Lectures on Atomic Physics

Walter R. Johnson  
Department of Physics, University of Notre Dame  
Notre Dame, Indiana 46556, U.S.A.

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# Contents

Preface ix

1 Angular Momentum 1

1.1 Orbital Angular Momentum - Spherical Harmonics 1

1.1.1 Quantum Mechanics of Angular Momentum 2

1.1.2 Spherical Coordinates - Spherical Harmonics 4

1.2 Spin Angular Momentum 7

1.2.1 Spin 1/2 and Spinors 7

1.2.2 Infinitesimal Rotations of Vector Fields 9

1.2.3 Spin 1 and Vectors 10

1.3 Clebsch-Gordan Coefficients 11

1.3.1 Three-j symbols 15

1.3.2 Irreducible Tensor Operators 17

1.4 Graphical Representation - Basic rules 19

1.5 Spinor and Vector Spherical Harmonics 21

1.5.1 Spherical Spinors 21

1.5.2 Vector Spherical Harmonics 23

2 Central-Field Schrödinger Equation 25

2.1 Radial Schrödinger Equation 25

2.2 Coulomb Wave Functions 27

2.3 Numerical Solution to the Radial Equation 31

2.3.1 Adams Method (ADAMS) 33

2.3.2 Starting the Outward Integration (OUTSCH) 36

2.3.3 Starting the Inward Integration (INSCH) 38

2.3.4 Eigenvalue Problem (MASTER) 39

2.4 Potential Models 41

2.4.1 Parametric Potentials 42

2.4.2 Thomas-Fermi Potential 44

2.5 Separation of Variables for Dirac Equation 48

2.6 Radial Dirac Equation for a Coulomb Field 49

2.7 Numerical Solution to Dirac Equation 53

2.7.1 Outward and Inward Integrations (ADAMS, OUTDIR, INDIR) 54

2.7.2 Eigenvalue Problem for Dirac Equation (MASTER) 57
2.7.3 Examples using Parametric Potentials ............... 58

3 Self-Consistent Fields ........................................... 61
3.1 Two-Electron Systems ......................................... 61
3.2 HF Equations for Closed-Shell Atoms ....................... 67
3.3 Numerical Solution to the HF Equations ................... 77
  3.3.1 Starting Approximation (HART) ......................... 77
  3.3.2 Refining the Solution (NRHF) ........................ 79
3.4 Atoms with One Valence Electron ........................... 82
3.5 Dirac-Fock Equations .......................................... 86

4 Atomic Multiplets .................................................. 95
4.1 Second-Quantization ........................................... 95
4.2 6-j Symbols ...................................................... 99
4.3 Two-Electron Atoms ............................................ 102
4.4 Atoms with One or Two Valence Electrons .................... 106
4.5 Particle-Hole Excited States ................................ 110
4.6 9-j Symbols ...................................................... 113
4.7 Relativity and Fine Structure ................................ 115
  4.7.1 He-like ions .............................................. 115
  4.7.2 Atoms with Two Valence Electrons ....................... 119
  4.7.3 Particle-Hole States ..................................... 120
4.8 Hyperfine Structure .............................................. 121
  4.8.1 Atoms with One Valence Electron ....................... 126

5 Radiative Transitions ............................................. 131
5.1 Review of Classical Electromagnetism ....................... 131
  5.1.1 Electromagnetic Potentials ............................... 132
  5.1.2 Electromagnetic Plane Waves ............................. 133
5.2 Quantized Electromagnetic Field .............................. 134
  5.2.1 Eigenstates of $N_i$ ...................................... 135
  5.2.2 Interaction Hamiltonian ................................ 136
  5.2.3 Time-Dependent Perturbation Theory .................... 137
  5.2.4 Transition Matrix Elements ............................... 138
  5.2.5 Gauge Invariance ....................................... 142
  5.2.6 Electric Dipole Transitions .............................. 143
  5.2.7 Magnetic Dipole and Electric Quadrupole Transitions . 149
  5.2.8 Nonrelativistic Many-Body Amplitudes .................. 154
5.3 Theory of Multipole Transitions .............................. 159

6 Introduction to MBPT ............................................... 167
6.1 Closed-Shell Atoms .............................................. 168
  6.1.1 Angular Momentum Reduction ............................ 170
  6.1.2 Example: 2nd-order Correlation Energy in Helium ...... 172
6.2 B-Spline Basis Sets ............................................. 173
6.3 Hartree-Fock Equation and B-splines ......................... 176
CONTENTS

6.4 Atoms with One Valence Electron ......................... 178
   6.4.1 Second-Order Energy ............................ 179
   6.4.2 Angular Momentum Decomposition ................. 180
   6.4.3 Quasi-Particle Equation and Brueckner-Orbitals ...... 181
   6.4.4 Monovalent Negative Ions ...................... 183
6.5 CI Calculations ........................................ 186

A ......................................................... 189
   A.1 Problems ........................................... 189
   A.2 Examinations ....................................... 193
   A.3 Answers to Problems ................................ 195
   A.4 Answers to Exams .................................. 209


List of Tables

1.1 $C(l, 1/2, j; m - m_s, m_s, m)$ .............................................. 13
1.2 $C(l, 1, j; m - m_s, m_s, m)$ .............................................. 14

2.1 Adams-Moulton integration coefficients ................................. 35
2.2 Comparison of $n = 3$ and $n = 4$ levels (a.u.) of sodium calculated using parametric potentials with experiment. ......................... 43
2.3 Parameters for the Tietz and Green potentials. ....................... 58
2.4 Energies obtained using the Tietz and Green potentials. .......... 59

3.1 Coefficients of the exchange Slater integrals in the nonrelativistic Hartree-Fock equations: $\Lambda_{l_{a}l_{b}}$. These coefficients are symmetric with respect to any permutation of the three indices. ................. 74
3.2 Energy eigenvalues for neon. The initial Coulomb energy eigenvalues are reduced to give model potential values shown under $U(r)$. These values are used as initial approximations to the HF eigenvalues shown under $V_{HF}$. ............................... 78
3.3 HF eigenvalues $\epsilon_{nl}$, average values of $r$ and $1/r$ for noble gas atoms. The negative of the experimental removal energies $-B_{exp}$ from Bearden and Burr (1967, for inner shells) and Moore (1957, for outer shells) is also listed for comparison. ......................... 84
3.4 Energies of low-lying states of alkali-metal atoms as determined in a $V_{HF}^{N-1}$ Hartree-Fock calculation. ............................. 86
3.5 Dirac-Fock eigenvalues (a.u.) for mercury, $Z = 80$. $E_{tot} = -19648.8585$ a.u.. For the inner shells, we also list the experimental binding energies from Bearden and Burr (1967) for comparison. .......................... 92
3.6 Dirac-Fock eigenvalues $\epsilon$ of valence electrons in Cs ($Z = 55$) and theoretical fine-structure intervals $\Delta$ are compared with measured energies (Moore). $\Delta_{nl} = \epsilon_{nlj=l+1/2} - \epsilon_{nlj=l-1/2}$ .................. 93

4.1 Energies of (1$s1d$) singlet and triplet states of helium (a.u.). Comparison of a model-potential calculation with experiment (Moore, 1957). .............................................................. 105
4.2 Comparison of $V_{HF}^{N-1}$ energies of (3$s2p$) and (3$p2p$) particle-hole excited states of neon and neonlike ions with measurements. . . . 112
4.3 First-order relativistic calculations of the \( (1s^2s) \) and \( (1s^2p) \) states of heliumlike neon \( (Z = 10) \), illustrating the fine-structure of the \( ^3P \) multiplet. .......................................................... 118

4.4 Nonrelativistic HF calculations of the magnetic dipole hyperfine constants \( a \) (MHz) for ground states of alkali-metal atoms compared with measurements. .................................................. 129

5.1 Reduced oscillator strengths for transitions in hydrogen ................ 147
5.2 Hartree-Fock calculations of transition rates \( A_{if} \) \( [\text{s}^{-1}] \) and lifetimes \( \tau \) \( [\text{s}] \) for levels in lithium. Numbers in parentheses represent powers of ten. ............................................................ 148

5.3 Wavelengths and oscillator strengths for transitions in heliumlike ions calculated in a central potential \( v_0(1s, r) \). Wavelengths are determined using first-order energies. ................................. 158

6.1 Eigenvalues of the generalized eigenvalue problem for the B-spline approximation of the radial Schrödinger equation with \( l = 0 \) in a Coulomb potential with \( Z = 2 \). Cavity radius is \( R = 30 \) a.u. We use 40 splines with \( k = 7 \). .......................................................... 175

6.2 Comparison of the HF eigenvalues from numerical integration of the HF equations (HF) with those found by solving the HF eigenvalue equation in a cavity using B-splines (spline). Sodium, \( Z = 11 \), in a cavity of radius \( R = 40 \) a.u. .................................................. 178

6.3 Contributions to the second-order correlation energy for helium. 179

6.4 Hartree-Fock eigenvalues \( \epsilon_v \) with second-order energy corrections \( E_v^{(2)} \) are compared with experimental binding energies for a few low-lying states in atoms with one valence electron. ........ 181

6.5 Expansion coefficients \( c_n \), \( n = 1 \cdot 20 \) of the 5s state of Pd\(^-\) in a basis of HF orbitals for neutral Pd confined to a cavity of radius \( R = 50 \) a.u. .......................................................... 184

6.6 Contribution \( \delta E_l \) of \( (nlml) \) configurations to the CI energy of the helium ground state. The dominant contributions are from the \( l = 0 \) \( nsm\) configurations. Contributions of configurations with \( l \geq 7 \) are estimated by extrapolation. ....................... 187
List of Figures

1.1 Transformation from rectangular to spherical coordinates. .... 4

2.1 Hydrogenic Coulomb wave functions for states with \( n = 1, 2 \) and \( 3 \). .................................................. 30

2.2 The radial wave function for a Coulomb potential with \( Z = 2 \) is shown at several steps in the iteration procedure leading to the \( 4p \) eigenstate. ........................................... 40

2.3 Electron interaction potentials from Eqs.(2.94) and (2.95) with parameters \( a = 0.2683 \) and \( b = 0.4072 \) chosen to fit the first four sodium energy levels. ......................................... 43

2.4 Thomas-Fermi functions for the sodium ion, \( Z = 11, N = 10 \). Upper panel: the Thomas-Fermi function \( \phi(r) \). Center panel: \( N(r) \), the number of electrons inside a sphere of radius \( r \). Lower panel: \( U(r) \), the electron contribution to the potential. ........ 47

2.5 Radial Dirac Coulomb wave functions for the \( n = 2 \) states of hydrogenlike helium, \( Z = 2 \). The solid lines represent the large components \( P_{2\kappa}(r) \) and the dashed lines represent the scaled small components, \( Q_{2\kappa}(r)/\alpha Z \). ................................. 53

3.1 Relative change in energy \( (E^{(n)} - E^{(n-1)})/E^{(n)} \) as a function of the iteration step number \( n \) in the iterative solution of the HF equation for helium, \( Z = 2 \). ................................. 66

3.2 Solutions to the HF equation for helium, \( Z = 2 \). The radial HF wave function \( P_{1s}(r) \) is plotted in the solid curve and electron potential \( v_0(1s,r) \) is plotted in the dashed curve. ................. 67

3.3 Radial HF wave functions for neon and argon. ................... 83

3.4 Radial HF densities for beryllium, neon, argon and krypton. .... 83

4.1 Energy level diagram for helium. ...................................... 103

4.2 Variation with nuclear charge of the energies of \( 1s2p \) states in heliumlike ions. At low \( Z \) the states are \( LS \)-coupled states, while at high \( Z \), they become \( jj \)-coupled states. Solid circles \( ^1P_1 \); Hollow circles \( ^3P_0 \); Hollow squares \( ^3P_1 \); Hollow diamonds \( ^3P_2 \). ....... 119

5.1 Detailed balance for radiative transitions between two levels. .. 141
5.2 The propagation vector \( \hat{k} \) is along the \( z' \) axis, \( \hat{\epsilon}_1 \) is along the \( x' \) axis and \( \hat{\epsilon}_2 \) is along the \( y' \) axis. The photon angular integration variables are \( \phi \) and \( \theta \). .................................................. 152
5.3 Oscillator strengths for transitions in heliumlike ions. .................. 159

6.1 We show the \( n = 30 \) B-splines of order \( k = 6 \) used to cover the interval 0 to 40 on an “atomic” grid. Note that the splines sum to 1 at each point. .......................................................... 174
6.2 B-spline components of the \( 2s \) state in a Coulomb field with \( Z = 2 \) obtained using \( n = 30 \) B-splines of order \( k = 6 \). The dashed curve is the resulting \( 2s \) wave function. .................. 176
6.3 The radial charge density \( \rho_v \) for the \( 3s \) state in sodium is shown together with \( 10 \times \delta \rho_v \), where \( \delta \rho_v \) is the second-order Brueckner correction to \( \rho_v \). .......................................................... 183
6.4 Lower panel: radial density of neutral Pd (\( Z = 46 \)). The peaks corresponding to closed \( n = 1, 2, \cdots \) shells are labeled. Upper panel: radial density of the \( 5s \) ground-state orbital of Pd\(^-\). The \( 5s \) orbital is obtained by solving the quasi-particle equation. .... 185
Preface

This is a set of lecture notes prepared for Physics 607, a course on Atomic Physics for second-year graduate students, given at Notre Dame during the spring semester of 1994. My aim in this course was to provide opportunities for “hands-on” practice in the calculation of atomic wave functions and energies.

The lectures started with a review of angular momentum theory including the formal rules for manipulating angular momentum operators, a discussion of orbital and spin angular momentum, Clebsch-Gordan coefficients and three-j symbols. This material should have been familiar to the students from first-year Quantum Mechanics. More advanced material on angular momentum needed in atomic structure calculations followed, including an introduction to graphical methods, irreducible tensor operators, spherical spinors and vector spherical harmonics.

The lectures on angular momentum were followed by an extended discussion of the central-field Schrödinger equation. The Schrödinger equation was reduced to a radial differential equation and analytical solutions for Coulomb wave functions were obtained. Again, this reduction should have been familiar from first-year Quantum Mechanics. This preliminary material was followed by an introduction to the finite difference methods used to solve the radial Schrödinger equation. A subroutine to find eigenfunctions and eigenvalues of the Schrödinger equation was developed. This routine was used together with parametric potentials to obtain wave functions and energies for alkali atoms. The Thomas-Fermi theory was introduced and used to obtain approximate electron screening potentials. Next, the Dirac equation was considered. The bound-state Dirac equation was reduced to radial form and Dirac-Coulomb wave functions were determined analytically. Numerical solutions to the radial Dirac equation were considered and a subroutine to obtain the eigenvalues and eigenfunctions of the radial Dirac equation was developed.

In the third part of the course, many electron wave functions were considered and the ground-state of a two-electron atom was determined variationally. This was followed by a discussion of Slater-determinant wave functions and a derivation of the Hartree-Fock equations for closed-shell atoms. Numerical methods for solving the HF equations were described. The HF equations for atoms with one-electron beyond closed shells were derived and a code was developed to solve the HF equations for the closed-shell case and for the case of a single valence electron. Finally, the Dirac-Fock equations were derived and discussed.
The final section of the material began with a discussion of second-quantization. This approach was used to study a number of structure problems in first-order perturbation theory, including excited states of two-electron atoms, excited states of atoms with one or two electrons beyond closed shells and particle-hole states. Relativistic fine-structure effects were considered using the “no-pair” Hamiltonian. A rather complete discussion of the magnetic-dipole and electric quadrupole hyperfine structure from the relativistic point of view was given, and nonrelativistic limiting forms were worked out in the Pauli approximation.

Fortran subroutines to solve the radial Schrödinger equation and the Hartree-Fock equations were handed out to be used in connection with weekly homework assignments. Some of these assigned exercises required the student to write or use FORTRAN codes to determine atomic energy levels or wave functions. Other exercises required the student to write MAPLE routines to generate formulas for wave functions or matrix elements. Additionally, more standard “pencil and paper” exercises on Atomic Physics were assigned.

I was disappointed in not being able to cover more material in the course. At the beginning of the semester, I had envisioned being able to cover second- and higher-order MBPT methods and CI calculations and to discuss radiative transitions as well. Perhaps next year!

Finally, I owe a debt of gratitude to the students in this class for their patience and understanding while this material was being assembled, and for helping read through and point out mistakes in the text.

South Bend, May, 1994

The second time that this course was taught, the material in Chap. 5 on electromagnetic transitions was included and Chap. 6 on many-body methods was started. Again, I was dissapointed at the slow pace of the course.

South Bend, May, 1995

The third time through, additional sections of Chap. 6 were added.

South Bend, January 14, 2002
Chapter 1

Angular Momentum

Understanding the quantum mechanics of angular momentum is fundamental in theoretical studies of atomic structure and atomic transitions. Atomic energy levels are classified according to angular momentum and selection rules for radiative transitions between levels are governed by angular-momentum addition rules. Therefore, in this first chapter, we review angular-momentum commutation relations, angular-momentum eigenstates, and the rules for combining two angular-momentum eigenstates to find a third. We make use of angular-momentum diagrams as useful mnemonic aids in practical atomic structure calculations. A more detailed version of much of the material in this chapter can be found in Edmonds (1974).

1.1 Orbital Angular Momentum - Spherical Harmonics

Classically, the angular momentum of a particle is the cross product of its position vector $\mathbf{r} = (x, y, z)$ and its momentum vector $\mathbf{p} = (p_x, p_y, p_z)$:

$$ \mathbf{L} = \mathbf{r} \times \mathbf{p}. $$

The quantum mechanical orbital angular momentum operator is defined in the same way with $\mathbf{p}$ replaced by the momentum operator $\mathbf{p} \rightarrow -i\hbar \nabla$. Thus, the Cartesian components of $\mathbf{L}$ are

$$ L_x = \frac{\hbar}{i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad L_y = \frac{\hbar}{i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \quad L_z = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (1.1) $$

With the aid of the commutation relations between $\mathbf{p}$ and $\mathbf{r}$:

$$ [p_x, x] = -i\hbar, \quad [p_y, y] = -i\hbar, \quad [p_z, z] = -i\hbar, \quad (1.2) $$
one easily establishes the following commutation relations for the Cartesian components of the quantum mechanical angular momentum operator:

\[ L_x L_y - L_y L_x = i\hbar L_z, \quad L_y L_z - L_z L_y = i\hbar L_x, \quad L_z L_x - L_x L_z = i\hbar L_y. \]  

(1.3)

Since the components of \( \mathbf{L} \) do not commute with each other, it is not possible to find simultaneous eigenstates of any two of these three operators. The operator \( L^2 = L_x^2 + L_y^2 + L_z^2 \), however, commutes with each component of \( \mathbf{L} \). It is, therefore, possible to find a simultaneous eigenstate of \( L^2 \) and any one component of \( \mathbf{L} \). It is conventional to seek eigenstates of \( L^2 \) and \( L_z \).

### 1.1.1 Quantum Mechanics of Angular Momentum

Many of the important quantum mechanical properties of the angular momentum operator are consequences of the commutation relations (1.3) alone. To study these properties, we introduce three abstract operators \( J_x, J_y, \) and \( J_z \) satisfying the commutation relations,

\[ J_x J_y - J_y J_x = i J_z, \quad J_y J_z - J_z J_y = i J_x, \quad J_z J_x - J_x J_z = i J_y. \]  

(1.4)

The unit of angular momentum in Eq.(1.4) is chosen to be \( \hbar \), so the factor of \( \hbar \) on the right-hand side of Eq.(1.3) does not appear in Eq.(1.4). The sum of the squares of the three operators \( J^2 = J_x^2 + J_y^2 + J_z^2 \) can be shown to commute with each of the three components. In particular,

\[ [J^2, J_z] = 0. \]  

(1.5)

The operators \( J_+ = J_x + i J_y \) and \( J_- = J_x - i J_y \) also commute with the angular momentum squared:

\[ [J^2, J_\pm] = 0. \]  

(1.6)

Moreover, \( J_+ \) and \( J_- \) satisfy the following commutation relations with \( J_z \):

\[ [J_z, J_\pm] = \pm J_\pm. \]  

(1.7)

One can express \( J^2 \) in terms of \( J_+ \), \( J_- \) and \( J_z \) through the relations

\[ J^2 = J_+ J_- + J_z^2 - J_z, \]  

(1.8)

\[ J^2 = J_- J_+ + J_z^2 + J_z. \]  

(1.9)

We introduce simultaneous eigenstates \( |\lambda, m\rangle \) of the two commuting operators \( J^2 \) and \( J_z \):

\[ J^2 |\lambda, m\rangle = \lambda |\lambda, m\rangle, \]  

(1.10)

\[ J_z |\lambda, m\rangle = m |\lambda, m\rangle, \]  

(1.11)

and we note that the states \( J_\pm |\lambda, m\rangle \) are also eigenstates of \( J^2 \) with eigenvalue \( \lambda \). Moreover, with the aid of Eq.(1.7), one can establish that \( J_+ |\lambda, m\rangle \) and \( J_- |\lambda, m\rangle \) are eigenstates of \( J_z \) with eigenvalues \( m \pm 1 \), respectively:

\[ J_z J_+ |\lambda, m\rangle = (m + 1) J_+ |\lambda, m\rangle, \]  

(1.12)

\[ J_z J_- |\lambda, m\rangle = (m - 1) J_- |\lambda, m\rangle. \]  

(1.13)
Since $J_+$ raises the eigenvalue $m$ by one unit, and $J_-$ lowers it by one unit, these operators are referred to as raising and lowering operators, respectively. Furthermore, since $J^2_x + J^2_y$ is a positive definite hermitian operator, it follows that

$$\lambda \geq m^2.$$  

By repeated application of $J_-$ to eigenstates of $J_z$, one can obtain states of arbitrarily small eigenvalue $m$, violating this bound, unless for some state $|\lambda, m_1\rangle$, $J_-|\lambda, m_1\rangle = 0$.

Similarly, repeated application of $J_+$ leads to arbitrarily large values of $m$, unless for some state $|\lambda, m_2\rangle$, $J_+|\lambda, m_2\rangle = 0$.

Since $m^2$ is bounded, we infer the existence of the two states $|\lambda, m_1\rangle$ and $|\lambda, m_2\rangle$. Starting from the state $|\lambda, m_1\rangle$ and applying the operator $J_+$ repeatedly, one must eventually reach the state $|\lambda, m_2\rangle$; otherwise the value of $m$ would increase indefinitely. It follows that

$$m_2 - m_1 = k,$$

where $k \geq 0$ is the number of times that $J_+$ must be applied to the state $|\lambda, m_1\rangle$ in order to reach the state $|\lambda, m_2\rangle$. One finds from Eqs.(1.8,1.9) that

$$\lambda|\lambda, m_1\rangle = (m_2^2 - m_1^2)|\lambda, m_1\rangle,$$

$$\lambda|\lambda, m_2\rangle = (m_2^2 + m_2)|\lambda, m_2\rangle,$$

leading to the identities

$$\lambda = m_1^2 - m_1 = m_2^2 + m_2,$$

which can be rewritten

$$(m_2 - m_1 + 1)(m_2 + m_1) = 0.$$  

Since the first term on the left of Eq.(1.16) is positive definite, it follows that $m_1 = -m_2$. The upper bound $m_2$ can be rewritten in terms of the integer $k$ in Eq.(1.14) as

$$m_2 = k/2 = j.$$  

The value of $j$ is either integer or half integer, depending on whether $k$ is even or odd:

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots .$$

It follows from Eq.(1.15) that the eigenvalue of $J^2$ is

$$\lambda = j(j + 1).$$  

The number of possible $m$ eigenvalues for a given value of $j$ is $k + 1 = 2j + 1$. The possible values of $m$ are

$$m = j, j - 1, j - 2, \cdots , -j.$$
Since $J_+ = J_+^\dagger$, it follows that

$$J_+ |\lambda, m\rangle = \eta |\lambda, m + 1\rangle, \quad J_- |\lambda, m + 1\rangle = \eta^* |\lambda, m\rangle.$$ 

Evaluating the expectation of $J^2 = J_- J_+ + J_z^2 + J_z$ in the state $|\lambda, m\rangle$, one finds

$$|\eta|^2 = j(j + 1) - m(m + 1).$$

Choosing the phase of $\eta$ to be real and positive, leads to the relations

$$J_+ |\lambda, m\rangle = \sqrt{(j + m + 1)(j - m)} |\lambda, m + 1\rangle,$$

$$J_- |\lambda, m\rangle = \sqrt{(j - m + 1)(j + m)} |\lambda, m - 1\rangle.$$  

### 1.1.2 Spherical Coordinates - Spherical Harmonics

Let us apply the general results derived in Section 1.1.1 to the orbital angular momentum operator $\mathbf{L}$. For this purpose, it is most convenient to transform Eqs.(1.1) to spherical coordinates (Fig. 1.1):

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta,$$

$$r = \sqrt{x^2 + y^2 + z^2}, \quad \theta = \arccos \frac{z}{r}, \quad \phi = \arctan \frac{y}{x}.$$ 

In spherical coordinates, the components of $\mathbf{L}$ are

$$L_x = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right),$$

$$L_y = i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right),$$

$$L_z = -i\hbar \frac{\partial}{\partial \phi}.$$
and the square of the angular momentum is
\[
L^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right).
\]  
(1.23)

Combining the equations for \( L_x \) and \( L_y \), we obtain the following expressions for the orbital angular momentum raising and lowering operators:
\[
L_\pm = \hbar e^{\pm i\phi} \left( \pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right).
\]  
(1.24)

The simultaneous eigenfunctions of \( L^2 \) and \( L_z \) are called spherical harmonics. They are designated by \( Y_{lm}(\theta, \phi) \). We decompose \( Y_{lm}(\theta, \phi) \) into a product of a function of \( \theta \) and a function of \( \phi \):
\[
Y_{lm}(\theta, \phi) = \Theta_{l,m}(\theta) \Phi_m(\phi).
\]

The eigenvalue equation \( L_z Y_{l,m}(\theta, \phi) = \hbar m Y_{l,m}(\theta, \phi) \) leads to the equation
\[
- i \frac{d \Phi_m(\phi)}{d \phi} = m \Phi_m(\phi),
\]
for \( \Phi_m(\phi) \). The single valued solution to this equation, normalized so that
\[
\int_0^{2\pi} |\Phi_m(\phi)|^2 d\phi = 1,
\]
(1.26)
is
\[
\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi},
\]
(1.27)
where \( m \) is an integer. The eigenvalue equation \( L^2 Y_{l,m}(\theta, \phi) = \hbar^2 (l+1) Y_{l,m}(\theta, \phi) \) leads to the differential equation
\[
\left( \frac{1}{\sin \theta} \frac{d}{d \theta} \sin \theta \frac{d}{d \theta} - \frac{m^2}{\sin^2 \theta} + l(l+1) \right) \Theta_{l,m}(\theta) = 0,
\]
(1.28)
for the function \( \Theta_{l,m}(\theta) \). The orbital angular momentum quantum number \( l \) must be an integer since \( m \) is an integer.

One can generate solutions to Eq.(1.28) by recurrence, starting with the solution for \( m = -l \) and stepping forward in \( m \) using the raising operator \( L_+ \), or starting with the solution for \( m = l \) and stepping backward using the lowering operator \( L_- \). The function \( \Theta_{l,-l}(\theta) \) satisfies the differential equation
\[
L_- \Theta_{l,-l}(\theta) \Phi_{-l}(\phi) = \hbar \Phi_{-l+1}(\phi) \left( - \frac{d}{d \theta} + l \cot \theta \right) \Theta_{l,-l}(\theta) = 0,
\]
which can be easily solved to give \( \Theta_{l,-l}(\theta) = c \sin^l \theta \), where \( c \) is an arbitrary constant. Normalizing this solution so that
\[
\int_0^\pi |\Theta_{l,-l}(\theta)|^2 \sin \theta d\theta = 1,
\]
(1.29)
one obtains
\[ \Theta_{l,-l}(\theta) = \frac{1}{2^l l!} \sqrt{\frac{(2l+1)!}{2}} \sin^l \theta. \]  
(1.30)

Applying \( L^m_l \) to \( Y_{l,-l}(\theta,\phi) \), leads to the result
\[ \Theta_{l,m}(\theta) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} \sin^m \theta \frac{d^{l+m}}{d \cos \theta^{l+m}} \sin^2 \theta. \]  
(1.31)

For \( m = 0 \), this equation reduces to
\[ \Theta_{l,0}(\theta) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{2l+1}{2}} \frac{d^l}{d \cos \theta^l} \sin^2 \theta. \]  
(1.32)

This equation may be conveniently written in terms of Legendre polynomials \( P_l(x) \) as
\[ \Theta_{l,0}(\theta) = \sqrt{\frac{2l+1}{2}} P_l(\cos \theta). \]  
(1.33)

Here the Legendre polynomial \( P_l(x) \) is defined by Rodrigues’ formula
\[ P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l. \]  
(1.34)

For \( m = l \), Eq.(1.31) gives
\[ \Theta_{l,l}(\theta) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)!}{2}} \sin^l \theta. \]  
(1.35)

Starting with this equation and stepping backward \( l - m \) times leads to an alternate expression for \( \Theta_{l,m}(\theta) \):
\[ \Theta_{l,m}(\theta) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)(l+m)!}{2}} \sin^{-m} \theta \frac{d^{l-m}}{d \cos \theta^{l-m}} \sin^2 \theta. \]  
(1.36)

Comparing Eq.(1.36) with Eq.(1.31), one finds
\[ \Theta_{l,-m}(\theta) = \frac{(-1)^m}{\Theta_{l,m}(\theta)}. \]  
(1.37)

We can restrict our attention to \( \Theta_{l,m}(\theta) \) with \( m \geq 0 \) and use (1.37) to obtain \( \Theta_{l,m}(\theta) \) for \( m < 0 \). For positive values of \( m \), Eq.(1.31) can be written
\[ \Theta_{l,m}(\theta) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P^m_l(\cos \theta), \]  
(1.38)

where \( P^m_l(x) \) is an associated Legendre functions of the first kind, given in Abramowitz and Stegun (1964, chap. 8), with a different sign convention, defined by
\[ P^m_l(x) = (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_l(x). \]  
(1.39)
The general orthonormality relations \( \langle l, m | l', m' \rangle = \delta_{ll'} \delta_{mm'} \) for angular momentum eigenstates takes the specific form

\[
\int_0^\pi \int_0^{2\pi} \sin \theta d\theta d\phi Y_{l,m}(\theta, \phi) Y_{l',m'}^*(\theta, \phi) = \delta_{ll'} \delta_{mm'},
\]

for spherical harmonics. Comparing Eq.(1.31) and Eq.(1.36) leads to the relation

\[
Y_{l,-m}(\theta, \phi) = (-1)^m Y_{l,m}^*(\theta, \phi).
\]

The first few spherical harmonics are:

\begin{align*}
Y_{00} &= \sqrt{\frac{1}{4\pi}} \\
Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos \theta \\
Y_{20} &= \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \\
Y_{2\pm2} &= \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi} \\
Y_{30} &= \sqrt{\frac{7}{16\pi}} \cos \theta (5 \cos^2 \theta - 3) \\
Y_{3\pm2} &= \sqrt{\frac{105}{32\pi}} \cos \theta \sin^2 \theta e^{\pm 2i\phi} \\
Y_{3\pm3} &= \sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{\pm 3i\phi}
\end{align*}

### 1.2 Spin Angular Momentum

#### 1.2.1 Spin 1/2 and Spinors

The internal angular momentum of a particle in quantum mechanics is called spin angular momentum and designated by \( S \). Cartesian components of \( S \) satisfy angular momentum commutation rules (1.4). The eigenvalue of \( S^2 \) is \( \hbar^2 s(s+1) \) and the \( 2s+1 \) eigenvalues of \( S_z \) are \( \hbar m \) with \( m = -s, -s+1, \ldots, s \). Let us consider the case \( s = 1/2 \) which describes the spin of the electron. We designate the eigenstates of \( S^2 \) and \( S_z \) by two-component vectors \( \chi_\mu, \mu = \pm 1/2 \):

\[
\chi_{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.
\]

These two-component spin eigenfunctions are called spinors. The spinors \( \chi_\mu \) satisfy the orthonormality relations

\[
\chi_\mu \chi_\nu = \delta_{\mu\nu}.
\]

The eigenvalue equations for \( S^2 \) and \( S_z \) are

\[
S^2 \chi_\mu = \frac{3}{4} \hbar^2 \chi_\mu, \quad S_z \chi_\mu = \mu \hbar \chi_\mu.
\]
We represent the operators $S^2$ and $S_z$ as $2 \times 2$ matrices acting in the space spanned by $\chi_\mu$:

$$S^2 = \frac{3}{2} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad S_z = \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$  

One can use Eqs. (1.18, 1.19) to work out the elements of the matrices representing the spin raising and lowering operators $S_\pm$:

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$  

These matrices can be combined to give matrices representing $S_x = (S_+ + S_-)/2$ and $S_y = (S_+ - S_-)/2i$. The matrices representing the components of $\mathbf{S}$ are commonly written in terms of the Pauli matrices $\sigma = (\sigma_x, \sigma_y, \sigma_z)$, which are given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$  

through the relation

$$\mathbf{S} = \frac{1}{2} \hbar \mathbf{\sigma}. \quad (1.45)$$  

The Pauli matrices are both hermitian and unitary. Therefore,

$$\sigma_x^2 = I, \quad \sigma_y^2 = I, \quad \sigma_z^2 = I,$$  

where $I$ is the $2 \times 2$ identity matrix. Moreover, the Pauli matrices anticommute:

$$\sigma_y \sigma_x = -\sigma_x \sigma_y, \quad \sigma_z \sigma_y = -\sigma_y \sigma_z, \quad \sigma_x \sigma_z = -\sigma_z \sigma_x. \quad (1.47)$$  

The Pauli matrices also satisfy commutation relations that follow from the general angular momentum commutation relations (1.4):

$$\sigma_x \sigma_y - \sigma_y \sigma_x = 2i\sigma_z, \quad \sigma_y \sigma_z - \sigma_z \sigma_y = 2i\sigma_x, \quad \sigma_z \sigma_x - \sigma_x \sigma_z = 2i\sigma_y. \quad (1.48)$$  

The anticommutation relations (1.47) and commutation relations (1.48) can be combined to give

$$\sigma_x \sigma_y = i\sigma_z, \quad \sigma_y \sigma_z = i\sigma_x, \quad \sigma_z \sigma_x = i\sigma_y. \quad (1.49)$$

From the above equations for the Pauli matrices, one can show

$$\mathbf{\sigma} \cdot \mathbf{a} \mathbf{\sigma} \cdot \mathbf{b} = \mathbf{a} \cdot \mathbf{b} + i \mathbf{\sigma} \cdot [\mathbf{a} \times \mathbf{b}],$$  

for any two vectors $\mathbf{a}$ and $\mathbf{b}$.

In subsequent studies we will require simultaneous eigenfunctions of $L^2$, $L_z$, $S^2$, and $S_z$. These eigenfunctions are given by $Y_{lm}(\theta, \phi) \chi_\mu$. 

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**CHAPTER 1. ANGULAR MOMENTUM**
1.2.2 Infinitesimal Rotations of Vector Fields

Let us consider a rotation about the $z$ axis by a small angle $\delta \phi$. Under such a rotation, the components of a vector $\mathbf{r} = (x, y, z)$ are transformed to

$$
x' = x + \delta \phi y, \\
y' = -\delta \phi x + y, \\
z' = z,
$$
neglecting terms of second and higher order in $\delta \phi$. The difference $\delta \psi(x, y, z) = \psi(x', y', z') - \psi(x, y, z)$ between the values of a scalar function $\psi$ evaluated in the rotated and unrotated coordinate systems is (to lowest order in $\delta \phi$),

$$
\delta \psi(x, y, z) = -i \delta \phi [L_z \psi(x, y, z)] = -i \delta \phi L_z \psi(x, y, z).
$$

The operator $L_z$, in the sense of this equation, generates an infinitesimal rotation about the $z$ axis. Similarly, $L_x$ and $L_y$ generate infinitesimal rotations about the $x$ and $y$ axes. Generally, an infinitesimal rotation about an axis in the direction $\mathbf{n}$ is generated by $\mathbf{L} \cdot \mathbf{n}$.

Now, let us consider how a vector function $\mathbf{A}(x, y, z) = [A_x(x, y, z), A_y(x, y, z), A_z(x, y, z)]$ transforms under an infinitesimal rotation. The vector $\mathbf{A}$ is attached to a point in the coordinate system; it rotates with the coordinate axes on transforming from a coordinate system $(x, y, z)$ to a coordinate system $(x', y', z')$. An infinitesimal rotation $\delta \phi$ about the $z$ axis induces the following changes in the components of $\mathbf{A}$:

$$
\delta A_x = A_x(x', y', z') - \delta \phi A_y(x', y', z') - A_x(x, y, z) = -i \delta \phi [L_z A_x(x, y, z)], \\
\delta A_y = A_y(x', y', z') + \delta \phi A_x(x', y', z') - A_y(x, y, z) = -i \delta \phi [L_z A_y(x, y, z) + i A_y(x, y, z)], \\
\delta A_z = A_z(x', y', z') - A_z(x, y, z) = -i \delta \phi L_z A_z(x, y, z).
$$

Let us introduce the $3 \times 3$ matrix $s_z$ defined by

$$
s_z = \begin{pmatrix}
0 & -i & 0 \\
 i & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}.
$$

With the aid of this matrix, one can rewrite the equations for $\delta \mathbf{A}$ in the form $\delta \mathbf{A}(x, y, z) = -i \delta \phi J_z \mathbf{A}(x, y, z)$, where $J_z = L_z + s_z$. If we define angular momentum to be the generator of infinitesimal rotations, then the $z$ component
CHAPTER 1. ANGULAR MOMENTUM

of the angular momentum of a vector field is $J_z = L_z + s_z$. Infinitesimal rotations about the $x$ and $y$ axes are generated by $J_x = L_x + s_x$ and $J_z = L_y + s_y$, where

$$s_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad s_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}.$$

The matrices $s = (s_x, s_y, s_z)$ are referred to as the spin matrices. In the following paragraphs, we show that these matrices are associated with angular momentum quantum number $s = 1$.

1.2.3 Spin 1 and Vectors

The eigenstates of $S^2$ and $S_z$ for particles with spin $s = 1$ are represented by three-component vectors $\xi_\mu$, with $\mu = -1, 0, 1$. The counterparts of the three Pauli matrices for $s = 1$ are the $3 \times 3$ matrices $s = (s_x, s_y, s_z)$ introduced in the previous section. The corresponding spin angular momentum operator is $S = \hbar s$ where

$$s_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad s_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \quad s_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The matrix $s^2 = s_x^2 + s_y^2 + s_z^2$ is

$$s^2 = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}.$$

The three matrices $s_x, s_y, \text{and } s_z$ satisfy the commutation relations

$$s_x s_y - s_y s_x = i s_z, \quad s_y s_z - s_z s_y = i s_x, \quad s_z s_x - s_x s_z = i s_y.$$

It follows that $S = \hbar s$ satisfies the angular momentum commutation relations (1.4).

Eigenfunctions of $S^2$ and $S_z$ satisfy the matrix equations $s^2 \xi_\mu = 2 \xi_\mu$ and $s_z \xi_\mu = \mu \xi_\mu$. The first of these equations is satisfied by an arbitrary three-component vector. Solutions to the second are found by solving the corresponding $3 \times 3$ eigenvalue problem,

$$\begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \mu \begin{pmatrix} a \\ b \\ c \end{pmatrix}.$$

The three eigenvalues of this equation are $\mu = -1, 0, 1$ and the associated eigenvectors are

$$\xi_1 = -\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix}, \quad \xi_0 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad \xi_{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}.$$
1.3. CLEBSCH-GORDAN COEFFICIENTS

The phases of the three eigenvectors are chosen in accordance with Eq.(1.18), which may be rewritten \( s_+ \xi_\mu = \sqrt{2} \xi_{\mu+1} \). The vectors \( \xi_\mu \) are called spherical basis vectors. They satisfy the orthogonality relations

\[
\xi_\mu^\dagger \xi_{\nu} = \delta_{\mu\nu}.
\]

It is, of course, possible to expand an arbitrary three-component vector \( \mathbf{v} = (v_x, v_y, v_z) \) in terms of spherical basis vectors:

\[
\mathbf{v} = \sum_{\mu=-1}^{1} v^\mu \xi_\mu, \quad \text{where} \quad v^\mu = \xi_\mu^\dagger \mathbf{v}.
\]

Using these relations, one may show, for example, that the unit vector \( \hat{\mathbf{r}} \) expressed in the spherical basis is

\[
\hat{\mathbf{r}} = \sqrt{\frac{4\pi}{3}} \sum_{\mu=-1}^{1} Y^*_{1,\mu}(\theta, \phi) \xi_\mu.
\]

1.3 Clebsch-Gordan Coefficients

One common problem encountered in atomic physics calculations is finding eigenstates of the sum of two angular momenta in terms of products of the individual angular momentum eigenstates. For example, as mentioned in section (1.2.1), the products \( Y_{l,m}(\theta, \phi) \chi_\mu \) are eigenstates of \( L^2 \), and \( L_z \), as well as \( S^2 \), and \( S_z \). The question addressed in this section is how to combine product states such as these to find eigenstates of \( J^2 \) and \( J_z \), where \( \mathbf{J} = \mathbf{L} + \mathbf{S} \).

Generally, let us suppose that we have two commuting angular momentum vectors \( \mathbf{J}_1 \) and \( \mathbf{J}_2 \). Let \( |j_1, m_1 \rangle \) be an eigenstate of \( J_1^2 \) and \( J_{1z} \) with eigenvalues \( j_1(j_1+1) \) and \( m_1 \), respectively. Similarly, let \( |j_2, m_2 \rangle \) be an eigenstate of \( J_2^2 \) and \( J_{2z} \), with eigenvalues \( j_2(j_2+1) \) and \( m_2 \). We set \( \mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2 \) and attempt to construct eigenstates of \( J^2 \) and \( J_z \) as linear combinations of the product states \( |j_1, m_1 \rangle |j_2, m_2 \rangle \):

\[
|j, m \rangle = \sum_{m_1, m_2} C(j_1, j_2; j; m_1, m_2, m) |j_1, m_1 \rangle |j_2, m_2 \rangle.
\]

The expansion coefficients \( C(j_1, j_2; j; m_1, m_2, m) \), called Clebsch-Gordan coefficients, are discussed in many standard quantum mechanics textbooks (for example, Messiah, 1961, chap. 10). One sometimes encounters notation such as \( \langle j_1, m_1, j_2, m_2 | j, m \rangle \) for the Clebsch-Gordan coefficient \( C(j_1, j_2; j; m_1, m_2, m) \).

Since \( J_z = J_{1z} + J_{2z} \), it follows from Eq.(1.57) that

\[
m|j, m \rangle = \sum_{m_1, m_2} (m_1 + m_2) C(j_1, j_2; j; m_1, m_2, m) |j_1, m_1 \rangle |j_2, m_2 \rangle.
\]

(1.58)
CHAPTER 1. ANGULAR MOMENTUM

Since the states \( |j_1, m_1\rangle |j_2, m_2\rangle \) are linearly independent, one concludes from Eq. (1.58) that

\[
(m_1 + m_2 - m) C(j_1, j_2, j; m_1, m_2, m) = 0. \tag{1.59}
\]

It follows that the only nonvanishing Clebsch-Gordan coefficients are those for which \( m_1 + m_2 = m \). The sum in Eq. (1.57) can be expressed, therefore, as a sum over \( m_2 \) only, the value of \( m_1 \) being determined by \( m = m_1 - m_2 \). Consequently, we rewrite Eq. (1.57) as

\[
|j, m\rangle = \sum_{m_2} C(j_1, j_2, j; m - m_2, m_2, m) |j_1, m - m_2\rangle |j_2, m_2\rangle. \tag{1.60}
\]

If we demand that all of the states in Eq. (1.60) be normalized, then it follows from the relation

\[
\langle j', m'|j, m\rangle = \delta_{j', j} \delta_{m', m},
\]

that

\[
\sum_{m_2} C(j_1, j_2, j'; m - m_2, m_2, m') C(j_1, j_2, j; m - m_2, m_2, m) \times \langle j_1, m' - m_2|j, m_2\rangle \langle j_2, m_2' |j_2, m_2\rangle = \delta_{j', j} \delta_{m', m}.
\]

From this equation, one obtains the orthogonality relation:

\[
\sum_{m_1, m_2} C(j_1, j_2, j'; m_1, m_2, m') C(j_1, j_2, j; m_1, m_2, m) = \delta_{j', j} \delta_{m', m}. \tag{1.61}
\]

One can make use of this equation to invert Eq. (1.60). Indeed, one finds

\[
|j_1, m - m_2\rangle |j_2, m_2\rangle = \sum_j C(j_1, j_2, j; m - m_2, m_2, m) |j, m\rangle. \tag{1.62}
\]

From Eq. (1.62), a second orthogonality condition can be deduced:

\[
\sum_{j, m} C(j_1, j_2, j; m_1', m_2', m) C(j_1, j_2, j; m_1, m_2, m) = \delta_{m_1', m_1} \delta_{m_2, m_2}. \tag{1.63}
\]

The state of largest \( m \) is the “extended state” \( |j_1, j_1\rangle |j_2, j_2\rangle \). With the aid of the decomposition, \( J^2 = J_1^2 + J_2^2 + 2J_1 J_2 + J_1^2 + J_2^2 + J_1 - J_2 \), one may establish that this state is an eigenstate of \( J^2 \) with eigenvalue \( j = j_1 + j_2 \); it is also, obviously, an eigenstate of \( J_z \) with eigenvalue \( m = j_1 + j_2 \). The state \( J_+ |j_1, j_1\rangle |j_2, j_2\rangle \) is also an eigenstate of \( J^2 \) with eigenvalue \( j = j_1 + j_2 \). It is an eigenstate of \( J_z \) but with eigenvalue \( m = j_1 + j_2 - 1 \). The corresponding normalized eigenstate is

\[
|j_1 + j_2, j_1 + j_2 - 1\rangle = \frac{j_1}{j_1 + j_2} |j_1, j_1 - 1\rangle |j_2, j_2\rangle + \frac{j_2}{j_1 + j_2} |j_1, j_1\rangle |j_2, j_2 - 1\rangle. \tag{1.64}
\]
By repeated application of $J_-$ to the state $|j_1, j_1\rangle|j_2, j_2\rangle$, one generates, in this way, each of the $2j + 1$ eigenstates of $J_z$ with eigenvalues $m = j_1 + j_2, j_1 + j_2 - 1, \ldots, -j_1 - j_2$. The state

$$ |j_1 + j_2 - 1, j_1 + j_2 - 1\rangle = -\sqrt{\frac{j_2}{j_1 + j_2}} |j_1, j_1 - 1\rangle|j_2, j_2\rangle + \sqrt{\frac{j_1}{j_1 + j_2}} |j_1, j_1\rangle|j_2, j_2 - 1\rangle, \quad (1.65)$$

is an eigenstate of $J_z$ with eigenvalue $j_1 + j_2 - 1$, constructed to be orthogonal to (1.64). One easily establishes that this state is an eigenstate of $J^2$ corresponding to eigenvalue $j = j_1 + j_2 - 1$. By repeated application of $J_-$ to this state, one generates the $2j + 1$ eigenstates of $J_z$ corresponding to $j = j_1 + j_2 - 1$. We continue this procedure by constructing the state orthogonal to the two states $|j_1 + j_2, j_1 + j_2 - 2\rangle$ and $|j_1 + j_2 - 1, j_1 + j_2 - 2\rangle$, and then applying $J_-$ successively to generate all possible $m$ states for $j = j_1 + j_2 - 2$. Continuing in this way, we construct states with $j = j_1 + j_2, j_1 + j_2 - 1, j_1 + j_2 - 2, \ldots, j_{\text{min}}$. The algorithm terminates when we have exhausted all of the $(2j_1 + 1)(2j_2 + 1)$ possible linearly independent states that can be made up from products of $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$. The limiting value $j_{\text{min}}$ is determined by the relation

$$ \sum_{j=j_{\text{min}}}^{j_1+j_2} (2j + 1) = (j_1 + j_2 + 2)(j_1 + j_2) - j_{\text{min}}^2 + 1 = (2j_1 + 1)(2j_2 + 1), \quad (1.66)$$

which leads to the $j_{\text{min}} = |j_1 - j_2|$. The possible eigenvalues of $J^2$ are, therefore, given by $j(j + 1)$, with $j = j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2|$.  

Values of the Clebsch-Gordan coefficients can be determined from the construction described above; however, it is often easier to proceed in a slightly different way. Let us illustrate the alternative for the case $\mathbf{J} = \mathbf{L} + \mathbf{S}$, with $s = 1/2$. In this case, the possible values $j$ are $j = l + 1/2$ and $j = l - 1/2$. Eigenstates of $J^2$ and $J_z$ constructed by the Clebsch-Gordan expansion are also eigenstates of

$$ \Lambda = 2\mathbf{L} \cdot \mathbf{S} = 2L_zS_z + L_+S_- + L_-S_+.$$
The eigenvalues of $\Lambda$ are $\lambda = j(j + 1) - l(l + 1) - 3/4$. Thus for $j = l + 1/2$, we find $\lambda = l$; for $j = l - 1/2$, we find $\lambda = -l - 1$. The eigenvalue equation for $\Lambda$,

$$\Lambda |j,m \rangle = \lambda |j,m \rangle$$

may be rewritten as a set of two homogeneous equations in two unknowns: $x = C(l,1/2,j;m-1/2,1/2,m)$ and $y = C(l,1/2,j;m+1/2,-1/2,m)$:

$$\begin{align*}
\lambda x &= (m - 1/2)x + \sqrt{(l - m + 1/2)(l + m + 1/2)}y \\
\lambda y &= \sqrt{(l - m + 1/2)(l + m + 1/2)}x - (m + 1/2)y.
\end{align*}$$

The solutions to this equation are:

$$y/x = \begin{cases} 
\sqrt{\frac{l+m+1/2}{l-m+1/2}} & \text{for } \lambda = l, \\
-\sqrt{\frac{l-m+1/2}{l+m+1/2}} & \text{for } \lambda = -l - 1.
\end{cases} \quad (1.67)$$

We normalize these solutions so that $x^2 + y^2 = 1$. The ambiguity in phase is resolved by the requirement that $y > 0$. The resulting Clebsch-Gordan coefficients are listed in Table 1.1.

This same technique can be applied in the general case. One chooses $j_2$ and $j_1$ so that $j_2 < j_1$. The eigenvalue equation for $\Lambda$ reduces to a set of $2j_2 + 1$ equations for $2j_2 + 1$ unknowns $x_k$, the Clebsch-Gordan coefficients for fixed $j$ and $m$ expressed in terms of $m_2 = j_2 + 1 - k$. The $2j_2 + 1$ eigenvalues of $\Lambda$ can be determined from the $2j_2 + 1$ possible values of $j$ by $\lambda = j(j + 1) - j_1(j_1 + 1) - j_2(j_2 + 1)$. One solves the resulting equations, normalizes the solutions to $\sum_k x_k^2 = 1$ and settles the phase ambiguity by requiring that the Clebsch-Gordan coefficient for $m_2 = -j_2$ is positive; e.g., $x_{2j_2+1} > 0$. As a second example of this method, we give in Table 1.2 the Clebsch-Gordan coefficients for $\mathbf{J} = \mathbf{L} + \mathbf{S}$, with $s = 1$.

A general formula for the Clebsch-Gordan coefficients is given in Wigner (1931). Another equivalent, but more convenient one, was obtained later by
1.3. CLEBSCH-GORDAN COEFFICIENTS

Racah (1942):

\[ C(j_1, j_2, j; m_1, m_2, m) = \delta_{m_1 + m_2, m} \sqrt{(j_1 + j_2 - j)!(j_1 + j - m_1)!(j_2 + j - m_2)!} \frac{(2j + 1)!}{(j + 1)! (j + j_1 + j_2 +1)!} \sum_k (-1)^k \sqrt{(j_1 + m_1)!(j_1 - m_1)!(j_2 + m_2)!(j_2 - m_2)!(j + m)!(j - m)!!} \frac{1}{k!(j_1 + j_2 - j - k)!(j_1 - m_1 - k)!(j_2 + m_2 - k)!(j - j_2 + m_1 + k)!(j - j_1 - m_2 + k)!}. \]

With the aid of this formula, the following symmetry relations between Clebsch-Gordan coefficients (see Rose, 1957, chap. 3) may be established:

\[ C(j_1, j_2, j; -m_1, -m_2, -m) = (-1)^{j_1 + j_2 - j} C(j_1, j_2, j; m_1, m_2, m), \quad (1.69) \]
\[ C(j_2, j_1, j; m_2, m_1, m) = (-1)^{j_1 + j_2 - j} C(j_1, j_2, j; m_1, m_2, m), \quad (1.70) \]
\[ C(j_1, j; j_2; m_1, -m, -m_2) = (-1)^{j_1 - m_1} \sqrt{\frac{2j_2 + 1}{2j + 1}} C(j_1, j_2, j; m_1, m_2, m). \quad (1.71) \]

Expressions for other permutations of the arguments can be inferred from these basic three. As an application of these symmetry relations, we combine the easily derived equation

\[ C(j_1, 0; j; m_1, 0, m) = \delta_{j_1, j} \delta_{m_1, m}, \quad (1.72) \]
with Eq.(1.71) to give

\[ C(j_1, 0; m_1, -m, 0) = \frac{(-1)^{j_1 - m_1}}{\sqrt{2j + 1}} \delta_{j_1, j} \delta_{m_1, m}. \quad (1.73) \]

Several other useful formulas may also be derived directly from Eq. (1.68):

\[ C(j_1, j_2, j_1 + j_2; m_1, m_2, m_1 + m_2) = \sqrt{\frac{(2j_1)!(2j_2)!(j_1 + j_2 + m_1 + m_2)!(j_1 + j_2 - m_1 - m_2)!}{(2j_1 + 2j_2)!(j_1 - m_1)!(j_1 + m_1)!(j_2 - m_2)!(j_2 + m_2)!}}, \quad (1.74) \]
\[ C(j_1, j_2, j; j_1, m - j_1, m) = \sqrt{\frac{(2j + 1)!(j_2 - j_2 + j)!(j_1 + j_2 - m)!(j + m)!}{(j_1 + j_2 - j)!(j_1 - j_2 + j)!(j_1 + j_2 + j + 1)!(j_2 - j_1 + m)!(j - m)!}}. \quad (1.75) \]

### 1.3.1 Three-j symbols

The symmetry relations between the Clebsch-Gordan coefficients are made more transparent by introducing the Wigner three-j symbols defined by:

\[ \left( \begin{array}{ccc} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{array} \right) = \frac{(-1)^{j_1 - j_2 - m_3}}{\sqrt{2j_3 + 1}} C(j_1, j_2, j_3; m_1, m_2, -m_3). \quad (1.76) \]

The three-j symbol vanishes unless

\[ m_1 + m_2 + m_3 = 0. \quad (1.77) \]
The three-j symbols have a high degree of symmetry under interchange of columns; they are symmetric under even permutations of the indices (1, 2, 3):

\[
\begin{pmatrix}
  j_3 & j_1 & j_2 \\
  m_3 & m_1 & m_2
\end{pmatrix}
= \begin{pmatrix}
  j_2 & j_3 & j_1 \\
  m_2 & m_3 & m_1
\end{pmatrix}
= \begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix},
\] (1.78)

and they change by a phase under odd permutations of (1, 2, 3), e.g.:

\[
\begin{pmatrix}
  j_2 & j_1 & j_3 \\
  m_2 & m_1 & m_3
\end{pmatrix}
= (-1)^{j_1 + j_2 + j_3} \begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}.
\] (1.79)

On changing the sign of \(m_1, m_2\) and \(m_3\), the three-j symbols transform according to

\[
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  -m_1 & -m_2 & -m_3
\end{pmatrix}
= (-1)^{j_1 + j_2 + j_3} \begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}.
\] (1.80)

The orthogonality relation (1.61) may be rewritten in terms of three-j symbols as

\[
\sum_{m_1, m_2} \begin{pmatrix}
  j_1 & j_2 & j_3' \\
  m_1 & m_2 & m_3'
\end{pmatrix}
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
= \frac{1}{2j_3 + 1} \delta_{j_3 j_3'} \delta_{m_3 m_3'},
\] (1.81)

and the orthogonality relation (1.63) can be rewritten

\[
\sum_{j_3, m_3} (2j_3 + 1) \begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
\begin{pmatrix}
  j_1 & j_2 & j_3' \\
  m_1' & m_2' & m_3'
\end{pmatrix}
= \delta_{m_1 m_1'} \delta_{m_2 m_2'}. \] (1.82)

We refer to these equations as “orthogonality relations for three-j symbols”.

The following specific results for three-j symbols are easily obtained from Eqs. (1.73-1.75) of the previous subsection:

\[
\begin{pmatrix}
  j & j & 0 \\
  m & -m & 0
\end{pmatrix}
= \frac{(-1)^{j-m}}{\sqrt{2j+1}} \delta_{j1, j} \delta_{m1, m},
\] (1.83)

\[
\begin{pmatrix}
  j_1 & j_2 & j_1 + j_2 \\
  m_1 & m_2 & -m_1 - m_2
\end{pmatrix}
= (-1)^{j_1 - j_2 + m_1 + m_2} \times
\sqrt{\frac{(2j_1)!(2j_2)!(j_1 + j_2 + m_1 + m_2)!(j_1 + j_2 - m_1 - m_2)!}{(2j_1 + 2j_2 + 1)!(j_1 - m_1)!(j_1 + m_1)!(j_2 - m_2)!(j_2 + m_2)!}},
\] (1.84)

\[
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
= (-1)^{-j_2 + j_3 + m_3} \times
\sqrt{\frac{(2j_1)! (j_2 - j_1 + j_3)!(j_1 + j_2 + m_3)!(j_3 - m_3)!}{(j_1 + j_2 + j_3 + 1)!(j_1 - j_2 + j_3)!(j_1 + j_2 - j_3)!(j_2 - j_1 + j_3)!(j_2 - j_1 - m_3)!(j_3 + m_3)!}}.
\] (1.85)

From the symmetry relation (1.80), it follows that

\[
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  0 & 0 & 0
\end{pmatrix}
= 0,
\]
unless \( J = j_1 + j_2 + j_3 \) is even. In that case, we may write

\[
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  0 & 0 & 0
\end{pmatrix}
= (-1)^{J/2} \sqrt{\frac{(J - 2j_1)!(J - 2j_2)!(J - 2j_3)!}{(J+1)!}}
\frac{(J/2)!}{(J/2 - j_1)!(J/2 - j_2)!(J/2 - j_3)!}.
\] (1.86)

Two Maple programs, based on Eq. (1.68), to evaluate Clebsch-Gordan coefficients (CGC.map) and three-\( j \) symbols (THREEJ.map), are provided as part of the course material.

### 1.3.2 Irreducible Tensor Operators

A family of \( 2k + 1 \) operators \( T^k_q \), with \( q = -k, -k + 1, \ldots, k \), satisfying the commutation relations

\[
[J_z, T^k_q] = qT^k_q, \quad (1.87)
\]

\[
[J_{\pm}, T^k_q] = \sqrt{(k \pm q + 1)(k \mp q)} T^{k \pm 1}_q, \quad (1.88)
\]

with the angular momentum operators \( J_z \) and \( J_{\pm} = J_x \pm iJ_y \), are called irreducible tensor operators of rank \( k \). The spherical harmonics \( Y_{lm}(\theta, \phi) \) are, according to this definition, irreducible tensor operators of rank \( l \). The operators \( J_\mu \) defined by

\[
J_\mu = \begin{cases} 
-\frac{1}{\sqrt{2}}(J_x + iJ_y), & \mu = +1, \\
J_z, & \mu = 0, \\
\frac{1}{\sqrt{2}}(J_x - iJ_y), & \mu = -1,
\end{cases}
\] (1.89)

are also irreducible tensor operators; in this case of rank 1.

Matrix elements of irreducible tensor operators between angular momentum states are evaluated using the Wigner-Eckart theorem (Wigner, 1931; Eckart, 1930):

\[
\langle j_1, m_1 | T^k_q | j_2, m_2 \rangle = (-1)^{j_1 - m_1} \begin{pmatrix}
  j_1 & k & j_2 \\
  -m_1 & q & m_2
\end{pmatrix} \langle j_1 || T^k || j_2 \rangle. \quad (1.90)
\]

In this equation, the quantity \( \langle j_1 || T^k || j_2 \rangle \), called the reduced matrix element of the tensor operator \( T^k \), is independent of the magnetic quantum numbers \( m_1 \), \( m_2 \) and \( q \).

To prove the Wigner-Eckart theorem, we note that the matrix elements \( \langle j_1 m_1 | T^k_q | j_2 m_2 \rangle \) satisfies the recurrence relations

\[
\sqrt{(j_1 \mp m_1 + 1)(j_1 \pm m_1)} \langle j_1 m_1 \pm 1 | T^k_q | j_2 m_2 \rangle = \\
\sqrt{(j_2 \mp m_2 + 1)(j_2 \pm m_2)} \langle j_1 m_1 | T^k_q | j_2 m_2 \pm 1 \rangle \\
+ \sqrt{(k \mp q + 1)(k \pm q)} \langle j_1 m_1 | T^k_{q \pm 1} | j_2 m_2 \rangle. \quad (1.91)
\]
They are, therefore, proportional to the Clebsch-Gordan coefficients
\[ C(j_2, k, j_1; m_2, q, m_1) = \sqrt{2j_1 + 1} (-1)^{j_1 - m_1} \left( \begin{array}{ccc} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{array} \right), \] (1.92)
the proportionality in Eq.(1.90) is established.

As a first application of the Wigner-Eckart theorem, consider the matrix
element of the irreducible tensor operator \( J_\mu \):
\[ \langle j_1, m_1 | J_\mu | j_2, m_2 \rangle = (-1)^{j_1 - m_1} \left( \begin{array}{ccc} j_1 & 1 & j_2 \\ -m_1 & 0 & m_1 \end{array} \right) \langle j_1 || J || j_2 \rangle. \] (1.93)
The reduced matrix element \( \langle j_1 || J || j_2 \rangle \) can be determined by evaluating both
sides of Eq.(1.93) in the special case \( \mu = 0 \). We find
\[ \langle j_1 || J || j_2 \rangle = \sqrt{j_1(j_1 + 1)(2j_1 + 1)} \delta_{j_1 j_2}, \] (1.94)
where we have made use of the fact that
\[ \left( \begin{array}{ccc} j_1 & 1 & j_2 \\ -m_1 & 0 & m_1 \end{array} \right) = (-1)^{j_1 - m_1} \frac{m_1}{\sqrt{j_1(j_1 + 1)(2j_1 + 1)}}. \] (1.95)

As a second application, we consider matrix elements of the irreducible tensor
operator \( C^k_q \),
\[ C^k_q = \sqrt{\frac{4\pi}{2k + 1}} Y_{kq}(\theta, \phi), \]
between orbital angular momentum eigenstates:
\[ \langle l_1 m_1 | C^k_q | l_2 m_2 \rangle = (-1)^{l_1 - m_1} \left( \begin{array}{ccc} l_1 & k & l_2 \\ -m_1 & q & m_2 \end{array} \right) \langle l_1 || C^k || l_2 \rangle. \] (1.96)
The left-hand side of Eq.(1.96) is (up to a factor) the integral of three spherical
harmonics. It follows that
\[ Y_{kq}(\Omega) Y_{l_2 m_2}(\Omega) = \sum_{l_1} \sqrt{\frac{2k + 1}{4\pi}} \times \]
\[ (-1)^{l_1 - m_1} \left( \begin{array}{ccc} l_1 & k & l_2 \\ -m_1 & q & m_2 \end{array} \right) \langle l_1 || C^k || l_2 \rangle Y_{l_1 m_1}(\Omega), \] (1.97)
where we use the symbol \( \Omega \) to designate the angles \( \theta \) and \( \phi \). With the aid of
the orthogonality relation (1.81) for the three-j symbols, we invert Eq.(1.97) to
find
\[ \sum_{m_2 q} \left( \begin{array}{ccc} l_1 & k & l_2 \\ -m_1 & q & m_2 \end{array} \right) Y_{kq}(\Omega) Y_{l_2 m_2}(\Omega) = \]
\[ \sqrt{\frac{2k + 1}{4\pi}} \frac{(-1)^{l_1 - m_1}}{2l_1 + 1} \langle l_1 || C^k || l_2 \rangle Y_{l_1 m_1}(\Omega). \] (1.98)
Evaluating both sides of this equation at $\theta = 0$, we obtain
\[
\langle l_1|C^k|l_2 \rangle = (-1)^{l_1} \sqrt{(2l_1 + 1)(2l_2 + 1)} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix}.
\] (1.99)

1.4 Graphical Representation - Basic rules

In subsequent chapters we will be required to carry out sums of products of three-j symbols over magnetic quantum numbers $m_j$. Such sums can be formulated in terms of a set of graphical rules, that allow one to carry out the required calculations efficiently. There are several ways of introducing graphical rules for angular momentum summations (Judd, 1963; Jucys et al., 1964; Varshalovich et al., 1988). Here, we follow those introduced by Lindgren and Morrison (1985).

The basic graphical element is a line segment labeled at each end by a pair of angular momentum indices $j_m$. The segment with $j_1 m_1$ at one end and $j_2 m_2$ at the other end is the graphical representation of $\delta_{j_1 j_2} \delta_{m_1 m_2}$; thus
\[
\begin{align*}
\sum_{m_2} j_1 m_1 j_2 m_2 j_3 m_3 &= \delta_{j_3 j_2} \delta_{m_1 m_2}. \\
\end{align*}
\] (1.100)

A directed line segment, which is depicted by attaching an arrow to a line segment, is a second important graphical element. An arrow pointing from $j_1 m_1$ to $j_2 m_2$ represents the identity:
\[
\begin{align*}
\sum_{m_2} j_1 m_1 j_2 m_2 j_3 m_3 &= \delta_{j_3 j_2} \delta_{m_1 m_2}. \\
\end{align*}
\] (1.101)

Reversing the direction of the arrow leads to
\[
\begin{align*}
\sum_{m_2} j_1 m_1 j_2 m_2 j_3 m_3 &= (-1)^{j_2 m_2} \delta_{j_1 j_2} \delta_{m_1 m_2}. \\
\end{align*}
\] (1.102)

Connecting together two line segments at ends carrying identical values of $j m$ is the graphical representation of a sum over the magnetic quantum number $m$. Therefore,
\[
\begin{align*}
\sum_{m_2} j_1 m_1 j_2 m_2 j_3 m_3 &= \delta_{j_3 j_2} \delta_{m_1 m_2}. \\
\end{align*}
\] (1.103)

It follows that two arrows directed in the same direction give an overall phase,
\[
\begin{align*}
\sum_{m_2} j_1 m_1 j_2 m_2 &= (-1)^{j_2 m_2} \delta_{j_1 j_2} \delta_{m_1 m_2}, \\
\end{align*}
\] (1.104)

and that two arrows pointing in opposite directions cancel,
\[
\begin{align*}
\sum_{m_2} j_1 m_1 j_2 m_2 &= \delta_{j_1 j_2} \delta_{m_1 m_2}. \\
\end{align*}
\] (1.105)

Another important graphical element is the three-j symbol, which is represented as
\[
\binom{j_1 \ j_2 \ j_3}{m_1 \ m_2 \ m_3} = \binom{j_1 m_3}{j_2 m_2}.
\] (1.106)
The + sign designates that the lines associated with \( j_1 m_1, j_2 m_2, \) and \( j_3 m_3 \) are oriented in such a way that a counter-clockwise rotation leads from \( j_1 m_1 \) to \( j_2 m_2 \) to \( j_3 m_3 \). We use a − sign to designate that a clockwise rotation leads from \( j_1 m_1 \) to \( j_2 m_2 \) to \( j_3 m_3 \). Thus, we can rewrite Eq.(1.106) as

\[
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix} = - \frac{j_1 m_1}{j_1 m_3} .
\]

The symmetry relation of Eq.(1.78) is represented by the graphical identity:

\[
\begin{pmatrix}
  j_1 m_1 \\
  j_1 m_2 \\
  j_2 m_2 \\
  j_3 m_3
\end{pmatrix} = \begin{pmatrix}
  j_1 m_1 \\
  j_1 m_2 \\
  j_2 m_2 \\
  j_3 m_3
\end{pmatrix} .
\]

The symmetry relation (1.79) leads to the graphical relation:

\[
\begin{pmatrix}
  j_1 m_1 \\
  j_1 m_2 \\
  j_2 m_2 \\
  j_3 m_3
\end{pmatrix} = (-1)^{j_1 + j_2 + j_3} \begin{pmatrix}
  j_1 m_1 \\
  j_1 m_2 \\
  j_2 m_2 \\
  j_1 m_1
\end{pmatrix} .
\]

One can attach directed lines and three-j symbols to form combinations such as

\[
\begin{pmatrix}
  j_1 m_1 \\
  j_2 m_2 \\
  j_3 m_3
\end{pmatrix} = (-1)^{j_1 - m_1} \begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix} .
\]

Using this, the Wigner-Eckart theorem can be written

\[
\langle j_1 m_1 | T^k_q | j_2 m_2 \rangle = - \frac{k}{j_2 m_2} \langle j_1 || T^k || j_2 \rangle .
\]

Furthermore, with this convention, we can write

\[
C(j_1, j_2, j_3; m_1, m_2, m_3) = \sqrt{2j_3 + 1} - \frac{j_3 m_3}{j_2 m_2} .
\]

Factors of \( \sqrt{2j_3 + 1} \) are represented by thickening part of the corresponding line segment. Thus, we have the following representation for a Clebsch-Gordan coefficient:

\[
C(j_1, j_2, j_3; m_1, m_2, m_3) = - \frac{j_3 m_3}{j_2 m_2} .
\]
The orthogonality relation for three-j symbols (1.81) can be written in graphical terms as

\[
\sum_{m_1 m_2} j_1' m_1' \quad j_3' m_3' \quad j_1 \quad j_2 \quad j_3 \quad j_3' \quad j_1' \quad j_2' \quad j_3' = \frac{1}{2 j_3 + 1} \delta_{j_3 j_3'} \delta_{m_3 m_3'} .
\]  
(1.114)

Another very useful graphical identity is

\[
\begin{aligned}
&\sum_{j_1' m_1'} j_1' m_1' \quad j_2' m_2' \quad j_3' m_3' \quad j_1 \quad j_2 \quad j_3 \quad j_3' = \\
&\quad \delta_{j_1 j_2} \delta_{m_1 m_2} \delta_{j_0} \sqrt{\frac{2 j_3 + 1}{2 j_1 + 1}} .
\end{aligned}
\]  
(1.115)

### 1.5 Spinor and Vector Spherical Harmonics

#### 1.5.1 Spherical Spinors

We combine spherical harmonics, which are eigenstates of \( L^2 \) and \( L_z \), and spinors, which are eigenstates of \( S^2 \) and \( S_z \) to form eigenstates of \( J^2 \) and \( J_z \), referred to as spherical spinors. Spherical spinors are denoted by \( \Omega_{jlm}(\theta, \phi) \) and are defined by the equation

\[
\Omega_{jlm}(\theta, \phi) = \sum_{\mu} C(l, 1/2, j; m - \mu, \mu, m) Y_{l,m-\mu}(\theta, \phi) \chi_\mu .
\]  
(1.116)

From Table 1.1, we obtain the following explicit formulas for spherical spinors having the two possible values, \( j = l \pm 1/2 \):

\[
\begin{align*}
\Omega_{l+1/2,l,m}(\theta, \phi) &= \left( \begin{array}{c} \sqrt{\frac{l+m+1/2}{2l+1}} Y_{l,m-1/2}(\theta, \phi) \\ \sqrt{\frac{l-m+1/2}{2l+1}} Y_{l,m+1/2}(\theta, \phi) \end{array} \right) , \\
\Omega_{l-1/2,l,m}(\theta, \phi) &= \left( \begin{array}{c} -\sqrt{\frac{l+m+1/2}{2l+1}} Y_{l,m-1/2}(\theta, \phi) \\ \sqrt{\frac{l-m+1/2}{2l+1}} Y_{l,m+1/2}(\theta, \phi) \end{array} \right) .
\end{align*}
\]  
(1.117, 1.118)

Spherical spinors are eigenfunctions of \( \sigma \cdot L \) and, therefore, of the operator

\[ K = -1 - \sigma \cdot L . \]

The eigenvalue equation for \( K \) is

\[
K \Omega_{jlm}(\theta, \phi) = \kappa \Omega_{jlm}(\theta, \phi) ,
\]  
(1.119)

where the (integer) eigenvalues are \( \kappa = -l - 1 \) for \( j = l + 1/2 \), and \( \kappa = l \) for \( j = l - 1/2 \). These values can be summarized as \( \kappa = \mp (j + 1/2) \) for \( j = l \pm 1/2 \). The value of \( \kappa \) determines both \( j \) and \( l \). Consequently, the more compact notation, \( \Omega_{\kappa m} = \Omega_{jlm} \) can be used.
Spherical spinors satisfy the orthogonality relations

\[ \int_{0}^{\pi} \sin \theta \, d\theta \int_{0}^{2\pi} d\phi \, \Omega_{\kappa m'}^{\dagger}(\theta, \phi) \Omega_{\kappa m}(\theta, \phi) = \delta_{\kappa', \kappa} \delta_{m', m}. \]  

(1.120)

The parity operator \( P \) maps \( r \to -r \). In spherical coordinates, the operator \( P \) transforms \( \phi \to \phi + \pi \) and \( \theta \to \pi - \theta \). Under a parity transformation,

\[ PY_{lm}(\theta, \phi) = Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi). \]  

(1.121)

It follows that the spherical spinors are eigenfunctions of \( P \) having eigenvalues \( p = (-1)^l \). The two spinors \( \Omega_{\kappa m}(\theta, \phi) \) and \( \Omega_{-\kappa m}(\theta, \phi) \), corresponding to the same value of \( j \), have values of \( l \) differing by one unit and, therefore, have opposite parity.

It is interesting to examine the behavior of spherical spinors under the operator \( \sigma \cdot \hat{r} \), where \( \hat{r} = r/r \). This operator satisfies the identity

\[ \sigma \cdot \hat{r} \sigma \cdot \hat{r} = 1, \]  

(1.122)

which follows from the commutation relations for the Pauli matrices. Furthermore, the operator \( \sigma \cdot \hat{r} \) commutes with \( J \) and, therefore, leaves the value of \( j \) unchanged. The parity operation changes the sign of \( \sigma \cdot \hat{r} \). Since the value of \( j \) remains unchanged, and since the sign of \( \sigma \cdot \hat{r} \) changes under the parity transformation, it follows that

\[ \sigma \cdot \hat{r} \Omega_{\kappa m}(\theta, \phi) = a\Omega_{-\kappa m}(\theta, \phi), \]  

where \( a \) is a constant. Evaluating both sides of Eq.(1.123) in a coordinate system where \( \theta = 0 \), one easily establishes \( a = -1 \). Therefore,

\[ \sigma \cdot \hat{r} \Omega_{\kappa m}(\theta, \phi) = -\Omega_{-\kappa m}(\theta, \phi). \]  

(1.124)

Now, let us consider the operator \( \sigma \cdot p \). Using Eq.(1.122), it follows that

\[ \sigma \cdot p = \sigma \cdot \hat{r} \sigma \cdot p \sigma \cdot \hat{r} = -i\sigma \cdot \hat{r} \left( i\hat{r} \cdot p - \frac{\sigma \times p}{r} \right). \]  

(1.125)

In deriving this equation, we have made use of the identity in Eq.(1.50).

From Eq.(1.125), it follows that

\[ \sigma \cdot p f(r) \Omega_{\kappa m}(\theta, \phi) = i \left( \frac{d f}{d r} + \frac{\kappa + 1}{r} f \right) \Omega_{-\kappa m}(\theta, \phi). \]  

(1.126)

This identities (1.124) and (1.126) are important in the reduction of the central-field Dirac equation to radial form.
1.5. Vector Spherical Harmonics

Following the procedure used to construct spherical spinors, one combines spherical harmonics with spherical basis vectors to form vector spherical harmonics $Y_{JLM}(\theta, \phi)$:

$$Y_{JLM}(\theta, \phi) = \sum_\sigma C(L, 1, J; M - \sigma, \sigma, M) Y_{LM-\sigma}(\theta, \phi) \xi_\sigma.$$  \hspace{1cm} (1.127)

The vector spherical harmonics are eigenfunctions of $J^2$ and $J_z$. The eigenvalues of $J^2$ are $J(J + 1)$, where $J$ is an integer. For $J > 0$, there are three corresponding values of $L$: $L = J \pm 1$ and $L = J$. For $J = 0$, the only possible values of $L$ are $L = 0$ and $L = 1$. Explicit forms for the vector spherical harmonics can be constructed with the aid of Table 1.2. Vector spherical harmonics satisfy the orthogonality relations

$$\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta Y_{J'L'M'}^*(\theta, \phi) Y_{JLM}(\theta, \phi) = \delta_{J'J} \delta_{L'L} \delta_{M'M}. \hspace{1cm} (1.128)$$

Vector functions, such as the electromagnetic vector potential, can be expanded in terms of vector spherical harmonics. As an example of such an expansion, let us consider

$$\hat{\mathbf{r}} Y_{lm}(\theta, \phi) = \sum_{JLM} a_{JLM} Y_{JLM}(\theta, \phi). \hspace{1cm} (1.129)$$

With the aid of the orthogonality relation, this equation can be inverted to give

$$a_{JLM} = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta Y_{JLM}^* \hat{\mathbf{r}} Y_{lm}(\theta, \phi).$$

This equation can be rewritten with the aid of (1.56) as

$$a_{JLM} = \sum_{\mu \nu} C(L, 1, J; M - \mu, \mu, M) \xi_\mu^\dagger \xi_\nu \langle l, m | C_\nu^1 | L, M - \mu \rangle. \hspace{1cm} (1.130)$$

Using the known expression for the matrix element of the $C_\nu^1$ tensor operator from Eqs.(1.96,1.99), one obtains

$$a_{JLM} = \sqrt{\frac{2L + 1}{2l + 1}} C(L, 1, l; 0, 0, 0) \delta_{Jl} \delta_{Mm} \hspace{1cm} (1.131)$$

$$= \left( \sqrt{\frac{l}{2l + 1}} \delta_{ll-1} - \sqrt{\frac{l + 1}{2l + 1}} \delta_{ll+1} \right) \delta_{Jl} \delta_{Mm}. \hspace{1cm} (1.132)$$

Therefore, one may write

$$\hat{\mathbf{r}} Y_{J'M'}(\theta, \phi) = \sqrt{\frac{J}{2J + 1}} Y_{JJ-1M}(\theta, \phi) - \sqrt{\frac{J + 1}{2J + 1}} Y_{JJ+1M}(\theta, \phi). \hspace{1cm} (1.133)$$
This vector is in the direction \( \hat{\mathbf{r}} \) and is, therefore, referred to as a longitudinal vector spherical harmonic. Following the notation of Akhiezer and Berestetsky, we introduce \( Y_{JM}^{(-1)}(\theta, \phi) = \hat{\mathbf{r}} Y_{JM}(\theta, \phi) \). The vector \( Y_{JM}(\theta, \phi) \) is orthogonal to \( Y_{JM}^{(-1)}(\theta, \phi) \), and is, therefore, transverse. The combination
\[
\sqrt{\frac{J+1}{2J+1}} Y_{J-J+1M}(\theta, \phi) + \sqrt{\frac{J}{2J+1}} Y_{J+1J+1M}(\theta, \phi).
\]
is also orthogonal to \( Y_{JM}^{(-1)}(\theta, \phi) \) and gives a second transverse spherical vector. It is easily shown that the three vector spherical harmonics
\[
Y_{JM}^{(-1)}(\theta, \phi) = \sqrt{\frac{J}{2J+1}} Y_{J-J+1M}(\theta, \phi) - \sqrt{\frac{J+1}{2J+1}} Y_{J+1J+1M}(\theta, \phi)
\]
\[
Y_{JM}^{(0)}(\theta, \phi) = Y_{JM}(\theta, \phi)
\]
\[
Y_{JM}^{(1)}(\theta, \phi) = \sqrt{\frac{J+1}{2J+1}} Y_{J-J+1M}(\theta, \phi) + \sqrt{\frac{J}{2J+1}} Y_{J+1J+1M}(\theta, \phi)
\]
satisfy the orthonormality relation:
\[
\int d\Omega Y_{J-M}^{(\lambda)\dagger}(\Omega) Y_{J-M'}^{(\lambda')}(\Omega) = \delta_{JJ'} \delta_{MM'} \delta_{\lambda\lambda'}.
\]
The following three relations may be also be proven without difficulty:
\[
Y_{JM}^{(-1)}(\theta, \phi) = \hat{\mathbf{r}} Y_{JM}(\theta, \phi),
\]
\[
Y_{JM}^{(0)}(\theta, \phi) = \frac{1}{\sqrt{J(J+1)}} \mathbf{L} Y_{JM}(\theta, \phi),
\]
\[
Y_{JM}^{(1)}(\theta, \phi) = \frac{r}{\sqrt{J(J+1)}} \nabla Y_{JM}(\theta, \phi).
\]
The first of these is just a definition; we leave the proof of the other two as exercises.
Chapter 2

Central-Field Schrödinger Equation

We begin the present discussion with a review of the Schrödinger equation for a single electron in a central potential $V(r)$. First, we decompose the Schrödinger wave function in spherical coordinates and set up the equation governing the radial wave function. Following this, we consider analytical solutions to the radial Schrödinger equation for the special case of a Coulomb potential. The analytical solutions provide a guide for our later numerical analysis. This review of basic quantum mechanics is followed by a discussion of the numerical solution to the radial Schrödinger equation.

The single-electron Schrödinger equation is used to describe the electronic states of an atom in the independent-particle approximation, a simple approximation for a many-particle system in which each electron is assumed to move independently in a potential that accounts for the nuclear field and the field of the remaining electrons. There are various methods for determining an approximate potential. Among these are the Thomas-Fermi theory and the Hartree-Fock theory, both of which will be taken up later. In the following section, we assume that an appropriate central potential has been given and we concentrate on solving the resulting single-particle Schrödinger equation.

2.1 Radial Schrödinger Equation

First, we review the separation in spherical coordinates of the Schrödinger equation for an electron moving in a central potential $V(r)$. We assume that $V(r) = V_{\text{nuc}}(r) + U(r)$ is the sum of a nuclear potential

$$V_{\text{nuc}}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r},$$

and an average potential $U(r)$ approximating the electron-electron interaction.
We let $\psi(r)$ designate the single-particle wave function. In the sequel, we refer to this wave function as an orbital to distinguish it from a many-particle wave function. The orbital $\psi(r)$ satisfies the Schrödinger equation

$$h\psi = E\psi,$$

(2.1)

where the Hamiltonian $h$ is given by

$$h = \frac{p^2}{2m} + V(r).$$

(2.2)

In Eq.(2.2), $p = -i\hbar \nabla$ is the momentum operator and $m$ is the electron’s mass. The Schrödinger equation, when expressed in spherical coordinates, $(r, \theta, \phi)$, becomes

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V(r)) \psi = 0.$$

(2.3)

We seek a solution $\psi(r, \theta, \phi)$ that can be expressed as a product of a function $P$ of $r$ only, and a function $Y$ of the angles $\theta$ and $\phi$:

$$\psi(r) = \frac{1}{r} P(r) Y(\theta, \phi).$$

(2.4)

Substituting this ansatz into Eq.(2.3), we obtain the following pair of equations for the functions $P$ and $Y$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \lambda Y = 0,$$

(2.5)

$$\frac{d^2 P}{dr^2} + \frac{2m}{\hbar^2} \left( E - V(r) - \frac{\lambda \hbar^2}{2mr^2} \right) P = 0,$$

(2.6)

where $\lambda$ is an arbitrary separation constant.

If we set $\lambda = \ell(\ell + 1)$, where $\ell = 0, 1, 2, \cdots$ is an integer, then the solutions to Eq.(2.5) that are finite and single valued for all angles are the spherical harmonics $Y_{\ell m}(\theta, \phi)$.

The normalization condition for the wave function $\psi(r)$ is

$$\int d^3r |\psi(r)|^2 = 1,$$

(2.7)

which leads to normalization condition

$$\int_0^\infty dr P^2(r) = 1,$$

(2.8)

for the radial function $P(r)$. 


The expectation value $\langle O \rangle$ of an operator $O$ in the state $\psi$ is given by

$$\langle O \rangle = \int d^3r \psi^\dagger(r) O \psi(r).$$  \hspace{1cm} (2.9)

In the state described by $\psi(r) = \frac{P(r)}{r} Y_\ell m(\theta, \phi)$, we have

$$\langle L^2 \rangle = \ell(\ell+1)\hbar^2,$$  \hspace{1cm} (2.10)

$$\langle L_z \rangle = m\hbar.$$  \hspace{1cm} (2.11)

### 2.2 Coulomb Wave Functions

The basic equation for our subsequent numerical studies is the radial Schrödinger equation (2.6) with the separation constant $\lambda = \ell(\ell+1)$:

$$\frac{d^2 P}{dr^2} + \frac{2m}{\hbar^2} \left( E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2mr^2} \right) P = 0.$$  \hspace{1cm} (2.12)

We start our discussion of this equation by considering the special case $V(r) = V_{\text{nuc}}(r)$.

**Atomic Units**: Before we start our analysis, it is convenient to introduce atomic units in order to rid the equation of unnecessary physical constants. Atomic units are defined by requiring that the electron’s mass $m$, the electron’s charge $|e|/\sqrt{4\pi\epsilon_0}$, and Planck’s constant $\hbar$, all have the value 1. The atomic unit of length is the Bohr radius, $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 0.529177\ldots \text{Å}$, and the atomic unit of energy is $me^4/(4\pi\epsilon_0\hbar)^2 = 27.2114\ldots \text{eV}$. Units for other quantities can be readily worked out from these basic few. For example, the atomic unit of velocity is $c\alpha$, where $c$ is the speed of light and $\alpha$ is Sommerfeld’s fine structure constant: $\alpha = e^2/4\pi\epsilon_0\hbar c = 1/137.0359895\ldots$.

In atomic units, Eq.(2.12) becomes

$$\frac{d^2 P}{dr^2} + 2 \left( E + \frac{Z}{r} - \frac{\ell(\ell+1)}{2r^2} \right) P = 0.$$  \hspace{1cm} (2.13)

We seek solutions to the radial Schrödinger equation (2.13) that satisfy the normalization condition (2.8). Such solutions exist only for certain discrete values of the energy, $E = E_{n\ell}$, the energy eigenvalues. Our problem is to determine these energy eigenvalues and the associated eigenfunctions, $P_{n\ell}(r)$. If we have two eigenfunctions, $P_{n\ell}(r)$ and $P_{m\ell}(r)$, belonging to the same angular momentum quantum number $\ell$ but to distinct eigenvalues, $E_{n\ell} \neq E_{m\ell}$, then it follows from Eq.(2.13) that

$$\int_0^\infty dr P_{n\ell}(r) P_{m\ell}(r) = 0.$$  \hspace{1cm} (2.14)
Near $r = 0$, solutions to Eq. (2.13) take on one of the following limiting forms:

$$P(r) \to \begin{cases} r^{\ell+1} & \text{regular at the origin, or} \\ r^{-\ell} & \text{irregular at the origin} \end{cases}$$

(2.15)

Since we seek normalizable solutions, we must require that our solutions be of the first type, regular at the origin. The desired solution grows as $r^{\ell+1}$ as $r$ moves outward from the origin while the complementary solution decreases as $r^{-\ell}$ as $r$ increases.

Since the potential vanishes as $r \to \infty$, it follows that

$$P(r) \to \begin{cases} e^{-\lambda r} & \text{regular at infinity, or} \\ e^{\lambda r} & \text{irregular at infinity} \end{cases}$$

(2.16)

where $\lambda = \sqrt{-2E}$. Again, the normalizability constraint (2.8) forces us to seek solutions of the first type, regular at infinity. Substituting

$$P(r) = r^{\ell+1} e^{-\lambda r} F(r)$$

(2.17)

into Eq. (2.13), we find that $F(x)$ satisfies Kummer’s equation

$$x \frac{d^2 F}{dx^2} + (b - x) \frac{dF}{dx} - aF = 0,$$

(2.18)

where $x = 2\lambda r$, $a = \ell + 1 - Z/\lambda$, and $b = 2(\ell + 1)$. The solutions to Eq. (2.18) that are regular at the origin are the Confluent Hypergeometric functions (Magnus and Oberhettinger, 1949, chap. VI):

$$F(a, b, x) = 1 + \frac{a}{b} x + \frac{a(a + 1)}{b(b + 1)} \frac{x^2}{2!} + \frac{a(a + 1)(a + 2)}{b(b + 1)(b + 2)} \frac{x^3}{3!} + \cdots$$

$$+ \frac{a(a + 1) \cdots (a + k - 1)}{b(b + 1) \cdots (b + k - 1)} \frac{x^k}{k!} + \cdots.$$  

(2.19)

This series has the asymptotic behavior

$$F(a, b, x) \to \frac{\Gamma(b)}{\Gamma(a)} e^x x^{a-b} [1 + O(|x|^{-1})],$$

(2.20)

for large $|x|$. The resulting radial wave function, therefore, grows exponentially unless the coefficient of the exponential in Eq. (2.20) vanishes. Since $\Gamma(b) \neq 0$, we must require $\Gamma(a) = \infty$ to obtain normalizable solutions. The function $\Gamma(a) = \infty$ when $a$ vanishes or when $a$ is a negative integer. Thus, normalizable wave functions are only possible when $a = -n_r$ with $n_r = 0, 1, 2, \cdots$. The quantity $n_r$ is called the radial quantum number. With $a = -n_r$, the Confluent Hypergeometric function in Eq. (2.19) reduces to a polynomial of degree $n_r$. The integer $n_r$ equals the number of nodes (zeros) of the radial wave function for $r > 0$. From $a = \ell + 1 - Z/\lambda$, it follows that

$$\lambda = \lambda_n = \frac{Z}{n_r + \ell + 1} = \frac{Z}{n},$$
2.2. COULOMB WAVE FUNCTIONS

with \( n = n_r + \ell + 1 \). The positive integer \( n \) is called the principal quantum number. The relation \( \lambda = \sqrt{-2E} \) leads immediately to the energy eigenvalue equation

\[
E = E_n = -\frac{\lambda^2}{2} = -\frac{Z^2}{2n^2}.
\]  

(2.21)

There are \( n \) distinct radial wave functions corresponding to \( E_n \). These are the functions \( P_{n\ell}(r) \) with \( \ell = 0, 1, \ldots, n-1 \). The radial function is, therefore, given by

\[
P_{n\ell}(r) = N_{n\ell} (2Zr/n)^{\ell+1}e^{-Zr/n} F(-n + \ell + 1, 2\ell + 2, 2Zr/n),
\]  

(2.22)

where \( N_{n\ell} \) is a normalization constant. This constant is determined by requiring

\[
N_{n\ell}^2 \int_0^\infty dx (2Zr/n)^{2\ell+2}e^{-2Zr/n} F^2(-n + \ell + 1, 2\ell + 2, 2Zr/n) = 1.
\]  

(2.23)

This integral can be evaluated analytically to give

\[
N_{n\ell} = \frac{1}{n(2\ell + 1)!} \sqrt{\frac{Z(n + \ell)!}{(n - \ell - 1)!}}.
\]  

(2.24)

The radial functions \( P_{n\ell}(r) \) for the lowest few states are found to be:

\[
P_{10}(r) = 2Z^{3/2}re^{-Zr},
\]  

(2.25)

\[
P_{20}(r) = \frac{1}{\sqrt{2}}Z^{3/2}re^{-Zr/2} \left( 1 - \frac{1}{2}Zr \right),
\]  

(2.26)

\[
P_{21}(r) = \frac{1}{2\sqrt{6}}Z^{5/2}r^2e^{-Zr/2},
\]  

(2.27)

\[
P_{30}(r) = \frac{2}{3\sqrt{3}}Z^{3/2}re^{-Zr/3} \left( 1 - \frac{2}{3}Zr + \frac{2}{27}Z^2r^2 \right),
\]  

(2.28)

\[
P_{31}(r) = \frac{8}{27\sqrt{6}}Z^{5/2}r^3e^{-Zr/3} \left( 1 - \frac{1}{6}Zr \right),
\]  

(2.29)

\[
P_{32}(r) = \frac{4}{81\sqrt{30}}Z^{7/2}r^3e^{-Zr/3}.
\]  

(2.30)

In Fig. 2.1, we plot the Coulomb wave functions for the \( n = 1, 2 \) and 3 states of hydrogen, \( Z = 1 \). In this figure, the angular momentum states are labeled using spectroscopic notation: states with \( l = 0, 1, 2, 3, 4, \ldots \) are given the labels \( s, p, d, f, g, \ldots \), respectively. It should be noted that the radial functions with the lowest value of \( l \) for a given \( n \), have no nodes for \( r > 0 \), corresponding to the fact that \( n_r = 0 \) for such states. The number of nodes is seen to increase in direct proportion to \( n \) for a fixed value of \( l \). The outermost maximum of each wave function is seen to occur at increasing distances from the origin as \( n \) increases.

The expectation values of powers of \( r \), given by

\[
\langle r^\nu \rangle_{n\ell} = N_{n\ell}^2 \left( \frac{n}{2Z} \right)^{\nu+1} \int_0^\infty dx x^{2\ell+2+\nu}e^{-x} F^2(-n + \ell + 1, 2\ell + 2, x),
\]  

(2.31)
can be evaluated analytically. One finds:

\[
\langle r^2 \rangle_{n\ell} = \frac{n^2}{2Z^2} [5n^2 + 1 - 3\ell(\ell + 1)],
\]

(2.32)

\[
\langle r \rangle_{n\ell} = \frac{1}{2Z} [3n^2 - \ell(\ell + 1)],
\]

(2.33)

\[
\langle \frac{1}{r} \rangle_{n\ell} = \frac{Z}{n^2},
\]

(2.34)

\[
\langle \frac{1}{r^2} \rangle_{n\ell} = \frac{Z^2}{n^3(\ell + 1/2)},
\]

(2.35)

\[
\langle \frac{1}{r^3} \rangle_{n\ell} = \frac{Z^3}{n^3(\ell + 1)(\ell + 1/2)}, \quad \ell > 0,
\]

(2.36)

\[
\langle \frac{1}{r^4} \rangle_{n\ell} = \frac{Z^4[3n^2 - \ell(\ell + 1)]}{2n^5(\ell + 3/2)(\ell + 1)(\ell + 1/2)(\ell - 1/2)}, \quad \ell > 0.
\]

(2.37)

These formulas follow from the expression for the expectation value of a power of \( r \) given by Bethe and Salpeter (1957):

\[
\langle r^\nu \rangle = \left( \frac{n}{2Z} \right)^\nu \frac{J_{n+1,2\ell+1}^{(\nu+1)}}{J_{n+1,2\ell+1}^{(1)}},
\]

(2.38)
where, for $\sigma \geq 0$,

$$
J_{\lambda,\mu}^{(\sigma)} = (-1)^{\sigma} \frac{\lambda! \sigma!}{(\lambda - \mu)!} \sum_{\beta=0}^{\sigma} (-1)^{\beta} \binom{\sigma}{\beta} \left( \binom{\lambda + \beta}{\sigma} \right) \left( \binom{\lambda + \beta - \mu}{\sigma} \right), \quad (2.39)
$$

and for $\sigma = -(s + 1) \leq -1$,

$$
J_{\lambda,\mu}^{(\sigma)} = \frac{\lambda!}{(\lambda - \mu)! (s + 1)!} \sum_{\gamma=0}^{s} (-1)^{s-\gamma} \binom{s}{\gamma} \left( \begin{array}{c} \lambda - \mu + \gamma \\ s \\ \end{array} \right) \left( \begin{array}{c} s \\ \mu + s - \gamma \\ s + 1 \\ \end{array} \right). \quad (2.40)
$$

In Eqs. (2.39-2.40),

$$
\binom{a}{b} = \frac{a! (b-a)!}{b!} \quad (2.41)
$$
designates the binomial coefficient.

### 2.3 Numerical Solution to the Radial Equation

Since analytical solutions to the radial Schrödinger equation are known for only a few central potentials, such as the Coulomb potential or the harmonic oscillator potential, it is necessary to resort to numerical methods to obtain solutions in practical cases.

We use finite difference techniques to find numerical solutions to the radial equation on a finite grid covering the region $r = 0$ to a practical infinity, $a_\infty$, a point determined by requiring that $P(r)$ be negligible for $r > a_\infty$.

Near the origin, there are two solutions to the radial Schrödinger equation, the desired solution which behaves as $r^{\ell+1}$, and an irregular solution, referred to as the complementary solution, which diverges as $r^{-\ell}$ as $r \to 0$. Numerical errors near $r = 0$ introduce small admixtures of the complementary solution into the solution being sought. Integrating outward from the origin keeps such errors under control, since the complementary solution decreases in magnitude as $r$ increases. In a similar way, in the asymptotic region, we integrate inward from $a_\infty$ toward $r = 0$ to insure that errors from small admixtures of the complementary solution, which behaves as $e^{\lambda r}$ for large $r$, decrease as the integration proceeds from point to point. In summary, one expects the point-by-point numerical integration outward from $r = 0$ and inward from $r = \infty$ to yield solutions that are stable against small numerical errors.

The general procedure used to solve Eq.(2.13) is to integrate outward from the origin, using an appropriate point-by-point scheme, starting with solutions that are regular at the origin. The integration is continued to the outer classical turning point, the point beyond which classical motion in the potential $V(r) + \ell(\ell + 1)/2r^2$ is impossible. In the region beyond the classical turning point, the equation is integrated inward, again using a point-by-point integration scheme, starting from $r = a_\infty$ with an approximate solution obtained from an asymptotic
series. Typically, we choose $a_\infty$ so that the dimensionless quantity $\lambda r \approx 40$ for the first few steps of the inward integration. With this choice, $P(r)$ is roughly $10^{-12}$ of its maximum value near $a_\infty$. The solutions from the inward and outward integrations are matched at the classical turning point. The energy is then adjusted until the derivative of $P(r)$ is continuous at the matching point.

The resulting function $P(r)$ is an eigenfunction and the corresponding energy $E$ is its eigenvalue. To find a particular eigenfunction, we make use of the fact that different eigenfunctions have different numbers of nodes for $r > 0$. For a given value of $\ell$, the lowest energy eigenfunction has no node, the next higher energy eigenfunction has one node, and so on. We first make a preliminary adjustment of the energy to obtain the desired number of nodes and then make a final fine adjustment to match the slope of the wave function at the classical turning point.

The radial wave function increases rapidly at small values of $r$ then oscillates in the classically allowed region and gradually decreases beyond the classical turning point. To accommodate this behavior, it is convenient to adopt a nonuniform integration grid, more finely spaced at small $r$ than at large $r$. Although there are many possible choices of grid, one that has proven to be both convenient and flexible is

$$r[i] = r_0 (e^{t[i]} - 1), \quad \text{where}$$

$$t[i] = (i - 1)h, \quad i = 1, 2, \ldots, N.$$  \hspace{1cm} (2.42)

We typically choose $r_0 = 0.0005$ a.u., $h = 0.02 - 0.03$, and extend the grid to $N = 500$ points. These choices permit the radial Schrödinger equation to be integrated with high accuracy (parts in $10^{12}$) for energies as low as 0.01 a.u.

We rewrite the radial Schrödinger equation as the equivalent pair of first order radial differential equations:

$$\frac{dP}{dr} = Q(r),$$  \hspace{1cm} (2.43)

$$\frac{dQ}{dr} = -2 \left( E - V(r) - \frac{\ell(\ell + 1)}{2r^2} \right) P(r).$$  \hspace{1cm} (2.44)

On the uniformly-spaced $t$-grid, this pair of equations can be expressed as a single, two-component equation

$$\frac{dy}{dt} = f(y, t),$$  \hspace{1cm} (2.45)

where $y$ is the array,

$$y(t) = \begin{bmatrix} P(r(t)) \\ Q(r(t)) \end{bmatrix}.$$  \hspace{1cm} (2.46)

The two components of $f(y, t)$ are given by

$$f(y, t) = \frac{d}{dt} \begin{bmatrix} Q(r(t)) \\ -2 \left( E - V(r) - \frac{\ell(\ell + 1)}{2r^2} \right) P(r(t)) \end{bmatrix}.$$  \hspace{1cm} (2.47)
2.3. NUMERICAL SOLUTION TO THE RADIAL EQUATION

We can formally integrate Eq.(2.45) from one grid point, \( t[n] \), to the next, \( t[n+1] \), giving

\[
y[n+1] = y[n] + \int_{t[n]}^{t[n+1]} f(y(t), t) \, dt.
\]

(2.48)

2.3.1 Adams Method

To derive the formula used in practice to carry out the numerical integration in Eq.(2.48), we introduce some notation from finite difference theory. More complete discussions of the calculus of difference operators can be found in textbooks on numerical methods such as Dahlberg and Bjöck (1974, chap. 7).

Let the function \( f(x) \) be given on a uniform grid and let \( f[n] = f(x[n]) \) be the value of \( f(x) \) at the \( n \)th grid point. We designate the backward difference operator by \( \nabla \):

\[
\nabla f[n] = f[n] - f[n-1].
\]

(2.49)

Using this notation, \( (1 - \nabla)f[n] = f[n-1] \). Inverting this equation, we may write,

\[
\begin{align*}
  f[n+1] &= (1 - \nabla)^{-1} f[n], \\
  f[n+2] &= (1 - \nabla)^{-2} f[n], \\
  & \vdots
\end{align*}
\]

(2.50)

or more generally,

\[
  f[n+x] = (1 - \nabla)^{-x} f[n].
\]

(2.51)

In these expressions, it is understood that the operators in parentheses are to be expanded in a power series in \( \nabla \), and that Eq.(2.49) is to be used iteratively to determine \( \nabla^k \).

Equation(2.51) is a general interpolation formula for equally spaced points. Expanding out a few terms, we obtain from Eq.(2.51)

\[
\begin{align*}
  f[n+x] &= \left( 1 + \frac{x}{1!} \nabla + \frac{x(x+1)}{2!} \nabla^2 + \frac{x(x+1)(x+2)}{3!} \nabla^3 + \cdots \right) f[n], \\
  &= \left( 1 + x + \frac{x(x+1)}{2!} + \frac{x(x+1)(x+2)}{3!} + \cdots \right) f[n] \\
  & \quad - \left( x + \frac{2x(x+1)}{2!} + \frac{3x(x+1)(x+2)}{3!} + \cdots \right) f[n-1] \\
  & \quad + \left( \frac{x(x+1)}{2!} + \frac{3x(x+1)(x+2)}{3!} + \cdots \right) f[n-2] \\
  & \quad - \left( \frac{x(x+1)(x+2)}{3!} + \cdots \right) f[n-3] + \cdots
\end{align*}
\]

(2.52)

Truncating this formula at the \( k \)th term leads to a polynomial of degree \( k \) in \( x \) that passes through the points \( f[n], f[n-1], \ldots, f[n-k] \), as \( x \) takes on the values 0, -1, -2, \ldots, -\( k \), respectively. We may use the interpolation formula
(2.51) to carry out the integration in Eq.(2.48), analytically leading to the result:
(Adams-Bashforth)
\[
y[n+1] = y[n] - \frac{h\nabla}{(1-\nabla)\log(1-\nabla)} f[n],
\]
\[
y[n] + h(1 + \frac{1}{2} \nabla + \frac{5}{12} \nabla^2 + \frac{9}{24} \nabla^3 + \cdots) f[n].
\]
(2.53)

This equation may be rewritten, using the identity \((1-\nabla)^{-1} f[n] = f[n+1]\), as an interpolation formula: (Adams-Moulton)
\[
y[n+1] = y[n] - \frac{h\nabla}{\log(1-\nabla)} f[n+1],
\]
\[
y[n] + h(1 - \frac{1}{2} \nabla - \frac{1}{12} \nabla^2 - \frac{1}{24} \nabla^3 + \cdots) f[n+1].
\]
(2.54)

Keeping terms only to third-order and using Eqs.(2.53-2.54), we obtain the four-point (fifth-order) predict-correct formulas
\[
y[n+1] = y[n] + \frac{h}{24} \left(55f[n] - 59f[n-1] + 37f[n-2] - 9f[n-3]\right)
\]
\[
+ \frac{251}{720} h^5 y^{(5)}[n],
\]
(2.55)
\[
y[n+1] = y[n] + \frac{h}{24} \left(9f[n+1] + 19f[n] - 5f[n-1] + f[n-2]\right)
\]
\[
- \frac{19}{720} h^5 y^{(5)}[n].
\]
(2.56)

The error terms in Eqs.(2.55-2.56) are obtained by evaluating the first neglected term in Eqs.(2.53-2.54) using the approximation
\[
\nabla^k f[n] \approx h^k \left(\frac{d^k f}{dt^k}\right) [n] = h^k \left(\frac{d^{k+1} y}{dt^{k+1}}\right) [n].
\]
(2.57)

The magnitude of the error in Eq.(2.56) is smaller (by an order of magnitude) than that in Eq.(2.55), since interpolation is used in Eq.(2.56), while extrapolation is used in Eq.(2.55). Often, the less accurate extrapolation formula (2.55) is used to advance from point \(t[n]\) (where \(y[n], f[n], f[n-1], f[n-2],\) and \(f[n-3]\) are known) to the point \(t[n+1]\). Using the predicted value of \(y[n+1]\), one evaluates \(f[n+1]\). The resulting value of \(f[n+1]\) can then be used in the interpolation formula (2.56) to give a more accurate value for \(y[n+1]\).

In our application of Adams method, we make use of the linearity of the differential equations (2.45) to avoid the extrapolation step altogether. To show how this is done, we first write the \(k+1\) point Adams-Moulton interpolation formula from Eq.(2.54) in the form,
\[
y[n+1] = y[n] + \frac{h}{D} \sum_{j=1}^{k+1} a[j] f[n - k + j].
\]
(2.58)
Table 2.1: Adams-Moulton integration coefficients

<table>
<thead>
<tr>
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<td>-863/60480</td>
</tr>
</tbody>
</table>

The coefficients $a[j]$ for 2-point to 7-point Adams-Moulton integration formulas are given in Table 2.1, along with the divisors $D$ used in Eq.(2.58), and the coefficient of $h^{k+2}y^{(k+2)}[n]$ in the expression for the truncation error.

Setting $f(y,t) = G(t)y$, where $G$ is a $2 \times 2$ matrix, we can take the $k+1$ term from the sum to the left-hand side of Eq.(2.58) to give

$$
\left(1 - \frac{ha[k+1]}{D}G[n+1]\right)y[n+1] = y[n] + \frac{h}{D} \sum_{j=1}^{k} a[j] f[n - k + j].
$$

From Eq.(2.47), it follows that $G$ is an off-diagonal matrix of the form

$$
G = \begin{pmatrix} 0 & b \\ c & 0 \end{pmatrix},
$$

for the special case of the radial Schrödinger equation. The coefficients $b(t)$ and $c(t)$ can be read from Eq.(2.47):

$$
b(t) = \frac{dr}{dt}, \quad c(t) = -2 \frac{dr}{dt} \left(E - V(r) - \frac{\ell(\ell+1)}{2r^2}\right).
$$

The matrix

$$
M[n+1] = 1 - \frac{ha[k+1]}{D}G[n+1]
$$

on the left-hand side of Eq.(2.59) is readily inverted to give

$$
M^{-1}[n+1] = \frac{1}{\Delta[n+1]} \begin{pmatrix} 1 & \lambda b[n+1] \\ \lambda c[n+1] & 1 \end{pmatrix},
$$

where

$$
\Delta[n+1] = 1 - \lambda^2 b[n+1]c[n+1], \\
\lambda = \frac{ha[k+1]}{D}.
$$

Equation (2.59) is solved to give

$$
y[n+1] = M^{-1}[n+1] \left(y[n] + \frac{h}{D} \sum_{j=1}^{k} a[j] f[n - k + j]\right).
$$
This is the basic algorithm used to advance the solution to the radial Schrödinger equation from one point to the next. Using this equation, we achieve the accuracy of the predict-correct method without the necessity of separate predict and correct steps. To start the integration using Eq. (2.64), we must give initial values of the two-component function \( f(t) \) at the points \( 1, 2, \ldots, k \). The subroutine \textsc{adams} is designed to implement Eq. (2.64) for values of \( k \) ranging from 0 to 8.

### 2.3.2 Starting the Outward Integration (OUTSCH)

The \( k \) initial values of \( y[j] \) required to start the outward integration using the \( k+1 \) point Adams method are obtained using a scheme based on Lagrangian differentiation formulas. These formulas are easily obtained from the basic finite difference expression for interpolation, Eq. (2.51). Differentiating this expression, we find

\[
\frac{dy}{dx}[n-j] = -\log(1 - \nabla)(1 - \nabla)^j y[n]. \tag{2.65}
\]

If Eq. (2.65) is expanded to \( k \) terms in a power series in \( \nabla \), and evaluated at the \( k+1 \) points, \( j = 0, 1, 2, \ldots, k \), we obtain the \( k+1 \) point Lagrangian differentiation formulas. For example, with \( k = 3 \) and \( n = 3 \) we obtain the formulas:

\[
\frac{dy}{dt}[0] = \frac{1}{6h}(-11y[0] + 18y[1] - 9y[2] + 2y[3]) - \frac{1}{4}h^3y^{(4)} \tag{2.66}
\]

\[
\frac{dy}{dt}[1] = \frac{1}{6h}(-2y[0] - 3y[1] + 6y[2] - 3y[3]) + \frac{1}{12}h^3y^{(4)} \tag{2.67}
\]

\[
\frac{dy}{dt}[2] = \frac{1}{6h}(y[0] - 6y[1] + 3y[2] + 2y[3]) - \frac{1}{12}h^3y^{(4)} \tag{2.68}
\]

\[
\frac{dy}{dt}[3] = \frac{1}{6h}(-2y[0] + 9y[1] - 18y[2] + 11y[3]) + \frac{1}{4}h^3y^{(4)}. \tag{2.69}
\]

The error terms in Eqs. (2.66-2.69) are found by retaining the next higher-order differences in the expansion of Eq. (2.65) and using the approximation (2.57). Ignoring the error terms, we write the general \( k+1 \) point Lagrangian differentiation formula as

\[
\left(\frac{dy}{dt}\right)[i] = \sum_{j=0}^{k} m[ij] y[j], \tag{2.70}
\]

where \( i = 0, 1, \ldots, k \), and where the coefficients \( m[ij] \) are determined from Eq. (2.65).

To find the values of \( y[j] \) at the first few points along the radial grid, first we use the differentiation formulas (2.70) to eliminate the derivative terms from the differential equations at the points \( j = 1, \ldots, k \), then we solve the resulting linear algebraic equations using standard methods.

Factoring \( r^{\ell+1} \) from the radial wave function \( P(r) \),

\[
P(r) = r^{\ell+1} p(r), \tag{2.71}
\]
we may write the radial Schrödinger equation as

\[
\frac{dp}{dt} = \frac{dr}{dt} q(t), \quad (2.72)
\]
\[
\frac{dq}{dt} = -2 \frac{dr}{dt} \left[ (E - V(r)) p(t) + \left( \frac{\ell + 1}{r} \right) q(t) \right]. \quad (2.73)
\]

Substituting for the derivatives from Eq.(2.70), we obtain the $2k \times 2k$ system of linear equations

\[
\sum_{j=1}^{k} m[i,j] p[j] - b[i] q[i] = -m[i0] p[0], \quad (2.74)
\]
\[
\sum_{j=1}^{k} m[i,j] q[j] - c[i] p[i] - d[i] q[i] = -m[i0] q[0], \quad (2.75)
\]

where

\[
b(t) = \frac{dr}{dt},
\]
\[
c(t) = -2 \frac{dr}{dt} [E - V(r)],
\]
\[
d(t) = -2 \frac{dr}{dt} \left( \frac{\ell + 1}{r} \right), \quad (2.76)
\]

and where $p[0]$ and $q[0]$ are the initial values of $p(t)$ and $q(t)$, respectively. If we assume that as $r \to 0$, the potential $V(r)$ is dominated by the nuclear Coulomb potential,

\[
V(r) \to -\frac{Z}{r}, \quad (2.77)
\]

then from Eq.(2.73) it follows that the initial values must be in the ratio

\[
\frac{q[0]}{p[0]} = -\frac{Z}{\ell + 1}. \quad (2.78)
\]

We choose $p[0] = 1$ arbitrarily and determine $q[0]$ from Eq.(2.78).

The $2k \times 2k$ system of linear equations (2.74-2.75) are solved using standard methods to give $p[i]$ and $q[i]$ at the points $j = 1, \cdots, k$ along the radial grid. From these values we obtain

\[
P[i] = r^{\ell+1}[i] p[i], \quad (2.79)
\]
\[
Q[i] = r^{\ell+1}[i] \left( q[i] + \frac{\ell + 1}{r[i]} p[i] \right). \quad (2.80)
\]

These are the $k$ initial values required to start the outward integration of the radial Schrödinger equation using the $k+1$ point Adams method. The routine OUTSCH implements the method described here to start the outward integration.
There are other ways to determine solutions to the second-order differential equations at the first $k$ grid points. One obvious possibility is to use a power series representation for the radial wave function at small $r$. This method is not used since we must consider cases where the potential at small $r$ is very different from the Coulomb potential and has no simple analytical structure. Such cases occur when we treat self-consistent fields or nuclear finite-size effects.

Another possibility is to start the outward integration using Runge-Kutta methods. Such methods require evaluation of the potential between the grid points. To obtain such values, for cases where the potential is not known analytically, requires additional interpolation. The present scheme is simple, accurate, and avoids such unnecessary interpolation.

### 2.3.3 Starting the Inward Integration (InSch)

To start the inward integration using the $k + 1$ point Adams method, we need $k$ values of $P[i]$ and $Q[i]$ in the asymptotic region just preceding the practical infinity. We determine these values using an asymptotic expansion of the Schrödinger wave function. Let us suppose that the potential $V(r)$ in the asymptotic region, $r \approx a_\infty$, takes the limiting form,

$$V(r) \to -\frac{\zeta}{r},$$

where $\zeta$ is the charge of the ion formed when one electron is removed. The radial Schrödinger equation in this region then becomes

$$\frac{dP}{dr} = Q(r),$$

$$\frac{dQ}{dr} = -2 \left( E + \frac{\zeta}{r} - \frac{\ell(\ell + 1)}{2r^2} \right)P(r).$$

We seek an asymptotic expansion of $P(r)$ and $Q(r)$ of the form:

$$P(r) = r^\sigma e^{-\lambda r} \left\{ a_0 + \frac{a_1}{r} + \cdots + \frac{a_k}{r^k} + \cdots \right\},$$

$$Q(r) = r^\sigma e^{-\lambda r} \left\{ b_0 + \frac{b_1}{r} + \cdots + \frac{b_k}{r^k} + \cdots \right\}.$$

Substituting the expansions (2.84-2.85) into the radial equations (2.82-2.83) and matching the coefficients of the two leading terms, we find that such an expansion is possible only if

$$\lambda = \sqrt{-2E},$$

$$\sigma = \frac{\zeta}{\lambda}.$$
2.3. NUMERICAL SOLUTION TO THE RADIAL EQUATION

Using these values for $\lambda$ and $\sigma$, the following recurrence relations for $a_k$ and $b_k$ are obtained by matching the coefficients of $r^{-k}$ in Eqs.(2.82-2.83):

\begin{align*}
a_k &= \frac{\ell(\ell + 1) - (\sigma - k)(\sigma - k + 1)}{2k\lambda} a_{k-1}, \quad (2.87) \\
b_k &= \frac{(\sigma + k)(\sigma - k + 1) - \ell(\ell + 1)}{2k} a_{k-1}. \quad (2.88)
\end{align*}

We set $a_0 = 1$ arbitrarily, $b_0 = -\lambda$, and use Eqs.(2.87-2.88) to generate the coefficients of higher-order terms in the series. Near the practical infinity, the expansion parameter $2\lambda r$ is large ($\approx 80$), so relatively few terms in the expansion suffice to give highly accurate wave functions in this region. The asymptotic expansion is used to evaluate $P_i$ and $Q_i$ at the final $k$ points on the radial grid. These values are used in turn to start a point-by-point inward integration to the classical turning point using the $k+1$ point Adams method. In the routine insch, the asymptotic series is used to obtain the values of $P(r)$ and $Q(r)$ at large $r$ to start the inward integration using Adams method.

2.3.4 Eigenvalue Problem (MASTER)

To solve the eigenvalue problem, we:

1. Guess the energy $E$.

2. Use the routine outsch to obtain values of the radial wave function at the first $k$ grid points, and continue the integration to the outer classical turning point ($a_c$) using the routine adams.

3. Use the routine insch to obtain the values of the wave function at the last $k$ points on the grid, and continue the inward solution to $a_c$ using the routine adams.

4. Multiply the wave function and its derivative obtained in step 3 by a scale factor chosen to make the wave function for $r < a_c$ from step 2, and that for $r > a_c$ from step 3, continuous at $r = a_c$.

If the energy guessed in step 1 happened to be an energy eigenvalue, then not only the solution, but also its derivative, would be continuous at $r = a_c$. If it were the desired eigenvalue, then the wave function would also have the correct number of radial nodes, $n_r = n - \ell - 1$.

Generally the energy $E$ in step 1 is just an estimate of the eigenvalue, so the numerical values determined by following steps 2 to 4 above give a wave function having an incorrect number of nodes and a discontinuous derivative at $a_c$. This is illustrated in Fig. 2.2. In the example shown there, we are seeking the $4p$ wave function in a Coulomb potential with $Z = 2$. The corresponding radial wave function should have $n_r = n - l - 1 = 2$ nodes. We start with the guess $E = -0.100$ a.u. for the energy and carry out steps 2 to 4 above. The resulting function, which is represented by the thin solid curve in the figure, has three nodes instead of two and has a discontinuous derivative at $a_c \approx 19$ a.u.
The number of nodes increases with increasing energy. To reduce the number of nodes, we must, therefore, lower the energy. We do this by multiplying $E$ (which is of course negative) by a factor of 1.1. Repeating steps 2 - 4 with $E = -0.110$ a.u., leads to the curve shown in the dot-dashed curve in the figure. The number of nodes remains $n_r = 3$, so we repeat the steps again with $E = 1.1(-0.110) = -0.121$ a.u.. At this energy, the number of nodes $n_r = 2$ is correct, as shown in the dashed curve in Fig. 2.2; however, the derivative of the wave function is still discontinuous at $a_c$. To achieve a wave function with a continuous derivative, we make further corrections to $E$ using a perturbative approach.

If we let $P_1(r)$ and $Q_1(r)$ represent the radial wave function and its derivative at $E_1$, respectively, and let $P_2(r)$ and $Q_2(r)$ represent the same two quantities at $E_2$, then it follows from the radial Schrödinger equation that

$$\frac{d}{dr}(Q_2 P_1 - P_2 Q_1) = 2(E_1 - E_2)P_1 P_2.$$  

(2.89)

From this equation, we find that

$$2(E_1 - E_2) \int_{a_c}^{\infty} P_1 P_2 \, dr = -(Q_2 P_1 - P_2 Q_1)^{+},$$  

(2.90)

and

$$2(E_1 - E_2) \int_{0}^{a_c} P_1 P_2 \, dr = (Q_2 P_1 - P_2 Q_1)^{-},$$  

(2.91)
2.4. POTENTIAL MODELS

where the superscripts ± indicate that the quantities in parentheses are to be evaluated just above or just below \(a_c\). These equations are combined to give

\[
E_1 - E_2 = \frac{(Q_1^- - Q_1^+)P_2(a_c) + (Q_2^- - Q_2^+)P_1(a_c)}{2 \int_0^\infty P_1 P_2 \, dr}.
\]

Suppose that the derivative \(Q_1\) is discontinuous at \(a_c\). If we demand that \(Q_2\) be continuous at \(a_c\), then the term \(Q_2^- - Q_2^+\) in the numerator of (2.92) vanishes. Approximating \(P_2\) by \(P_1\) in this equation, we obtain

\[
E_2 \approx E_1 + \frac{(Q_1^- - Q_1^+)P_1(a_c)}{2 \int_0^\infty P_1^2 \, dr},
\]

as an approximation for the eigenenergy. We use this approximation iteratively until the discontinuity in \(Q(r)\) at \(r = a_c\) is reduced to an insignificant level.

The program \textsc{master} is designed to determine the wave function and the corresponding energy eigenvalue for specified values of \(n\) and \(\ell\) by iteration. In this program, we construct an energy trap that reduces \(E\) (by a factor of 1.1) when there are too many nodes at a given step of the iteration, or increases \(E\) (by a factor of 0.9) when there are too few nodes. When the number of nodes is correct, the iteration is continued using Eq.(2.93) iteratively until the discontinuity in \(Q(r)\) at \(r = a_c\) is reduced to a negligible level. In the routine, we keep track of the least upper bound on the energy \(E_u\) (too many nodes) and the greatest lower bound \(E_l\) (too few nodes) as the iteration proceeds. If increasing the energy at a particular step of the iteration would lead to \(E > E_u\), then we simply replace \(E\) by \((E + E_u)/2\), rather than following the above rules. Similarly, if decreasing \(E\) would lead to \(E < E_l\), then we replace \(E\) by \((E + E_l)/2\).

For the example shown in the Fig. 2.2, it required 8 iterations to obtain the energy \(E_{4p} = -1/8\) a.u. to 10 significant figures starting from the estimate \(E = -100\) a.u.. The resulting wave function is shown in the heavy solid line in the figure.

It is only necessary to normalize \(P(r)\) and \(Q(r)\) to obtain the desired radial wave function and its derivative. The normalization integral,

\[
N^{-2} = \int_0^\infty P^2 \, dr,
\]

is evaluated using the routine \textsc{rint}; a routine based on the trapezoidal rule with endpoint corrections that will be discussed later. As a final step in the routine \textsc{master}, the wave function and its derivative are multiplied by \(N\) to give a properly normalized numerical solution to the radial Schrödinger equation.

2.4 Potential Models

The potential experienced by a bound atomic electron near \(r = 0\) is dominated by the nuclear Coulomb potential, so we expect

\[
V(r) \approx -\frac{Z}{r},
\]

where the superscripts ± indicate that the quantities in parentheses are to be evaluated just above or just below \(a_c\). These equations are combined to give

\[
E_1 - E_2 = \frac{(Q_1^+ - Q_1^-)P_2(a_c) + (Q_2^- - Q_2^+)P_1(a_c)}{2 \int_0^\infty P_1 P_2 \, dr}.
\]
for small $r$. At large $r$, on the other hand, an electron experiences a potential that is the sum of the attractive nuclear Coulomb potential and the sum of the repulsive potentials of the remaining electrons, so we expect

$$\lim_{r \to \infty} V(r) = -\frac{\zeta}{r},$$

with $\zeta = Z - N + 1$ for an $N$ electron atom with nuclear charge $Z$. The transition from a nuclear potential to an ionic potential is predicted by the Thomas-Fermi model, for example. However, it is possible to simply approximate the potential in the intermediate region by a smooth function of $r$ depending on several parameters that interpolates between the two extremes. One adjusts the parameters in this potential to fit the observed energy spectrum as well as possible. We examine this approach in the following section.

### 2.4.1 Parametric Potentials

It is a simple matter to devise potentials that interpolate between the nuclear and ionic potentials. Two simple one-parameter potentials are:

$$V_a(r) = -\frac{Z}{r} + \frac{(Z - \zeta)}{a^2 + r^2},$$

(2.94)

$$V_b(r) = -\frac{Z}{r} + \frac{Z - \zeta}{r} (1 - e^{-r/b}).$$

(2.95)

The second term in each of these potentials approximates the electron-electron interaction. As an exercise, let us determine the values of the parameters $a$ and $b$ in Eqs.(2.94) and (2.95) that best represent the four lowest states (3s, 3p, 4s and 3d) in the sodium atom. For this purpose, we assume that the sodium spectrum can be approximated by that of a single valence electron moving in one of the above parametric potentials. We choose values of the parameters to minimize the sum of the squares of the differences between the observed levels and the corresponding numerical eigenvalues of the radial Schrödinger equation.

To solve the radial Schrödinger equation, we use the routine MASTER described above. To carry out the minimization, we use the subroutine GOLDEN from the NUMERICAL RECIPES library. This routine uses the golden mean technique to find the minimum of a function of a single variable, taken to be the sum of the squares of the energy differences considered as a function of the parameter in the potential.

We find that the value $a = 0.2683$ a.u. minimizes the sum of the squares of the differences between the calculated and observed terms using the potential $V_a$ from Eq.(2.94). Similarly, $b = 0.4072$ a.u. is the optimal value of the parameter in Eq.(2.95). In Table 2.2, we compare the observed sodium energy level with values calculated using the two potentials. It is seen that the calculated and observed levels agree to within a few percent for both potentials, although $V_b$ leads to better agreement.

The electron-electron interaction potential for the two cases is shown in Fig. 2.3. These two potentials are completely different for $r < 1$ a.u., but agree
2.4. POTENTIAL MODELS

Table 2.2: Comparison of \( n = 3 \) and \( n = 4 \) levels (a.u.) of sodium calculated using parametric potentials with experiment.

<table>
<thead>
<tr>
<th>State</th>
<th>( V_a )</th>
<th>( V_b )</th>
<th>Exp.</th>
</tr>
</thead>
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<td>3s</td>
<td>-0.1919</td>
<td>-0.1881</td>
<td>-0.1889</td>
</tr>
<tr>
<td>3p</td>
<td>-0.1072</td>
<td>-0.1124</td>
<td>-0.1106</td>
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<tr>
<td>4s</td>
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<td>-0.0717</td>
<td>-0.0716</td>
</tr>
<tr>
<td>3d</td>
<td>-0.0575</td>
<td>-0.0557</td>
<td>-0.0559</td>
</tr>
</tbody>
</table>

Figure 2.3: Electron interaction potentials from Eqs.(2.94) and (2.95) with parameters \( a = 0.2683 \) and \( b = 0.4072 \) chosen to fit the first four sodium energy levels.

closely for \( r > 1 \) a.u., where the \( n = 3 \) and \( n = 4 \) wave functions have their maxima.

Since the two potentials are quite different for small \( r \), it is possible to decide which of the two is more reasonable by comparing predictions of levels that have their maximum amplitudes at small \( r \) with experiment. Therefore, we are led to compare the \( 1s \) energy from the two potentials with the experimentally measured \( 1s \) binding energy \( E_{1s}^{\exp} = -39.4 \) a.u. We find upon solving the radial Schrödinger equation that

\[
E_{1s} = \begin{cases} 
-47.47 \text{a.u.} & \text{for } V_a, \\
-40.14 \text{a.u.} & \text{for } V_b.
\end{cases}
\]

It is seen that potential \( V_b(r) \) predicts an energy that is within 2\% of the experimental value, while \( V_a \) leads to a value of the \( 1s \) energy that disagrees with experiment by about 18\%. As we will see later, theoretically determined potentials are closer to case \( b \) than to case \( a \), as one might expect from the comparison here.
One can easily devise multi-parameter model potentials, with parameters adjusted to fit a number of levels precisely, and use the resulting wave functions to predict atomic properties. Such a procedure is a useful first step in examining the structure of an atom, but because of the ad hoc nature of the potentials being considered, it is difficult to assess errors in predictions made using such potentials.

2.4.2 Thomas-Fermi Potential

A simple approximation to the atomic potential was derived from a statistical model of the atom by L.H Thomas and independently by E. Fermi in 1927. This potential is known as the Thomas-Fermi potential. Although there has been a revival of research interest in the Thomas-Fermi method in recent years, we will consider only the most elementary version of the theory here to illustrate an ab-initio calculation of an atomic potential.

We suppose that bound electrons in an atom behave in the same way as free electrons confined to a box of volume $V$. For electrons in a box, the number of states $d^3N$ available in a momentum range $d^3p$ is given by

$$d^3N = 2\frac{V}{(2\pi)^3}d^3p,$$  \hspace{1cm} (2.96)

where the factor 2 accounts for the two possible electron spin states. Assuming the box to be spherically symmetric, and assuming that all states up to momentum $p_f$ (the Fermi momentum) are filled, it follows that the particle density $\rho$ is

$$\rho = \frac{N}{V} = \frac{1}{\pi^2} \int_0^{p_f} p^2 dp = \frac{1}{3\pi^2} p_f^3.$$  \hspace{1cm} (2.97)

Similarly, the kinetic energy density is given by

$$\epsilon_k = \frac{E_k}{V} = \frac{1}{\pi^2} \int_0^{p_f} \frac{p^2}{2} dp = \frac{1}{10\pi^2} p_f^5.$$  \hspace{1cm} (2.98)

Using Eq.(2.97), we can express the kinetic energy density in terms of the particle density through the relation

$$\epsilon_k = \frac{3}{10}(3\pi^2)^{2/3} \rho^{5/3}.$$  \hspace{1cm} (2.99)

In the Thomas-Fermi theory, it is assumed that this relation between the kinetic-energy density and the particle density holds not only for particles moving freely in a box, but also for bound electrons in the nonuniform field of an atom. In the atomic case, we assume that each electron experiences a spherically symmetric field and, therefore, that $\rho = \rho(r)$ is independent of direction.

The electron density $\rho(r)$ is assumed to vanish for $r \geq R$, where $R$ is determined by requiring

$$\int_0^R 4\pi r'^2 \rho(r')dr' = N,$$  \hspace{1cm} (2.100)
where \( N \) is the number of bound electrons in the atom.

In the Thomas-Fermi theory, the electronic potential is given by the classical potential of a spherically symmetric charge distribution:

\[
V_e(r) = \int_0^R \frac{1}{r'} 4\pi r'^2 \rho(r')dr',
\]

(2.101)

where \( r_\geq = \max(r, r') \). The total energy of the atom in the Thomas-Fermi theory is obtained by combining Eq.(2.99) for the kinetic energy density with the classical expressions for the electron-nucleus potential energy and the electron-electron potential energy to give the following semi-classical expression for the energy of the atom:

\[
E = \int_0^R \left\{ \frac{3}{10} \left(3\pi^2 \right)^{2/3} \rho^{2/3} - \frac{Z}{r} + \frac{1}{2} \int_0^R \frac{1}{r'} 4\pi r'^2 \rho(r')dr' \right\} 4\pi r^2 \rho(r)dr.
\]

(2.102)

The density is determined from a variational principle; the energy is required to be a minimum with respect to variations of the density, with the constraint that the number of electrons is \( N \). Introducing a Lagrange multiplier \( \lambda \), the variational principal \( \delta (E - \lambda N) = 0 \) can be written

\[
\int_0^R \left\{ \frac{1}{2} \left(3\pi^2 \right)^{2/3} \rho^{2/3} - \frac{Z}{r} + \int_0^R \frac{1}{r'} 4\pi r'^2 \rho(r')dr' - \lambda \right\} 4\pi r^2 \delta \rho(r)dr = 0.
\]

(2.103)

Requiring that this condition be satisfied for arbitrary variations \( \delta \rho(r) \) leads to the following integral equation for \( \rho(r) \):

\[
\frac{1}{2} \left(3\pi^2 \right)^{2/3} \rho^{2/3} - \frac{Z}{r} + \int_0^R \frac{1}{r'} 4\pi r'^2 \rho(r')dr' = \lambda.
\]

(2.104)

Evaluating this equation at the point \( r = R \), where \( \rho(R) = 0 \), we obtain

\[
\lambda = \frac{Z}{R} + \frac{1}{R} \int_0^R 4\pi r'^2 \rho(r')dr' = -\frac{Z}{R} = V(R),
\]

(2.105)

where \( V(r) \) is the sum of the nuclear and atomic potentials at \( r \). Combining (2.105) and (2.104) leads to the relation between the density and potential,

\[
\frac{1}{2} \left(3\pi^2 \right)^{2/3} \rho^{2/3} = V(R) - V(r).
\]

(2.106)

Since \( V(r) \) is a spherically symmetric potential obtained from purely classical arguments, it satisfies the radial Laplace equation,

\[
\frac{1}{r} \frac{d}{dr} r V(r) = -4\pi \rho(r),
\]

(2.107)

which can be rewritten

\[
\frac{1}{r} \frac{d}{dr} [r V(R) - V(r)] = 4\pi \rho(r).
\]

(2.108)
CHAPTER 2. CENTRAL-FIELD SCHRÖDINGER EQUATION

Substituting for $\rho(r)$ from (2.106) leads to

$$\frac{d^2}{dr^2} r[V(R) - V(r)] = \frac{8\sqrt{2}}{3\pi} \frac{(r[V(R) - V(r)])^{3/2}}{r^{1/2}}. \quad (2.109)$$

It is convenient to change variables to $\phi$ and $x$, where

$$\phi(r) = \frac{r[V(R) - V(r)]}{Z}, \quad (2.110)$$

and

$$x = r/\xi, \quad (2.111)$$

with

$$\xi = \left(\frac{9\pi^2}{128Z}\right)^{1/3}. \quad (2.112)$$

With the aid of this transformation, we can rewrite the Thomas-Fermi equation (2.109) in dimensionless form:

$$\frac{d^2 \phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}}, \quad (2.113)$$

Since $\lim_{r \to 0} r[V(r) - V(R)] = -Z$, the desired solution to (2.113) satisfies the boundary condition $\phi(0) = 1$. From $\rho(R) = 0$, it follows that $\phi(X) = 0$ at $X = R/\xi$.

By choosing the initial slope appropriately, we can find solutions to the Thomas-Fermi equation that satisfy the two boundary conditions for a wide range of values $X$. The correct value of $X$ is found by requiring that the normalization condition (2.100) is satisfied. To determine the point $X$, we write Eq. (2.108) as

$$r \frac{d^2 \phi}{dr^2} = \frac{1}{Z} 4\pi r^2 \rho(r). \quad (2.114)$$

From this equation, it follows that $N(r)$, the number of electrons inside a sphere of radius $r$, is given by

$$\frac{N(r)}{Z} = \int_0^r r \frac{d^2 \phi(r)}{dr^2} dr \quad (2.115) = \left(\frac{d\phi}{dr} - \phi\right)_0^r \quad (2.116) = r \frac{d\phi}{dr} - \phi(r) + 1. \quad (2.117)$$

Evaluating this expression at $r = R$, we obtain the normalization condition

$$X \left(\frac{d\phi}{dx}\right)_X = -\frac{Z - N}{Z}. \quad (2.118)$$

An iterative scheme is set up to solve the Thomas-Fermi differential equation. First, two initial values of $X$ are guessed: $X = X_a$ and $X = X_b$. The
2.4. POTENTIAL MODELS

Figure 2.4: Thomas-Fermi functions for the sodium ion, Z = 11, N = 10. Upper panel: the Thomas-Fermi function \( \phi(r) \). Center panel: \( N(r) \), the number of electrons inside a sphere of radius \( r \). Lower panel: \( U(r) \), the electron contribution to the potential.

The Thomas-Fermi equation (2.113) is integrated inward to \( r = 0 \) twice: the first time starting at \( x = X_a \), using initial conditions \( \phi(X_a) = 0 \), \( d\phi/dx(X_a) = -(Z - N)/X_a Z \), and the second time starting at \( x = X_b \), using initial conditions \( \phi(X_b) = 0 \), \( d\phi/dx(X_b) = -(Z - N)/X_b Z \). We examine the quantities \( \phi(0) - 1 \) in the two cases. Let us designate this quantity by \( f \); thus, \( f_a \) is the value of \( \phi(0) - 1 \) for the first case, where initial conditions are imposed at \( x = X_a \), and \( f_b \) is the value of \( \phi(0) - 1 \) in the second case. If the product \( f_a f_b > 0 \), we choose two new points and repeat the above steps until \( f_a f_b < 0 \). If \( f_a f_b < 0 \), then it follows that the correct value of \( X \) is somewhere in the interval between \( X_a \) and \( X_b \). Assuming that we have located such an interval, we continue the iteration by interval halving: choose \( X = (X_a + X_b)/2 \) and integrate inward, test the sign of \( f f_a \) and \( f f_b \) to determine which subinterval contains \( X \) and repeat the above averaging procedure. This interval halving is continued until \(|f| < \epsilon \), where \( \epsilon \) is a tolerance parameter. The value chosen for \( \epsilon \) determines how well the boundary condition at \( x = 0 \) is to be satisfied.

In the routine \textsc{thomas}, we use the fifth-order Runge-Kutta integration scheme given in Abramowitz and Stegun to solve the Thomas-Fermi equation. We illustrate the solution obtained for the sodium ion, Z = 11, N = 10 in Fig. 2.4. The value of \( R \) obtained on convergence was \( R = 2.914 \) a.u.. In the top panel, we show \( \phi(r) \) in the interval 0 - \( R \). In the second panel, we show the corresponding value of \( N(r) \), the number of electrons inside a sphere of radius \( r \). In the bottom panel, we give the electron contribution to the potential. Comparing with Fig. 2.3, we see that the electron-electron potential \( U(r) \) from the Thomas-Fermi potential has the same general shape as the electron-
interaction contribution to the parametric potential $V_b(r)$. This is consistent with the previous observation that $V_b(r)$ led to an accurate inner-shell energy for sodium.

2.5 Separation of Variables for Dirac Equation

To describe the fine structure of atomic states from first principles, it is necessary to treat the bound electrons relativistically. In the independent particle picture, this is done by replacing the one-electron Schrödinger orbital $\psi(r)$ by the corresponding Dirac orbital $\varphi(r)$. The orbital $\varphi(r)$ satisfies the single-particle Dirac equation

$$ h_D \varphi = E \varphi, \quad (2.119) $$

where $h_D$ is the Dirac Hamiltonian. In atomic units, $h_D$ is given by

$$ h_D = c \alpha \cdot \mathbf{p} + \beta c^2 + V(r). \quad (2.120) $$

The constant $c$ is the speed of light; in atomic units, $c = 137.0359895 \ldots$. The quantities $\alpha$ and $\beta$ in Eq. (2.120) are $4 \times 4$ Dirac matrices:

$$ \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.121) $$

The $2 \times 2$ matrix $\sigma$ is the Pauli spin matrix, discussed in Sec. 1.2.1.

The total angular momentum is given by $J = L + S$, where $L$ is the orbital angular momentum, and $S$ is the $4 \times 4$ spin angular momentum matrix,

$$ S = \frac{1}{2} \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix}. \quad (2.122) $$

It is not difficult to show that $J$ commutes with the Dirac Hamiltonian. We may, therefore, classify the eigenstates of $h_D$ according to the eigenvalues of energy, $J^2$ and $J_z$. The eigenstates of $J^2$ and $J_z$ are easily constructed using the two-component representation of $S$. They are the spherical spinors $\Omega_{\kappa m}(\hat{r})$.

If we seek a solution to the Dirac equation (2.120) having the form

$$ \varphi_\kappa(r) = \frac{1}{r} \begin{pmatrix} i P_\kappa(r) \\ Q_\kappa(r) \end{pmatrix}, \quad (2.123) $$

then we find, with the help of the identities (1.124,1.126), that the radial functions $P_\kappa(r)$ and $Q_\kappa(r)$ satisfy the coupled first-order differential equations:

$$ (V + c^2) P_\kappa + c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_\kappa = EP_\kappa \quad (2.124) $$

$$ -c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_\kappa + (V - c^2) Q_\kappa = EQ_\kappa \quad (2.125) $$
where \( V(r) = V_{\text{nucl}}(r) + U(r) \). The normalization condition for the orbital \( \varphi_\kappa(r) \),

\[
\int \varphi_\kappa^\dagger(r) \varphi_\kappa(r) d^3r = 1, \tag{2.126}
\]
can be written

\[
\int_0^\infty [P_\kappa^2(r) + Q_\kappa^2(r)] dr = 1, \tag{2.127}
\]
when expressed in terms of the radial functions \( P_\kappa(r) \) and \( Q_\kappa(r) \). The radial eigenfunctions and their associated eigenvalues, \( E \), can be determined analytically for a Coulomb potential. In practical cases, however, the eigenvalue problem must be solved numerically.

### 2.6 Radial Dirac Equation for a Coulomb Field

In this section, we seek analytical solutions to the radial Dirac equations (2.124) and (2.125) for the special case \( V(r) = -Z/r \). As a first step in our analysis, we examine these equations at large values of \( r \). Retaining only dominant terms as \( r \to \infty \), we find

\[
c - \frac{dQ_\kappa}{dr} = (E - c^2) P_\kappa, \tag{2.128}
\]
\[
c - \frac{dP_\kappa}{dr} = -(E + c^2) Q_\kappa. \tag{2.129}
\]

This pair of equations can be converted into the second-order equation

\[
c^2 \frac{d^2 P_\kappa}{dr^2} + (E^2 - c^4) P_\kappa = 0, \tag{2.130}
\]
which has two linearly independent solutions, \( e^{\pm \lambda r} \), with \( \lambda = \sqrt{c^2 - E^2/c^2} \). The physically acceptable solution is

\[
P_\kappa(r) = e^{-\lambda r}. \tag{2.131}
\]

The corresponding solution \( Q_\kappa \) is given by

\[
Q_\kappa(r) = \sqrt{\frac{c^2 - E}{c^2 + E}} e^{-\lambda r}. \tag{2.132}
\]

Factoring the asymptotic behavior, we express the radial functions in the form

\[
P_\kappa = \sqrt{1 + E/c^2} e^{-\lambda x} (F_1 + F_2), \tag{2.133}
\]
\[
Q_\kappa = \sqrt{1 - E/c^2} e^{-\lambda x} (F_1 - F_2). \tag{2.134}
\]

Substituting this ansatz into (2.124) and (2.125), we find that the functions \( F_1 \) and \( F_2 \) satisfy the coupled equations

\[
\frac{dF_1}{dx} = \frac{EZ}{c^2 \lambda x} F_1 + \left( \frac{Z}{\lambda x} - \frac{\kappa}{x} \right) F_2, \tag{2.135}
\]
\[
\frac{dF_2}{dx} = - \left( \frac{Z}{\lambda x} + \frac{\kappa}{x} \right) F_1 + \left( 1 - \frac{EZ}{c^2 \lambda x} \right) F_2. \tag{2.136}
\]
where \( x = 2\lambda r \).

We seek solutions to Eqs. (2.135, 2.136) that have the limiting forms \( F_1 = a_1 x^\gamma \) and \( F_2 = a_2 x^\gamma \) as \( x \to 0 \). Substituting these expressions into (2.135) and (2.136) and retaining only the most singular terms, we find:

\[
\frac{a_2}{a_1} = \frac{\gamma - EZ/c^2\lambda}{-\kappa + Z/\lambda} = \frac{-\kappa - Z/\lambda}{\gamma + EZ/c^2\lambda}.
\]

(2.137)

Clearing fractions in the right-hand equality, leads to the result \( \gamma^2 = \kappa^2 - Z^2/c^2 = \kappa^2 - \alpha^2Z^2 \). Here, we have used the fact that \( c = 1/\alpha \) in atomic units. The physically acceptable value of \( \gamma \) is given by the positive square root, \( \gamma = \sqrt{\kappa^2 - \alpha^2Z^2} \). Next, we use Eq. (2.135) to express \( F_2 \) in terms of \( F_1 \),

\[
F_2 = \frac{1}{-\kappa + Z/\lambda} \left[ x \frac{dF_1}{dx} - \frac{EZ}{c^2\lambda} F_1 \right].
\]

(2.138)

This equation, in turn, can be used to eliminate \( F_2 \) from Eq. (2.136), leading to

\[
x \frac{d^2F_1}{dx^2} + (1 - x) \frac{dF_1}{dx} - \left( \frac{\gamma^2}{x^2} - \frac{EZ}{c^2\lambda} \right) F_1 = 0.
\]

(2.139)

Finally, we write

\[
F_1(x) = x^\gamma F(a, b, x),
\]

(2.140)

and find that the function \( F(x) \) satisfies the Kummer’s equation,

\[
x \frac{d^2F}{dx^2} + (b - x) \frac{dF}{dx} - aF = 0,
\]

(2.141)

where \( a = \gamma - EZ/c^2\lambda \), and \( b = 2\gamma + 1 \). This equation is identical to Eq. (2.18) except for the values of the parameters \( a \) and \( b \). The solutions to Eq. (2.141) that are regular at the origin are the Confluent Hypergeometric functions written out in Eq. (2.19). Therefore,

\[
F_1(x) = x^\gamma F(a, b, x).
\]

(2.142)

The function \( F_2(x) \) can also be expressed in terms of Confluent Hypergeometric functions. Using Eq. (2.138), we find

\[
F_2(x) = \frac{x^\gamma}{(-\kappa + Z/\lambda)} \left[ x \frac{dF}{dx} + aF \right] = \frac{(\gamma - EZ/c^2\lambda)}{(-\kappa + Z/\lambda)} x^\gamma F(a + 1, b, x).
\]

(2.143)

Combining these results, we obtain the following expressions for the radial Dirac functions:

\[
P_\kappa(r) = \sqrt{1 + E/c^2 e^{-x^2/2} x^\gamma} [(-\kappa + Z/\lambda) F(a, b, x) + (\gamma - EZ/c^2\lambda) F(a + 1, b, x)],
\]

(2.144)

\[
Q_\kappa(r) = \sqrt{1 - E/c^2 e^{-x^2/2} x^\gamma} [(-\kappa + Z/\lambda) F(a, b, x) - (\gamma - EZ/c^2\lambda) F(a + 1, b, x)].
\]

(2.145)
These solutions have yet to be normalized.

We now turn to the eigenvalue problem. First, we examine the behavior of the radial functions at large $r$. We find:

\[ F(a, b, x) \rightarrow \frac{\Gamma(b)}{\Gamma(a)} e^{x a - b [1 + O(|x|^{-1})]}, \]  
\[ aF(a + 1, b, x) \rightarrow \frac{\Gamma(b)}{\Gamma(a)} e^{x (a + 1) - b [1 + O(|x|^{-1})]}. \]  

From these equations, it follows that the radial wave functions are normalizable if, and only if, the coefficients of the exponentials in Eqs.(2.146) and (2.147) vanish. As in the nonrelativistic case, this occurs when $a = -n_r$, where $n_r = 0, -1, -2, \ldots$. We define the principal quantum number $n$ through the relation, $n = k + n_r$, where $k = |\kappa| = j + 1/2$. The eigenvalue equation, therefore, can be written

\[ EZ/c^2 \lambda = \gamma + n - k. \]  

The case $a = -n_r = 0$ requires special attention. In this case, one can solve the eigenvalue equation to find $k = Z/\lambda$. From this, it follows that the two factors $-\kappa + Z/\lambda$ and $\gamma - EZ/c^2 \lambda$ in Eqs.(2.144) and (2.145) vanish for $\kappa = k > 0$. States with $n_r = 0$ occur only for $\kappa < 0$. Therefore, for a given value of $n > 0$ there are $2n - 1$ possible eigenfunctions: $n$ eigenfunctions with $\kappa = -1, -2, \ldots - n$, and $n - 1$ eigenfunctions with $\kappa = 1, 2, \ldots n - 1$.

Solving the eigenvalue equation for $E$, we obtain

\[ E_{n\kappa} = \frac{c^2}{\sqrt{1 + \frac{\alpha^2 Z^2}{(\gamma + n - k)^2}}}. \]  

It is interesting to note that the Dirac energy levels depend only on $k = |\kappa|$. Those levels having the same values of $n$ and $j$, but different values of $\ell$ are degenerate. Thus, for example, the $2s_{1/2}$ and $2p_{1/2}$ levels in hydrogenlike ions are degenerate. By contrast, levels with the same value of $n$ and $\ell$ but different values of $j$, such as the $2p_{1/2}$ and $2p_{3/2}$ levels, have different energies. The separation between two such levels is called the fine-structure interval.

Expanding (2.148) in powers of $\alpha Z$, we find

\[ E_{n\kappa} = c^2 - \frac{Z^2}{2n^2} - \frac{\alpha^2 Z^4}{2n^3} \left( \frac{1}{k} - \frac{3}{4n} \right) + \cdots. \]  

The first term in this expansion is just the electron’s rest energy $(mc^2)$ expressed in atomic units. The second term is precisely the nonrelativistic Coulomb-field binding energy. The third term is the leading fine-structure correction. The fine-structure energy difference between the $2p_{3/2}$ and $2p_{1/2}$ levels in hydrogen is predicted by this formula to be

\[ \Delta E_{2p} = \frac{\alpha^2}{32} \text{ a.u.} = 0.3652 \text{ cm}^{-1}, \]
in close agreement with the measured separation. The separation of the \(2s_{1/2}\) and \(2p_{1/2}\) levels in hydrogen is measured to be 0.0354 cm\(^{-1}\). The degeneracy between these two levels predicted by the Dirac equation is lifted by the Lamb-shift!

Let us introduce the (noninteger) parameter \(N = Z/\lambda = (\gamma + n - k)c^2/E\). From (2.148), we find \(N = \sqrt{n^2 - 2(n - k)(k - \gamma)}\). Thus, \(N = n\) when \(n = k\). With this definition, the coefficients of the hypergeometric functions in Eqs. (2.144) and (2.145) can be written

\[
(-\kappa + Z/\lambda) = (N - \kappa), \quad (\gamma - EZ/c^2\lambda) = -(n - k). \quad (2.150)
\]

Introducing the normalization factor

\[
N_{nk} = \frac{1}{N\Gamma(2\gamma + 1)} \sqrt{\frac{Z\Gamma(2\gamma + 1 + n - k)}{2(n - k)! (N - \kappa)}}, \quad (2.152)
\]

we can write the radial Dirac Coulomb wave functions as

\[
P_{nk}(r) = \sqrt{1 + E_{nk}/c^2} N_{nk}e^{-x/2}x^{\gamma} ((N - \kappa)F(-n + k, 2\gamma + 1, x)\nonumber \\
\quad - (n - k)F(-n + k + 1, 2\gamma + 1, x)), \quad (2.153)
\]

\[
Q_{nk}(r) = \sqrt{1 - E_{nk}/c^2} N_{nk}e^{-x/2}x^{\gamma} ((N - \kappa)F(-n + k, 2\gamma + 1, x)\nonumber \\
\quad + (n - k)F(-n + k + 1, 2\gamma + 1, x)). \quad (2.154)
\]

These functions satisfy the normalization condition (2.127). It should be noticed that the ratio of the scale factors in (2.153) and (2.154) is \(\sqrt{(1 - E_{nk}/c^2)/(1 + E_{nk}/c^2)} \approx \alpha Z/2n\). Thus, \(Q_{nk}(r)\) is several orders of magnitude smaller than \(P_{nk}(r)\) for \(Z = 1\). For this reason, \(P_{nk}\) and \(Q_{nk}\) are referred to as the large and small components of the radial Dirac wave function, respectively.

As a specific example, let us consider the \(1s_{1/2}\) ground state of an electron in a hydrogenlike ion with nuclear charge \(Z\). For this state, \(n = 1, \kappa = -1, k = 1, \gamma = \sqrt{1 - \alpha^2Z^2}, E_{nk}/c^2 = \gamma, N = 1, \lambda = Z\) and \(x = 2Zr\). Therefore,

\[
P_{1-1}(r) = \sqrt{\frac{1 + \gamma}{2}} \frac{2Z}{\Gamma(2\gamma + 1)} (2Zr)^{\gamma} e^{-Zr},
\]

\[
Q_{1-1}(r) = \sqrt{\frac{1 - \gamma}{2}} \frac{2Z}{\Gamma(2\gamma + 1)} (2Zr)^{\gamma} e^{-Zr}.
\]

In Fig. 2.5, we plot the \(n = 2\) Coulomb wave functions for nuclear charge \(Z = 2\). The small components \(Q_{2n}(r)\) in the figure are scaled up by a factor of \(1/\alpha Z\) to make them comparable in size to the large components \(P_{2n}(r)\). The large components are seen to be very similar to the corresponding nonrelativistic Coulomb wave functions \(P_{2n}(r)\), illustrated in Fig. 2.1. The number of nodes in the \(P_{nk}(r)\) is \(n - \ell - 1\). The number of nodes in \(Q_{nk}(r)\) is also \(n - \ell - 1\).
2.7 Numerical Solution to Dirac Equation

The numerical treatment of the radial Dirac equation closely parallels that used previously to solve the radial Schrödinger equation. The basic point-by-point integration of the radial equations is performed using the Adams-Moulton scheme (ADAMS). We obtain the values of the radial functions near the origin necessary to start the outward integration using an algorithm based on Lagrangian differentiation (OUTDIR). The corresponding values of the radial functions near the practical infinity, needed to start the inward integration, are obtained from an asymptotic expansion of the radial functions (INDIR). A scheme following the pattern of the nonrelativistic routine MASTER is then used to solve the eigenvalue problem. In the paragraphs below we describe the modifications of the nonrelativistic routines that are needed in the Dirac case.

Figure 2.5: Radial Dirac Coulomb wave functions for the $n = 2$ states of hydrogenlike helium, $Z = 2$. The solid lines represent the large components $P_{2\kappa}(r)$ and the dashed lines represent the scaled small components, $Q_{2\kappa}(r)/\alpha Z$. for $\kappa < 0$, but is $n - \ell$ for $\kappa > 0$. These rules for the nodes will be useful in designing a numerical eigenvalue routine for the Dirac equation. It should be noticed that, except for sign, the large components of the $2p_{1/2}$ and $2p_{3/2}$ radial wave functions are virtually indistinguishable.
To make comparison with nonrelativistic calculations easier, we subtract the rest energy $c^2$ a.u. from $E_\kappa$ in our numerical calculations. In the sequel, we use $W_\kappa = E_\kappa - c^2$ instead of $E$ as the value of the energy in the relativistic case.

The choice of radial grid is identical to that used in the nonrelativistic case; $r(t)$ gives the value of the distance coordinate on the uniformly-spaced $t$ grid. The radial Dirac equations on the $t$ grid take the form

$$\frac{dy}{dt} = f(y, t), \quad (2.155)$$

where $y(t)$ and $f(y, t)$ are the two-component arrays:

$$y = \begin{pmatrix} P_\kappa \\ Q_\kappa \end{pmatrix}, \quad (2.156)$$

$$f(y, t) = r'(\frac{-\kappa}{r}) P_\kappa(r) - a[W_\kappa - V(r) + 2\alpha^{-2}] Q_\kappa(r) + (\frac{\kappa}{r}) Q_\kappa(r) + \alpha[W_\kappa - V(r)] P_\kappa(r), \quad (2.157)$$

where, $r'(t) = \frac{dr}{dt}$.

### 2.7.1 Outward and Inward Integrations (ADAMS, OUTDIR, INDIR)

**ADAMS:** We integrate Eqs.(2.156) and(2.157) forward using the Adams-Moulton algorithm given in Eq.(2.58):

$$y[n + 1] = y[n] + \frac{h}{D} \sum_{j=1}^{k+1} a[j] f[n - k + j]. \quad (2.158)$$

The coefficients $a[j]$ and $D$ for this integration formula are given in Table 2.1. Writing $f(y, t) = G(t) y$, equation (2.158) can be put in the form (2.59),

$$\left(1 - \frac{ha[k+1]}{D} G[n+1]\right) y[n+1] = y[n] + \frac{h}{D} \sum_{j=1}^{k} a[j] f[n - k + j], \quad (2.159)$$

where $G$ is the $2 \times 2$ matrix

$$G(t) = \begin{pmatrix} a(t) & b(t) \\ c(t) & d(t) \end{pmatrix}, \quad (2.160)$$

with

$$a(t) = -r'(\kappa/r), \quad b(t) = -\alpha r'(W_\kappa - V(r) + 2\alpha^{-2}),$$

$$c(t) = \alpha r'(W_\kappa - V(r)), \quad d(t) = r'(\kappa/r). \quad (2.161)$$

The matrix $M[n+1] = 1 - \frac{ha[k+1]}{D} G[n+1]$ on the left-hand side of Eq.(2.160) can be inverted to give

$$M^{-1}[n+1] = \frac{1}{\Delta[n+1]} \begin{pmatrix} 1 - \lambda d[n+1] & \lambda b[n+1] \\ \lambda c[n+1] & 1 - \lambda a[n+1] \end{pmatrix}, \quad (2.162)$$
where
\[ \Delta[n + 1] = 1 - \lambda^2(b[n + 1]c[n + 1] - a[n + 1]d[n + 1]), \]
\[ \lambda = \frac{ha[k + 1]}{D}. \]

With these definitions, the radial Dirac equation can be written in precisely the same form as the radial Schrödinger equation (2.64)
\[ y[n + 1] = M^{-1}[n + 1] \left( y[n] + \frac{h}{D} \sum_{j=1}^{k} a[j] f[n - k + j] \right). \tag{2.163} \]

This formula is used in the relativistic version of the routine ADAMS to carry out the step-by-step integration of the Dirac equation.

As in the nonrelativistic case, we must supply values of \( y_n \) at the first \( k \) grid points. This is done by adapting the procedure used to start the outward integration of the Schrödinger equation to the Dirac case.

**OUTDIR:** The values of \( y_n \) at the first \( k \) grid points, needed to start the outward integration using (2.163), are obtained using Lagrangian integration formulas. As a preliminary step, we factor \( r^\gamma \) from the radial functions \( P_\kappa(r) \) and \( Q_\kappa(r) \), where \( \gamma = \sqrt{k^2 - (\alpha Z)^2} \). We write:
\[ P_\kappa(r) = r^\gamma u(r(t)), \tag{2.164} \]
\[ Q_\kappa(r) = r^\gamma v(r(t)). \tag{2.165} \]

and find,
\[ \frac{du}{dt} = a(t)u(t) + b(t)v(t), \tag{2.166} \]
\[ \frac{dv}{dt} = c(t)u(t) + d(t)v(t). \tag{2.167} \]

where,
\[ a(t) = -(\gamma + \kappa)r'/r, \tag{2.168} \]
\[ b(t) = -\alpha(W - V(r) + 2\alpha^{-2})r', \tag{2.169} \]
\[ c(t) = \alpha(W - V(r))r', \tag{2.170} \]
\[ d(t) = -(\gamma - \kappa)r'/r. \tag{2.171} \]

We normalize our solution so that, at the origin, \( u_0 = u(0) = 1 \). It follows that \( v_0 = v(0) \) takes the value
\[ v_0 = -(\kappa + \gamma)/\alpha Z, \quad \text{for } \kappa > 0, \tag{2.172} \]
\[ = \alpha Z/(\gamma - \kappa), \quad \text{for } \kappa < 0, \tag{2.173} \]

provided the potential satisfies
\[ V(r) \to -\frac{Z}{r}. \]
as \( r \to 0 \). The two equations (2.172) and (2.173) lead to identical results mathematically; however, (2.172) is used for \( \kappa > 0 \) and (2.173) for \( \kappa < 0 \) to avoid unnecessary loss of significant figures by cancellation for small values of \( \alpha Z \). One can express \( du/dt \) and \( dv/dt \) at the points \( t[i], i = 0, 1, \cdots, k \) in terms of \( u[i] = u(t[i]) \) and \( v[i] = v(t[i]) \) using the Lagrangian differentiation formulas written down in Eq.(2.70). The differential equations thereby become inhomogeneous matrix equations giving the vectors \((u[1], u[2], \cdots, u[k])\) and \((v[1], v[2], \cdots, v[k])\) in terms of initial values \( u[0] \) and \( v[0] \):

\[
\sum_{j=1}^{k} m[ij] u[j] - a[i] u[i] - b[i] v[i] = -m[i0] u[0], \quad (2.174)
\]

\[
\sum_{j=1}^{k} m[ij] v[j] - c[i] u[i] - d[i] v[i] = -m[i0] v[0]. \quad (2.175)
\]

This system of \( 2k \times 2k \) inhomogeneous linear equations can be solved by standard routines to give \( u[i] \) and \( v[i] \) at the points \( i = 1, 2, \cdots, k \). The corresponding values of \( P_\kappa \) and \( Q_\kappa \) are given by

\[
P_\kappa(r[i]) = r[i]^\gamma u[i], \quad (2.176)
\]

\[
Q_\kappa(r[i]) = r[i]^\gamma v[i]. \quad (2.177)
\]

These equations are used in the routine \textsc{outdir} to give the \( k \) values required to start the outward integration using a \( k + 1 \)-point Adams-Moulton scheme.

\textsc{indir:} The inward integration is started using an asymptotic expansion of the radial Dirac functions. The expansion is carried out for \( r \) so large that the potential \( V(r) \) takes on its asymptotic form

\[ V(r) = -\frac{\zeta}{r}, \]

where \( \zeta = Z - N + 1 \) is the ionic charge of the atom. We assume that the asymptotic expansion of the radial Dirac functions takes the form

\[
P_\kappa(r) = r^\sigma e^{-\lambda r} \left\{ \sqrt{\frac{c^2 + E}{2c^2}} \left[ 1 + \frac{a_1}{r} + \frac{a_2}{r^2} + \cdots \right] \\
+ \sqrt{\frac{c^2 - E}{2c^2}} \left[ \frac{b_1}{r} + \frac{b_2}{r^2} + \cdots \right] \right\}, \quad (2.178)
\]

\[
Q_\kappa(r) = r^\sigma e^{-\lambda r} \left\{ \sqrt{\frac{c^2 + E}{2c^2}} \left[ 1 + \frac{a_1}{r} + \frac{a_2}{r^2} + \cdots \right] \\
- \sqrt{\frac{c^2 - E}{2c^2}} \left[ \frac{b_1}{r} + \frac{b_2}{r^2} + \cdots \right] \right\}, \quad (2.179)
\]
where $\lambda = \sqrt{c^2 - E^2/c^2}$. The radial Dirac equations admit such a solution only if $\sigma = E\zeta/c^2\lambda$. The expansion coefficients can be shown to satisfy the following recursion relations:

\begin{align}
    b_1 &= \frac{1}{2c} \left( \kappa + \frac{\zeta}{\lambda} \right), \\
    b_{n+1} &= \frac{1}{2n\lambda} \left( \kappa^2 - (n - \sigma)^2 - \frac{\zeta^2}{c^2} \right) b_n, \quad n = 1, 2, \cdots, \\
    a_n &= \frac{c}{n\lambda} \left( \kappa + (n - \sigma)\frac{E}{c^2} - \frac{\zeta\lambda}{c^2} \right) b_n, \quad n = 1, 2, \cdots.
\end{align}

In the routine INDIR, Eqs. (2.178) and (2.179) are used to generate the $k$ values of $P_\kappa(r)$ and $Q_\kappa(r)$ needed to start the inward integration.

### 2.7.2 Eigenvalue Problem for Dirac Equation (MASTER)

The method that we use to determine the eigenfunctions and eigenvalues of the radial Dirac equation is a modification of that used in the nonrelativistic routine MASTER to solve the eigenvalue problem for the Schrödinger equation. We guess an energy, integrate the equation outward to the outer classical turning point $a_c$ using OUTDIR, integrate inward from the practical infinity $a_\infty$ to $a_c$ using INDIR and, finally, scale the solution in the region $r > a_c$ so that the large component $P(r)$ is continuous at $a_c$. A preliminary adjustment of the energy is made to obtain the correct number of nodes ($= n - l - 1$) for $P(r)$ by adjusting the energy upward or downward as necessary. At this point we have a continuous large component function $P(r)$ with the correct number of radial nodes; however, the small component $Q(r)$ is discontinuous at $r = a_c$. A fine adjustment of the energy is made using perturbation theory to remove this discontinuity.

If we let $P_1(r)$ and $Q_1(r)$ be solutions to the radial Dirac equation corresponding to energy $W_1$ and let $P_2(r)$ and $Q_2(r)$ be solutions corresponding to energy $W_2$, then it follows from the radial Dirac equations that

\begin{equation}
    \frac{d}{dr}(P_1Q_2 - P_2Q_1) = \frac{1}{c}(W_2 - W_1)(P_1P_2 + Q_1Q_2).
\end{equation}

Integrating both sides of this equation from $0$ to $a_c$ and adding the corresponding integral of both sides from $a_c$ to infinity, we obtain the identity

\begin{equation}
    P_1(a_c)(Q_2^+ - Q_2^-) + P_2(a_c)(Q_1^+ - Q_1^-) = \frac{1}{c}(W_2 - W_1) \int_0^\infty (P_1P_2 + Q_1Q_2) dr,
\end{equation}

where $Q_1^+$ and $Q_2^+$ are the values of the small components at $a_c$ obtained from inward integration, and $Q_1^-$ and $Q_2^-$ are the values at $a_c$ obtained from outward integration. If we suppose that $Q_1$ is discontinuous at $a_c$ and if we require that $Q_2$ be continuous, then we obtain from (2.184) on approximating $P_2(r)$ and $Q_2(r)$ by $P_1(r)$ and $Q_1(r)$,

\begin{equation}
    W_2 \approx W_1 + \frac{cP_1(a_c)(Q_1^+ - Q_1^-)}{\int_0^\infty (P_1^2 + Q_1^2) dr}.
\end{equation}
The approximation (2.185) is used iteratively to reduce the discontinuity in \( Q(r) \) at \( r = a_c \) to insignificance. The Dirac eigenvalue routine \texttt{dmaster} is written following the pattern of the nonrelativistic eigenvalue routine \texttt{master}, incorporating the routines \texttt{outdir} and \texttt{indir} to carry out the point-by-point integration of the radial equations and using the approximation (2.185) to refine the solution.

### 2.7.3 Examples using Parametric Potentials

As in the nonrelativistic case, it is possible to devise parametric potentials to approximate the effects of the electron-electron interaction. Two potentials that have been used with some success to describe properties of large atoms having one valence electron are the Tietz potential

\begin{equation}
V(r) = -\frac{1}{r} \left[ 1 + \frac{(Z - 1)e^{-\gamma r}}{(1 + tr)^2} \right],
\end{equation}

and the Green potential

\begin{equation}
V(r) = -\frac{1}{r} \left[ 1 + \frac{Z - 1}{He^{r/d} - 1 + 1} \right].
\end{equation}

Each of these potentials contain two parameters that can be adjusted to fit experimentally measured energy levels. In Table 2.3, we list values of the parameters for rubidium (\( Z=37 \)), cesium (\( Z=55 \)), gold (\( Z=79 \)) and thallium (\( Z=81 \)). Energies of low-lying states of these atoms obtained by solving the Dirac equation in the two potentials are listed in Table 2.4. Wave functions obtained by solving the Dirac equation in parametric potentials have been successfully employed to predict properties of heavy atoms (such as hyperfine constants) and to describe the interaction of atoms with electromagnetic fields. The obvious disadvantage of treating atoms using parametric potentials is that there is no \textit{a priori} reason to believe that properties, other than those used as input data in the fitting procedure, will be predicted accurately. In the next chapter, we take up the Hartree-Fock theory, which provides an \textit{ab-initio} method for calculating electronic potentials, atomic energy levels and wave functions.
2.7. **NUMERICAL SOLUTION TO DIRAC EQUATION**

Table 2.4: Energies obtained using the Tietz and Green potentials.

<table>
<thead>
<tr>
<th>State</th>
<th>Tietz</th>
<th>Green</th>
<th>Exp.</th>
<th>State</th>
<th>Tietz</th>
<th>Green</th>
<th>Exp.</th>
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<td></td>
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Chapter 3

Self-Consistent Fields

In this chapter, we consider the problem of determining an approximate wave function for an \( N \)-electron atom. We assume that each electron in the atom moves independently in the nuclear Coulomb field and the average field of the remaining electrons. We approximate the electron-electron interaction by a central potential \( U(r) \), and we construct an \( N \)-electron wave function for the atomic ground state as an antisymmetric product of one-electron orbitals. Next, we evaluate the energy of the atom in its ground state using this wave function. We invoke the variational principle, requiring that the energy be stationary with respect to small changes in the orbitals with the constraint that the wave function remain normalized, to determine the orbitals. This leads to the Hartree-Fock (HF) equations. Solving the HF equations, we determine the one-electron orbitals, the one-electron energies, and the central potential \( U(r) \) self-consistently.

3.1 Two-Electron Systems

Let us start our discussion of many-electron atoms by considering a two-electron (heliumlike) ion with nuclear charge \( Z \). The two-electron Hamiltonian may be written

\[
H(r_1, r_2) = h_0(r_1) + h_0(r_2) + \frac{1}{r_{12}}, \quad (3.1)
\]

with

\[
h_0(r) = -\frac{1}{2} \nabla^2 - \frac{Z}{r}. \quad (3.2)
\]

The term \( 1/r_{12} \) in Eq.(3.1) is the Coulomb repulsion between the two electrons. The two-electron wave function \( \Psi(r_1, r_2) \) satisfies the Schrödinger equation

\[
H(r_1, r_2)\Psi(r_1, r_2) = E\Psi(r_1, r_2). \quad (3.3)
\]

We seek bound-state solutions to this equation.
The two-electron Hamiltonian is symmetric with respect to the interchange of the coordinates \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \). It follows that \( \Psi(\mathbf{r}_2, \mathbf{r}_1) \) is an eigenfunction of \( H \) having the same eigenvalue as \( \Psi(\mathbf{r}_1, \mathbf{r}_2) \). Moreover, the symmetric and antisymmetric combinations,

\[
\Psi(\mathbf{r}_1, \mathbf{r}_2) \pm \Psi(\mathbf{r}_2, \mathbf{r}_1), \quad (3.4)
\]

are also eigenfunctions, energy degenerate with \( \Psi(\mathbf{r}_1, \mathbf{r}_2) \). The symmetric combination in Eq.(3.4) gives the two-particle wave function appropriate to a system of two interacting bosons; for example, an atom consisting of two \( \pi^- \) mesons in a nuclear Coulomb field repelling one another by the Coulomb force. For electrons and other fermions, the antisymmetric combination in Eq.(3.4) is the appropriate choice.

As an approximation to the two-electron Hamiltonian in Eq.(3.1), let us consider the Independent-Particle Hamiltonian

\[
H_0(\mathbf{r}_1, \mathbf{r}_2) = h(\mathbf{r}_1) + h(\mathbf{r}_2), \quad (3.5)
\]

where

\[
h(\mathbf{r}) = h_0(\mathbf{r}) + U(\mathbf{r}) = -\frac{1}{2} \nabla^2 + V(\mathbf{r}). \quad (3.6)
\]

The Hamiltonian \( H_0 \) describes the independent motion of two particles in a potential \( V(\mathbf{r}) = -Z/r + U(\mathbf{r}) \). The potential \( U(\mathbf{r}) \) is chosen to approximate the effect of the Coulomb repulsion \( 1/r^{12} \). The full Hamiltonian \( H \) is then given by

\[
H = H_0 + V(\mathbf{r}_1, \mathbf{r}_2),
\]

and

\[
V(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r_{12}} - U(\mathbf{r}_1) - U(\mathbf{r}_2). \quad (3.7)
\]

If we let the orbital \( \psi_a(\mathbf{r}) \) represent a solution to the one-electron Schrödinger equation,

\[
h(\mathbf{r}) \psi_a(\mathbf{r}) = \epsilon_a \psi_a(\mathbf{r}), \quad (3.8)
\]

belonging to eigenvalue \( \epsilon_a \), then the product wave function \( \Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \) is a solution to the two-electron problem,

\[
H_0 \Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = E_{ab} \Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2), \quad (3.9)
\]

belonging to energy \( E_{ab}^{(0)} = \epsilon_a + \epsilon_b \).

The lowest energy two-electron eigenstate of \( H_0 \) is a product of the two lowest energy one-electron orbitals. For atomic potentials, these are the \( 1s \) orbitals corresponding to the two possible orientations of spin, \( \psi_{1s\mu}(\mathbf{r}) = (P_{1s}(r)/r)Y_{\mu0}(\hat{r})\chi_\mu \), with \( \mu = \pm 1/2 \). The corresponding antisymmetric product state is

\[
\Psi_{1s,1s}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4\pi} \frac{1}{r_1} P_{1s}(r_1) \frac{1}{r_2} P_{1s}(r_2)
\]

\[
\frac{1}{\sqrt{2}} (\chi_{1/2}(1)\chi_{-1/2}(2) - \chi_{-1/2}(1)\chi_{1/2}(2)). \quad (3.10)
\]
The factor $1/\sqrt{2}$ is introduced here to insure that $(\Psi_{1s1s}|\Psi_{1s1s}) = 1$. The wave function in Eq.(3.10) is an approximation to the ground-state wave function for a two-electron ion.

The orbital angular momentum vector $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$ and the spin angular momentum $\mathbf{S} = \frac{1}{2}\sigma_1 + \frac{1}{2}\sigma_2$ commute with $H$ as well as $H_0$. It follows that the eigenstates of $H$ and $H_0$ can also be chosen as eigenstates of $L^2$, $L_z$, $S^2$ and $S_z$. The combination of spin functions in Eq.(3.10),

$$\frac{1}{\sqrt{2}}(\chi_{1/2}(1)\chi_{-1/2}(2) - \chi_{-1/2}(1)\chi_{1/2}(2)),$$

is an eigenstate of $S^2$ and $S_z$ with eigenvalues 0 and 0, respectively. Similarly, the product of spherical harmonics $Y_{00}^{(1)}(\hat{r}_1)Y_{00}^{(2)}(\hat{r}_2)$ is an eigenstate of $L^2$ and $L_z$ with eigenvalues 0 and 0, respectively.

Let us approximate the electron interaction by simply replacing the charge $Z$ in the Coulomb potential by an effective charge $\zeta = Z - \sigma$. This corresponds to choosing the electron-electron potential $U(r) = (Z - \zeta)/r$. The potential $V(r)$ in the single-particle Hamiltonian is $V(r) = -\zeta/r$. The one-electron solutions to Eq.(3.8) are then known analytically; they are

$$P_{1s}(r) = 2\zeta^{3/2} re^{-\zeta r}.$$

The corresponding two-electron energy eigenvalue is $E_{1s1s}^{(0)} = -\zeta^2$ a.u. We can easily obtain the first-order correction to this energy by applying first-order perturbation theory:

$$E_{1s1s}^{(1)} = (\Psi_{1s1s}| \frac{1}{\sqrt{12}} - U(r_1) - U(r_2)|\Psi_{1s1s}).$$ (3.13)

The first term in (3.13) can be written

$$\langle \Psi_{1s1s}| \frac{1}{r_{12}} |\Psi_{1s1s}\rangle = \frac{1}{4\pi^2} \int dr_1 d\Omega_1 \int dr_2 d\Omega_2 P_{1s}^2(r_1) P_{1s}^2(r_2) \frac{1}{r_{12}}.$$

The Coulomb interaction in this equation can be expanded in terms of Legendre polynomials to give

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos \theta),$$

where $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$, and where $\theta$ is the angle between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. With the aid of this expansion, the angular integrals can be carried out to give

$$\langle \Psi_{1s1s}| \frac{1}{r_{12}} |\Psi_{1s1s}\rangle = \int_0^\infty dr_1 P_{1s}^2(r_1) \int_0^\infty dr_2 P_{1s}^2(r_2) \frac{1}{r_>}$$. (3.16)

It should be noted that after the angular integrations, only the monopole contribution from (3.15) survives. The function

$$v_0(1s, r_1) = \int_0^\infty dr_2 P_{1s}^2(r_2) \frac{1}{r_>}$$. (3.17)
CHAPTER 3. SELF-CONSISTENT FIELDS

is just the potential at \( r_1 \) of a spherically symmetric charge distribution having radial density \( P_{1s}(r) \). In terms of this function, we may write

\[
\langle \Psi_{1s1s} \left| \frac{1}{r_{12}} \right| \Psi_{1s1s} \rangle = \int_0^\infty P_{1s}^2(r) v_0(1s, r) \, dr. \tag{3.18}
\]

The two remaining integrals in Eq.(3.13) are easily evaluated. We find

\[
\langle \Psi_{1s1s} | U(r_1) | \Psi_{1s1s} \rangle = \langle \Psi_{1s1s} | U(r_2) | \Psi_{1s1s} \rangle = \int_0^\infty P_{1s}^2(r) U(r) \, dr. \tag{3.19}
\]

Combining (3.18) and (3.19), we obtain the following expression for the first-order energy:

\[
E_{1s1s}^{(1)} = \int_0^\infty P_{1s}^2(r) (v_0(1s, r) - 2U(r)) \, dr. \tag{3.20}
\]

Using the specific form of the 1s radial wave function given in Eq.(3.12), we can evaluate \( v_0(1s, r) \) analytically using Eq.(3.17) to obtain

\[
v_0(1s, r) = (1 - e^{-2\zeta r})/r - \zeta e^{-2\zeta r}. \tag{3.21}
\]

Using this result, we find

\[
\int_0^\infty P_{1s}^2(r) v_0(1s, r) \, dr = \frac{5}{8} \zeta. \tag{3.22}
\]

The integral of \( U(r) = (Z - \zeta)/r \) in Eq.(3.20) can be evaluated using the fact that \( \langle 1s | 1/r | 1s \rangle = \zeta \). Altogether, we find

\[
E_{1s1s}^{(1)} = \frac{5}{8} \zeta - 2(Z - \zeta)\zeta. \tag{3.23}
\]

Combining this result with the expression for the lowest-order energy, we obtain

\[
E_{1s1s} = E_{1s1s}^{(0)} + E_{1s1s}^{(1)} = -\zeta^2 + \frac{5}{8} \zeta - 2(Z - \zeta)\zeta. \tag{3.24}
\]

The specific value of \( \zeta \) in this equation is determined with the aid of the variational principle, which requires that the parameters in the approximate wave function be chosen to minimize the energy. The value of \( \zeta \) which minimizes the energy in Eq.(3.24) is found to be \( \zeta = Z - 5/16 \). The corresponding value of the energy is \( E_{1s1s} = -(Z - 5/16)^2 \). For helium, \( Z = 2 \), this leads to a prediction for the ground-state energy of \( E_{1s1s} = -2.848 \) a.u., which is within 2% of the experimentally measured energy \( E_{1s1s}^{exp} = -2.903 \) a.u.

Generally, in the independent-particle approximation, the energy can be expressed in terms of the radial wave function as

\[
E_{1s1s} = \langle \Psi_{1s1s} | h_0(r_1) + h_0(r_2) + \frac{1}{r_{12}} | \Psi_{1s1s} \rangle. \tag{3.25}
\]
3.1. TWO-ELECTRON SYSTEMS

The expectation values of the single-particle operators \( h_0(r_1) \) and \( h_0(r_2) \) are identical. The first term in (3.25) can be reduced to

\[
\langle \Psi_{1s1s} | h_0 | \Psi_{1s1s} \rangle = \int_0^\infty dr \left( -\frac{1}{2} \frac{d^2 P_{1s}}{dr^2} - \frac{Z}{r} P_{1s}^2 \right).
\]

Integrating by parts, and making use of the previously derived expression for the Coulomb interaction in (3.18), we obtain

\[
E_{1s1s} = \int_0^\infty dr \left[ \left( \frac{dP_{1s}}{dr} \right)^2 - 2 \frac{Z}{r} P_{1s}^2(r) + v_0(1s, r) P_{1s}^2(r) \right].
\]

The requirement that the two-particle wave function be normalized, \( \langle \Psi_{1s1s} | \Psi_{1s1s} \rangle = 1 \), leads to the constraint on the single electron orbital

\[
N_{1s} = \int_0^\infty P_{1s}(r)^2 dr = 1.
\]

We now invoke the variational principle to determine the radial wave functions. We require that the energy be stationary with respect to variations of the radial function subject to the normalization constraint. Introducing the Lagrange multiplier \( \lambda \), the variational principle may be written

\[
\delta(E_{1s1s} - \lambda N_{1s}) = 0.
\]

We designate the variation in the function \( P_{1s}(r) \) by \( \delta P_{1s}(r) \), and we require \( \delta P_{1s}(0) = \delta P_{1s}(\infty) = 0 \). Further, we note the identity

\[
\delta \frac{dP_{1s}}{dr} = \frac{d}{dr} \delta P_{1s}.
\]

With the aid of (3.30) we obtain

\[
\delta(E_{1s1s} - \lambda N_{1s}) = 2 \int_0^\infty \left( -\frac{d^2 P_{1s}}{dr^2} - 2 \frac{Z}{r} P_{1s}(r) \right. \\
+ 2v_0(1s, r) P_{1s}(r) - \lambda P_{1s}(r) \left. \right) \delta P_{1s}(r).
\]

Requiring that this expression vanish for arbitrary variations \( \delta P_{1s}(r) \) satisfying the boundary conditions leads to the Hartree-Fock equation

\[
-\frac{1}{2} \frac{d^2 P_{1s}}{dr^2} - \frac{Z}{r} P_{1s}(r) + v_0(1s, r) P_{1s}(r) = \epsilon_{1s} P_{1s}(r),
\]

where we have defined \( \epsilon_{1s} = \lambda/2 \). The HF equation is just the radial Schrödinger equation for a particle with orbital angular momentum 0 moving in the potential

\[
V(r) = -\frac{Z}{r} + v_0(1s, r).
\]
CHAPTER 3. SELF-CONSISTENT FIELDS

Figure 3.1: Relative change in energy \((E^{(n)} - E^{(n-1)})/E^{(n)}\) as a function of the iteration step number \(n\) in the iterative solution of the HF equation for helium, \(Z = 2\).

The HF equation is solved iteratively. We start the iterative solution by approximating the radial HF function \(P_{1s}(r)\) with a screened 1s Coulomb function having effective charge \(\zeta = Z - 5/16\). We use this wave function to evaluate \(v_0(1s,r)\). We then solve (3.32) using the approximate potential \(v_0(1s,r)\). The resulting radial function \(P_{1s}(r)\) is used to construct a second approximation to \(v_0(1s,r)\), and the iteration is continued until self-consistent values of \(P_{1s}(r)\) and \(v_0(1s,r)\) are obtained. The pattern of convergence for this iteration procedure is illustrated in Fig. 3.1 where we plot the relative change in the single-particle energy as a function of the iteration step. After 18 steps, the energy has converged to 10 figures.

The resulting value of single-particle energy is found to be \(\epsilon_a = -0.9179\ldots\) a.u.. The total energy of the two-electron system can be written

\[
E_{1s1s} = \langle 1s | 2h_0 + v_0(1s,r) | 1s \rangle = 2\epsilon_{1s} - \langle 1s | v_0(1s,r) | 1s \rangle. \tag{3.34}
\]

From this, we find \(E_{1s1s} = -2.861\ldots\) a.u., only a slight improvement over the value obtained previously using a screened Coulomb field to approximate the electron-electron interaction. The HF energy is the most accurate that can be obtained within the framework of the independent-particle model. To achieve greater accuracy, we must go beyond the independent-particle model and treat the correlated motion of the two electrons.

In Fig. 3.2, we plot the functions \(P_{1s}(r)\) and \(v_0(1s,r)\) found by solving the HF equation for neutral helium, \(Z = 2\). The potential \(v_0(1s,r)\) has the following limiting values:

\[
\lim_{r \to 0} v_0(1s,r) = \langle 1s | \frac{1}{r} | 1s \rangle, \tag{3.35}
\]

\[
\lim_{r \to \infty} v_0(1s,r) = \frac{1}{r}. \tag{3.36}
\]
3.2. HF EQUATIONS FOR CLOSED-SHELL ATOMS

For a system of $N$-electrons, the Hamiltonian is

$$ H(r_1, r_2, \cdots, r_N) = \sum_{i=1}^{N} h_0(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}, \quad (3.37) $$

where $h_0$ is the single-particle operator for the sum of the kinetic energy and the electron-nucleus interaction given in Eq.(3.2), and where $1/r_{ij}$ is the Coulomb interaction energy between the $i^{th}$ and $j^{th}$ electrons. We seek approximate solutions to the $N$-electron Schrödinger equation

$$ H(r_1, r_2, \cdots, r_N)\Psi(r_1, r_2, \cdots, r_N) = E\Psi(r_1, r_2, \cdots, r_N). \quad (3.38) $$

The solutions corresponding to electrons (and other fermions) are completely antisymmetric with respect to the interchange of any two coordinates

$$ \Psi(r_1, \cdots, r_i, \cdots, r_j, \cdots, r_N) = -\Psi(r_1, \cdots, r_j, \cdots, r_i, \cdots, r_N). \quad (3.39) $$

It is perhaps worthwhile repeating here an observation by Hartree (1957, p. 16) concerning “exact” solutions to Eq.(3.38) in the many-electron case. If we consider, for example, the 26 electron iron atom, the function $\Psi(r_1, r_2, \cdots, r_N)$ depends on $3 \times 26 = 78$ variables. Using a course grid of only 10 points for each variable, it would require $10^{78}$ numbers to tabulate the wave function for iron. Since this number exceeds the estimated number of particles in the solar system, it is difficult to understand how the wave function would be stored even if it could be calculated! Of more practical interest are approximations to “exact” solutions and methods for systematically improving the accuracy of such approximations.

Figure 3.2: Solutions to the HF equation for helium, $Z = 2$. The radial HF wave function $P_{1s}(r)$ is plotted in the solid curve and electron potential $v_0(1s, r)$ is plotted in the dashed curve.

3.2. HF Equations for Closed-Shell Atoms

For a system of $N$-electrons, the Hamiltonian is

$$ H(r_1, r_2, \cdots, r_N) = \sum_{i=1}^{N} h_0(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}, \quad (3.37) $$

where $h_0$ is the single-particle operator for the sum of the kinetic energy and the electron-nucleus interaction given in Eq.(3.2), and where $1/r_{ij}$ is the Coulomb interaction energy between the $i^{th}$ and $j^{th}$ electrons. We seek approximate solutions to the $N$-electron Schrödinger equation

$$ H(r_1, r_2, \cdots, r_N)\Psi(r_1, r_2, \cdots, r_N) = E\Psi(r_1, r_2, \cdots, r_N). \quad (3.38) $$

The solutions corresponding to electrons (and other fermions) are completely antisymmetric with respect to the interchange of any two coordinates

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Figure 3.2: Solutions to the HF equation for helium, $Z = 2$. The radial HF wave function $P_{1s}(r)$ is plotted in the solid curve and electron potential $v_0(1s, r)$ is plotted in the dashed curve.
Again, we start with the independent-particle approximation. We write $H = H_0 + V$, with

$$H_0(r_1, r_2, \cdots, r_N) = \sum_{i=1}^{N} h(r_i), \quad (3.40)$$

$$V(r_1, r_2, \cdots, r_N) = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} - \sum_{i=1}^{N} U(r_i), \quad (3.41)$$

where, as in the previous section, $U(r)$ is an appropriately chosen approximation to the electron interaction potential and where $h(r) = h_0 + U(r)$. If we let $\psi_a(r)$ be an eigenfunction of $h$ having eigenvalue $\epsilon_a$, then

$$\psi_a(r_1)\psi_b(r_2)\cdots\psi_n(r_N) \quad (3.42)$$

is an eigenfunction of $H_0$ with eigenvalue

$$E^{(0)}_{ab\cdots n} = \epsilon_a + \epsilon_b + \cdots + \epsilon_n.$$

Moreover, each of the $N!$ product functions obtained by permuting the indices $r_1, r_2, \cdots, r_N$ in the wave function (3.42), is degenerate in energy with that wave function. A completely antisymmetric product wave function is given by the Slater determinant

$$\Psi_{ab\cdots n}(r_1, r_2, \cdots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(r_1) & \psi_b(r_1) & \cdots & \psi_n(r_1) \\ \psi_a(r_2) & \psi_b(r_2) & \cdots & \psi_n(r_2) \\ \vdots & & & \vdots \\ \psi_a(r_N) & \psi_b(r_N) & \cdots & \psi_n(r_N) \end{vmatrix}. \quad (3.43)$$

The antisymmetric two-particle wave function $\Psi_{1a1b}(r_1, r_2)$ used in the previous section is a special case of a Slater-determinant wave function with $n_a = 1, l_a = 0, m_a = 0, \mu_a = 1/2$ and $n_b = 1, l_b = 0, m_b = 0, \mu_b = -1/2$. Here, we specify the orbitals by their quantum numbers; for example, $a = (n_a, l_a, m_a, \mu_a)$. Since the determinant vanishes if two columns are identical, it follows that the quantum numbers $a, b, \cdots, n$ must be distinct. The fact that the quantum numbers of the orbitals in an antisymmetric product wave function are distinct is called the Pauli exclusion principle.

In the following paragraphs, we will need to evaluate diagonal and off-diagonal matrix elements of many-particle operators between Slater-determinant wave functions. Many-particle operators $F$ of the form

$$F = \sum_{i=1}^{N} f(r_i), \quad (3.44)$$

such as $H_0$ itself, are called one-particle operators. Operators $G$ of the form

$$G = \frac{1}{2} \sum_{i \neq j} g(r_{ij}), \quad (3.45)$$

are called two-particle operators.
such as the Coulomb interaction energy, are called two-particle operators. The following rules will help us evaluate matrix elements of one- and two-particle operators:

**Rule 1**
\[
\langle \Psi_{a'b'...n'} | F | \Psi_{ab...n} \rangle = 0,
\]
if the indices \(\{a',b',...,n'\}\) and \(\{a,b,...,n\}\) differ in more than one place.

**Rule 2**
\[
\langle \Psi_{ab...k...n} | F | \Psi_{ab...k...n} \rangle = f_{k'k},
\]
if only the two indices \(k\) and \(k'\) differ.

**Rule 3**
\[
\langle \Psi_{ab...n} | F | \Psi_{ab...n} \rangle = \sum_{i=a}^{n} f_{ii},
\]
if the indices in the two sets are identical.

**Rule 4**
\[
\langle \Psi_{a'b'...n'} | G | \Psi_{ab...n} \rangle = 0,
\]
if the indices \(\{a',b',...,n'\}\) and \(\{a,b,...,n\}\) differ in more than two places.

**Rule 5**
\[
\langle \Psi_{ab...k'...l'...n} | G | \Psi_{ab...k...l...n} \rangle = g_{k'l'ki} - g_{k'li'k},
\]
if only the pairs \(k,l\) and \(k',l'\) in the two sets differ.

**Rule 6**
\[
\langle \Psi_{ab...k'...n} | G | \Psi_{ab...k...n} \rangle = \sum_{i=a}^{n} (g_{k'iki} - g_{k'iik}),
\]
if only the indices \(k\) and \(k'\) in the two sets differ.

**Rule 7**
\[
\langle \Psi_{ab...n} | G | \Psi_{ab...n} \rangle = \frac{1}{2} \sum_{i,j} (g_{ijji} - g_{ijij}),
\]
if the two sets are identical, where both sums extend over all of the indices \(\{a,b,...,n\}\)

In the above rules, we have introduced the notation:

\[
f_{ab} = \langle a | f | b \rangle = \int d^3 r \psi_a^\dagger(r) f(r) \psi_b(r),
\]
\[
g_{abcd} = \langle ab | g | cd \rangle = \int d^3 r_1 \int d^3 r_2 \psi_a^\dagger(r_1) \psi_b^\dagger(r_2) g(r_{12}) \psi_c(r_1) \psi_d(r_2).
\]
With the aid of these rules, we easily work out the expectation value of the $H_0$ and $H$, using a Slater determinant wave function:

$E^{(0)}_{ab\cdots n} = \sum_a (h_0)_{aa} + \sum_a U_{aa}$, \hspace{1cm} (3.48)

$E^{(1)}_{ab\cdots n} = \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}) - \sum_a U_{aa}$, \hspace{1cm} (3.49)

$E_{ab\cdots n} = \sum_a (h_0)_{aa} + \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba})$, \hspace{1cm} (3.50)

where the sums extend over all one-electron orbital quantum numbers in the set \{a, b, \cdots, n\}. The terms $g_{abab}$ and $g_{abba}$ are matrix elements of the Coulomb interaction $g(r_{12}) = \frac{1}{r_{12}}$. The term $g_{abab}$ is called the direct matrix element of the operator $g(r_{12})$ and $g_{abba}$ is called the exchange matrix element.

The lowest-energy eigenstate of $H_0$ for an $N$-electron atom is a product of the $N$ lowest-energy one-electron orbitals. For two-electron atoms, these are the two 1s orbitals with different spin projections. In atomic model potentials, such as those discussed in the previous chapter, the lowest few orbital eigenvalues are ordered in the sequence $\epsilon_{1s} < \epsilon_{2s} < \epsilon_{2p} < \epsilon_{3s} < \epsilon_{3p}$. (The ordering beyond this point depends on the potential to some extent and will be considered later.)

For three- or four-electron atoms (lithium and beryllium), the ground state-wave function is taken to be a Slater determinant made up of two 1s orbitals, and one or two 2s orbitals. The radial probability density functions for these atoms have two distinct maxima, one corresponding to the 1s electrons near $1/Z$ a.u., and a second corresponding to the 2s electron near 1 a.u.. This variation of the density is referred to as the atomic shell structure. Electronic orbitals having the same principal quantum number $n$ belong to the same shell; their contribution to the radial density is localized. Orbitals having the same principal quantum number, but different angular quantum numbers, belong to different subshells. They contribute fine structure to the radial density function of the atom. The 2s subshell is complete after including the two 2s orbitals with different spin projections. We continue through the first row of the periodic table, adding successive 2p electrons with different values of $m$ and $\mu$ until the $n = 2$ shell is complete at neon, $Z = 10$. This building up scheme can be continued throughout the periodic system.

Slater-determinant wave functions for atoms with closed subshells can be shown to be eigenstates of $L^2, L_z, S^2$ and $S_z$. The eigenvalues of all four of these operators are 0. Similarly, Slater-determinant wave function for atoms with one electron beyond closed subshells, or for atoms with a single hole in an otherwise filled subshell, are also angular momentum eigenstates. To construct angular momentum eigenstates for other open-shell atoms, linear combinations of Slater determinants, coupled together with Clebsch-Gordan coefficients, are used. We defer further discussion of open-shell atoms until the next chapter and concentrate here on the case of atoms with closed subshells.

We define the configuration of an atomic state to be the number and type of one-electron orbitals present in the Slater-determinant wave function represent-
ing that state. A configuration having \( k \) orbitals with principal quantum number \( n \) and angular quantum number \( l \) is designated by \( (nl)^k \). The configurations of the ground states of the closed-shell atoms being considered are: helium \((1s)^2\); beryllium \((1s)^2(2s)^2\); neon \((1s)^2(2s)^2(2p)^6\); magnesium \((1s)^2(2s)^2(2p)^6(3s)^2\); argon \((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6\), calcium \((1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2\); and so forth.

The orbitals \( \psi_n(r) \) are decomposed into radial, angular, and spin components as 
\[
\psi_n(r) = (P_{n,la}(\hat{r}_1)/r_1)Y_{l,m}^a(\hat{r}_1)\chi_{\mu_a}(\hat{r}_1),
\]
and the terms in the expression for the energy (3.50) are worked out. First, we evaluate \( (h_0)_{aa} \) to obtain:

\[
(h_0)_{aa} = \int_0^\infty dr P_{n,la} \left( \frac{1}{2} \frac{d^2 P_{n,la}}{dr^2} + \frac{l_a(l_a + 1)}{2r^2} P_{n,la} - \frac{Z}{r} P_{n,la} \right). \tag{3.51}
\]

We note that this term has the same value for each of the \( 2(2l_a + 1) \) orbitals in the \( n, l_a \) subshell. The integral on the right-hand side of this equation is often denoted by \( I(n, l_a) \). On integrating by parts, we can rewrite Eq. (3.51) as

\[
I(n, l_a) = \int_0^\infty dr \left[ \frac{1}{2} \left( \frac{dP_{n,la}}{dr} \right)^2 + \frac{l_a(l_a + 1)}{2r^2} P_{n,la}^2 - \frac{Z}{r} P_{n,la}^2 \right]. \tag{3.52}
\]

We will need this term later in this section.

Next, we examine the direct Coulomb matrix element \( g_{abab} \). To evaluate this quantity, we make use of the decomposition of \( 1/r_{12} \) given in Eq.(3.15). Further, we use the well-known identity

\[
P_l(\cos \theta) = \sum_{m=-l}^{l} (-1)^m C_{-m}^l(\hat{r}_1) C_m^l(\hat{r}_2),
\]

(3.53)

to express the Legendre polynomial of \( \cos \theta \), where \( \theta \) is the angle between the two vectors \( \hat{r}_1 \) and \( \hat{r}_2 \), in terms of the angular coordinates of the two vectors in an arbitrary coordinate system. Here, as in Chapter 1, the quantities \( C_m^l(\hat{r}) \) are tensor operators, defined in terms of spherical harmonics by:

\[
C_m^l(\hat{r}) = \sqrt{\frac{4\pi}{2l + 1}} Y_{lm}(\hat{r}).
\]

With the aid of the above decomposition, we find:

\[
g_{abab} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-1)^m \int_0^\infty dr_1 P_{n,la}^2(\hat{r}_1) \int d\Omega_1 Y_{l,m_a}^*(\hat{r}_1) C_{-m}^l(\hat{r}_1) Y_{l,m_a}(\hat{r}_1) \int_0^\infty dr_2 P_{n,la}^2(\hat{r}_2) \left( \frac{r_1}{r_2} \right) \int d\Omega_2 Y_{l,m_b}^*(\hat{r}_2) C_m^l(\hat{r}_2) Y_{l,m_b}(\hat{r}_2). \tag{3.54}
\]

The angular integrals can be expressed in terms of reduced matrix elements of
the tensor operator $C_{m}^{l}$ using the Wigner-Eckart theorem. We find

$$g_{abab} = \sum_{l=0}^{\infty} \frac{l_{a}m_{a}l_{b}m_{b}}{l_{a}m_{a}l_{b}m_{b}} \langle l_{a}||C^{l}||l_{b} \rangle \langle l_{b}||C^{l}||l_{a} \rangle R_{l}(n_{a}l_{a}, n_{b}l_{b}, n_{a}l_{a}, n_{b}l_{b}),$$

where

$$R_{l}(a, b, c, d) = \int_{0}^{\infty} dr_{1} P_{a}(r_{1}) P_{c}(r_{1}) \int_{0}^{\infty} dr_{2} P_{b}(r_{2}) P_{d}(r_{2}) \left( \frac{r_{l}^{2}}{r_{l}^{2} + 1} \right).$$

These integrals of products of four radial orbitals are called Slater integrals. The Slater integrals can be written in terms of multipole potentials. We define the potentials $v_{l}(a, b, r)$ by

$$v_{l}(a, b, r_{1}) = \int_{0}^{\infty} dr_{2} P_{a}(r_{2}) P_{b}(r_{2}) \left( \frac{r_{l}^{2}}{r_{l}^{2} + 1} \right).$$

We may then write

$$R_{l}(a, b, c, d) = \int_{0}^{\infty} dr P_{a}(r) P_{c}(r) v_{l}(b, d, r)$$

$$= \int_{0}^{\infty} dr P_{b}(r) P_{d}(r) v_{l}(a, c, r).$$

The potentials $v_{l}(a, b, r)$ are often expressed in the form $v_{l}(a, b, r) = Y_{l}(a, b, r)/r$. The functions $Y_{l}(a, b, r)$ are called Hartree screening functions. Later, we will designate the functions $v_{l}(a, a, r)$ using the slightly simpler notation $v_{l}(a, r)$. The function $v_{0}(a, r)$ is the potential at $r$ due to a spherically symmetric charge distribution with radial density $P_{a}(r)^{2}$. The functions $v_{l}(b, r)$ have the following limiting forms which will be used later:

$$\lim_{r \to 0} v_{l}(a, r) = r^{l} \langle a|\frac{1}{r^{l+1}}|a \rangle,$$

$$\lim_{r \to \infty} v_{l}(a, r) = \frac{1}{r^{l+1}} \langle a|r^{l}|a \rangle.$$

Following the outline of the calculation for the direct integral $g_{abab}$, we may write the exchange integral $g_{abba}$ as

$$g_{abba} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \delta_{\mu_{a}=\mu_{b}} \frac{l_{a}m_{a}l_{b}m_{b}}{l_{a}m_{a}l_{b}m_{b}} \langle l_{b}||C^{l}||l_{a} \rangle^{2} R_{l}(n_{a}l_{a}, n_{b}l_{b}, n_{b}l_{b}, n_{a}l_{a}).$$

Let us carry out the sum over the magnetic quantum numbers $m_{b}$ and $\mu_{b}$ in Eq.(3.55). We make use of the identity

$$\delta_{l_{b}l_{b}10} = \delta_{l_{b}} \sqrt{2l_{b} + 1}$$
to obtain
\[
\sum_{m_b\mu_b} g_{abab} = 2\sqrt{2l_b + 1} \frac{|l_a||C^0||l_b||C^0|}{2l_a + 1} R_0(n_a l_a, n_b l_b, n_a l_a, n_b l_b)
\]
\[
= 2(2l_b + 1) R_0(n_a l_a, n_b l_b, n_a l_a, n_b l_b) .
\] (3.64)

To carry out the sum over the magnetic quantum numbers \(m_b\) and \(\mu_b\) and \(m\) in Eq.(3.62), we use the identity
\[
l_a m_a - \sum_{l} l = \frac{2l_a + 1}{2}.
\] (3.65)
and find
\[
\sum_{m_b\mu_b} g_{abba} = \sum_{l} \frac{(l_b||C^l||l_a)^2}{2l_a + 1} R_l(n_a l_a, n_b l_b, n_b l_b, n_a l_a) .
\] (3.66)
The sum over \(l\) extends over all values permitted by the angular momentum and parity selection rules contained in \(l_a||C^l||l_a\), namely, \(|l_a - l_b| \leq l \leq l_a + l_b\), with the constraint that the sum \(l_a + l_b + l\) is an even integer.

We are now in a position to evaluate the expression for the energy given in Eq.(3.50). We find
\[
E_{ab\cdots n} = \sum_{n_a l_a} 2(2l_a + 1) \left\{ I(n_a l_a) + \sum_{n_b l_b} (2l_b + 1) \left( R_0(n_a l_a, n_b l_b, n_a l_a, n_b l_b)
- \sum_{l} \Lambda_{l_a l_b} R_l(n_a l_a, n_b l_b, n_b l_b, n_a l_a) \right) \right\},
\] (3.67)
with
\[
\Lambda_{l_a l_b} = \frac{(l_a||C^l||l_b)^2}{2(2l_a + 1)(2l_b + 1)} = \frac{1}{2} \left( \begin{array}{ccc} l_a & l & l_b \\ 0 & 0 & 0 \end{array} \right)^2 .
\] (3.68)
The coefficients \(\Lambda_{l_a l_b}\) are symmetric with respect to an arbitrary interchange of indices. Values of \(\Lambda_{l_a l_b}\) for \(0 \leq l_a \leq l_b \leq 4\) are given in Table 3.1.

To maintain normalization of the many-electron wave function, we must require that the radial functions corresponding to a fixed value of \(l\) be orthonormal. Therefore,
\[
N_{n_a l_a, n_b l_b} = \int_0^{\infty} dr P_{n_a l_a}(r) P_{n_b l_b}(r) = \delta_{n_a n_b} .
\] (3.69)

Introducing Lagrange multipliers to accommodate the constraints in Eq.(3.69), we can express the variational principle as:
\[
\delta(E_{ab\cdots n} - \sum_{n_a n_b l_a} \lambda_{n_a l_a, n_b l_b} N_{n_a l_a, n_b l_b}) = 0 ,
\] (3.70)
and we demand \(\lambda_{n_a l_a, n_b l_b} = \lambda_{n_b l_b, n_a l_a}\).
Table 3.1: Coefficients of the exchange Slater integrals in the nonrelativistic Hartree-Fock equations: $\Lambda_{l_a l_b l_c}$. These coefficients are symmetric with respect to any permutation of the three indices.

<table>
<thead>
<tr>
<th>$l_a$</th>
<th>$l_b$</th>
<th>$l_c$</th>
<th>$\Lambda_{l_a l_b l_c}$</th>
<th>$l_a$</th>
<th>$l_b$</th>
<th>$l_c$</th>
<th>$\Lambda_{l_a l_b l_c}$</th>
<th>$l_a$</th>
<th>$l_b$</th>
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The equation obtained by requiring that this expression be stationary with respect to variations $\delta P_{n_a l_a}(r)$ is found to be

$$-\frac{1}{2} \frac{d^2 P_{n_a l_a}(r)}{dr^2} + \frac{l_a(l_a + 1)}{2r^2} P_{n_a l_a}(r) - \frac{Z}{r} P_{n_a l_a}(r) + \sum_{n_b l_b} (4l_b + 2) \left( v_0(n_b l_b, r) P_{n_b l_b}(r) - \sum_{l_c} \Lambda_{l_a l_b l_c} v_l(n_b l_b, n_a l_a, r) P_{n_b l_b}(r) \right) = \epsilon_{n_a l_a} P_{n_a l_a}(r) + \sum_{n_b \neq n_a} \epsilon_{n_a l_a, n_b l_b} P_{n_b l_b}(r), \quad (3.71)$$

where $\epsilon_{n_a l_a, n_b l_b} = \lambda_{n_a l_a, n_b l_b} / (4l_a + 2)$ and $\epsilon_{n_a l_a} = \lambda_{n_a l_a, n_a l_a} / (4l_a + 2)$.

For orientation, let us examine several special cases. Let us first consider the case of helium for which there is a single 1s orbital and a single HF equation. The only nonvanishing angular coefficient in the second line of Eq.(3.71) is $\Lambda_{000} = 1/2$. The entire second row of the equation reduces to

$$2 \left( v_0(1s, r) P_{1s}(r) - \frac{1}{2} v_0(1s, r) P_{1s}(r) \right) = v_0(1s, r) P_{1s}(r).$$

The HF equation, Eq.(3.71), reduces to Eq.(3.32) derived in the previous section.

For the case of beryllium, there are two distinct radial orbitals for the 1s
and 2s shells, respectively. The second line of Eq.(3.71) takes the form
\[
\left( v_0(1s, r) + 2v_0(2s, r) \right) P_{1s} - v_0(2s, 1s, r) P_{2s}(r), \quad \text{for } n_a l_a = 1s,
\]
\[
2v_0(1s, r) + v_0(2s, r) \right) P_{2s} - v_0(1s, 2s, r) P_{1s}(r), \quad \text{for } n_a l_a = 2s.
\]

The two HF equations for beryllium become
\[
\frac{1}{2} \frac{d^2 P_{1s}}{dr^2} + \left( -\frac{Z}{r} + v_0(1s, r) + 2v_0(2s, r) \right) P_{1s} - v_0(2s, 1s, r) P_{2s}(r) = \epsilon_{1s} P_{1s}(r) + \epsilon_{1s, 2s} P_{2s}(r), \quad (3.72)
\]
\[
\frac{1}{2} \frac{d^2 P_{2s}}{dr^2} + \left( -\frac{Z}{r} + 2v_0(1s, r) + v_0(2s, r) \right) P_{2s} - v_0(1s, 2s, r) P_{1s}(r) = \epsilon_{1s, 2s} P_{1s}(r) + \epsilon_{2s} P_{2s}(r). \quad (3.73)
\]

The off-diagonal Lagrange multiplier \( \epsilon_{1s, 2s} \) is chosen so as to insure the orthogonality of the 1s and 2s radial orbitals. Multiplying Eq.(3.72) by \( P_{2s}(r) \) and Eq.(3.73) by \( P_{1s}(r) \), subtracting the resulting equations, and integrating from 0 to \( \infty \), we obtain the identity
\[
(\epsilon_{1s} - \epsilon_{2s}) \int_0^\infty dr P_{1s}(r) P_{2s}(r) = -\frac{1}{2} \left( P_{2s} \frac{dP_{1s}}{dr} - P_{1s} \frac{dP_{2s}}{dr} \right)_0^\infty. \quad (3.74)
\]

For solutions regular at 0 and \( \infty \), the right-hand side of this equation vanishes. Since \( \epsilon_{2s} \neq \epsilon_{1s} \), the solutions to Eqs.(3.72) and (3.73) are orthogonal for arbitrary values of the off-diagonal Lagrange multiplier. We make the simplest choice here, namely, \( \epsilon_{1s, 2s} = 0 \). The HF equations then reduce to a pair of radial Schrödinger equations coupled together by the potential function \( v_0(1s, 2s, r) = v_0(2s, 1s, r) \).

As in the example of beryllium, it is easily shown for a general closed-shell atom that the orbitals associated with a specific value of \( l \) and different values of \( n \) are orthogonal no matter what value is chosen for the off-diagonal Lagrange multipliers. We take advantage of this fact to simplify the HF equations by choosing \( \epsilon_{n_a l_a, n_b l_b} = 0 \) for all values of \( n_a, n_b \) and \( l_a \).

Generally, we define the Hartree-Fock potential \( V_{HF} \) by specifying its action on an arbitrary radial orbital \( P_*(r) \). Writing \( V_{HF} P_*(r) = V_{\text{dir}} P_*(r) + V_{\text{exc}} P_*(r) \) we find,
\[
V_{\text{dir}} P_*(r) = \sum_b (4l_b + 2) v_0(b, r) P_*(r), \quad (3.75)
\]
\[
V_{\text{exc}} P_*(r) = \sum_b (4l_b + 2) \sum_l \Lambda_{l_b l, l} v_l(b, *, r) P_l(r). \quad (3.76)
\]

In the above equations, the sum over \( b \) is understood to mean a sum over \( n_b \) and \( l_b \). The direct potential \( V_{\text{dir}} \) is a multiplicative operator. It is just the potential
due to the spherically averaged charge distribution of all atomic electrons. The exchange potential $V_{\text{exc}}$ is, by contrast, a nonlocal operator defined by means of an integral. The direct part of the HF potential has the following limits

$$\lim_{r \to 0} V_{\text{dir}}(r) = \sum_b (4l_b + 2) \frac{1}{r} \langle b | b \rangle,$$

$$\lim_{r \to \infty} V_{\text{dir}}(r) = \frac{N}{r},$$

where $N = \sum_b (4l_b + 2)$ = number of electrons in the atom. For neutral atoms, the direct part of the HF potential precisely cancels the nuclear potential at large $r$. The asymptotic potential for a neutral atom is, therefore, dominated by the monopole parts of the exchange potential at large $r$. Using the fact that $\Lambda_{l_b l_a} = \frac{\delta_{l_b l_a}}{4l_a + 2}$, and the fact that the limiting value of $v_0(n_b l_a, n_a l_a, r)$ is

$$\lim_{r \to \infty} v_0(n_b l_a, n_a l_a, r) = \frac{1}{r} \int_0^\infty dr P_{n_b l_a}(r) P_{n_a l_a}(r) = \frac{\delta_{n_b n_a}}{r},$$

we find that

$$\lim_{r \to \infty} V_{\text{exc}} P_a(r) = -\frac{1}{r} P_a(r).$$

The sum of the nuclear potential and the HF potential, therefore, approaches the ionic potential $(N - 1)/r$ for large $r$. With the above definitions, we may write the HF equation for an atom with closed subshells as

$$-\frac{1}{2} \frac{d^2 P_a}{dr^2} + \left( V_{\text{HF}} - \frac{Z}{r} + \frac{l_a(l_a + 1)}{2r^2} \right) P_a(r) = \epsilon_a P_a(r),$$

where the index $a$ ranges over the occupied subshells $(n_a l_a)$. The HF equations are a set of radial Schrödinger equations for electrons moving in a common central potential $V(r) = -Z/r + U(r)$. By comparison with Eq.(2.12), the “best” value for the average central potential $U(r)$ is seen to be the nonlocal HF potential $V_{\text{HF}}$.

Once the HF equations have been solved, the energy can be determined from Eq.(3.50), which may be written in terms of radial orbitals as

$$E_{ab\cdots n} = \sum_a \epsilon_a - \sum_a (V_{\text{HF}})_{aa} + \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba})$$

$$= \sum_a \epsilon_a - \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}).$$

Here, we have made use of the fact that $(V_{\text{HF}})_{aa} = \sum_b (g_{abab} - g_{abba})$. Expressing the energy in terms of Slater integrals, we find

$$E_{ab\cdots n} = \sum_a 2l_a \left[ \epsilon_a - \sum_b [l_b] \left( R_0(a, b, a, b) - \sum_l \Lambda_{l_b l_a} R_l(a, b, b, a) \right) \right],$$

with $[l_a] = 2l_a + 1$. 

76  

CHAPTER 3. SELF-CONSISTENT FIELDS
The HF energy eigenvalue $\epsilon_c$ is related to the energy required to remove an electron from the subshell $c$. If we calculate the energy of an ion with closed subshells except for a vacancy in subshell $c$, using a Slater determinant wave function, then we obtain

$$E_{\text{ion}} = \sum_a \langle a | h_0 | a \rangle - \langle c | h_0 | c \rangle + \frac{1}{2} \sum_{ab} (g_{abab} - g_{baba}) - \sum_a (g_{acac} - g_{caac}). \quad (3.85)$$

Let us use the orbitals from the closed-shell HF approximation for the atom to evaluate this expression. We then obtain

$$E_{\text{ion}} - E_{\text{atom}} = -\langle c | h_0 | c \rangle - \sum_a (g_{acac} - g_{caac}) = -\langle c | h_0 + V_{\text{HF}} | c \rangle = -\epsilon_c. \quad (3.86)$$

Thus we find that the removal energy, calculated using HF wave functions for the atom, is the negative of the corresponding HF eigenvalue. This result is called Koopmans’ theorem.

In Section 3.1, we have discussed the numerical solution to the HF equation for the $1s$ orbital in helium. In Section 3.3, we discuss the numerical solution to the coupled system of HF equations that arise for other closed-subshell atoms and ions.

### 3.3 Numerical Solution to the HF Equations

As in the case of helium, the Hartree-Fock equations (3.81) for a general closed-shell atom are solved iteratively. We approximate the HF orbitals by unscreened Coulomb field orbitals initially. This is a fair approximation for the innermost $1s$ orbitals, but a very poor approximation for the outer orbitals. To create a more realistic starting potential, we do a preliminary self-consistent calculation of the direct part of the HF potential scaled to give the correct ionic charge. The Coulomb orbitals are gradually modified until self-consistency at the level is achieved at a level of 1 part in $10^3$. The resulting potential is a good local approximation to HF potential and the resulting orbitals are good approximations to the final HF orbitals for outer as well as inner shells. Moreover, orbitals with the same value of $l$ but different values of $n$ are orthogonal. These screened orbitals are used to start the iterative solution of the HF equations. The iteration of the HF equations, including both direct and exchange terms, is then performed until self-consistency is achieved at a level of 1 part in $10^9$.

#### 3.3.1 Starting Approximation (HART)

As outlined above, we carry out a self-consistent calculation of single-particle orbitals in a model potential $U(r)$ as a preliminary step in the solution to the HF equations. The model potential is obtained by scaling the direct part of the HF potential to give a potential with the proper asymptotic behavior.

We choose $U(r) = 0$, initially, and use the routine master to solve the radial Schrödinger equation in the unscreened nuclear Coulomb field $V(r) = -Z/r$ for
Table 3.2: Energy eigenvalues for neon. The initial Coulomb energy eigenvalues are reduced to give model potential values shown under $U(r)$. These values are used as initial approximations to the HF eigenvalues shown under $V_{\text{HF}}$.

<table>
<thead>
<tr>
<th>State</th>
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<th>$V_{\text{HF}}$</th>
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<td>1s</td>
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<td>-12.50000</td>
<td>-0.65093</td>
<td>-0.85041</td>
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</table>

each occupied orbital $P_a(r)$. We accumulate the radial charge density $\rho(r) = \sum_a (4l_a + 2)P_a(r)^2$. The direct part of the HF potential is given in terms of $\rho(r)$ by

$$V_{\text{dir}}(r) = \int_0^{\infty} dr' \frac{\rho(r')}{r}.$$  \hfill (3.87)

Asymptotically, $\lim_{r \to \infty} V_{\text{dir}}(r) = N/r$, where $N$ is the number of atomic electrons. To create a model potential with the correct asymptotic behavior, we multiply $V_{\text{dir}}$ by the factor $(N-1)/N$. We use the potential $U(r) = (1-1/N)V_{\text{dir}}(r)$, calculated self-consistently, as our starting approximation. We add $U(r)$ to the nuclear potential and solve the radial equations once again to obtain a second approximation. This second approximation is used to obtain new values of $\rho(r)$ and $U(r)$. These values are used to obtain a third approximation. This iteration procedure is continued until the potential is stable to some desired level of accuracy.

Since this potential is only used as an initial approximation in solving the HF equations, it is not necessary to carry out the self-consistent iteration accurately. We terminate the iterative solution to the equations when the relative change in the eigenvalue for each orbital, from loop to loop in the iteration, is less than 1 part in $10^3$.

The iteration procedure described above does not converge in general, but oscillates from loop to loop with increasing amplitude. To eliminate such oscillations, we change the initial Coulomb interaction gradually. If we designate the value of $U(r)$ from the $n$th iteration loop as $U^{(n)}(r)$, then at the $(n+1)^{\text{st}}$ loop we use the combination

$$U(r) = \eta U^{(n+1)}(r) + (1 - \eta)U^{(n)}(r)$$

rather than $U^{(n+1)}(r)$ to continue the iteration. Choosing $\eta$ in the range $0.375 - 0.5$ leads to convergence in all cases.

The subroutine HART is designed to carry out the iteration. For the case of neon, it required 13 iterations to obtain the model potential $U(r)$ self-consistent to 1 part in $10^3$ using $\eta = 0.5$. The resulting eigenvalues are compared with the initial Coulomb eigenvalues and the final HF eigenvalues in Table 3.2.
A comment should be made in connection with the use of the subroutine master. As discussed previously, the routine master itself uses an iterative procedure to determine the radial wave functions. master requires only a few iterations if an accurate estimate of the eigenvalue is provided initially. To produce such an estimate, we use perturbation theory to determine the change in the eigenvalues induced by changing the potential. A small loop is introduced after $U(r)$ is changed at the end of an iteration step to calculate the first-order change in each of the energy eigenvalues. Perturbation theory gives

$$
\delta \epsilon_a = \int_0^\infty dr \left[ U^{(n+1)}(r) - U^{(n)}(r) \right] P_a^2(r).
$$

(3.88)

This correction to the energy at the end of the $n^{th}$ iteration is added to the output energy $\epsilon_a$ from master and used as the input energy for the $(n + 1)^{st}$ loop.

After the iteration in the routine hart is completed, we have a model potential $U(r)$ and a set of orbitals $P_a(r)$ and energies $\epsilon_a$ that provide a suitable starting point for the iterative solution to the HF equations.

### 3.3.2 Refining the Solution (NRHF)

The HF equation for orbital $P_a$ is written as a pair of inhomogeneous differential equations

$$
\frac{dP_a}{dr} - Q_a = 0,
$$

(3.89)

$$
\frac{dQ_a}{dr} + f_a P_a = 2(V_{\text{HF}} - U)P_a,
$$

(3.90)

where

$$
f_a(r) = 2 \left( \epsilon_a - \frac{l_a(l_a + 1)}{2r^2} + \frac{Z}{r} - U(r) \right).
$$

(3.91)

These equations are to be solved iteratively. We start with functions $P_a^{(0)}(r)$ and $\epsilon_a^{(0)}$ obtained from the routine hart described in the previous section. To solve the HF equations, we set up an iteration scheme in which $P_a(r)$ is replaced by $P_a^{(n-1)}(r)$ on the right-hand side of Eq.(3.90) in the $n^{th}$ approximation. Thus we write,

$$
\frac{dP_a^{(n)}}{dr} - Q_a^{(n)} = 0,
$$

(3.92)

$$
\frac{dQ_a^{(n)}}{dr} + f_a^{(n)} P_a^{(n)} = 2(V_{\text{HF}}^{(n-1)} - U)P_a^{(n-1)},
$$

(3.93)

where $f_a^{(n)}$ is given by Eq.(3.91) with $\epsilon_a$ replaced by $\epsilon_a^{(n)}$. The functions $P_a^{(0)}(r)$ and $Q_a^{(0)}(r)$ satisfy the homogeneous equations obtained from Eqs.(3.89-3.90)
by dropping the right-hand side and replacing \( f_a \) by \( f^{(0)} \). From Eqs.(3.92-3.93), we readily obtain the relation

\[
\epsilon_a^{(n)} = \epsilon_a^{(0)} + \frac{\int_0^\infty dr P_a^{(n)}(r) \left( V_{HF}(r)^{(n-1)} - U(r) \right) P_a^{(n-1)}(r)}{\int_0^\infty dr P_a^{(0)}(r) P_a^{(n)}(r)}.
\] (3.94)

We use this equation, with \( P_a^{(n)}(r) \) replaced by \( P_a^{(n-1)}(r) \) in the denominator, to obtain an approximate value of \( \epsilon_a^{(n)} \) to use in the function \( f_a^{(n)}(r) \). This approximate value of \( \epsilon_a^{(n)} \) will be readjusted later in the iteration step to give a properly normalized orbital. The equations (3.92-3.93) are solved by using the method of variation of parameters.

**Solving the inhomogeneous equations:** Consider the pair of inhomogeneous differential equations

\[
dP(r) - Q(r) = 0, \tag{3.95}
\]
\[
dQ(r) + f(r)P(r) = R(r). \tag{3.96}
\]

We can obtain solutions to the homogeneous equations (obtained by setting \( R(r) = 0 \)) that are regular at the origin using the routine `OUTSCH` described in Chapter 2. We designate these solutions by \( P_0 \) and \( Q_0 \). Similarly, we can obtain solutions to the homogeneous equations that are regular at infinity by inward integration using the routine `INSCCH`. We designate these solutions by \( P_\infty \) and \( Q_\infty \). We seek a solution to the inhomogeneous equations (3.95-3.96) in the form

\[
P(r) = A(r)P_0(r) + B(r)P_\infty(r), \tag{3.97}
\]
\[
Q(r) = A(r)Q_0(r) + B(r)Q_\infty(r), \tag{3.98}
\]

where \( A(r) \) and \( B(r) \) are functions that are to be determined. Substituting into Eqs.(3.95-3.96), we find that the functions \( A(r) \) and \( B(r) \) satisfy the differential equations

\[
\frac{dA}{dr} = -\frac{1}{W}P_\infty(r)R(r), \tag{3.99}
\]
\[
\frac{dB}{dr} = \frac{1}{W}P_0(r)R(r). \tag{3.100}
\]

where \( W = P_0(r)Q_\infty(r) - Q_0(r)P_\infty(r) \) is a constant (independent of \( r \)) known as the Wronskian of the two solutions. Integrating Eqs.(3.99-3.100), we obtain
3.3. NUMERICAL SOLUTION TO THE HF EQUATIONS

a solution to Eqs.(3.95-3.96) regular at the origin and infinity:

\[
P(r) = \frac{1}{W} \left( P_\infty(r) \int_0^r dr' P_0(r') R(r') \right. \\
\left. + P_0(r) \int_r^\infty dr' P_\infty(r') R(r') \right), \quad (3.101)
\]

\[
Q(r) = \frac{1}{W} \left( Q_\infty(r) \int_0^r dr' P_0(r') R(r') \right. \\
\left. + Q_0(r) \int_r^\infty dr' P_\infty(r') R(r') \right). \quad (3.102)
\]

This method of solving a linear inhomogeneous set of equations is known as the method of variation of parameters. We use the resulting formulas to obtain numerical solutions to Eqs.(3.92-3.93) at each stage of iteration.

**Normalizing the orbitals:** The orbitals obtained using Eqs.(3.101-3.102) are regular at the origin and infinity, however, they are not properly normalized. To obtain normalized orbitals at the \(n\)\(^{th}\) step of iteration, it is necessary to adjust the eigenvalue \(\epsilon_a(n)\) from the approximate value given in (3.94). Let us suppose that the norm of the solution to the inhomogeneous equations is

\[
\int_0^\infty dr P^2(r) = N \neq 1. \quad (3.103)
\]

We modify the energy eigenvalue by a small amount \(\delta \epsilon\). This induces small changes \(\delta P\) and \(\delta Q\) in the radial functions \(P(r)\) and \(Q(r)\). These small changes in the solution satisfy the pair of inhomogeneous equations

\[
\frac{d\delta P}{dr} - \delta Q(r) = 0, \quad (3.104)
\]

\[
\frac{d\delta Q}{dr} + f(r) \delta P(r) = -2\delta \epsilon P(r). \quad (3.105)
\]

The solution to this equation, found by variation of parameters, is

\[
\delta P(r) = -2\delta \epsilon \hat{P}(r), \quad (3.106)
\]

\[
\delta Q(r) = -2\delta \epsilon \hat{Q}(r), \quad (3.107)
\]

with

\[
\hat{P}(r) = \frac{1}{W} \left( P_\infty(r) \int_0^r dr' P_0(r') P(r') \right. \\
\left. + P_0(r) \int_r^\infty dr' P_\infty(r') P(r') \right), \quad (3.108)
\]

\[
\hat{Q}(r) = \frac{1}{W} \left( Q_\infty(r) \int_0^r dr' P_0(r') P(r') \right. \\
\left. + Q_0(r) \int_r^\infty dr' P_\infty(r') P(r') \right). \quad (3.109)
\]
CHAPTER 3. SELF-CONSISTENT FIELDS

We must choose $\delta \epsilon$ to insure that the orbital $P + \delta P$ is properly normalized. Thus, we require (neglecting terms of order $\delta P^2$) that

$$\int_0^{\infty} dr P(r)^2 + 2 \int_0^{\infty} dr P(r) \delta P(r) = 1.$$  \hspace{1cm} (3.110)

This equation can be rewritten as

$$\delta \epsilon = \frac{N - 1}{4 \int_0^{\infty} dr P(r) \hat{P}(r)}.$$  \hspace{1cm} (3.111)

Equation (3.111) is itself used iteratively to obtain a properly normalized orbital. Usually a single iteration is sufficient to obtain functions normalized to parts in $10^{12}$, although occasionally two iterations are required to obtain this accuracy.

Once starting orbitals have been obtained from the routine HART, first-order and second-order corrections are made to each orbital. A selection scheme is then set up in which the orbitals with the largest values of the relative change in energy are treated in order. For example, if we are considering the Be atom which has 2 orbitals, we iterate the 1s orbital twice then we iterate the 2s orbital twice. At this point, we chose the orbital with the largest value of $|\epsilon_a^{(2)} - \epsilon_a^{(1)}|/|\epsilon_a^{(2)}|$ and iterate this orbital until the relative change in energy is no longer the larger of the two. We then iterate the other orbital until the relative change in energy is no longer the larger. The selection procedure continues until the changes in relative energies of both orbitals are less than one part in $10^9$.

Once the iteration has converged to this level of accuracy, we calculate the total energy, check the orthogonality and normalization of the orbitals, and write the radial functions to an output data file for use in other applications.

In Table 3.3, we list the HF eigenvalues and total energies for the noble gases helium, neon, argon, krypton and xenon. In this table, we also give the average values of $r$ and $1/r$ for each individual subshell. It should be noticed that $\langle nl|r|nl \rangle$ and $\langle nl|1/r|nl \rangle$ depend strongly on the principal quantum number $n$ but only weakly on the angular momentum quantum number $l$ within a shell. For comparison, we also give the negative of the removal energy ($-B_{nl}$) for an electron in the shell $nl$ which, according to Koopmans’ theorem, is approximately the HF eigenvalue $\epsilon_{nl}$. The experimental binding energies presented in this table are averages over the fine-structure components.

In Fig. 3.3, we show the radial wave functions for the occupied orbitals in neon and argon. The 1s orbitals peak at about $1/Z$ a.u. whereas the outer orbitals peak at about 1 a.u. and become insignificant beyond 4 a.u. for both elements. In Fig. 3.4, we plot the radial densities for the elements beryllium, neon, argon and krypton. The shell structure of these elements is evident in the figure.

### 3.4 Atoms with One Valence Electron

Let us consider the alkali-metal atoms lithium, sodium, potassium, rubidium and cesium, all of which have one valence electron outside of closed shells. We
3.4. ATOMS WITH ONE VALENCE ELECTRON

Figure 3.3: Radial HF wave functions for neon and argon.

Figure 3.4: Radial HF densities for beryllium, neon, argon and krypton.
Table 3.3: HF eigenvalues $\epsilon_{nl}$, average values of $r$ and $1/r$ for noble gas atoms. The negative of the experimental removal energies $-B_{\text{exp}}$ from Bearden and Burr (1967, for inner shells) and Moore (1957, for outer shell) is also listed for comparison.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$nl$</th>
<th>$\epsilon_{nl}$</th>
<th>$\langle r \rangle$</th>
<th>$\langle 1/r \rangle$</th>
<th>$-B_{\text{exp}}$</th>
</tr>
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<td>Helium</td>
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<td></td>
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<td>Krypton</td>
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<td>$E_{\text{tot}}$</td>
<td></td>
<td></td>
<td></td>
<td>-2752.054983</td>
</tr>
<tr>
<td>Xenon</td>
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<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>$E_{\text{tot}}$</td>
<td></td>
<td></td>
<td></td>
<td>-7232.138370</td>
</tr>
</tbody>
</table>
3.4. ATOMS WITH ONE VALENCE ELECTRON

take the wave function of an alkali-metal atom to be a Slater determinant composed of orbitals from the closed shells and a single valence orbital $\psi_v$. The energy is given by the expression

$$E_{ab\ldots n\nu} = \sum_a \langle a|h_0|a\rangle + \langle \nu|h_0|\nu\rangle + \frac{1}{2} \sum_{ab} (g_{baba} - g_{abba}) + \sum_a (g_{avav} - g_{vava}),$$

(3.112)

where the sums over $a$ and $b$ extend over all closed subshells. We can use the results from the previous section to carry out the sums over the magnetic substates of the closed shells to obtain

$$E_{ab\ldots n\nu} = E_{ab\ldots n} + I(n_\nu l_\nu) + \sum_{n_a l_a} 2[l_a] \left( R_0(avav) - \sum_k \Lambda_{l_a k l} R_k(vaav) \right),$$

(3.113)

where $E_{ab\ldots n}$ is the energy of the closed core given in Eq.(3.67). Let us assume that the orbitals for the closed shells have been determined from a HF calculation for the closed ionic core. The core energy in Eq.(3.113) is then fixed. The valence orbital in Eq.(3.113) is determined variationally. The requirement that the energy be stationary under variations of the valence electron radial function $P_v(r)$, subject to the constraint that the valence orbital remain normalized, leads to the differential equation

$$-\frac{1}{2} \frac{d^2 P_v}{dr^2} + \left( V_{HF} - \frac{Z}{r} + \frac{l_v(l_v + 1)}{2r^2} \right) P_v = \epsilon_v P_v,$$

(3.114)

where $V_{HF}$ is the core HF potential written down in Eqs.(3.75-3.76). This homogeneous equation can be solved using the variation of parameters scheme described in the previous section, once the core orbitals are known. Since the equation is homogeneous, the solution can be trivially normalized. The potential in Eq.(3.113) is the HF potential of the $N-1$ electron ion; it is referred to as the $V_{HF}^{N-1}$ potential.

Since the valence electron and those core electrons that have the same orbital angular momentum as the valence electron move in precisely the same potential, it follows that the corresponding radial functions are orthogonal. Thus,

$$\int_0^\infty dr P_v(r) P_a(r) = 0 \text{ for } l_a = l_v.$$  

(3.115)

The total energy of the atom can be expressed in terms of the HF eigenvalue $\epsilon_v$ as

$$E_{ab\ldots n\nu} = E_{ab\ldots n} + \epsilon_v,$$

(3.116)

where, again, $E_{ab\ldots n}$ is the energy of the ionic core. It follows that the binding energy of the valence electron is just the negative of the corresponding eigenvalue $B_v = E_{\text{ion}} - E_{\text{atom}} = -\epsilon_v$.

Eigenvalues of the low-lying states of the alkali-metal atoms are presented in Table 3.4. These values agree with measured binding energies at the level of a few percent for lithium. This difference between HF eigenvalues and experiment grows to approximately 10% for cesium.
Table 3.4: Energies of low-lying states of alkali-metal atoms as determined in a $V_{\text{HF}}^{N^{-1}}$ Hartree-Fock calculation.

<table>
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<tr>
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<th>Lithium</th>
<th>Sodium</th>
<th>Potassium</th>
<th>Rubidium</th>
<th>Cesium</th>
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<td>$nl$</td>
<td>$\epsilon_{nl}$</td>
<td>$nl$</td>
<td>$\epsilon_{nl}$</td>
</tr>
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<td>4s</td>
<td>-.146954</td>
</tr>
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</tr>
</tbody>
</table>

3.5 Dirac-Fock Equations

The Hartree-Fock theory is easily extended to include relativistic effects. We start with a many-body Hamiltonian patterned after its nonrelativistic counterpart:

$$H(r_1, r_2, \cdots, r_N) = \sum_{i=1}^{N} h_0(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}.$$  \hspace{1cm} (3.117)

In the relativistic case, the one-electron Hamiltonian $h_0(r)$ is taken to be the Dirac Hamiltonian

$$h_0(r) = c \alpha \cdot p + \beta c^2 - \frac{Z}{r}.$$  \hspace{1cm} (3.118)

The resulting many-body Hamiltonian is called the Dirac-Coulomb Hamiltonian. It provides a useful starting point for discussions of relativistic effects in atoms. The Dirac-Coulomb Hamiltonian must be supplemented by the Breit interaction to understand fine-structure corrections precisely. We will ignore the Breit interaction initially, and return to it after we have derived the Dirac-Fock equations.

The reader must be cautioned that there are difficulties associated with applications of the Dirac-Coulomb Hamiltonian (with or without the Breit Interaction) in higher-order perturbation theory calculations. These difficulties can only be resolved by recourse to Quantum Electrodynamics. We will discuss these difficulties and their solution when we take up relativistic many-body perturbation theory. For doing calculations at the Hartree-Fock level of approximation,
the Dirac-Coulomb Hamiltonian is the appropriate point of departure.

As in the nonrelativistic case, we introduce an average central potential \( U(r) \) and the corresponding one-electron Hamiltonian \( h(r) \):

\[
h(r) = \alpha \mathbf{p} + \beta c^2 + V(r),
\]

(3.119)

with \( V(r) = -Z/r + U(r) \). The Dirac-Coulomb Hamiltonian can then be written as \( H = H_0 + V \) with

\[
H_0 = \sum_i h(r_i)
\]

(3.120)

\[
V = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} - \sum_i U(r_i).
\]

(3.121)

If \( \varphi_a(r) \) is an eigenfunction of the one-electron Dirac Hamiltonian \( h(r) \) with eigenvalue \( \epsilon_a \), then the product wave function

\[
\varphi_a(r_1) \varphi_b(r_2) \cdots \varphi_n(r_N)
\]

(3.122)

is an eigenfunction of \( H_0 \) with eigenvalue

\[
E^{(0)}_{ab \cdots n} = \epsilon_a + \epsilon_b + \cdots + \epsilon_n.
\]

A properly antisymmetrized product wave function is given by the Slater determinant:

\[
\Psi_{ab \cdots n}(r_1, r_2, \cdots, r_N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{ccc}
\varphi_a(r_1) & \varphi_b(r_1) & \cdots & \varphi_n(r_1) \\
\varphi_a(r_2) & \varphi_b(r_2) & \cdots & \varphi_n(r_2) \\
\vdots & \vdots & & \vdots \\
\varphi_a(r_N) & \varphi_b(r_N) & \cdots & \varphi_n(r_N)
\end{array} \right|.
\]

(3.123)

We take the wave function for the ground-state of a closed-shell atom to be a Slater determinant formed from the \( N \) lowest-energy single-particle orbitals and evaluate the expectation value of the energy. We find that

\[
E_{ab \cdots n} = \sum_a \langle a | h_0 | a \rangle + \frac{1}{2} \sum_{ab} \left( g_{abab} - g_{abba} \right).
\]

(3.124)

This is just the expression obtained previously in the nonrelativistic case. Here, however, the Coulomb matrix elements \( g_{abcd} \) are to be evaluated using Dirac orbitals rather than nonrelativistic orbitals. As in Chapter 2, we write the one-electron Dirac orbital \( \varphi_a(r) \) in terms of spherical spinors as

\[
\varphi_a(r) = \frac{1}{r} \left( \begin{array}{c}
i P_a(r) \Omega_{\kappa_a \kappa_a} (\hat{r}) \\
Q_a(r) \Omega_{-\kappa_a \kappa_a} (\hat{r})
\end{array} \right).
\]

(3.125)

Before we can carry out the sums over magnetic quantum numbers, it is necessary to do an angular momentum decomposition of the Coulomb integrals.
In making this decomposition, we use the fact that
\[
\varphi^+_a(r) \varphi_c(r) = \frac{1}{r^2} [P_a(r)P_c(r) \Omega^\dagger_{\kappa_a m_a}(\hat{r}) \Omega_{\kappa_c m_c}(\hat{r}) + Q_a(r)Q_c(r) \Omega^\dagger_{-\kappa_a m_a}(\hat{r}) \Omega_{-\kappa_c m_c}(\hat{r})]
\]
\[
= \frac{1}{r^2} [P_a(r)P_c(r) + Q_a(r)Q_c(r)] \Omega^\dagger_{\kappa_a m_a}(\hat{r}) \Omega_{\kappa_c m_c}(\hat{r}).
\] (3.126)

Introducing the expansion
\[
\frac{1}{r_{12}} = \sum_{kq} \frac{r_{kq}}{r_{kq}^2} (-1)^q C^k_{-q}(\hat{r}_1) C^k_q(\hat{r}_2),
\] (3.127)
the Coulomb integral \(g_{abcd}\) can be written
\[
g_{abcd} = \sum_{kq} (-1)^q \langle \kappa_a m_a | C^k_{-q} | \kappa_c m_c \rangle \langle \kappa_b m_b | C^k_q | \kappa_d m_d \rangle R_k(abc) d, \quad (3.128)
\]
where \(R_k(abc) d\) is the (relativistic) Slater integral defined by
\[
R_k(abc) d = \int_0^\infty dr_1 [P_a(r_1)P_c(r_1) + Q_a(r_1)Q_c(r_1)]
\times
\int_0^\infty dr_2 \frac{r^k_{kq}}{r_{kq}^2} [P_b(r_2)P_d(r_2) + Q_b(r_2)Q_d(r_2)]. \quad (3.129)
\]

The angular matrix elements in Eq.(3.128) are given by
\[
\langle \kappa_a m_a | C^k_q | \kappa_c m_c \rangle = \int d\Omega \Omega^\dagger_{\kappa_a m_a}(\hat{r}) C^k_q(\hat{r}) \Omega_{\kappa_c m_c}(\hat{r}). \quad (3.130)
\]

Since the spherical spinors are angular momentum eigenstates and since the functions \(C^k_q(\hat{r})\) are spherical tensor operators, the Wigner-Eckart theorem may be used to infer the dependence on the magnetic quantum numbers. We obtain,
\[
\langle \kappa_a m_a | C^k_q | \kappa_b m_b \rangle = -\frac{j_a m_a}{j_b m_b} \langle \kappa_a | C^k | \kappa_b \rangle. \quad (3.131)
\]

The reduced matrix element \(\langle \kappa_a | C^k | \kappa_b \rangle\) is found to be
\[
\langle \kappa_a | C^k | \kappa_b \rangle = (-1)^{j_a+1/2} \sqrt{|j_a||j_b|} \begin{pmatrix} j_a & j_b & k \\ -1/2 & 1/2 & 0 \end{pmatrix} \Pi(l_a + l_b) d, \quad (3.132)
\]
where
\[
\Pi(l) = \begin{cases} 1, & \text{if } l \text{ is even} \\ 0, & \text{if } l \text{ is odd} \end{cases}
\] (3.133)

With these definitions, we may write
\[
g_{abcd} = \sum_k \frac{j_{a m_a} j_{b m_b}}{j_{c m_c} j_{d m_d}} X_k(abc) d, \quad (3.134)
\]
where
\[ X_k(abcd) = (-1)^k \langle \kappa_a || C^k || \kappa_b \rangle \langle \kappa_b || C^k || \kappa_d \rangle R_k(abcd). \] (3.135)

Let us carry out the sum over \( m_b \) of the direct and exchange Coulomb matrix elements in Eq.(3.124). To this end, we make use of the easily verified identities
\[ \sum m_b g_{abab} = \sqrt{[ja][jb]} X_0(abab) = [jb] R_0(abab), \] (3.136)

where we have used the fact that
\[ \langle \kappa_a || C^0 || \kappa_a \rangle \] (3.139)

Using the second graphical identity above, we find that
\[ \sum m_b g_{abba} = \sum_k (-1)^{j_a - j_b + k} \frac{1}{[ja]} X_k(abba) = [jb] \sum_k \Lambda_{\kappa_a \kappa_b} R_k(abba), \] (3.141)

with
\[ \Lambda_{\kappa_a \kappa_b} = \frac{\langle \kappa_a || C^k || \kappa_b \rangle^2}{[ja][jb]} = \begin{pmatrix} j_a & j_b & k \\ -1/2 & 1/2 & 0 \end{pmatrix}^2 \Pi(l_a + k + l_b). \] (3.142)

It is now a simple matter to carry out the double sum over magnetic quantum numbers in the expression for the Coulomb energy in Eq.(3.124). We obtain
\[ \frac{1}{2} \sum_{m_a, m_b} (g_{abab} - g_{abba}) = \frac{1}{2} [ja][jb] \left( R_0(abab) - \sum_k \Lambda_{\kappa_a \kappa_b} R_k(abba) \right). \] (3.143)

The terms \( \langle a || h_0 || a \rangle \) in Eq.(3.124) are independent of \( m_a \). They are given by the radial integral
\[ I_a = \langle a || h_0 || a \rangle = \int_0^\infty dr \left\{ P_a \left( -\frac{Z}{r} + c^2 \right) P_a + cP_a \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_a - cQ_a \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_a + Q_a \left( -\frac{Z}{r} - c^2 \right) Q_a \right\}. \] (3.144)
The energy can therefore be expressed as

\[ E_{ab\ldots n} = \sum_a [j_a] \left\{ I_a + \frac{1}{2} \sum_b [j_b] \left[ R_0(abab) - \sum_k \Lambda_{\kappa_a\kappa_b} R_k(abba) \right] \right\}, \quad (3.145) \]

where the indices \(a\) and \(b\) refer to \((n_a\kappa_a)\) and \((n_b\kappa_b)\), respectively.

Again, as in the nonrelativistic case, we require that \(E_{ab\ldots n}\) be stationary with the constraint that the radial functions having the same angular quantum number \(\kappa\) but different principal quantum numbers \(n\) be orthogonal. This requirement is combined with the normalization condition in the equation

\[ N_{n_a\kappa_a, n_b\kappa_b} = \int_0^\infty dr[P_{n_a\kappa_a}(r)P_{n_b\kappa_b}(r) + Q_{n_a\kappa_a}(r)Q_{n_b\kappa_b}(r)] = \delta_{n_a n_b}. \quad (3.146) \]

Introducing Lagrange multipliers \(\lambda_{n_a\kappa_a, n_b\kappa_b}\) (assumed to be symmetric with respect to \(n_a\) and \(n_b\)), the variational condition is

\[ \delta(E_{ab\ldots n} - \sum_{ab} \delta_{n_a\kappa_b} \lambda_{n_a\kappa_a, n_b\kappa_b} N_{n_a\kappa_a, n_b\kappa_b}) = 0, \quad (3.147) \]

with respect to variations in the radial functions \(P_a\) and \(Q_a\). The variations \(\delta P_a(r)\) and \(\delta Q_a(r)\) are required to vanish at the origin and infinity. After an integration by parts, the variational condition immediately leads to the “Dirac-Fock” differential equations

\[ \left(V_{HF} - \frac{Z}{r} + c^2 \right) P_a + c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_a = \epsilon_a P_a + \sum_{n_b \neq n_a} \epsilon_{n_a\kappa_a, n_b\kappa_b} P_{n_b\kappa_b} \quad (3.148) \]

\[ -c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_a + \left(V_{HF} - \frac{Z}{r} - c^2 \right) Q_a = \epsilon_a Q_a + \sum_{n_b \neq n_a} \epsilon_{n_a\kappa_a, n_b\kappa_b} Q_{n_b\kappa_b}. \quad (3.149) \]

Here, the HF potential \(V_{HF}\) is defined by its action on a radial orbital. Thus, if \(R_a(r)\) represents either the large component radial function \(P_a(r)\) or the small component function \(Q_a(r)\), then

\[ V_{HF} R_a(r) = \sum_{b} [j_b] \left( v_b(b, b, r) R_a(r) - \sum_k \Lambda_{\kappa_a\kappa_b} v_k(b, a, r) R_b(r) \right). \quad (3.150) \]

The (relativistic) screening potentials in this equation are given by

\[ v_k(a, b, r) = \int_0^\infty dr' \int_{r_{k+1}}^{r_k} \frac{dr''}{r''} \left[ P_a(r') P_b(r'') + Q_a(r') Q_b(r'') \right]. \quad (3.151) \]

In Eqs.(3.148, 3.149), we have introduced the notation \(\epsilon_a = \lambda_{n_a\kappa_a, n_a\kappa_a}/[j_a]\) and \(\epsilon_{n_a\kappa_a, n_b\kappa_b} = \lambda_{n_a\kappa_a, n_b\kappa_b}/[j_a]\).
Just as in the nonrelativistic case, the radial orbitals belonging to a particular value of the angular quantum number \( \kappa \) but different values of the principal quantum number \( n \) are orthogonal for arbitrary values of the off-diagonal Lagrange multiplier \( \epsilon_{n_a \kappa_a, n_b \kappa_a} \). We make the simplest choice here, namely, \( \epsilon_{n_a \kappa_a, n_b \kappa_a} = 0 \). With this choice, the Dirac-Fock equations become a set of coupled, non-linear eigenvalue equations. These equations are to be solved self-consistently to obtain the occupied orbitals and the associated energy eigenvalues.

The total energy of the atom may be easily calculated, once the Dirac-Fock equations have been solved using Eq.(3.145). Alternatively, it can be written in terms of the Dirac-Fock eigenvalues as

\[
E_{ab...n} = \sum_a [j_a] \epsilon_a - \frac{1}{2} \sum_{ab} [j_a][j_b] \left( R_0(abab) - \sum_k \Lambda_{\kappa_a \kappa_b} R_{k} (abba) \right). \tag{3.152}
\]

As in the nonrelativistic case, Koopmans’ theorem leads to the interpretation of the energy eigenvalue \( \epsilon_a \) as the negative of the removal energy of an electron from subshell \( a \) \((-B_a)\).

**Numerical Considerations:** The numerical techniques used to solve the Dirac-Fock equations are similar to those used in the nonrelativistic case. Starting from Coulomb wave functions, a model potential \( U(r) \), taken to be the direct part of the HF potential scaled to give the correct asymptotic behavior, is obtained iteratively using the Dirac routine MASTER. The Dirac-Fock equations are rewritten as inhomogeneous equations, in a form suitable for iteration starting from the model-potential orbitals:

\[
\left( U - \frac{Z}{r} + c^2 - \epsilon^{(n)}_a \right) P^{(n)}_a + c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q^{(n)}_a =
- \left( V^{(n-1)}_{HF} - U \right) P^{(n-1)}_a \tag{3.153}
\]

\[
-c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P^{(n)}_a + \left( U - \frac{Z}{r} - c^2 - \epsilon^{(n)}_a \right) Q^{(n)}_a =
- \left( V^{(n-1)}_{HF} - U \right) Q^{(n-1)}_a. \tag{3.154}
\]

These equations are solved at each stage of iteration and the energy adjusted using a variation of parameters scheme similar to that used in the nonrelativistic case. We leave it to the reader to write out the detailed formulas for solving the inhomogeneous equations. The iteration procedure is continued until the relative change in energy for each orbital is less than one part in \( 10^9 \). At this point the total energy is calculated, the orthogonality of the orbitals is checked and the wave functions are written to an external file for use in other applications.

As an example, we present the eigenvalues obtained from a Dirac-Fock calculation of the closed-shell mercury atom \((Z=80)\) in Table 3.5. These eigenvalues
Table 3.5: Dirac-Fock eigenvalues (a.u.) for mercury, $Z = 80$. $E_{\text{tot}} = -19648.8585$ a.u.. For the inner shells, we also list the experimental binding energies from Bearden and Burr (1967) for comparison.

<table>
<thead>
<tr>
<th>$nl_j$</th>
<th>$\epsilon_{nl_j}$</th>
<th>$-B_{nl_j}$</th>
<th>$nl_j$</th>
<th>$\epsilon_{nl_j}$</th>
<th>$-B_{nl_j}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s1/2</td>
<td>-3074.2259</td>
<td>-3054.03</td>
<td>2s1/2</td>
<td>-550.2508</td>
<td>-545.35</td>
</tr>
<tr>
<td>3s1/2</td>
<td>-133.1130</td>
<td>-125.86</td>
<td>4s1/2</td>
<td>-30.6482</td>
<td>-27.88</td>
</tr>
<tr>
<td>5s1/2</td>
<td>-5.1030</td>
<td>-3.96</td>
<td>6s1/2</td>
<td>-0.3280</td>
<td>-0.384</td>
</tr>
<tr>
<td>2p1/2</td>
<td>-526.8546</td>
<td>-522.17</td>
<td>2p3/2</td>
<td>-455.1566</td>
<td>-451.44</td>
</tr>
<tr>
<td>3p1/2</td>
<td>-122.6388</td>
<td>-120.48</td>
<td>3p3/2</td>
<td>-106.5451</td>
<td>-104.63</td>
</tr>
<tr>
<td>5p1/2</td>
<td>-3.5379</td>
<td>-2.64</td>
<td>5p3/2</td>
<td>-2.8420</td>
<td>-2.12</td>
</tr>
<tr>
<td>3d3/2</td>
<td>-89.4368</td>
<td>3d5/2</td>
<td>-86.0201</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4d3/2</td>
<td>-14.7967</td>
<td>4d5/2</td>
<td>-14.0526</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5d3/2</td>
<td>-0.6501</td>
<td>5d5/2</td>
<td>-0.5746</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4f5/2</td>
<td>-4.4729</td>
<td>4f7/2</td>
<td>-4.3117</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

are also compared with experimental removal energies in the table. The ground-state configuration consists of 22 subshells: $(1s_{1/2})^2 \cdots (5d_{3/2})^4(5d_{5/2})^6(6s_{1/2})^2$. The fine-structure splitting between levels having the same $n$ and $l$ but different $j$ is evident in both the theoretical and experimental energies. The differences between the experimental and theoretical energies is partly due to the approximation involved in interpreting energy eigenvalues as binding energies (Koopmans’ theorem) and partly to the neglect of the Breit interaction and QED corrections. When these effects are considered, the agreement between theory and experiment improves to one part in $10^5$ the inner electrons.

**Nuclear Finite Size:** In this example, we have included the effects of nuclear finite size by replacing the nuclear Coulomb potential $-Z/r$ with the potential of a finite charge distribution. We assume that the nucleus is described by a uniform ball of charge of radius $R$. Under this assumption, the nuclear potential can be written

$$V_{\text{nucl}}(r) = \begin{cases} 
-Z/R \left(3/2 - r^2/2R^2\right) & r < R \\
-Z/r & r \geq R
\end{cases} \quad (3.155)$$

The root-mean-square radius of a uniform charge distribution $R_{\text{rms}}$ is related to its radius $R$ through

$$R = \sqrt{\frac{5}{3}} R_{\text{rms}}. \quad (3.156)$$
3.5. DIRAC-FOCK EQUATIONS

Table 3.6: Dirac-Fock eigenvalues \( \epsilon \) of valence electrons in Cs (\( Z = 55 \)) and theoretical fine-structure intervals \( \Delta \) are compared with measured energies (Moore).

\[
\Delta_{nl} = \epsilon_{nlj=l+1/2} - \epsilon_{nlj=l-1/2}
\]

<table>
<thead>
<tr>
<th>( nl_j )</th>
<th>( \epsilon )</th>
<th>( \Delta_{nl} )</th>
<th>( -B_{\text{exp}} )</th>
<th>( \Delta_{\text{exp}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6s_{1/2}</td>
<td>-0.1273680</td>
<td>-0.143100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6p_{1/2}</td>
<td>-0.0856159</td>
<td>-0.092168</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6p_{3/2}</td>
<td>-0.0837855</td>
<td>0.001830</td>
<td>-0.089643</td>
<td>0.02525</td>
</tr>
<tr>
<td>5d_{3/2}</td>
<td>-0.0644195</td>
<td>-0.077035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5d_{5/2}</td>
<td>-0.0645296</td>
<td>-0.000110</td>
<td>-0.076590</td>
<td>0.000445</td>
</tr>
<tr>
<td>7s_{1/2}</td>
<td>-0.0551873</td>
<td>-0.058646</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7p_{1/2}</td>
<td>-0.0420214</td>
<td>-0.043928</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7p_{3/2}</td>
<td>-0.0413681</td>
<td>0.000653</td>
<td>-0.043103</td>
<td>0.000825</td>
</tr>
<tr>
<td>6d_{3/2}</td>
<td>-0.0360870</td>
<td>-0.040177</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6d_{5/2}</td>
<td>-0.0360899</td>
<td>-0.000029</td>
<td>-0.039981</td>
<td>0.000196</td>
</tr>
<tr>
<td>8s_{1/2}</td>
<td>-0.0309524</td>
<td>-0.032302</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4f_{5/2}</td>
<td>-0.0312727</td>
<td>-0.031596</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4f_{7/2}</td>
<td>-0.0312737</td>
<td>0.000000</td>
<td>-0.031595</td>
<td>-0.000001</td>
</tr>
</tbody>
</table>

High-energy electron-nucleus scattering experiments and measurements of energies of muonic x-rays allow one to determine \( R_{\text{rms}} \) for many nuclei reliably.

A tabulation of \( R \) and \( R_{\text{rms}} \) throughout the periodic table by analysis of such experiments is given by Johnson and Soff. The radii of nuclei for which no direct measurements are available can be estimated using the empirical formula

\[
R_{\text{rms}} = 0.836A^{1/3} + 0.570 \text{ fm} \quad A > 9,
\]

which fits the available data to \( \pm 0.05 \) fm.

**Atoms with One-Valence Electron:** Again, in parallel with the nonrelativistic theory, we can obtain wave functions for atoms with one-electron beyond closed shells by solving the valence orbital Dirac-Fock equations in the fixed \( V_{\text{HF}} \) potential of the closed shell ion. As an example, we show the Dirac-Fock eigenvalues for the 13 lowest states in Cs (\( Z = 55 \)) in Table 3.6. For this atom, theoretical eigenvalues and experimental removal energies agree to about 10%. The theoretical fine-structure splitting for \( np \) levels (\( \Delta_{np} = \epsilon_{np_{3/2}} - \epsilon_{np_{1/2}} \)) agrees with experiment only in order of magnitude, whereas, the fine-structure interval for \( nd \) levels disagrees with experiment even in sign. To understand these differences, we must consider correlation effects as well as the Breit interaction. In the following chapter, we introduce perturbation theoretic methods for treating correlation corrections.
Chapter 4

Atomic Multiplets

In this chapter, we extend the study of atomic structure from atoms with one valence electron to those with two or more valence electrons. As illustrated in the two previous chapters, excited states of one valence electron atoms having a given angular momentum and parity can be described in the independent-particle model using a single Slater determinant. For atoms with two or more electrons, a linear combination of two or more Slater determinants are typically needed to describe a particular state. In addition to the state of interest, this linear combination describes one or more closely related states; the collection of states given by the linear combination of Slater determinants is referred to as a multiplet. To study multiplets, it is convenient to replace the description of states using Slater determinants by the equivalent second-quantization description of the following section. The rules of second-quantization rules are familiar from studies of the harmonic oscillator in quantum mechanics. A more complete discussion may be found in Lindgren and Morrison (1985).

4.1 Second-Quantization

We start our discussion of second quantization by examining the description of one- and two-electron states. As in the previous chapters, we let a single index $k$ designate the set of one-particle quantum numbers $(n_k l_k m_k \mu_k)$. The one-electron state $|k\rangle$, describe by its wave function $\psi_k(r)$ previously, is represented in second quantization by an operator $a_k^\dagger$ acting on the vacuum state $|0\rangle$

$$|k\rangle = a_k^\dagger |0\rangle.$$  \hfill (4.1)

The vacuum state is the state in which there are no electrons; it is assumed to be normalized

$$\langle 0 | 0 \rangle = 1.$$  \hfill (4.2)

The adjoint to the state $|k\rangle$ is given by

$$\langle k | = \langle 0 | a_k.$$  \hfill (4.3)
We assume that $a_k$ operating on the vacuum state vanishes; therefore,

$$a_k|0\rangle = 0 \quad \text{and} \quad \langle 0|a_k^\dagger = 0. \quad (4.4)$$

The operators $a_k^\dagger$ and $a_k$ are called creation and annihilation operators, respectively. The creation and annihilation operators are assumed to satisfy the following anticommutation relations:

$$\{a_j^\dagger, a_k^\dagger\} = a_j^\dagger a_k + a_k^\dagger a_j^\dagger = 0, \quad (4.5)$$

$$\{a_j, a_k\} = a_j a_k + a_k a_j = 0, \quad (4.6)$$

$$\{a_j, a_k^\dagger\} = a_j a_k^\dagger + a_k^\dagger a_j = \delta_{jk}. \quad (4.7)$$

The third of these relations (4.7) can be used to prove the orthonormality of the one-electron states $|j\rangle$ and $|k\rangle$:

$$\langle j|k \rangle = \langle 0|a_j a_k^\dagger|0\rangle = \langle 0|\delta_{jk} - a_k^\dagger a_j|0\rangle = \delta_{jk}\langle 0|0\rangle = \delta_{jk}. \quad (4.8)$$

The antisymmetric two-electron state, represented previously by a Slater determinant $\Psi_{jk}(r_1, r_2)$, is represented in second quantization by

$$|jk\rangle = a_j^\dagger a_k^\dagger|0\rangle. \quad (4.9)$$

The anticommutation relations (4.5) insure the antisymmetry of the state $|jk\rangle$. Similarly, the antisymmetry of the adjoint state follows from the relation (4.6). The normalization condition for a two-electron state $|jk\rangle$ can be written:

$$\langle jk|jk \rangle = \langle 0|a_k a_k^\dagger a_j a_j^\dagger|0\rangle = \langle 0|a_k a_k^\dagger - a_k^\dagger a_k a_j a_j^\dagger|0\rangle = \langle 0|1 - a_k^\dagger a_k - a_j^\dagger a_j + a_j^\dagger a_k a_k a_j^\dagger|0\rangle = 1. \quad (4.10)$$

If we define the number operator for a state $|k\rangle$ by $\mathcal{N}_k = a_k^\dagger a_k$, then, by virtue of the anticommutation relations, we obtain

$$\mathcal{N}_k^2 = a_k^\dagger a_k a_k a_k^\dagger = a_k^\dagger a_k - a_k^\dagger a_k a_k a_k^\dagger = a_k^\dagger a_k = \mathcal{N}_k. \quad (4.11)$$

Therefore, the number operator satisfies the identity $\mathcal{N}_k^2 - \mathcal{N}_k = 0$. If $n_k$ is an eigenvalue of $\mathcal{N}_k$, then $n_k$ satisfies the same equation, $n_k^2 - n_k = 0$. From this, it follows that the possible eigenvalues of $\mathcal{N}_k$ are 0 and 1. The one-electron state $|k\rangle$ is an eigenstate of $\mathcal{N}_k$ with eigenvalue 1,

$$\mathcal{N}_k|k\rangle = a_k^\dagger a_k a_k a_k^\dagger|0\rangle = (a_k^\dagger - a_k^\dagger a_k a_k^\dagger)|0\rangle = a_k^\dagger a_k^\dagger|0\rangle = |k\rangle. \quad (4.12)$$

A general N-particle state described by a Slater determinant wave function formed from a product of the orbitals $\psi_a \psi_b \cdots \psi_n$ is represented in second quantization as

$$|ab \cdots n\rangle = a_a^\dagger a_b^\dagger \cdots a_n^\dagger|0\rangle. \quad (4.13)$$
This state is antisymmetric with respect to the interchange of any two indices; moreover, it is normalized to 1. Defining the number operator $\mathcal{N}$ by

$$\mathcal{N} = \sum_k N_k = \sum_k a_k^\dagger a_k ,$$

(4.14)

where the sum extends over all single-particle quantum numbers, it can easily be shown that $|ab\cdots n\rangle$ is an eigenstate of $\mathcal{N}$ with eigenvalue $N$. In a similar way, we see that the state $|ab\cdots n\rangle$ is an eigenstate of the unperturbed Hamiltonian operator $H_0$ defined by

$$H_0 = \sum_k \epsilon_k a_k^\dagger a_k ,$$

(4.15)

with eigenvalue

$$E^{(0)} = \epsilon_a + \epsilon_b + \cdots + \epsilon_n .$$

(4.16)

Here $\epsilon_k$ is the eigenvalue of the one-electron Hamiltonian $h(r)$ belonging to the eigenfunction $\psi_k(r)$:

$$h\psi_k(r) = \epsilon_k \psi_k(r) .$$

Equation (4.15) gives the representation of the unperturbed Hamiltonian $H_0$ in second quantization. This equation can be rewritten

$$H_0 = \sum_k \langle k|h|k \rangle a_k^\dagger a_k .$$

(4.17)

A general single-particle operator $F = \sum_{i=1}^N f(r_i)$ is represented in second quantization as

$$F = \sum_{kl} \langle k|f|l \rangle a_k^\dagger a_l .$$

(4.18)

This operator acting on the state $|ab\cdots n\rangle$ gives

$$F |ab\cdots n\rangle = \sum_{kc} \langle k|f|c \rangle |ab\cdots c \rightarrow k\cdots n \rangle ,$$

(4.19)

where $|ab\cdots c \rightarrow k\cdots n\rangle$ is identical to the state $|ab\cdots n\rangle$ with the operator $a^\dagger_c$ replaced by $a^\dagger_k$. In this expression, $c$ is a state occupied in $|ab\cdots n\rangle$ and the sum extends over all such states. The state $k$ is either identical to $c$ or is a state not occupied in $|ab\cdots n\rangle$. The matrix element of $F$ between a state $|a'\cdots n'\rangle$ and $|ab\cdots n\rangle$ is nonvanishing only if the sets $\{ab\cdots n\}$ and $\{a'\cdots n'\}$ differ in at most one place. Thus

$$\langle ab\cdots c'\cdots n|F|ab\cdots c\cdots n\rangle = \langle c'|f|c \rangle .$$

(4.20)

Furthermore,

$$\langle ab\cdots n|F|ab\cdots n\rangle = \sum_c \langle c|f|c \rangle .$$

(4.21)

These rules are precisely the same as those developed in Chapter 2 to calculate matrix-elements of single-particle operators between Slater determinant wave functions.
The two-particle operator,
\[
G = \frac{1}{2} \sum_{i \neq j} g(r_{ij}) ,
\]
is represented in second quantization by:
\[
G = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^{\dagger} a_j^{\dagger} a_l a_k ,
\tag{4.22}
\]
where, as before,
\[
g_{ijkl} = \int d^3r_1 d^3r_2 \psi_i^\dagger(r_1) \psi_j^\dagger(r_2) g(r_{12}) \psi_k(r_1) \psi_l(r_2) .
\]
Again, it is simple to verify that matrix elements of \(G\) satisfy precisely the rules written down in the previous chapter for calculating matrix elements of two-particle operators between determinant wave functions. As an example, let us consider the expectation value of \(G\) in the two-particle state \(|ab\rangle\).
\[
\langle ab|G|ab\rangle = \frac{1}{2} \sum_{ijkl} g_{ijkl} \langle 0|a_b a_a a_i^{\dagger} a_j^{\dagger} a_l a_k a_i^{\dagger} a_j^{\dagger}|0\rangle .
\tag{4.23}
\]
With the aid of the anticommutation relations, the product \(a_b a_a a_i^{\dagger} a_j^{\dagger}\) on the left in Eq.(4.23) can be rearranged to give
\[
a_b a_a a_i^{\dagger} a_j^{\dagger} = \delta_{ia} \delta_{jb} - \delta_{ib} \delta_{ja} - \delta_{ia} a_j^{\dagger} a_b + \delta_{ib} a_i^{\dagger} a_a + \delta_{ja} a_l a_k - \delta_{ja} a_l a_k .
\tag{4.24}
\]
Since \langle 0|a_j^{\dagger} = 0, only the first two terms on the right-hand side of this equation contribute in (4.23). Similarly, the product of operators \(a_l a_k a_i^{\dagger} a_j^{\dagger}\) can be written
\[
a_l a_k a_i^{\dagger} a_j^{\dagger} = \delta_{ka} \delta_{lb} - \delta_{ka} \delta_{kb} - \delta_{ia} a_l a_k + \delta_{ib} a_i^{\dagger} a_l + \delta_{ia} \delta_{ka} - \delta_{ia} \delta_{ka} + a_i^{\dagger} a_j^{\dagger} a_k a_l .
\tag{4.25}
\]
Only the first two terms in this expression contribute to (4.23) since \(a_k|0\rangle = 0\). Therefore,
\[
\langle ab|G|ab\rangle = \frac{1}{2} \sum_{ijkl} g_{ijkl} \langle 0|\delta_{ia} \delta_{jb} - \delta_{ia} \delta_{ja} - \delta_{ia} a_l a_k - \delta_{ja} a_l a_k + a_i^{\dagger} a_j^{\dagger} a_l a_k \rangle = g_{bab} - g_{aba} .
\tag{4.26}
\]
This is precisely the result that we obtain in configuration space using a Slater determinant wave function.
4.2. 6-J SYMBOLS

Schrödinger Hamiltonian: With the aid of the second quantization expressions for one- and two-body operators, we write the expression for the Hamiltonian in second quantization as $H = H_0 + V$, where

$$H_0 = \sum_k \epsilon_k a_k^\dagger a_k,$$  

(4.27)

$$V = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k - \sum_{ik} U_{ik} a_i^\dagger a_k.$$  

(4.28)

Here, $\epsilon_k$ is the eigenvalue of the one-electron Schrödinger equation in a potential $-Z/r + U(r)$, the quantity $g_{ijkl}$ is a two-electron matrix element of the Coulomb potential $g(r_{12}) = 1/r_{12}$ and $U_{ik}$ is the one-electron matrix element of the background potential $U(r)$:

$$U_{ik} = \int d^3r \psi_i^\dagger(r) U(r) \psi_k(r).$$  

(4.29)

No-Pair Hamiltonian: The Dirac-Coulomb Hamiltonian of the previous chapter can also be cast in second-quantized form. Again, $H = H_0 + V$, where $H_0$ and $V$ are given by the formulas (4.27-4.28). For the Dirac case, $\epsilon_k$ in (4.27) is an eigenvalue of the one-electron Dirac Hamiltonian in a potential $-Z/r + U(r)$, and $g_{ijkl}$ is a two-electron Coulomb integral evaluated with Dirac orbitals. In the expression for the Hamiltonian, the operators are restricted to be creation and annihilation operators for positive-energy solutions to the Dirac equation. These are the solutions associated with electron states. Contributions from negative-energy (positron) states are omitted from the Hamiltonian entirely. The resulting Hamiltonian is called the no-pair Hamiltonian. Since positron states are not present in the no-pair Hamiltonian, effects of virtual electron-positron pairs on atomic structure are omitted. To account for these small effects, we must carry out a separate QED calculation. The no-pair Hamiltonian is free from the problems mentioned in the previous chapter in connection with the Dirac-Coulomb Hamiltonian; it can be used in higher-order perturbation theory calculations. The no-pair Hamiltonian was introduced in a slightly different form by Brown and Ravenhall (1951) and has been discussed in great detail by Mittleman (1971, 1972, 1981) and Sucher (1980).

4.2 6-j Symbols

Before continuing our discussion of many-body techniques, it is necessary to make a short digression into angular momentum theory to describe various ways of combining more than two angular momentum eigenstates to form a product state that is also an angular momentum eigenstate. The Wigner 6-j symbols arise when we consider coupling three states to give a state of definite angular momentum. It is clear that we can couple three states with angular momenta $j_1$, $j_2$ and $j_3$ to a total angular momentum $J$ in various ways. For example, we
can first couple \( j_1 \) and \( j_2 \) to an intermediate angular momentum \( J_{12} \), and then couple \( J_{12} \) and \( j_3 \) to \( J \) and \( M \), leading to the state

\[
| (j_1 j_2)_{J_{12} j_3} , JM \rangle = \sum_{m_1=-m_{12}}^{m_{12}} \left[ \begin{array}{c} j_1 m_1 \\ J_{12} m_{12} \\ j_2 m_2 \\ j_3 m_3 \end{array} \right] | j_1 m_1 \rangle | j_2 m_2 \rangle | j_3 m_3 \rangle .
\]

(4.30)

Alternatively, we can couple \( j_2 \) and \( j_3 \) to \( J_{23} \), and then couple \( j_1 \) to \( J_{23} \) to give the resulting value of \( J \) and \( M \). This order of coupling leads to the state

\[
| j_1 (j_2 j_3)_{J_{23}} , JM \rangle = \sum_{m_2=-m_{23}}^{m_{23}} \left[ \begin{array}{c} j_2 m_2 \\ J_{23} m_{23} \\ j_3 m_3 \end{array} \right] | j_1 m_1 \rangle | j_2 m_2 \rangle | j_3 m_3 \rangle .
\]

(4.31)

States obtained from either of these two coupling schemes can be expressed as linear combinations of states obtained using the other scheme. Thus, for example, we may write

\[
| j_1 (j_2 j_3)_{J_{23}} , JM \rangle = \sum_{J_{12}} | (j_1 j_2)_{J_{12} j_3} , JM \rangle \langle (j_1 j_2)_{J_{12} j_3} , JM | j_1 (j_2 j_3)_{J_{23}} , JM \rangle .
\]

(4.32)

The resulting recoupling coefficient \( \langle (j_1 j_2)_{J_{12} j_3} , JM | j_1 (j_2 j_3)_{J_{23}} , JM \rangle \) is independent of \( M \). We evaluate this coefficient by connecting the lines corresponding to \( j_1, j_2 \) and \( j_3 \) in the graphs from (4.30) and (4.31) above. The resulting graph has two free ends, both labeled by \( JM \). Since the recoupling coefficient is independent of \( M \), we may obtain the coefficient by averaging over \( M \). This is done by connecting the free ends and dividing by \( [J] \). The resulting coefficient can be expressed as

\[
\langle (j_1 j_2)_{J_{12} j_3} , JM | j_1 (j_2 j_3)_{J_{23}} , JM \rangle = (-1)^{j_1 + j_2 + j_3 + J_{12}} [J_{23}] \{ \begin{array}{ccc} j_1 & j_2 & J_{12} \\ j_3 & J & J_{23} \end{array} \},
\]

(4.33)

where the expression in curly brackets can be brought into the graphical form

\[
\left\{ \begin{array}{ccc} j_1 & j_2 & J_{12} \\ j_3 & J & J_{23} \end{array} \right\} = \frac{1}{2} \left( \begin{array}{c} j_1 \\ J_{12} \\ j_2 \\ J_{23} \\ j_3 \\ J \end{array} \right) + \frac{1}{2} \left( \begin{array}{c} j_1 \\ J_{12} \\ j_2 \\ J_{23} \\ j_3 \\ J \end{array} \right).
\]

(4.34)

The quantity

\[
\left\{ \begin{array}{ccc} j_1 & j_2 & J_{12} \\ j_3 & J & J_{23} \end{array} \right\}
\]
is a 6-j symbol. This quantity vanishes unless angular momentum triangle inequalities are satisfied by the triples \(j_1 j_2 J_1, j_3 J_1 j_2, j_3 j_2 J_3\) and \(j_1 J_1 J_3\). Moreover, the 6-j symbols satisfy the symmetry relations

\[
\begin{align*}
\begin{array}{c}
\{j_a, j_b, j_c \} \\
\{l_a, l_b, l_c \}
\end{array}
= \begin{array}{c}
\{j_b, j_a, j_c \} \\
\{l_b, l_a, l_c \}
\end{array}
= \begin{array}{c}
\{j_c, j_b, j_a \} \\
\{l_c, l_b, l_a \}
\end{array}.
\end{align*}
\]

(4.35)

In other words, the 6-j symbol is invariant with respect to a permutation (even or odd) of columns. Further, the 6-j symbol satisfies the symmetry relations

\[
\begin{align*}
\begin{array}{c}
\{j_a, j_b, j_c \} \\
\{l_a, l_b, l_c \}
\end{array}
= \begin{array}{c}
\{l_a, j_b, l_c \} \\
\{l_a, j_b, l_a \}
\end{array}
= \begin{array}{c}
l_a \\
\{j_a, j_b, l_c \}
\end{array}.
\end{align*}
\]

(4.36)
i.e, the 6-j symbol is invariant under inversion of the arguments in any two columns.

The graphical representation of the 6-j symbol leads to its analytical expression in terms of 3-j symbols

\[
\begin{align*}
\begin{array}{c}
\{j_a, j_b, j_c \} \\
\{j_d, j_e, j_f \}
\end{array}
= \sum_{m,s} (-1)^K \times
\left[
\begin{array}{ccc}
-1 & -1 & -1 \\
-1 & -1 & -1 \\
-1 & -1 & -1
\end{array}
\right] \\
\left[
\begin{array}{ccc}
j_a & j_b & j_c \\
j_d & j_e & j_f
\end{array}
\right] \\
\left[
\begin{array}{ccc}
j_a & j_b & j_c \\
j_d & j_e & j_f
\end{array}
\right],
\end{align*}
\]

(4.37)

with

\[
K = j_a - m_a + j_b - m_b + j_c - m_c + j_d - m_d + j_e - m_e + j_f - m_f
\]

A useful formula (Edmonds, 1974) for calculating 6-j symbols is

\[
\begin{align*}
\begin{array}{c}
\{j_a, j_b, j_c \} \\
\{j_d, j_e, j_f \}
\end{array}
= \Delta(j_a j_b j_c) \Delta(j_d j_e j_f) \Delta(j_d j_e j_c) \times
\sum_k \left[
\begin{array}{c}
-1 \times
\frac{(k - j_a - j_b - j_c)!}{(k - j_a - j_d - j_f)!} \\
\frac{1}{(j_b + j_c + j_f - k)! (j_c + j_a + j_f + j_d - k)!}
\end{array}
\right],
\end{align*}
\]

(4.38)

where

\[
\Delta(j_a j_b j_c) = \sqrt{\frac{(j_a + j_b - j_c)! (j_a - j_b + j_c)! (j_a + j_b + j_c)!}{(j_a + j_b + j_c + 1)!}}.
\]

(4.39)

The 6-j symbols satisfy the following orthogonality relation

\[
\sum_{j_f} [j_c] [j_f] \{j_a, j_b, j_c \} \{j_d, j_e, j_f \} = \delta_{j_c, j' c}.
\]

(4.40)
Additionally, they satisfy the following two sum rules: (Racah)
\[ \sum_{j_f} (-1)^{j_a+j_b+j_f} \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ j_d & j_e & j_f \end{array} \right\} = \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ j_d & j_e & j_f \end{array} \right\}, \] (4.41)
and (Biedenharn, 1953; Elliott, 1953)
\[ \sum_k (-1)^{S+k} \left\{ \begin{array}{ccc} l_1 & j_2 & l_3 \\ l'_1 & l'_2 & l'_3 \end{array} \right\} = \left\{ \begin{array}{ccc} l_1 & j_2 & l_3 \\ l'1 & l'_2 & l'_3 \end{array} \right\}, \] (4.42)
where \( S = j_1 + j_2 + j_3 + l_1 + l_2 + l_3 + l'_1 + l'_2 + l'_3 \). The following special case is often useful
\[ \left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ l_1 & l_2 & 0 \end{array} \right\} = \delta_{j_1 l_1} \delta_{j_2 l_2} (-1)^{j_1+j_2+j_3} \frac{(-j_1+j_2+j_3)}{\sqrt{j_1 j_2}}. \] (4.43)

### 4.3 Two-Electron Atoms

In this Section, we use second quantization to study the excited states of two-electron atoms and ions. We start our discussion by considering a two-electron state \(|ab\rangle\). This is an eigenstate of \(H_0\), with eigenvalue \(E^{(0)}_{ab} = \epsilon_a + \epsilon_b\):
\[ H_0 |ab\rangle = (\epsilon_a + \epsilon_b) |ab\rangle. \] (4.44)

The state \(|ab\rangle\) is \(2|l_a\rangle \times 2|l_b\rangle\)-fold degenerate. It is not necessarily an angular momentum eigenstate. We make use of the degeneracy to construct eigenstates of \(L^2, L_z, S^2\) and \(S_z\) from \(|ab\rangle\). To this end, we first couple \(l_a\) and \(l_b\) to give an eigenstate of \(L^2\) and \(L_z\), then we couple \(s_a\) (\(s_a = 1/2\)) and \(s_b\) (\(s_b = 1/2\)) to give an eigenstate of \(S^2\) and \(S_z\). The possible eigenvalues of \(S^2\) are \(S(S + 1)\), where \(S = 0\) or \(1\). States with \(S = 0\) are referred to as singlet states, since there is only one such state with \(M_S = 0\). States with \(S = 1\) are called triplet states. The resulting eigenstates of \(L^2, L_z, S^2\) and \(S_z\) are called \(LS\)-coupled states. Singlet states are also eigenstates of \(J (J = L + S)\) with \(J = L\). Triplet states can be further combined to give eigenstates of \(J\) having eigenvalues \(L - 1, L, L + 1\). Nonrelativistically, the triplet states with different values of \(J\) are degenerate. This degeneracy is lifted in relativistic calculations. The observed spectrum of helium consists of singlets and triplets of various angular symmetries \(S, P, \ldots\) corresponding to \(L = 0, 1, \ldots\). The triplets are slightly split by relativistic effects. \(LS\)-coupled states with orbital angular momentum \(L\), spin angular momentum \(S\), and total angular momentum \(J\) are designated by the spectroscopic notation \(^{2S+1}L_J\). In Fig. 4.1, we show the approximate ordering of the low-lying singlet and triplet levels of helium in an energy level (or Grotrian) diagram.
To form the LS-coupled states, we combine the degenerate states according to
\[ |ab, LM, SM_S⟩ = \eta \sum_{m_a m_b \mu_a \mu_b} t_{a m_a} L_{M L} \left[ \frac{1}{2 \mu_a} S_{M S} \right] a^{\dagger}_{a m_a} a^{\dagger}_{b m_b} |0⟩ . \] (4.45)

Here, \( \eta \) is a normalization factor. The norm of this coupled state is easily shown to be
\[ \langle ab, LM, SM_S | ab, LM, SM_S⟩ = \eta^2 (1 + (-1)^{L+S} \delta_{n_a n_b} \delta_{l_a l_b}) . \] (4.46)

For states with \( n_b \neq n_a \) or \( l_b \neq l_a \), we obtain a normalized state by choosing \( \eta = 1 \). For states formed from identical orbitals (\( n_b = n_a \) and \( l_b = l_a \)), the sum \( L + S \) must be even in order to have a normalizable state. To normalize such a state, we choose \( \eta = 1/\sqrt{2} \). An example of a state formed from identical orbitals is the \((1s)^2\) ground state. This state has \( L = 0 \) and \( S = 0 \); it is a \( ^1S_0 \) state.

The first-order correction to the energy of an LS-coupled state is given by
\[ E^{(1)}_{ab,LS} = \langle ab, LM, SM_S | V | ab, LM, SM_S⟩ . \] (4.47)

This result can be written
\[ E^{(1)}_{ab,LS} = \eta^2 \sum_{m' q' s'} \left[ t_{a m_a} t_{b m_b} \right] \left[ \frac{1}{2 \mu_a} S_{M S} \right] \left[ \frac{1}{2 \mu_b} S_{M S} \right] \left[ U_{aa} + U_{bb} \right] . \]

We make use of the identity
\[ g_{abcd} = \sum_k \left[ t_{a m_a} t_{b m_b} \right] L_{k m_c m_d} + X_k(abc) , \] (4.48)
where

\[ X_k(abcd) = (-1)^k \langle l_a || C^k || l_b \rangle \langle l_b || C^k || l_a \rangle R_k(abcd). \] (4.49)

Substituting this into the expression for the first-order energy, we find

\[ E^{(1)}_{ab,LS} = \eta^2 \sum_k \left[ (-1)^{L+k+l_a+l_b} \left\{ \begin{array}{ccc} l_a & l_b & L \\ l_a & l_b & k \end{array} \right\} X_k(abab) \right. \]

\[ + (-1)^{S+k+l_a+l_b} \left\{ \begin{array}{ccc} l_a & l_b & L \\ l_a & l_b & k \end{array} \right\} X_k(abba) \] \left. - U_{aa} - U_{bb} \right]. \] (4.50)

Let us consider the special case where \( a \) is a \( 1s \) state and \( b \) is an \( nl \) excited state. Such states are single-particle excitations of the helium ground state. All of the bound levels of helium are of this type; doubly-excited states of helium are not bound! We, therefore, set \( l_a = 0 \) and \( l_b = l \) in Eq.(4.50). In the first term, \( k = 0 \) so the sum reduces to

\[ R_0(1s, nl, 1s, nl) . \]

Here, we have made use of Eq.(4.43) and the fact that \( \langle s || C^k || s \rangle = \delta_{k0} \) and \( \langle l || C^0 || l \rangle = \sqrt{l!} \). In the second term, we find from Eq.(4.43) that \( k = L = l \). Furthermore, \( \langle l || C^l || l \rangle = 1 \), and \( \langle s || C^l || l \rangle = (-1)^l \). Therefore, the second term reduces to

\[ (-1)^S \frac{1}{l!} R_1(1s, nl, nl, 1s) \delta_{ll}. \] (4.51)

Combining these results, we obtain for \((1snl)\) states

\[ E^{(1)}_{1snl,LS} = \left[ \eta^2 \left( R_0(1s, nl, 1s, nl) + (-1)^S \frac{1}{l!} R_1(1s, nl, nl, 1s) \right) \right. \]

\[ - U_{1s1s} - U_{nlnl} \delta_{ll}. \] (4.51)

First, let us consider the case \( nl = 1s \). In this case, as discussed above, \( S = 0 \) and \( \eta = 1/\sqrt{2} \), leading to the result

\[ E^{(1)}_{1s1s,00} = R_0(1s, 1s, 1s, 1s) - 2U_{1s1s} . \] (4.52)

This is precisely the expression obtained in the previous section for the first-order correction to the ground-state energy of a heliumlike ion. For states with \( nl \neq 1s \), \( \eta = 1 \) and we find

\[ E^{(1)}_{1snl,LS} = \left( R_0(1s, nl, 1s, nl) + (-1)^S \frac{1}{l!} R_1(1s, nl, nl, 1s) \right. \]

\[ - U_{1s1s} - U_{nlnl} \delta_{ll}. \] (4.53)

The lowest-order energy of these states, \( \epsilon_{1s} + \epsilon_{nl} \), is independent of \( S \). The separation between the singlet and triplet states is, therefore, given by

\[ \Delta E = E_{1snl,S=0} - E_{1snl,S=1} = \frac{2}{l!} R_1(1s, nl, nl, 1s) . \]
4.3. TWO-ELECTRON ATOMS

Table 4.1: Energies of \((1s nl)\) singlet and triplet states of helium (a.u.). Comparison of a model-potential calculation with experiment (Moore, 1957).

<table>
<thead>
<tr>
<th>(nl)</th>
<th>Singlet</th>
<th>Triplet</th>
<th>(\Delta E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theory</td>
<td>Exp.</td>
<td>Theory</td>
</tr>
<tr>
<td>2s</td>
<td>-1.1537</td>
<td>-1.4595</td>
<td>-1.172019</td>
</tr>
<tr>
<td>3s</td>
<td>-1.0632</td>
<td>-1.0612</td>
<td>-1.068014</td>
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<td>4s</td>
<td>-1.0343</td>
<td>-1.0358</td>
<td>-1.036265</td>
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<td>5s</td>
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<td>-1.0211</td>
<td>-1.022502</td>
</tr>
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<td>2p</td>
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<td>-1.1238</td>
<td>-1.130465</td>
</tr>
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<td>4p</td>
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<td>-1.0310</td>
<td>-1.032022</td>
</tr>
<tr>
<td>5p</td>
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<td>-1.020400</td>
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</tr>
<tr>
<td>5f</td>
<td>-1.0200</td>
<td>-1.0200</td>
<td>-1.020005</td>
</tr>
</tbody>
</table>

In Table 4.1, we compare a first-order perturbation theory calculation of the energies of the singlet and triplet \(S, P, D,\) and \(F\) states of helium with experiment. For the purposes of this calculation, we assume that the 1s electron moves in the unscreened potential of the nucleus, but that the excited \(nl\) electrons move in the field of the nucleus screened by the monopole potential \(v_0(1s, r)\) of the 1s electron. This somewhat exotic potential can be formally described in terms of projection operators. We let \(P = |1s\rangle \langle 1s|\) be the projection operator onto the 1s state, and \(Q\) be the projection operator onto the complement to the 1s state:

\[
Q = \sum_{nl \neq 1s} |nl\rangle \langle nl|.
\]

It follows that \(P + Q = 1\). We represent the screening potential by

\[
U = Q v_0 Q = v_0 - P v_0 - v_0 P + P v_0 P.
\]  

(4.54)

Note that

\[
U |1s\rangle = v_0 |1s\rangle - |1s\rangle \langle 1s| v_0 |1s\rangle - v_0 |1s\rangle + |1s\rangle \langle 1s| v_0 |1s\rangle = 0,
\]  

(4.55)

while for \(nl \neq 1s\) we find,

\[
U |nl\rangle = v_0 |nl\rangle - |1s\rangle \langle 1s| v_0 |nl\rangle.
\]  

(4.56)
For states with $l \neq 0$, the second term in the above expression vanishes and $U = v_0(1s, r)$. For states with $l = 0$, the second term insures that the resulting radial wave function is orthogonal to the $1s$ wave function. Notice that $U_{1s1s} = 0$ for this potential, and that $U_{nlnl} = R_0(1s, nl, 1s, nl)$. For comparison with experiment, we evaluate the energy relative to that of the hydrogenlike ion formed when the $nl$ electron is removed. The energy of the hydrogenic ion is precisely $\epsilon_{1s}$. The energy relative to the ion in this model potential is, therefore, given by

$$E_{1snl,LS} - E_{ion} = \epsilon_{nl} + (-1)^{S} \frac{1}{[l]} R_l(1s, nl, nl, 1s).$$

(4.57)

Values obtained from this formula are tabulated in Table 4.1. As seen from this Table, this simple model potential suffices to predict the multiplet structure in helium at the few-percent level of accuracy.

### 4.4 Atoms with One or Two Valence Electrons

In this section, we study states of atoms that have one or two valence electrons beyond closed shells. For atoms with one valence electron, the present section is an extension of our previous discussion using the $V_{HF}^{N-1}$ potential. For atoms with two valence electrons, the material here is an extension of the discussion of excited states of helium given in the previous section.

We let $|0_c\rangle$ represent the ionic core, which is assumed to consists of filled subshells,

$$|0_c\rangle = a_a^\dagger a_b^\dagger \cdots |0\rangle.$$  

(4.58)

The states of interest can then be described as

$$|v\rangle = a_v^\dagger |0_c\rangle,$$

$$|vw\rangle = a_v^\dagger a_w^\dagger |0_c\rangle,$$

(4.59)

(4.60)

where the indices $v$ and $w$ designate orbitals that are different from any of those occupied in the core. Here and later, we adopt the notation that letters at the beginning of the alphabet $a, b, \cdots$, designate core orbitals, letters in the middle of the alphabet $i, j, \cdots$, designate either core or excited (outside of the core) orbitals, letters $m, n, \cdots$, represent excited orbitals, and letters at the end of the alphabet $v, w, \cdots$, represent valence orbitals. Valence orbitals are, of course, special cases of excited orbitals.

It is useful to introduce the normal product of operators here. The normal product of two operators is defined as the product rearranged so that core creation operators are always put to the right of core annihilation operators and excited state annihilation operators are always put to the right of excited state creation operators. In carrying out that rearrangement, a sign change is made for each operator transposition. Normal products are designated by enclosing the operators between pairs of colons; thus : $a_a^\dagger a_n^\dagger :$ represents the normal product of the operators $a_a^\dagger$ and $a_n^\dagger$. Normal products of two creation
operators or two annihilation operators are just the product of the two operators. Moreover,

\[ a_m^\dagger a_n = a_m^\dagger a_n , \]
\[ a_n a_m^\dagger = -a_n^\dagger a_m , \]
\[ a_n^\dagger a_b = -a_b a_n^\dagger , \]
\[ a_b a_n^\dagger = a_n a_b^\dagger . \]

This definition can be extended to arbitrary products of operators. The normal product of \( N \) operators is the product of the \( N \) operators rearranged so that core creation operators are to the right of core annihilation operators and excited state annihilation operators are to the right of excited state creation operators with a sign change for each transposition of two operators. With this definition, it follows that the expectation value of the normal product of two operators calculated in the core state vanishes:

\[ \langle 0_c | a_1 a_2 \cdots a_l | 0_c \rangle = 0. \] (4.61)

Here \( a_i \) designates either a creation operator \( a_i^\dagger \) or an annihilation operator \( a_i \).

The Hamiltonian \( H \) can be expressed in terms of normal products by

\[ H = H_0 + V, \]

\[ H_0 = E_0 + \sum_k \epsilon_k : a_k^\dagger a_k : , \]

\[ V = \frac{1}{2} \sum_{ijkl} g_{ijkl} : a_i^\dagger a_j^\dagger a_l a_k : + \sum_{ij} (V_{HF} - U)_{ij} : a_i^\dagger a_j : + V_0. \] (4.64)

Here

\[ E_0 = \sum_a \epsilon_a , \]

and

\[ V_0 = \sum_a \left[ \frac{1}{2} (V_{HF})_{aa} - U_{aa} \right] . \]

In the above equations we have used the notation

\[ (V_{HF})_{ij} = \sum_b (g_{ibjb} - g_{ibbj}) . \] (4.65)

The quantity \( V_{HF} \) is just the Hartree-Fock potential of the closed core. We should notice that

\[ E_{core} = \langle 0_c | H | 0_c \rangle = E_0 + V_0 = \sum_a \epsilon_a + \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}) - \sum_a U_{aa} . \] (4.66)

This result was derived previously by manipulating Slater determinants.
One valence electron: Let us first consider an atom with one valence electron in a state \( v \). To help evaluate the expectation value of \( H_0 \), we make use of the easily established identity

\[
a_v : a_k^\dagger a_k : a_v^\dagger = a_v a_k^\dagger a_k a_v^\dagger + \delta_{kv} : a_k^\dagger a_k : a_v^\dagger + : a_k^\dagger a_k : + \delta_{kv}. \tag{4.67}
\]

From this identity, it follows that

\[
\left\langle v \right| a_k^\dagger a_k : \left| v \right\rangle = \left\langle 0_c \right| a_v : a_k^\dagger a_k : a_v^\dagger \left| 0_c \right\rangle = \delta_{kv}.
\tag{4.68}
\]

Therefore, from Eq.(4.63) it follows that,

\[
E_v^{(0)} = \left\langle v \right| H_0 \left| v \right\rangle = E_0 + \epsilon_v.
\tag{4.69}
\]

To evaluate the first-order energy, we make use of the identities

\[
\left\langle 0_c \right| a_v : a_k^\dagger a_k : a_v^\dagger \left| 0_c \right\rangle = 0,
\tag{4.70}
\]

\[
\left\langle 0_c \right| a_v : a_j^\dagger : a_v^\dagger \left| 0_c \right\rangle = \delta_{iv} \delta_{jv}.
\tag{4.71}
\]

Combining these relations with the expression for \( V \) given in Eq.(4.64), we find

\[
E_v^{(1)} = \left\langle v \right| V \left| v \right\rangle = V_0 + (V_{HF} - U)_{vv}.
\tag{4.72}
\]

To first order, we therefore have

\[
E_v = E_{\text{core}} + \epsilon_v + (V_{HF} - U)_{vv}.
\tag{4.73}
\]

If we let \( U \) be the Hartree-Fock potential of the core, then the valence orbital is just the \( V_{HF}^{-1} \) orbital discussed in the previous section. As we found previously, \( \epsilon_v \) is the difference between the energy of the atom and ion. This rule will, of course, be modified when we consider corrections from higher-order perturbation theory. For atoms with one valence electron, the second-quantization approach leads easily to results obtained previously by evaluating matrix elements using Slater determinants.

Two valence electrons: Now, let us turn to atoms having two valence electrons. As an aid to evaluating the energy for such atoms, we make use of the identities

\[
\left\langle 0_c \right| a_w a_v : a_j^\dagger a_j : a_w^\dagger a_w^\dagger \left| 0_c \right\rangle = (\delta_{iv} \delta_{jw} - \delta_{jv} \delta_{iw}) \times
\]

\[
\left( \delta_{k_0} \delta_{l_w} - \delta_{l_v} \delta_{k_w} \right),
\tag{4.74}
\]

\[
\left\langle 0_c \right| a_w a_v : a_j^\dagger a_j : a_w^\dagger a_w^\dagger \left| 0_c \right\rangle = \delta_{iv} \delta_{jw} + \delta_{iw} \delta_{jv}.
\tag{4.75}
\]

From these identities, we find for the lowest-order energy,

\[
E_{vw}^{(0)} = \left\langle vw \right| H_0 \left| vw \right\rangle = E_0 + \epsilon_v + \epsilon_w.
\tag{4.76}
\]
and for the first-order energy,

\[ E_{vw}^{(1)} = (vw|V|vw) \]
\[ = V_0 + (V_{HF} - U)_{vw} + (V_{HF} - U)_{ww} + g_{vwvw} - g_{wvvw}. \]  

(4.77)

Combining, we find to first order

\[ E_{vw} = E_{\text{core}} + \epsilon_v + \epsilon_w + (V_{HF} - U)_{vv} + (V_{HF} - U)_{ww} + g_{vwvw} - g_{wvvw}. \]  

(4.78)

For the purpose of illustration, we assume that \( U = V_{HF} \) in Eq.(4.78), and we measure energies relative to the closed core. We then have

\[ E_{vw}^{(0)} = \epsilon_v + \epsilon_w \]
\[ E_{vw}^{(1)} = g_{vwvw} - g_{wvvw}. \]

As in the case of helium, the degenerate states \( v \) and \( w \) can be combined to form eigenstates of \( L^2 \), \( L_z \), \( S^2 \) and \( S_z \). The expression for \( E_{vw}^{(1)} \) in an \( LS \) basis is found from (4.50) to be:

\[ E_{vw,LS}^{(1)} = \eta^2 \sum_k \left[ (-1)^{L+k+l_v+l_w} \left\{ \begin{array}{ccc} l_v & l_w & L \\ l_w & l_v & k \end{array} \right\} X_k(vwvw) \right. 
\left. + (-1)^{S+k+l_v+l_w} \left\{ \begin{array}{ccc} l_v & l_w & L \\ l_w & l_v & k \end{array} \right\} X_k(vwvw) \right]. \]  

(4.79)

Here \( \eta = 1/\sqrt{2} \) for the case of identical particles (\( n_v = n_w \) and \( l_v = l_w \)), and \( \eta = 1 \) otherwise. For the identical-particle case, the sum \( L + S \) must be an even integer.

As specific examples, let us consider the atoms such as beryllium or magnesium which, in the ground state, have two \( s \) electrons outside closed shells. In the ground state, beryllium \((Z = 4)\) has two \( 2s \) electrons outside a heliumlike core and magnesium \((Z = 12)\) has two \( 3s \) electrons outside of a neonlike core. Other such atoms are calcium, zinc, mercury and radium. The low-lying excited states of these atoms are \((2snl)\) singlet or triplet states for beryllium, \((3snl)\) singlet or triplet states for magnesium, etc.. For such states, the expression for the first-order energy simplifies to a form similar to that obtained for helium:

\[ E_{ksnl,LS}^{(1)} = \eta^2 \left( R_0(k,s,n,l) + (-1)^{S} \frac{1}{[l]} R_l(k,s,n,l) \right) \delta_{LL} \]  

(4.80)

Combining this with the lowest-order energy, we find for the \((ks)^2\) ground-state energy,

\[ E_{kks,00} = 2\epsilon_{ks} + R_0(k,s,k,s,k,s), \]  

(4.81)

and for \((ksnl)\) excited states,

\[ E_{kksl,LS} = \epsilon_{ks} + \epsilon_{nl} + \left( R_0(k,s,n,l) + (-1)^{S} \frac{1}{[l]} R_l(k,s,n,l) \right) \delta_{LL} \]  

(4.82)

For beryllium, magnesium and calcium, doubly excited \(|(2p)^2,LS\rangle\), \(|(3p)^2,LS\rangle\) and \(|(4p)^2,LS\rangle\) states, respectively, are also observed in the bound state spectrum. Furthermore, doubly-excited \(|3d4p,LS\rangle\) states are observed in the spectrum of calcium.
For $(kp)^2$ configurations, the sum $L+S$ must be even. Therefore, the possible states are $1S$, $3P$ and $1D$. The first-order energy for these states is given by

$$E_{kpkp,00}^{(1)} = R_0(kp, kp, kp, kp) + \frac{2}{5} R_2(kp, kp, kp, kp),$$  \hspace{0.5cm} (4.83)

$$E_{kpkp,11}^{(1)} = R_0(kp, kp, kp, kp) - \frac{1}{5} R_2(kp, kp, kp, kp),$$  \hspace{0.5cm} (4.84)

$$E_{kpkp,20}^{(1)} = R_0(kp, kp, kp, kp) + \frac{1}{25} R_2(kp, kp, kp, kp).$$  \hspace{0.5cm} (4.85)

From this, it is predicted in first-order that the $3P$ state has the lowest energy and that the $1S$ state has the highest energy.

Both carbon ($Z = 6$) and silicon ($Z = 14$) have two $kp$ electrons beyond closed $(ks)^2$ shells in their ground states. We therefore expect the ground states of these atoms to be $3P$ state and we expect the next two excited states to be $1D$ and $1S$ states, respectively. The collection of states from the $(kp)^2$ configuration is called the ground-state multiplet.

The lowest state in the observed spectrum of both carbon and silicon is a $3P$ state as predicted, and the next two states are $1D$ and $1S$ states, as expected. From Eqs.(4.83-4.85), we predict that

$$R = \frac{E(kpkp,00) - E(kpdp,20)}{E(kpdp,00) - E(kpdp,11)} = \frac{3}{5}.$$  \hspace{0.5cm} (4.86)

For carbon the observed ratio is $R = 0.529$, while for silicon $R = 0.591$.

Another interesting example is titanium ($Z = 24$) which has a ground-state configuration $(3d)^2$. For this case, the ground-state multiplet consists of the $1S$, $3P$, $1D$, $3F$ and $1G$ states. The first-order energy is given by

$$E_{3d3d,00}^{(1)} = R_0 + \frac{2}{7} R_2 + \frac{2}{7} R_4,$$  \hspace{0.5cm} (4.87)

$$E_{3d3d,11}^{(1)} = R_0 + \frac{1}{7} R_2 - \frac{4}{21} R_4,$$  \hspace{0.5cm} (4.88)

$$E_{3d3d,20}^{(1)} = R_0 - \frac{3}{49} R_2 + \frac{4}{49} R_4,$$  \hspace{0.5cm} (4.89)

$$E_{3d3d,31}^{(1)} = R_0 - \frac{8}{49} R_2 - \frac{1}{49} R_4,$$  \hspace{0.5cm} (4.90)

$$E_{3d3d,40}^{(1)} = R_0 + \frac{4}{49} R_2 + \frac{1}{441} R_4,$$  \hspace{0.5cm} (4.91)

where $R_k \equiv R_k(3d, 3d, 3d, 3d)$. From Eqs.(4.86-4.90), we expect the order of the levels in the ground-state multiplet of titanium to be (from lowest to highest): $3F$, $1D$, $3P$, $1G$ and $1S$. This ordering of levels is indeed observed in the ground-state multiplet.

### 4.5 Particle-Hole Excited States

The low-lying excited states of noble gas atoms are those in which an outer-shell electron is promoted to a single-particle state outside of the core, leaving...
4.5. PARTICLE-HOLE EXCITED STATES

a vacancy (or hole) in the closed shell. The particle-hole state in which a core electron with quantum numbers \( a \) is excited to a state with quantum numbers \( v \) is represented by the state vector \( |va\rangle \):

\[
|va\rangle = a^\dagger_a |0_c\rangle
\]

This state is an eigenstate of \( H_0 \) with eigenvalue

\[
E^{(0)}_{va} = E_0 + \epsilon_v - \epsilon_a. 
\]

The state is \( 2|l_a| \times 2|l_a| \)-fold degenerate. Again, we make use of the degeneracy to form \( LS \)-coupled angular momentum states. Here, some caution is required. A state with a hole in substate \( \cdots m_a, \mu_a \), has angular momentum properties of a particle with angular momentum components \( \cdots -m_a, -\mu_a \). Moreover, if the state \( |0_c\rangle \) is formed by applying creation operators to the vacuum in descending order; namely,

\[
|0_c\rangle = \cdots a^\dagger_{n_a} a^\dagger{l_a}, 1/2 a^\dagger_{n_a} a^\dagger{l_a}, a^\dagger_{-1/2} a^\dagger_{n_a} a^\dagger{l_a}, a^\dagger_{-1/2} a^\dagger_{n_a} a^\dagger{l_a}, \ldots
\]

then an extra factor of

\[
(-1)^{l_a - m_a} \times (-1)^{1/2 - \mu_a}
\]

is obtained in transposing the operator \( a^\dagger_a \) to the position to the left of \( a^\dagger_y \) in the wave function, where we can replace the product \( a^\dagger_a a^\dagger_y \) by 1. Thus, the state vector corresponding to a particle with angular momentum \( l_v, m_v, \mu_v \) and hole with angular momentum \( l_a, -m_a, -\mu_a \) is

\[
(-1)^{l_a - m_a} (-1)^{1/2 - \mu_a} a^\dagger_v a^\dagger_a |0_c\rangle.
\]

States of this type can be combined to form an \( LS \) state. We find,

\[
|va, LS\rangle = \sum_{m_v, m_a} \left( -1 \right)^{l_a - m_a} LML \left( -1 \right)^{1/2 - \mu_a} \left( \frac{1}{2 \mu_v} \right)^{SM_S} a^\dagger_v a^\dagger_a |0_c\rangle
\]

\[
= \sum_{m_v, m_a} \left( \frac{1}{2 \mu_v} \right)^{SM_S} a^\dagger_v a^\dagger_a |0_c\rangle.
\]

These states are properly normalized:

\[
\langle va | va \rangle = 1.
\]

The first-order energy for the state \( |va, LS\rangle \) is evaluated using the relations

\[
\langle 0_c | a^\dagger_v a^\dagger_a | 0_c \rangle = \delta_{v a} - \delta_{a v},
\]

\[
\langle 0_c | a^\dagger_v a^\dagger_a a^\dagger_k | 0_c \rangle = \delta_{v a} \delta_{a k} - \delta_{a v} \delta_{k a}.
\]
Table 4.2: Comparison of $V_{\text{HF}}^{N-1}$ energies of (3s2p) and (3p2p) particle-hole excited states of neon and neonlike ions with measurements.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$V_{\text{HF}}^{N-1}$ (3s2p)</th>
<th>Exp.</th>
<th>$V_{\text{HF}}^{N-1}$ (3p2p)</th>
<th>Exp.</th>
<th>$V_{\text{HF}}^{N-1}$ (3s2p)</th>
<th>Exp.</th>
<th>$V_{\text{HF}}^{N-1}$ (3p2p)</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>1.9942 1.9424 2.0234 2.1778</td>
<td></td>
<td>2.1296 2.1962 2.4162 2.1296</td>
<td></td>
<td>2.1778 2.1296 2.4162 2.2073</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$^{+}$</td>
<td>1.2602 1.2089 1.2814 1.2246</td>
<td></td>
<td>1.2246 1.3360 1.5416 1.4073</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ne</td>
<td>0.6638 0.6118 0.6757 0.6192</td>
<td></td>
<td>0.6755 0.7263 0.6755 0.7927</td>
<td></td>
<td>0.7263 0.6755 0.7927 0.6970</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From these relations, we conclude that the matrix element of $V$ between uncoupled particle-hole states is

$$\langle wc | V | va \rangle = g_{wacv} - g_{wavc} + (V_{\text{HF}} - U)_{wv} \delta_{ac} - (V_{\text{HF}} - U)_{ac} \delta_{wv}.$$  \hfill (4.95)

For coupled states, we obtain

$$E_{va,LS}^{(1)} = - \sum_{m_{a} \mu_{a} m_{c} \mu_{c}} \frac{1}{2 \mu_{a}} L_{L} M_{L} S_{S} M_{S} \left[ g_{wacv} - g_{wavc} + (V_{\text{HF}} - U)_{wv} \delta_{ac} - (V_{\text{HF}} - U)_{ac} \delta_{wv} \right],$$ \hfill (4.96)

where $(n_{w}, l_{w}) = (n_{v}, l_{v})$ and $(n_{c}, l_{c}) = (n_{a}, l_{a})$. Carrying out the sums over magnetic substates, we obtain

$$E_{va,LS}^{(1)} = (-1)^{l_{v} + l_{a} + l_{w}} \delta_{S0} X_{L}(vaav) - \sum_{k} \left\{ \begin{array}{c} l_{v} \\ l_{a} \\ l_{v} \\ l_{v} \end{array} \right\} X_{k}(vaaa) + (V_{\text{HF}} - U)_{vv} - (V_{\text{HF}} - U)_{aa}.$$ \hfill (4.97)

This expression is simplified by choosing the potential $U$ to be the $V_{\text{HF}}^{N-1}$ potential, defined for closed shells as

$$V_{\text{HF}}^{N-1} \overset{\text{def}}{=} V_{\text{HF}} + Q \Delta V Q.$$ \hfill (4.98)

The term $Q \Delta V Q$ subtracts the contribution of one core electron (assumed to have quantum numbers $h$) from the HF potential, when it acts on an excited-state orbital:

$$\Delta V P_{n} = -v_{0}(h,r) P_{n} + \sum_{k} \Lambda_{lk} v_{k}(h,n,r) P_{k}.$$ \hfill (4.99)
4.6 9-J Symbols

In Eq.(4.98), $Q = 1 - P$ is the projection operator onto excited states:

$$P = \sum_a |a\rangle\langle a|, \quad (4.100)$$

$$Q = \sum_n |n\rangle\langle n|. \quad (4.101)$$

Setting $U = V_{HF}^{N-1}$, we obtain

$$UP_a = V_{HF} P_a, \quad (4.102)$$

$$UP_n = (V_{HF} + \Delta V) P_n - \sum_a \langle a|\Delta V|n\rangle P_a. \quad (4.103)$$

It follows that $(V_{HF} - U)_{aa} = 0$ and $(V_{HF} - U)_{vv} = -\Delta V_{vv}$.

As an example, let us consider the excited states of Ne (Z=10) and the neonlike ions Na$^+$ (Z=11) and Mg$^{2+}$ (Z=12). The low-lying states of these systems are the odd parity $(3s^2p)^{3P}$, $3^P$, $1^P$ states. Just above these states are the even parity $(3p^2p)^{3S}$, $3^D$, $1^D$, $3^P$, $1^P$ and $1^S$ states. In Table 4.2, we show the results of calculations of the energies of these states using Eq.(4.97) with a $V_{HF}^{N-1}$ potential. This model for the excited states of closed-shell systems leads to energies that agree with observation at the 10% level of accuracy. To improve the agreement, it is necessary to consider corrections from higher-order perturbation theory.

4.6 9-j Symbols

Let us consider the problem of coupling spin and orbital angular momenta of two electrons to total angular momentum $J$. This problem requires us to consider ways of coupling four angular momentum vectors, which can be done in several ways. For example, we may couple the orbital angular momenta $l_1$ and $s_1$ of the electrons to $L$, the spin angular momenta $s_1$ and $s_2$ to $S$, then couple the resulting $L$ and $S$ to a final $J$. This method of coupling the angular momenta of two electrons is referred to as $LS$ coupling. The angular part of the two-electron wave function for an $LS$-coupled state is

$$|[l_1l_2]L|(s_1s_2)SJM⟩ = \sum_{m_1,m_2\mu_1\mu_2} |l_1m_1⟩LML |s_1\mu_1⟩SM_\delta |l_2m_2⟩SM_\delta |s_2\mu_2⟩JM |l_1m_1⟩|l_2m_2⟩|s_1\mu_1⟩|s_2\mu_2⟩. \quad (4.104)$$

As an alternative to $LS$ coupling, we can first couple $l_1$ and $s_1$ to $j_1$, then couple $l_2$ and $s_2$ to $j_2$, and finally couple the resulting $j_1$ and $j_2$ to $J$. This is referred to as the $jj$ coupling scheme. The angular parts of the one-electron wave function that results from coupling $l_i$ and $s_i$ to $j_i$ are just the spherical spinors $\Omega_{\kappa_i m_i}$. 

The angular part of the two-electron wave function in the \(jj\) coupling scheme is

\[
|\langle l_1 s_1 j_1 | \langle l_2 s_2 j_2 J M \rangle = \sum_{m_1 m_2 \mu_1 \mu_2} \langle l_1 m_1 | l_2 m_2 | s_1 \mu_1 \rangle | s_2 \mu_2 \rangle|lm_1 \rangle |l_2 m_2 \rangle |s_1 \mu_1 \rangle |s_2 \mu_2 \rangle.
\]

Either scheme can be used to describe possible two-electron wave functions; the \(LS\) scheme is a more convenient starting point for describing states in atoms with low nuclear charge where relativistic (spin-orbit) effects are negligible, while the \(jj\) scheme is more convenient for atoms with high nuclear charge where relativistic effects are important. The natural starting point for relativistic calculations of two electron systems, where single-particle orbitals are taken from the Dirac equation, is the \(jj\)-scheme.

We may write each \(jj\) coupled wave functions as a linear combinations of \(LS\) wave functions:

\[
|\langle l_1 s_1 j_1 | \langle l_2 s_2 j_2 J M \rangle = \sum_{LS} \langle LSJ | j_1 j_2 J \rangle |\langle l_1 l_2 | \langle s_1 s_2 S J M \rangle \rangle,
\]

where the orthogonal matrix \(\langle LSJ | j_1 j_2 J \rangle\) is given diagrammatically by

\[
\langle LSJ | j_1 j_2 J \rangle = (-1)^R \sqrt{L(S)} |l_1 j_1 \rangle |j_2 j_2 \rangle.
\]

The phase factor \(R = l_1 + l_2 + s_1 + s_2 + j_1 + j_2 + L + S + J\) is the sum of all 9 angular momentum quantum numbers. The hexagonal diagram above serves to define the 9-j symbol:

\[
\{ a \ b \ c \ \ d \ e \ f \ \ g \ h \ j \} = \sum_x (-1)^{x+2} \{ a \ b \ c \ \ d \ e \ f \ \ g \ h \ j \}.
\]

The 9-j symbol can be expressed conveniently as a product of 3-j symbols:

\[
\{ a \ b \ c \ \ d \ e \ f \ \ g \ h \ j \} = \sum_x (-1)^{x+2} \{ a \ b \ c \ \ d \ e \ f \ \ g \ h \ j \}.
\]
R is the previously defined sum of nine angular momenta. The 9-j symbol is also symmetric with respect to a transposition of rows and columns. Thus, for example

\[
\begin{align*}
\begin{pmatrix}
  a & b & c \\
  d & e & f \\
  g & h & j
\end{pmatrix}
&= \begin{pmatrix}
  d & e & f \\
  g & h & j \\
  a & b & c
\end{pmatrix} = (-1)^R \begin{pmatrix}
  d & e & f \\
  a & b & c \\
  g & h & j
\end{pmatrix} = \begin{pmatrix}
  a & d & g \\
  b & e & h \\
  c & f & j
\end{pmatrix}
\end{align*}
\]

With the aid of the symmetry relations, we may write the transformation matrix from the \(LS\) to \(jj\) scheme as

\[
\langle LSJ | j_1 j_2 J \rangle = \sqrt{[L][S][j_1][j_2]} \begin{pmatrix}
  L \\
  S \\
  j_1 \\
  j_2
\end{pmatrix}. \tag{4.111}
\]

A useful special case to bear in mind is that in which one angular momentum is zero. In that case, one finds:

\[
\begin{pmatrix}
  a & b & c \\
  d & e & f \\
  g & h & 0
\end{pmatrix}
= \delta_{cf} \delta_{gh} (-1)^{b+d+c+g} \begin{pmatrix}
  a & b & c \\
  e & d & g
\end{pmatrix}. \tag{4.112}
\]

The transformation from \(LS\) to \(jj\) coupling leads us into a discussion of relativistic effects in atoms.

### 4.7 Relativity and Fine Structure

In the preceding (nonrelativistic) discussion of excited-state energy levels, we found that on transforming to \(LS\)-coupled states, the interaction Hamiltonian \(V\) became diagonal. Each of the resulting \(LS\) states is still \([L] \times [S]\)-fold degenerate. We can, of course, combine these degenerate \(LS\) states into eigenstates of \(J^2\) and \(J_z\), but the degeneracy of the resulting \([LS, JM]\) states (designated by the spectroscopic notation \(2S+1LJ\)) remains. In the case of one-electron atoms, where the eigenstates of orbital angular momentum split into eigenstates of \(J^2\) with \(j = l \pm 1/2\), the \(2|l|\) fold degeneracy of the orbital angular momentum eigenstates is removed. The splitting between the states with a given value of \(l\) but different values of \(j\) is referred to as the “fine-structure” splitting. In a similar way, nonrelativistic many-particle \(LS\) states split into fine-structure components having different \(J\) values when relativistic effects are introduced.

#### 4.7.1 He-like ions

Let us consider the relativistic two-particle state \(|ab\rangle = a^+_a a^+_b |0\rangle\), where the single-particle indices \(a = (n_a \kappa_a m_a)\) and \(b = (n_b \kappa_b m_b)\) refer to quantum numbers of Dirac orbitals. This state is an eigenstate of the unperturbed part, \(H_0\), of the no-pair Hamiltonian with eigenvalue \(E^{(0)} = \epsilon_a + \epsilon_b\):

\[
H_0 |ab\rangle = (\epsilon_a + \epsilon_b) |ab\rangle. \tag{4.113}
\]
The states \(|ab\rangle\) are \([j_a|\times [j_b]\)-fold degenerate. They can be combined to form eigenstates of \(J^2\) and \(J_z\) \((|ab, JM_J\rangle\) using Clebsch-Gordan coefficients. The resulting states are referred to as \(jj\)-coupled states. We have

\[
|ab, JM_J\rangle = \eta \sum_{m_a m_b}^{j_a m_a} \frac{J_{M J}}{j_{h m_b}} a_{j_a}^+ a_{j_b}^+ |0\rangle.
\] (4.114)

These states are also eigenstates of parity with eigenvalue \(P = (-1)^{I_a + I_b}\). The norm of the \(jj\) state in Eq.(4.114) is

\[
\langle ab, JM_J | ab, JM_J \rangle = 1 + (-1)^J \delta_{ab}.
\] (4.115)

Thus, identical-particle states \((n_b = n_a\) and \(\kappa_b = \kappa_a\) couple to even values of \(J\) only. It follows that we must introduce a normalization factor \(\eta = 1/\sqrt{2}\) for identical-particle states, and \(\eta = 1\) for other states. With this normalization, we obtain the following expression for the first-order energy:

\[
E_{ab,j}^{(1)} = \eta^2 \sum_k \left( (-1)^{J+k+j_a+j_b} \left\{ \begin{array}{ccc} j_a & j_b & J \\ j_b & j_a & k \end{array} \right\} X_k(abab) \\
+ (-1)^{k+j_a+j_b} \left\{ \begin{array}{ccc} j_a & j_b & J \\ j_b & j_a & k \end{array} \right\} X_k(aba) \right) - U_{aa} - U_{bb},
\] (4.116)

where the quantities \(X_k(abcd)\) are given by the Dirac counterpart of Eq.(4.49),

\[
X_k(abcd) = (-1)^k \langle \kappa_a || C^k || \kappa_b \rangle \langle \kappa_b || C^k || \kappa_d \rangle R_k(abcd).
\] (4.117)

For heliumlike ions, the ground state is a \((1s1s)_{J=0}\). Although it is possible to couple two \(j = 1/2\) states to form a \(J = 1\) state, the above rule \((J\) is even for identical-particle states) prohibits \(J = 1\) in the \((1s)^2\) configuration. The lowest excited state nonrelativistically is the \((1s2s)\) \(^3S_1\) state. Relativistically, this is the \((1s2s)_{J=1}\) state. The \((1s2s)\) \(^1S_0\) state has the \((1s2s)_{J=0}\) state as its relativistic counterpart. The relativistic \((1s2p_{1/2})_{J=0}\) and \((1s2p_{3/2})_{J=2}\) states correspond to the nonrelativistic \(^3P_0\) and \(^3P_2\), respectively. The correspondence between nonrelativistic and relativistic \((1s2p)\) states is ambiguous for the case \(J = 1\). Relativistically, we have two such states \((1s2p_{1/2})_1\) and \((1s2p_{3/2})_1\), while in the nonrelativistic case, we have the two states \(^3P_1\) and \(^1P_1\). On general grounds, we expect to be able to express the relativistic states that have \(^3P_1\) and \(^1P_1\) states as their nonrelativistic limits as linear combinations of the \((1s2p_{1/2})_1\) and \((1s2p_{3/2})_1\) states. Thus, we are led to consider the linear combination of relativistic states

\[
|1s2p, 1\rangle = c_1 |1s2p_{1/2}, 1\rangle + c_2 |1s2p_{3/2}, 1\rangle,
\] (4.118)

with \(c_1^2 + c_2^2 = 1\). The lowest-order energy in this state is given by

\[
E_{1s2p}^{(0)} = c_1^2 \epsilon_{2p_{1/2}} + c_2^2 \epsilon_{2p_{3/2}}.
\] (4.119)
and the corresponding interaction energy is given by

\[
E_{1s2p,1}^{(1)} = c_1^2 \langle 1s2p_{1/2},1|V|1s2p_{1/2},1 \rangle - U_{2p_{1/2},2p_{1/2}} + 2c_1c_2 \langle 1s2p_{3/2},1|V|1s2p_{1/2},1 \rangle + c_2^2 \langle 1s2p_{3/2},1|V|1s2p_{3/2},1 \rangle - U_{2p_{3/2},2p_{3/2}}. 
\]

In the first of these two equations we have dropped a term \(\epsilon_{1s}\), which is independent of the expansion coefficients \(c_1\) and \(c_2\), and, in the second equation, we have dropped a similar \(c\)-independent term \(-U_{1s,1s}\). Diagonalizing the energy \(E_{1s2p,1}^{(1)} + E_{1s2p,1}^{(0)}\) leads to the \(2 \times 2\) eigenvalue equation:

\[
\begin{pmatrix}
\epsilon_{2p_{1/2}} + V_{1/2,1/2} - U_{1/2,1/2} & V_{1/2,3/2} \\
V_{3/2,1/2} & \epsilon_{2p_{3/2}} + V_{3/2,3/2} - U_{3/2,3/2}
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix}
= E
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix},
\]

where

\[
U_{j,j'} = U_{2p_{1/2},2p_{j'/2}}, \quad (4.122)
\]

\[
V_{j,j'} = \langle 1s2p_{j'},1|V|1s2p_{j'},1 \rangle = R_0(1s,2p,j,1s,2p_j)\delta_{jj'} - 2 \left\{ \begin{array}{cc}
1/2 & j \\
1/2 & j'
\end{array} \right\} \left( \begin{array}{cc}
j & 1/2 & 1 \\
-1/2 & 1/2 & 0
\end{array} \right) \left( \begin{array}{cc}
j' & 1/2 & 1 \\
-1/2 & 1/2 & 0
\end{array} \right) \\
\times R_1(1s,2p_{j'},2p_{j'},1s). \quad (4.123)
\]

We must add \(\epsilon_{1s} - U_{1s,1s}\) to the eigenvalues of Eq. (4.121) to obtain the energies of the two relativistic \(J = 1\) states. This additive term is, of course, just the energy of the one-electron ion formed when the two-electron system is ionized and is omitted when energies are calculated relative to the ionization threshold.

It is instructive to consider the nonrelativistic limit of the energies of the four \(|1s2p_{j}, J\rangle\) states. For the \(J = 0\) and \(J = 2\) states, we find

\[
E_{1s2p_{1/2},0} = \epsilon_{2p} + R_0(1s,2p,1s,2p) - \frac{1}{3} R_1(1s,2p,2p,1s) - U_{2p,2p} \quad (4.124)
\]

\[
E_{1s2p_{3/2},2} = \epsilon_{2p} + R_0(1s,2p,1s,2p) - \frac{1}{3} R_1(1s,2p,2p,1s) - U_{2p,2p}. \quad (4.125)
\]

Since we are considering the nonrelativistic limit, we do not distinguish between \(2p_{1/2}\) and \(2p_{3/2}\). These two levels are degenerate in the nonrelativistic limit and have precisely the energy obtained in Eq. (4.53) for a nonrelativistic \(3P\) state. The \(2 \times 2\) eigenvalue problem for the \(J = 1\) case simplifies to

\[
(E - \epsilon_{2p} - R_0(1s2s1s2p) + U_{2p,2p}) \begin{pmatrix}
c_1 \\
c_2
\end{pmatrix}
= R_1(1s,2p,2p,1s) \begin{pmatrix}
-1/9 & \sqrt{8}/9 \\
\sqrt{8}/9 & 1/9
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix}. \quad (4.126)
\]
Table 4.3: First-order relativistic calculations of the \((1s^2s)\) and \((1s^2p)\) states of heliumlike neon \((Z = 10)\), illustrating the fine-structure of the \(3P\) multiplet.

<table>
<thead>
<tr>
<th>Term</th>
<th>(3S_1)</th>
<th>(3S_0)</th>
<th>(3P_0)</th>
<th>(3P_1)</th>
<th>(3P_2)</th>
<th>(3P_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E^{(0)})</td>
<td>-12.5209</td>
<td>-12.5209</td>
<td>-12.5209</td>
<td>-12.5125</td>
<td>-12.5042</td>
<td>-12.5125</td>
</tr>
<tr>
<td>(E^{(1)})</td>
<td>1.8834</td>
<td>2.3247</td>
<td>2.2641</td>
<td>2.2596</td>
<td>2.2592</td>
<td>2.6049</td>
</tr>
<tr>
<td>(E_{\text{tot}})</td>
<td>-10.6375</td>
<td>-10.1962</td>
<td>-10.2568</td>
<td>-10.2529</td>
<td>-10.2450</td>
<td>-9.9076</td>
</tr>
</tbody>
</table>

The eigenvalues of the small matrix on the right-hand side of this equation are \(\pm 1/3\). From this, it follows that the energies of the \(J = 1\) states are

\[
E_{1s^2p_{1/2}, 1} = \epsilon_{2p} + R_0(1s, 2p, 1s, 2p) \mp \frac{1}{3} R_1(1s, 2p, 2p, 1s) - U_{2p, 2p}. \tag{4.127}
\]

The energy associated with the \(-\) sign agrees with the energies of the \(|s_{1/2}p_{1/2}, 0\rangle\) and \(|s_{1/2}p_{3/2}, 2\rangle\) states given in Eq. (4.125) while the energy associated with the \(+\) sign agrees with the energy of the nonrelativistic \(1P\) state given in Eq (4.53). Thus, the energies predicted for the \(|1s^2p_j, 1\rangle\) states reduce to nonrelativistic values obtained previously. Furthermore, the orthogonal matrix that diagonalizes the small matrix in Eq. (4.126) is

\[
\begin{pmatrix}
\sqrt{1/3} & \sqrt{2/3} \\
\sqrt{2/3} & -\sqrt{1/3}
\end{pmatrix}.
\]

This is precisely the matrix, obtained in a more direct way in Sec. 4.6, that transforms the \(jj\) coupled states

\[
\begin{bmatrix}
(s_{1/2}p_{1/2})_1 \\
(s_{1/2}p_{3/2})_1
\end{bmatrix}
\]

to the \(LS\) coupled states

\[
\begin{bmatrix}
(sp)^{3P_1} \\
(sp)^{3P_1}
\end{bmatrix}.
\]

We leave it as an exercise to verify this assertion.

The degeneracy of \(LS\) multiplets is lifted in relativistic calculations, giving to a \(J\)-dependent fine-structure of \(2S+1L\) states. As a specific example, let us consider heliumlike neon \((Z = 10)\). For simplicity, we choose \(U = 0\), and calculate the energies of the two \((1s^2s)\) states and the four \((1s^2p)\) states. In Table 4.3, we show the lowest-order and first-order energies \(E^{(0)}\) and \(E^{(1)}\) together with the resulting sum. These energies are all given relative to the one-electron ion. The energies of the \(3P_1\) and \(1P_1\) states were obtained by solving the \(2 \times 2\) eigenvalue problem in Eq. (4.121). The three \(3P_j\) states have slightly different energies in this relativistic calculation; the \(J\)-dependent fine structure of the \(3P\) state obvious from the table.
Figure 4.2: Variation with nuclear charge of the energies of 1s2p states in heliumlike ions. At low Z the states are LS-coupled states, while at high Z, they become jj-coupled states. Solid circles $^1P_1$; Hollow circles $^3P_0$; Hollow squares $^3P_1$; Hollow diamonds $^3P_2$.

In Fig. 4.2, we illustrate the transition from LS to jj coupling as Z increases along the helium isoelectronic sequence by presenting the results of a series of calculations of the energies of (1s2p) states for two electron ions with nuclear charges ranging from Z = 4 to Z = 90. We plot the ratio of the energy of each of the four substates to the average energy of the states. For low values of Z, near the nonrelativistic limit, the states divide into a singlet state and a triplet state. As Z increases the triplet state splits apart into J dependent fine-structure components. For large Z, the states come together again to form the two jj states ($1s_{1/2}2p_{1/2}$) and ($1s_{1/2}2p_{3/2}$).

### 4.7.2 Atoms with Two Valence Electrons

The fine-structure of atoms with two valence electrons beyond closed shells can be treated in much the same way as the fine structure of heliumlike ions. Let us consider the nonrelativistic LS-coupled state $^2S+^1L$ (with $S = 0$ or $S = 1$) made up from the configurations $(n_v l_v n_w l_w)$. A single nonrelativistic two-electron configuration $(n_v l_v n_w l_w)$ corresponds to four relativistic configurations $(n_v l_v n_w l_w)$ with $j_v = l_v ± 1/2$ and $j_w = l_w ± 1/2$. A jj-coupled state having the state $^2S+^1L_J$ as its nonrelativistic limit is generally made up as a linear combination

$$|JM⟩ = ∑_{vw} c_{vw} |vw, J⟩.$$  \[4.128\]

Here $|vw, J⟩$ are normalized jj-coupled and $c_{vw}$ are expansion coefficients satisfying

$$∑_{vw} c_{vw}^2 = 1.$$  \[4.129\]
As a specific example, let us consider the even-parity \(^3D_2\) state obtained nonrelativistically from the configuration \((2p3p)\). There are three relativistic configurations contributing to this state; \((2p_{1/2}3p_{3/2})\), \((2p_{3/2}3p_{1/2})\), and \((2p_{3/2}3p_{3/2})\). The configuration \((2p_{1/2}3p_{1/2})\) cannot contribute since two single-particle states with \(j = 1/2\) cannot couple to \(J = 2\)!

The lowest-order energy for the state \(|JM\rangle\) in Eq.(4.128) is

\[
E^{(0)}_J = \sum_{vw} c_{vw}^2 (\epsilon_v + \epsilon_w).
\]

The first-order energy is given by the quadratic form

\[
E^{(1)}_J = \sum_{vw,xy} c_{vw} c_{xy} V_{vw,xy} + \sum_{vw} c_{vw}^2 \left[ (V_{HF} - U)_{vv} + (V_{HF} - U)_{ww} \right].
\]

The interaction potential \(V_{vw,xy}\) in Eq.(4.131) is given by

\[
V_{vw,xy} = \eta_v \eta_x \sum_k \left[ (-1)^{j_w + j_x + J + k} \begin{pmatrix} j_v & j_w & J \\ j_x & j_y & k \end{pmatrix} X_k(vwxy) + (-1)^{j_w + j_x + k} \begin{pmatrix} j_v & j_w & J \\ j_x & j_y & k \end{pmatrix} X_k(vwyx) \right],
\]

where, as usual, the normalization factor \(\eta_{vw} = 1/\sqrt{2}\) for identical particle configurations \((n_w = n_v \text{ and } \kappa_w = \kappa_v)\) and \(\eta_{vw} = 1\) otherwise. It can be easily seen that \(V_{vw,xy} = V_{xy,vw}\).

As in the mixed-configuration case described previously for heliumlike ions, diagonalizing the quadratic form in Eq.(4.131) leads to the algebraic eigenvalue equation for the energy:

\[
\sum_{xy} \left[ \epsilon_x + (V_{HF} - U)_{xx} + \epsilon_y + (V_{HF} - U)_{yy} \right] \delta_{vw,xy} + V_{vw,xy} c_{xy} = E c_{vw}.
\]

### 4.7.3 Particle-Hole States

Because of the relatively large separation between energies of subshells with a given value of \(l\) and different values of \(j\) in closed shell atoms (even an atom as light as neon), the fine-structure splitting of particle-hole states is particularly important. The arguments in the preceding paragraphs apply with obvious modifications to the particle-hole states as well.

First, we construct an angular momentum eigenstate as a linear combination of those relativistic particle-hole configurations \((n_v l_v n_a l_a)\) with \(j_v = l_v \pm 1/2\) and \(j_a = l_a \pm 1/2\) that couple to a given value of \(J\):

\[
|JM\rangle = \sum_{va} c_{va} |va, JM\rangle,
\]
where the expansion coefficients satisfy the normalization constraint $\sum_{va} c^2_{va} = 1$. Again, the first-order energy is a quadratic form in the expansion coefficients. Diagonalizing this quadratic form leads to an algebraic eigenvalue problem for the energy and the expansion coefficients. In the particle-hole case, the eigenvalue problem takes the form

$$\sum_{va} \left( (\epsilon_v + (V_{HF} - U)_{vv} - \epsilon_a - (V_{HF} - U)_{aa}) \delta_{vv} \delta_{ab} + V_{wb,va} \right) c_{va} = E c_{wb},$$

(4.135)

where the (symmetric) interaction matrix is given by

$$V_{wb,va} = (-1)^{J + j_w - j_b} \frac{1}{[J]} X_J(wabv)$$

$$+ \sum_k (-1)^{J + j_w - j_b} \left\{ j_w \ j_b \ j_a \ j_v \ k \right\} X_K(wamb),$$

(4.136)

### 4.8 Hyperfine Structure

The interaction of atomic electrons with the multipole moments of the nucleus leads to a nuclear spin-dependence of atomic energy levels referred to as the atomic hyperfine structure. The moments of a nucleus with angular momentum $I$ are limited by angular momentum selection rules to those with multipolarity $k \leq 2I$. Parity selection rules further limit the moments to even-order electric moments and odd-order magnetic moments. Thus a nucleus with $I = 0$ can have only an electric monopole moment, the nuclear charge $|e|Z$. A nucleus with angular momentum $I = 1/2$ can also have a magnetic dipole moment, while a nucleus with $I = 1$ can have a magnetic dipole moment and an electric quadrupole moment in addition to its charge. Low-order nuclear moments give the most significant contributions to the hyperfine interaction. Here, we concentrate on the dominant interactions, those of the magnetic dipole and electric quadrupole moments.

The hyperfine interaction of a (relativistic) electron with the nucleus is just the electromagnetic interaction with the scalar and vector potentials generated by the nuclear moments

$$h_{hfs}(r) = e \phi(r) - ec \alpha \cdot A(r).$$

(4.137)

Nonrelativistic limits can be worked out as needed.

If we let $\mu$ designate the nuclear magnetic moment, then the corresponding magnetic vector potential is given by

$$A(r) = \frac{\mu_0}{4\pi} \frac{[\mu \times r]}{r^3}.$$  

It is convenient to express the interaction $-ec \alpha \cdot A(r)$ in a spherical basis. For this purpose, we rewrite

$$\alpha \cdot [\mu \times r] = [r \times \alpha] \cdot \mu = \sum_{\lambda} (-1)^\lambda [r \times \alpha]_{\lambda} \mu_{-\lambda}.$$
For an arbitrary vector $\mathbf{v}$, one may show,

$$[\mathbf{r} \times \mathbf{v}]_\lambda = -i\sqrt{2} r \mathbf{C}_{1\lambda}^{(0)}(\hat{r}) \cdot \mathbf{v},$$

where $\mathbf{C}_{1\lambda}^{(0)}(\hat{r})$ is a normalized vector spherical harmonic defined by

$$\mathbf{C}_{kq}^{(0)}(\hat{r}) = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}^{(0)}(\hat{r}).$$

Using this relation, we can write the magnetic hyperfine interaction as:

$$\frac{e}{4\pi \epsilon_0} \sum_\lambda (-1)^\lambda \frac{i\sqrt{2}}{c^2} \left[\mathbf{\alpha} \cdot \mathbf{C}_{1\lambda}^{(0)}(\hat{r})\right] \mu_{-\lambda}.$$ 

The quantity $[\mathbf{\alpha} \cdot \mathbf{C}_{1\lambda}^{(0)}(\hat{r})]$ is an irreducible tensor operator of rank 1 acting in the space of electron coordinates and spin. Quantum mechanically, $\mu_\lambda$ is an irreducible tensor operator of rank 1 acting in the space of nuclear coordinates and spin. The c-number magnetic moment $\mu$ is the expectation value of the operator $\mu_0$ in the “extended” state of the nucleus, $M_I = I$:

$$\mu \overset{\text{def}}{=} \langle II|\mu_0|II\rangle.$$ 

(4.138)

The nuclear magnetic moment $\mu$ is measured in units of the nuclear magneton $\mu_N$:

$$\mu_N = \frac{|e|\hbar}{2M_p},$$

where $M_p$ is the mass of the proton. We write $\mu$ in terms of the angular momentum quantum number $I$ as:

$$\mu = g_I I \mu_N.$$ 

(4.139)

The dimensionless factor $g_I$ is called the gyromagnetic ratio. For the proton, the gyromagnetic ratio has the numerical value $g_I = 5.5856948(1)$.

If we let $Q_{ij}$ represent the nuclear quadrupole moment tensor, then the scalar potential is given by

$$\phi(\mathbf{r}) = \frac{1}{4\pi \epsilon_0} \sum_{ij} \frac{x_i x_j}{2r^3} Q_{ij}. $$

The quadrupole tensor $Q_{ij}$ is a traceless symmetric tensor of rank 2; it therefore has 5 independent components. For a classical charge distribution $\rho(\mathbf{r})$ the Cartesian components of the quadrupole tensor are given by

$$Q_{ij} = \int d^3r (3x_i x_j - r^2 \delta_{ij}) \rho(\mathbf{r}).$$

The components of this tensor can be transformed to a spherical basis and expressed in terms of the five components of the second-rank spherical tensor $Q_\lambda$ defined by,

$$Q_\lambda = \int d^3r r^2 C_\lambda^2(\hat{r}) \rho(\mathbf{r}).$$
where $C_2^2(\hat{r})$ is a normalized spherical tensor of rank 2. In particular, $Q_{33} = 2Q_0$. The potential due to the quadrupole, expressed in a spherical basis, is

$$
\phi(r) = \frac{1}{4\pi\varepsilon_0} \sum_\lambda (-1)^\lambda \frac{C_2^2(\hat{r})}{r^3} r Q_{-\lambda}.
$$

Here, $Q_\lambda$ is an irreducible tensor operator of rank 2 acting in the space of nucleon coordinates and spins. The c-number quadrupole moment of the nucleus $Q$ is given in terms of the expectation value of the operator $Q_0$ in the extended state:

$$
Q_{\text{def}} = 2\langle II|Q_0|II \rangle. \quad (4.140)
$$

The nuclear quadrupole moment $Q$ is dimensionally a charge times a length squared. It is commonly written in units of $|e| \times \text{barn}$.

The hyperfine interaction Hamiltonian for a relativistic electron with the nuclear magnetic dipole and electric quadrupole moments becomes

$$
h_{\text{hfs}}(r) = \frac{e}{4\pi\varepsilon_0} \left\{ \sum_\lambda (-1)^\lambda \frac{i\sqrt{2} [\alpha \cdot C_{2\lambda}^{(0)}(\hat{r})]}{cr^2} \mu_{-\lambda} + \sum_\lambda (-1)^\lambda \frac{C_2^2(\hat{r})}{r^3} Q_{-\lambda} \right\}.
$$

Both the electric and magnetic interactions are thereby expressed in terms of tensor operators and the hyperfine interaction Hamiltonian takes the form

$$
h_{\text{hfs}}(r) = \sum_{k\lambda} (-1)^\lambda t_k^\lambda(\hat{r}) T_k^\lambda,
$$

where $t_k^\lambda(r)$ is an irreducible tensor operator of rank $k$ that acts on electron coordinates and spin, and $T_k^\lambda$ is a rank $k$ irreducible tensor operator that acts on nuclear coordinates and spin. Here, $k = 1$ for the magnetic dipole interaction and $k = 2$ for the electric quadrupole interaction. Specifically,

$$
t_1^\lambda(r) = -\frac{|e|}{4\pi\varepsilon_0} \frac{i\sqrt{2} [\alpha \cdot C_{2\lambda}^{(0)}(\hat{r})]}{cr^2}, \quad (4.142)
$$

and

$$
t_2^\lambda(r) = -\frac{|e|}{4\pi\varepsilon_0} \frac{C_2^2(\hat{r})}{r^3}, \quad (4.143)
$$

and

$$
T_1^\lambda = \mu_\lambda, \quad (4.144)
$$

$$
T_2^\lambda = Q_\lambda. \quad (4.145)
$$

For a collection of $N$ electrons $h_{\text{hfs}}(r)$ is replaced by the single-particle operator

$$
H_{\text{hfs}} = \sum_{i=1}^N h_{\text{hfs}}(r_i) = \sum_\lambda (-1)^\lambda T_1^\lambda T_2^\lambda, \quad (4.146)
$$
with
\[ T_k^\lambda = \begin{cases} \sum_{i=1}^N t_k^\lambda (r_i) & \text{in first quantization,} \\ \sum_{ij} \langle i| t_k^\lambda |j\rangle a_i^\dagger a_j & \text{in second quantization.} \end{cases} \] (4.147)

Let us consider an atomic angular momentum eigenstate \(|J,M\rangle\) and a nuclear angular momentum eigenstate \(|I,M\rangle\). These states are coupled to give a eigenstate of total angular momentum \(F = I + J\),

\[ |(IJ),FM_F\rangle = \sum_{M_I M_J} \frac{FM_F}{J M_J} |I,M_I\rangle |J,M_J\rangle. \]

The first-order correction to the energy in this state is just the expectation value of \(H_{\text{hfs}}\), which is easily shown to be

\[ W_F = \langle (IJ),FM_F|H_{\text{hfs}}|(IJ),FM_F\rangle \]

\[ = \sum_k (-1)^{I+J+F} \left\{ \begin{array}{ccc} I & J & F \\ J & I & k \end{array} \right\} \langle J||T_k^0||J\rangle \langle I||T_k^0||I\rangle. \] (4.148)

We can write this equation in a somewhat more convenient way by introducing

\[ (-1)^{I+J+F} \left\{ \begin{array}{ccc} I & J & F \\ J & I & k \end{array} \right\} = \frac{(2I)!(2J)!}{\sqrt{(2I-k)!(2I+k+1)!}(2J-k)!(2J+k+1)!} M(IJ,Fk), \]

where

\[ M(IJ,Fk) = \begin{cases} \frac{K}{2I} & \text{for } k = 1, \\ \frac{6K(I+1)-8J(J+1)(I+1)}{2I(2I-1)2J(2J-1)} & \text{for } k = 2, \end{cases} \]

with \(K = F(F+1) - I(I+1) - J(J+1)\). With the aid of the identity

\[ \left( \begin{array}{ccc} J & k & J \\ -J & 0 & J \end{array} \right) = \frac{(2J)!}{\sqrt{(2J-k)!(2J+k+1)!}}, \] (4.149)

it follows that

\[ \langle JJ|T_0^k|JJ\rangle = \frac{(2J)!}{\sqrt{(2J-k)!(2J+k+1)!}} \langle J||T_k^0||J\rangle. \] (4.150)

Combining Eqs.(4.148) and (4.150), we obtain for the energy the expression

\[ W_F = \sum_k M(IJ,Fk) \langle JJ|T_0^k|JJ\rangle \langle II|T_0^k||II\rangle. \] (4.151)
The two terms in this sum can be written out explicitly as
\[ W_F = \frac{1}{2} Ka + \frac{1}{2} \frac{3K(K+1) - 4J(J+1)I(I+1)}{2I(2I-1)2J(2J-1)} b, \] (4.152)
where
\[ a = \frac{1}{IJ} \langle JJ|T_0^1|JJ\rangle \langle II|T_1^0|II\rangle = \mu \frac{IJ}{IJ} \langle JJ|T_0^1|JJ\rangle, \] (4.153)
\[ b = 4\langle JJ|T_0^2|JJ\rangle \langle II|T_2^0|II\rangle = 2Q \langle JJ|T_0^2|JJ \rangle. \] (4.154)

The problem of evaluating the energy shift due to the atomic hyperfine interaction is now reduced to that of determining the expectation values of the tensor operators \( T_0^k \) in atomic states.

Let us suppose that \( b = 0 \). The interaction energy then reduces to \( W_F = Ka/2 \), with \( K = F(F+1) - I(I+1) - J(J+1) \). This is precisely the energy that would have been obtained from an effective Hamiltonian of the form
\[ H_{\text{eff}} = a \mathbf{I} \cdot \mathbf{J}. \]

We find that an eigenstate of \( J \) breaks up into \( 2J+1 \) sublevels for the case \( I \geq J \) or \( 2I+1 \) sublevels for \( J < I \). Let us consider the case \( I \geq J = 1/2 \). In this case, an eigenstate of \( J \) breaks up into 2 sublevels,
\[ W_F = \begin{cases} 
\frac{Ja}{2} & \text{for } F = I + 1/2, \\
-(I+1)a/2 & \text{for } F = I - 1/2.
\end{cases} \]

The splitting between the two sublevels is \( \Delta W = (I + 1/2)a \). For \( I \geq J = 1 \), an eigenstate of \( J \) splits into three components separated by \( (I+1)a \) and \( Ia \), respectively. Generally, for the case \( I \geq J \), the hyperfine pattern has \( 2J+1 \) components; the splitting between two adjacent sublevels being \( W_{F+1} - W_F = Fa \). By counting the hyperfine components in the case \( J > I \) we can determine the nuclear angular momentum \( I \), while measurements of the separation between sublevels permits us to evaluate the nuclear gyromagnetic ratio \( g_I \).

**Units:** Dimensionally, the magnetic hyperfine interaction energy is given by
\[ [W_{\text{m.d.}}] = \frac{|e|}{4\pi \varepsilon_0} \frac{|e|\hbar c}{8M_p c a_0^2} = \frac{1}{2M_p c} = 1.987131 \times 10^{-6} \text{ a.u.} \]
\[ = 0.4361249 \text{ cm}^{-1} \]
\[ = 13074.69 \text{ MHz}. \]

Similarly, the electric quadrupole hyperfine interaction energy is, dimensionally,
\[ [W_{\text{e.q.}}] = \frac{|e|}{4\pi \varepsilon_0} |e| \times \text{barn} \frac{1}{a_0^2} = 3.571064 \times 10^{-8} \text{ a.u.} \]
\[ = 7.83758 \times 10^{-3} \text{ cm}^{-1} \]
\[ = 234.965 \text{ MHz}. \]
In the following, we express the nuclear magnetic moment in units of \(\mu_N\), the quadrupole moment in terms of \(|e| \times \text{barn}\), and omit the constants \(e/4\pi\epsilon_0\) and \(c\) in expressions given previously for the interaction. The results will then be in terms of the units given in this paragraph.

### 4.8.1 Atoms with One Valence Electron

We now turn to the problem of determining \(W_F\) for an atom having a single valence electron in the state \(v = (n_v\kappa_vm_v)\),

\[|v\rangle = a^\dagger_v|O_v\rangle.\]

The atomic angular momentum components \(J\) and \(M_J\) are given by \(j_v\) and \(m_v\) for this state, and the many-body expectation value of the tensor operator \(T^k_\lambda\) is given by

\[\langle v|T^k_\lambda|v\rangle = \langle v|t^k_\lambda(r)|v\rangle + \sum_a \langle a|t^k_\lambda(r)|a\rangle,\]

where the sum over \(a\) extends over all core states. The core sum is easily shown to vanish:

\[
\sum_a \langle a|t^k_\lambda(r)|a\rangle = \sum_{n_a\kappa_a} \delta_{k\lambda} \delta_{j\alpha} \langle j\alpha|t^k_\lambda(r)|j\alpha\rangle = 0.
\]

The expectation value of \(T^k_\lambda\), therefore reduces to the valence electron expectation value of \(t^k_\lambda(r)\). For a one valence electron atom, we therefore have,

\[a = \frac{g_v}{j_v}\langle n_v\kappa_vm_v = j_v|t^1_0|n_v\kappa_vm_v = j_v\rangle \times 13074.7 \text{ MHz},\quad (4.155)\]

\[b = 2Q\langle n_v\kappa_vm_v = j_v|t^2_0|n_v\kappa_vm_v = j_v\rangle \times 234.965 \text{ MHz}.\quad (4.156)\]

In the magnetic case, \(k = 1\), we obtain from Eq.(4.142)

\[
\langle w|t^1_\lambda(r)|v\rangle = -i\sqrt{2} \int \frac{dr}{r^2} \left( -iP_{\kappa_w\kappa_v}(r)Q_{\kappa_w\kappa_v}(r) \langle \kappa_w m_w | \sigma \cdot C_{10}^{(0)}(\hat{r}) | -\kappa_v m_v \rangle \right.
\]

\[
\left. + iQ_{\kappa_w\kappa_v}(r)P_{\kappa_w\kappa_v}(r) \langle -\kappa_w m_w | \sigma \cdot C_{10}^{(0)}(\hat{r}) | \kappa_v m_v \rangle \right), \quad (4.157)
\]

where, for example,

\[
\langle \kappa_w m_w | \sigma \cdot C_{kq}^{(0)}(\hat{r}) | -\kappa_v m_v \rangle = \int d\Omega \Omega_{\kappa_w m_w}^\dagger(\hat{r}) \sigma \cdot C_{kq}^{(0)}(\hat{r}) \Omega_{-\kappa_v m_v}(\hat{r}).
\]
4.8. HYPERFINE STRUCTURE

Often in relativistic calculations, one encounters angular matrix elements, such as those in the above equation, of \( \sigma \) times a normalized vector spherical harmonic \( C^{(\nu)}_{kq} \). Such matrix elements are easily reduced to matrix elements of normalized spherical harmonics. We find:

\[
\langle \kappa_b m_b | \sigma \cdot C^{(-1)}_{kq} | \kappa_a m_a \rangle = -\langle -\kappa_b m_b | C^k_q | \kappa_a m_a \rangle, \tag{4.158}
\]
\[
\langle \kappa_b m_b | \sigma \cdot C^{(0)}_{kq} | \kappa_a m_a \rangle = \frac{\kappa_a - \kappa_b}{\sqrt{k(k + 1)}} \langle \kappa_b m_b | C^k_q | \kappa_a m_a \rangle, \tag{4.159}
\]
\[
\langle \kappa_b m_b | \sigma \cdot C^{(1)}_{kq} | \kappa_a m_a \rangle = \frac{\kappa_a + \kappa_b}{\sqrt{k(k + 1)}} \langle -\kappa_b m_b | C^k_q | \kappa_a m_a \rangle. \tag{4.160}
\]

With the aid of Eq. (4.159), we obtain

\[
\langle w|t^1_\lambda(r)|v \rangle = (\kappa_v + \kappa_w) \langle -\kappa_w m_w | C^1_\lambda | \kappa_v m_v \rangle \left( \frac{1}{r^2} \right)_{wv}, \tag{4.161}
\]

where

\[
\left( \frac{1}{r^2} \right)_{wv} = \int_0^\infty \frac{dr}{r^2} (P_{n_w,\kappa_w}(r)Q_{n_w,\kappa_v}(r) + Q_{n_w,\kappa_w}(r)P_{n_w,\kappa_v}(r)). \tag{4.162}
\]

Here we have used the symmetry relation

\[
\langle -\kappa_w m_w | C^1_\lambda | \kappa_v m_v \rangle = \langle \kappa_w m_w | C^1_\lambda | -\kappa_v m_v \rangle. \tag{4.163}
\]

Therefore, we have in the case \( k = 1 \),

\[
\langle n_v \kappa_v j_v | t^1_0 | n_v \kappa_v j_v \rangle = 2\kappa_v \langle -\kappa_v j_v | C^1_0 | \kappa_v j_v \rangle \left( \frac{1}{r^2} \right)_{vv}. \tag{4.164}
\]

A similar, but simpler calculation for \( k = 2 \) gives

\[
\langle n_v \kappa_v j_v | t^2_0 | n_v \kappa_v j_v \rangle = -\langle \kappa_v j_v | C^2_0 | \kappa_v j_v \rangle \left( \frac{1}{r^3} \right)_{vv}, \tag{4.165}
\]

where

\[
\left( \frac{1}{r^3} \right)_{wv} = \int_0^\infty \frac{dr}{r^3} (P_{n_w,\kappa_w}(r)P_{n_w,\kappa_v}(r) + Q_{n_w,\kappa_w}(r)Q_{n_w,\kappa_v}(r)). \tag{4.166}
\]

The angular matrix elements in Eqs. (4.164) and (4.165) are evaluated to give

\[
\langle -\kappa_v j_v | C^1_0 | \kappa_v j_v \rangle = -\frac{1}{2j_v + 2},
\]
\[
\langle \kappa_v j_v | C^2_0 | \kappa_v j_v \rangle = -\frac{2j_v - 1}{4j_v + 4},
\]

from which it follows that

\[
a = -\frac{g_I}{j_v(j_v + 1)} \left( \frac{1}{r^2} \right)_{vv} \times 13074.7 \text{ MHz}, \tag{4.167}
\]
\[
b = Q \frac{2j_v - 1}{2j_v + 2} \left( \frac{1}{r^3} \right)_{vv} \times 234.965 \text{ MHz}. \tag{4.168}
\]
Pauli Approximation: To obtain the nonrelativistic limit of the expression for the dipole hyperfine constant $a$ in Eq.(4.167), we consider an approximation to the radial Dirac equation referred to as the Pauli approximation. We set $W_{n\kappa} = E_{n\kappa} - c^2$ and write the radial Dirac equations as

$$c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_{n\kappa} = (W_{n\kappa} - V) P_{n\kappa}, \quad (4.169)$$

$$2c^2 + W_{n\kappa} - V) Q_{n\kappa} = -c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_{n\kappa}. \quad (4.170)$$

The Pauli approximation consists of neglecting $W_{n\kappa} - V$ compared to $2c^2$ in Eq.(4.170), leading to the relation

$$Q_{n\kappa} \approx -\frac{1}{2c} \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_{n\kappa}. \quad (4.171)$$

Substituting this approximation into Eq.(4.170), gives the differential equation

$$\frac{1}{2} \frac{d^2 P_{n\kappa}}{dr^2} + \left( W_{n\kappa} - V - \frac{\kappa(\kappa + 1)}{2r^2} \right) P_{n\kappa} = 0, \quad (4.172)$$

for the large component radial function $P_{n\kappa}$. This is just the radial Schrödinger equation for orbital angular momentum $l$, since $\kappa(\kappa + 1) = l(l + 1)$ for the two possible $\kappa$ values associated with a given value of $l$ ($\kappa = l$ and $\kappa = -l - 1$). Therefore, in the Pauli approximation, the large component radial function $P_{n\kappa}$ goes over to the corresponding nonrelativistic radial function $P_{nl}$. The small component radial function in the Pauli approximation is found from Eq.(4.171) with $P_{n\kappa}$ replaced by $P_{nl}$. With the aid of the Pauli approximation, we therefore obtain

$$\left( \frac{1}{r^2} \right)_{vw} = -\frac{1}{2c} \int_0^\infty dr \frac{r}{r^2} \left[ P_{n_vl_v} \left( \frac{d}{dr} + \frac{\kappa_w}{r} \right) P_{n_wl_w} + P_{n_wl_w} \left( \frac{d}{dr} + \frac{\kappa_v}{r} \right) P_{n_vl_v} \right]$$

$$= -\frac{1}{2c} \int_0^\infty dr \left[ \frac{d}{dr} \left( \frac{P_{n_vl_v} P_{n_wl_w}}{r^2} \right) + \frac{\kappa_v + \kappa_w + 2}{r^3} P_{n_vl_v} P_{n_wl_w} \right]$$

$$= \frac{1}{2c} \left( \frac{P_{n_vl_v} P_{n_wl_w}}{r^2} \right)_{r=0} - \frac{\kappa_v + \kappa_w + 2}{2c} \left( \frac{1}{r^3} \right)_{vw}, \quad (4.173)$$

where the radial matrix element of $1/r^3$ on the last line is to be evaluated using nonrelativistic wave functions. The first term on the last line of Eq.(4.173) contributes if, and only if, both states $v$ and $w$ are $s$ states, since the nonrelativistic radial wave functions $P_{nl}(r)$ are proportional to $r^{l+1}$. Indeed, if we let

$$\lim_{r \to 0} \left( \frac{P_{nvl_v}(r)}{r} \right) = N_v \delta_{l_v,0},$$

then we obtain the following nonrelativistic limiting values for the dipole hyperfine constant:

$$a_{NR} = \frac{2}{3} g_i N_v^2 \times 95.4016 \text{ MHz}, \quad \text{for } l_v = 0, \quad (4.174)$$
Table 4.4: Nonrelativistic HF calculations of the magnetic dipole hyperfine constants $a$ (MHz) for ground states of alkali-metal atoms compared with measurements.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Z</th>
<th>A</th>
<th>I</th>
<th>State</th>
<th>$g_I$</th>
<th>$a_{NR}$</th>
<th>$a_{Exp.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3</td>
<td>7</td>
<td>3/2</td>
<td>$2s_{1/2}$</td>
<td>2.17065</td>
<td>284.2</td>
<td>401.752</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>23</td>
<td>3/2</td>
<td>$3s_{1/2}$</td>
<td>1.47749</td>
<td>615.9</td>
<td>885.813</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>39</td>
<td>3/2</td>
<td>$4s_{1/2}$</td>
<td>0.26064</td>
<td>140.8</td>
<td>230.860</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>85</td>
<td>5/2</td>
<td>$5s_{1/2}$</td>
<td>0.54121</td>
<td>542.0</td>
<td>1011.911</td>
</tr>
</tbody>
</table>

\[ a_{NR} = \frac{l_v(l_v+1)}{j_v(j_v+1)} g_I \left\langle \frac{1}{r^3} \right\rangle_{vv} \times 95.4016 \text{ MHz}, \text{ for } l_v \neq 0. \]  
\[ a_{NR} = \frac{2}{3} \times 5.5856948 \times 2^2 \times 95.4016 \text{ MHz} = 1421.16 \text{ MHz}. \]

This number is to be compared with the experimental value $a_{Exp.} = 1420.406 \text{ MHz}$. The difference between these values arises from radiative, reduced-mass and relativistic corrections. These corrections are discussed, for example, in Bethe and Salpeter (1957).

In Table 4.4, we compare results of HF calculations of the hyperfine constants for the ground states of alkali-metal atoms with measurements. These values are seen to be in only qualitative agreement with experiment. The agreement between theory and experiment can be improved to the level of 5% or better by including corrections from first-order and second-order perturbation theory. For the heavier alkali atoms, a significant part of the difference between calculation and measurement is due to the use of the nonrelativistic approximation. For example, if we use the relativistic expression Eq.(4.167) rather than Eq.(4.174) to evaluate $a$ for rubidium, we obtain $a = 643.9 \text{ MHz}$ instead of the value $a = 542.0 \text{ MHz}$ given in the table.
Chapter 5

Radiative Transitions

In this chapter, we study the absorption and emission of radiation by atoms. We start with a brief review of Maxwell’s equations for the radiation field and plane-wave solutions to these equations. We introduce the quantized electromagnetic field, and expand the atom-field interaction Hamiltonian in terms of photon creation and annihilation operators. The interaction between the atom and field is described using the perturbation expansion of the $S$-matrix. Spontaneous and induced emission are explained, and expressions for the Einstein $A$ and $B$ coefficients are derived. We give the multipole decomposition of the fields and discuss selection rules and intensity ratios. Detailed studies are made of transitions in one- and two-electron atoms.

5.1 Review of Classical Electromagnetism

The electric field $\mathbf{E}(r, t)$ and magnetic field $\mathbf{B}(r, t)$ (magnetic flux density vector) generated by a charge density $\rho(r, t)$ and a current density $\mathbf{J}(r, t)$ are governed by Maxwell’s equations, which (in S.I. units) are

$$
\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0} \rho,
\nabla \cdot \mathbf{B} = 0,

\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t},
\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}.
$$

(5.1)

These fields couple to the atomic electrons through the scalar and vector potentials, so let us start with a review of these potentials.
5.1.1 Electromagnetic Potentials

The fields \( \mathbf{E}(\mathbf{r}, t) \) and \( \mathbf{B}(\mathbf{r}, t) \) are represented in terms of a scalar potential \( \phi(\mathbf{r}, t) \) and a vector potential \( \mathbf{A}(\mathbf{r}, t) \) through the differential relations

\[
\mathbf{E}(\mathbf{r}, t) = -\nabla \phi(\mathbf{r}, t) - \frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t}, \quad (5.2)
\]
\[
\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t). \quad (5.3)
\]

The homogeneous Maxwell equations are satisfied identically by these relations and the inhomogeneous Maxwell equations can be written

\[
\nabla^2 \phi - \frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} = -\frac{1}{\epsilon_0} \rho(\mathbf{r}, t), \quad (5.4)
\]
\[
\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = -\mu_0 \mathbf{J}(\mathbf{r}, t), \quad (5.5)
\]

provided the potentials satisfy the Lorentz condition,

\[
\nabla \cdot \mathbf{A} + \frac{1}{c^2} \frac{\partial \phi}{\partial t} = 0. \quad (5.6)
\]

The electric and magnetic fields remain unchanged when the potentials are subjected to a gauge transformation,

\[
\mathbf{A}(\mathbf{r}, t) \rightarrow \mathbf{A}'(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t) + \nabla \chi(\mathbf{r}, t), \quad (5.7)
\]
\[
\phi(\mathbf{r}, t) \rightarrow \phi'(\mathbf{r}, t) = \phi(\mathbf{r}, t) - \frac{\partial \chi(\mathbf{r}, t)}{\partial t}. \quad (5.8)
\]

From the Lorentz condition, it follows that the gauge function \( \chi(\mathbf{r}, t) \) satisfies the wave equation,

\[
\nabla^2 \chi(\mathbf{r}, t) - \frac{1}{c^2} \frac{\partial^2 \chi(\mathbf{r}, t)}{\partial t^2} = 0. \quad (5.9)
\]

Let us consider harmonic electromagnetic fields with time dependence \( \exp(\mp i\omega t) \). The corresponding potentials are written

\[
\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_\pm(\mathbf{r}, \omega) e^{\mp i\omega t},
\]
\[
\phi(\mathbf{r}, t) = \phi_\pm(\mathbf{r}, \omega) e^{\mp i\omega t}.
\]

For such waves, the Lorentz condition becomes

\[
c \nabla \cdot \mathbf{A}_\pm(\mathbf{r}, \omega) \mp i k \phi_\pm(\mathbf{r}, \omega) = 0, \quad (5.10)
\]

where \( k = \omega/c \). Equations (5.7) and (5.8) describing a gauge transformation become

\[
\mathbf{A}_\pm(\mathbf{r}, \omega) \rightarrow \mathbf{A}'_\pm(\mathbf{r}, \omega) = \mathbf{A}_\pm(\mathbf{r}, \omega) + \nabla \chi_\pm(\mathbf{r}, \omega), \quad (5.11)
\]
\[
\phi_\pm(\mathbf{r}, \omega) \rightarrow \phi'_\pm(\mathbf{r}, \omega) = \phi_\pm(\mathbf{r}, \omega) \pm i\omega \chi_\pm(\mathbf{r}, \omega). \quad (5.12)
\]
and the wave equation (5.9) reduces to the Helmholtz equation

$$\nabla^2 \chi_{\pm}(r, \omega) + k^2 \chi_{\pm}(r, \omega) = 0. \quad (5.13)$$

Gauge transformations can be used to bring potentials into various convenient forms. One particularly important form, referred to as the *transverse gauge*, is defined by the condition

$$\nabla \cdot \mathbf{A}_{\pm}(r, \omega) = 0. \quad (5.14)$$

It follows from the Lorentz condition that, in the transverse gauge, the scalar potential vanishes:

$$\phi_{\pm}(r, \omega) = 0. \quad (5.15)$$

Any given set of potentials \((\mathbf{A}_{\pm}(r, \omega), \phi_{\pm}(r, \omega))\) satisfying the Lorentz condition can, of course, be transformed into the transverse gauge by a suitably chosen gauge transformation. In the transverse gauge, the electric and magnetic fields are given by

$$\mathbf{E}_{\pm}(r, \omega) = \pm i \omega \mathbf{A}_{\pm}(r, \omega), \quad (5.16)$$

$$\mathbf{B}_{\pm}(r, \omega) = \nabla \times \mathbf{A}_{\pm}(r, \omega). \quad (5.17)$$

### 5.1.2 Electromagnetic Plane Waves

Let us consider plane-wave solutions to the source-free Maxwell equations. If we suppose that these plane waves are propagating in the direction \(\hat{k}\), then the transverse-gauge vector potential is

$$\mathbf{A}_{\pm}(r, \omega) = \hat{\epsilon} e^{\pm i \mathbf{k} \cdot \mathbf{r}}. \quad (5.18)$$

The vector \(\mathbf{k} = k \hat{k}\) is called the propagation vector, and the unit vector \(\hat{\epsilon}\) is called the polarization vector. From the relation (5.14) it follows that the polarization vector is orthogonal to the propagation vector. The two-dimensional space perpendicular to \(\hat{k}\) is spanned by two orthogonal polarization vectors. If, for example, we suppose \(\hat{k}\) is along the \(z\) axis, then the unit vector along the \(x\) axis, \(\hat{i}\), and the unit vector along the \(y\) axis, \(\hat{j}\), span the two-dimensional space of polarization vectors. Fields described by these unit vectors are *linearly polarized* along the \(x\) axis and \(y\) axis, respectively. From Eqs.(5.16,5.17), it follows that for plane waves linearly polarized along direction \(\hat{i}\), the electric field \(\mathbf{E}\) is along \(\hat{i}\) and the magnetic field \(\mathbf{B}\) is along \(\hat{j} = [\hat{k} \times \hat{i}]\).

A *real* linear combination, \(\hat{\epsilon} = \cos \varphi \hat{i} + \sin \varphi \hat{j}\) describes a wave that is linearly polarized at angle \(\varphi\) to the \(x\) axis. Moreover, the combinations

$$\hat{\epsilon}_{\pm} = \frac{1}{\sqrt{2}} (\hat{i} \pm i \hat{j})$$

describe *left- and right-circularly polarized* waves, respectively. For circularly-polarized waves, the electric field vector at a fixed point in space rotates in a
circle in the plane perpendicular to \( \hat{k} \), the sense of rotation being positive or negative for left- or right-circularly polarized waves, respectively. Generally, we let \( \hat{\epsilon}_\lambda \) (with \( \lambda = \pm 1 \)) represent two orthogonal unit vectors, spanning the space of polarization vectors. We take these vectors to be either two real vectors describing linear polarization or the two complex vectors describing circular polarization. In either case we have

\[
\hat{\epsilon}_1^\ast \cdot \hat{\epsilon}_1 = 1, \quad \hat{\epsilon}_{-1}^\ast \cdot \hat{\epsilon}_{-1} = 1, \quad \hat{\epsilon}_1^\ast \cdot \hat{\epsilon}_{-1} = 0, \\
\hat{k} \cdot \hat{\epsilon}_1 = 0, \quad \hat{k} \cdot \hat{\epsilon}_{-1} = 0, \quad \hat{k} \cdot \hat{k} = 1.
\]

A plane-wave solution is, therefore, characterized by frequency \( \omega \), propagation direction \( \hat{k} \), and polarization vector \( \hat{\epsilon}_\lambda \). To simplify our notation somewhat, we use a single index \( i \) to refer to the entire set of parameters \( i = (\omega, \hat{k}, \hat{\epsilon}_\lambda) \).

The general solution to the time-dependent wave equation in the transverse gauge can be written as a superposition of plane wave solutions

\[
A(r, t) = \sum_i A_i(r, t),
\]

where

\[
A_i(r, t) = c_i \hat{\epsilon}_\lambda e^{ik \cdot r - i\omega t} + c_i^\ast \hat{\epsilon}_\lambda^\ast e^{-ik \cdot r + i\omega t}.
\]

The constants \( c_i \) and \( c_i^\ast \) are Fourier expansion coefficients. From Eq.(5.20), it follows that the vector potential is real.

### 5.2 Quantized Electromagnetic Field

We carry out the quantization of the electromagnetic field in a box of volume \( V \). The vector \( k \) in Eq.(5.20) then takes on discrete values depending on boundary conditions at the surface of the box, with the number of distinct vectors in the interval \( d^3k \) given by \( d^3n = V d^3k/(2\pi)^3 \). To quantize the field, we interpret the expansion coefficients \( c_i \) and \( c_i^\ast \) in Eq.(5.20) as quantum mechanical operators. In this way we obtain the operator \( A_i(r, t) \) representing a photon with frequency \( \omega \), propagation direction \( \hat{k} \), and polarization vector \( \hat{\epsilon}_\lambda \):

\[
A_i(r, t) = \sqrt{\frac{\hbar}{2\epsilon_0 \omega V}} \left[ c_i \hat{\epsilon}_\lambda e^{ik \cdot r - i\omega t} + c_i^\ast \hat{\epsilon}_\lambda^\ast e^{-ik \cdot r + i\omega t} \right].
\]

In this equation, \( c_i \) and \( c_i^\ast \) are photon annihilation and creation operators, respectively. These operators satisfy the commutation relations

\[
[c_i, c_j^\dagger] = 0, \quad [c_i^\dagger, c_j] = 0, \quad [c_i, c_j^\dagger] = \delta_{ij}.
\]

The coefficient \( \sqrt{\hbar/2\epsilon_0 \omega V} \) is chosen in such a way that the expression for the energy has an obvious interpretation in terms of photons.
The general expression for the quantized vector potential is a superposition of the photon potentials, as in Eq. (5.19),

\[ A(r, t) = \sum_i A_i(r, t). \]

The corresponding electric and magnetic fields are given by

\[ E(r, t) = i \sum_i \sqrt{\frac{\hbar \omega}{2 \epsilon_0 V}} \left[ c_i \hat{\epsilon}_\lambda e^{i \mathbf{k} \cdot \mathbf{r} - i \omega t} - c_i^\dagger \hat{\epsilon}_\lambda^* e^{-i \mathbf{k} \cdot \mathbf{r} + i \omega t} \right], \]

\[ B(r, t) = i \sum_i \sqrt{\frac{\hbar \omega}{2 \epsilon_0 V}} \left[ c_i [\hat{k} \times \hat{\epsilon}_\lambda] e^{i \mathbf{k} \cdot \mathbf{r} - i \omega t} - c_i^\dagger [\hat{k} \times \hat{\epsilon}_\lambda^*] e^{-i \mathbf{k} \cdot \mathbf{r} + i \omega t} \right]. \]

The Hamiltonian governing the electromagnetic field is

\[ H_{EM} = \frac{\epsilon_0}{2} \int d^3 r E(r, t) \cdot E(r, t) + \frac{1}{2 \mu_0} \int d^3 r B(r, t) \cdot B(r, t) \]
\[
= \frac{1}{4} \sum_i \hbar \omega \left( \hat{\epsilon}_\lambda \cdot \hat{\epsilon}_\lambda + [\hat{k} \times \hat{\epsilon}_\lambda] \cdot [\hat{k} \times \hat{\epsilon}_\lambda^*] \right) \left( c_i c_i^\dagger + c_i^\dagger c_i \right) \tag{5.23}
\]
\[
= \sum_i \hbar \omega \left( N_i + \frac{1}{2} \right),
\]

where \( N_i = c_i^\dagger c_i \) is the photon number operator.

### 5.2.1 Eigenstates of \( N_i \)

Let us say a few words about eigenstates of the number operator \( N_i \), which are also eigenstates of the electromagnetic Hamiltonian. For simplicity, we drop the subscript \( i \) and consider an eigenstate of the generic operator \( N = c^\dagger c \). If we let \( |\nu\rangle \) be an eigenstate of \( N \)

\[ N |\nu\rangle = \nu |\nu\rangle, \tag{5.24} \]

then it follows from the commutation relation \([c, c^\dagger] = 1\) that \( c |n\rangle \) is an eigenstate with eigenvalue \( \nu - 1 \) and \( c^\dagger |\nu\rangle \) is an eigenstate with eigenvalue \( \nu + 1 \). By applying \( c \) repeatedly to the state \( |\nu\rangle \), we generate a sequence of states with eigenvalues \( \nu - 1, \nu - 2, \cdots \). If we require that the eigenvalues of \( N \) (and therefore the energy) be nonnegative, then it follows that this sequence must terminate after a finite number of steps \( n \). This will happen only if \( \nu = n \). Thus, the eigenvalues of the number operator are integers.

We write

\[ c |n\rangle = \alpha |n - 1\rangle, \]
\[ c^\dagger |n\rangle = \beta |n + 1\rangle. \]

It is simple to evaluate the constants \( \alpha \) and \( \beta \). For this purpose, we consider

\[ n = \langle n | c^\dagger c |n\rangle = \alpha^2 \langle n - 1 | n - 1 \rangle = \alpha^2, \tag{5.25} \]
\[ = \langle n | (-1 + c c^\dagger) |n\rangle = -\langle n | n \rangle + \beta^2 \langle n + 1 | n + 1 \rangle = -1 + \beta^2, \tag{5.26} \]
From Eq. (5.25), it follows that $\alpha = \sqrt{n}$ and from Eq. (5.26) $\beta = \sqrt{n + 1}$. We therefore have

\[ c|n\rangle = \sqrt{n}|n - 1\rangle, \quad c^\dagger|n\rangle = \sqrt{n + 1}|n + 1\rangle. \quad (5.27) \]

The electromagnetic vacuum state $|0\rangle$ is the state for which $N_i|0\rangle = 0$ for all $i$. The vacuum state is an eigenstate of $H_{EM}$ having energy

\[ E_0 = \frac{1}{2} \sum_i \hbar \omega_i. \]

This is the (infinite) zero-point energy of the electromagnetic field. Since the zero-point energy is not measurable, it is convenient to subtract it from the electromagnetic Hamiltonian. This is accomplished by replacing the operator products in Eq. (5.23) by normal products. The modified electromagnetic Hamiltonian is

\[ H_{EM} = \sum_i \hbar \omega N_i \]

An eigenstate of the $H_{EM}$ corresponding to a photon in state $i$ with frequency $\omega$, propagation direction $\hat{k}$ and polarization vector $\hat{\epsilon}_\lambda$ is $|1_i\rangle = c_i^\dagger|0\rangle$. The corresponding eigenvalue is $\hbar \omega$. Generally, the state $|n_i\rangle$ is an eigenstate of $H_{EM}$ with eigenvalue $n_i \hbar \omega$.

### 5.2.2 Interaction Hamiltonian

The interaction of an electron with this external field is described by the Hamiltonian

\[ h_I(r, t) = -\epsilon c \alpha \cdot A(r, t) \]

\[ = \sum_i \left[ h_i(r, \omega) c_i e^{-i\omega t} + h_i^\dagger(r, \omega) c_i^\dagger e^{i\omega t} \right], \quad (5.29) \]

where

\[ h_i(r, \omega) = -\epsilon c \sqrt{\frac{\hbar}{2\epsilon_0 \omega V}} \alpha \cdot \hat{\epsilon}_\lambda e^{ikr}. \quad (5.30) \]

The corresponding many-electron interaction Hamiltonian in the Heisenberg representation is given by

\[ H_I(t) = \sum_k \left[ H_I^\dagger(\omega) c_k e^{-i\omega t} + H_I(\omega) c_k^\dagger e^{i\omega t} \right], \quad (5.31) \]

where $H_I(\omega)$ is a sum of one-electron terms,

\[ H_I(\omega) = \sum_{i=1}^N h_i(r_i, \omega). \quad (5.32) \]

The interaction Hamiltonian in the Schrödinger representation is just the interaction Hamiltonian in the Heisenberg representation evaluated at $t = 0$. 
5.2. QUANTIZED ELECTROMAGNETIC FIELD

5.2.3 Time-Dependent Perturbation Theory

Let us now consider the effect of adding the interaction Hamiltonian $H_I$ to the sum of the many-electron Hamiltonian $H_0 + V_I$ and the electromagnetic Hamiltonian $H_{EM}$,

$$H = H_0 + V_I + H_{EM}. \quad (5.33)$$

We let $\Psi_k$ represent an eigenfunction of $H_0 + V_I$ belonging to eigenvalue $E_k$,

$$(H_0 + V_I)\Psi_k = E_k \Psi_k, \quad (5.34)$$

and we let $|n_k\rangle$ be an $n_k$ photon eigenstate of $H_{EM}$ with eigenvalue $n_k\hbar\omega$,

$$H_{EM}|n_k\rangle = n_k\hbar\omega|n_k\rangle. \quad (5.35)$$

An eigenstate of $H$ corresponding to a many-electron atom in the state $\Psi_k$ and $n_k$ photons is the product state

$$\Phi_k \equiv \Psi_k |n_k\rangle. \quad (5.36)$$

This is an eigenstate of $H$ with eigenvalue $E_k + n_k\hbar\omega$. We are interested in transitions between such stationary states induced by the interaction $H_I$.

In the interaction representation, the Schrödinger equation for a state $\Phi(t)$ is written

$$i\hbar \frac{\partial \Phi(t)}{\partial t} = \hat{H}_I(t) \Phi(t), \quad (5.37)$$

where $\hat{H}_I(t)$ is the time-dependent interaction Hamiltonian

$$\hat{H}_I(t) = e^{iH_I/\hbar}H_I e^{-iH_I/\hbar}. \quad (5.38)$$

Let us introduce the unitary operator $U(t,t_0)$ describing the evolution of stationary states $\Phi_k$ prepared at $t = t_0$,

$$\Phi_k(t) = U(t,t_0) \Phi_k. \quad (5.39)$$

It follows from Eq.(5.35) that $U(t,t_0)$ satisfies

$$i\hbar \frac{\partial U(t,t_0)}{\partial t} = H_I U(t,t_0) \quad (5.40)$$

where $I$ is the identity operator. These equations can be rewritten as an equivalent integral equation

$$U(t,t_0) = I - \frac{i}{\hbar} \int_{t_0}^{t} dt_1 \hat{H}_I(t_1) U(t_1,t_0). \quad (5.41)$$

The iteration solution to Eq.(5.41) is

$$U(t,t_0) = I - \frac{i}{\hbar} \int_{t_0}^{t} dt_1 \hat{H}_I(t_1) + \frac{(-i)^2}{\hbar^2} \int_{t_0}^{t} dt_1 \hat{H}_I(t_1) \int_{t_0}^{t_1} dt_2 \hat{H}_I(t_2) U(t_2,t_0)$$

$$= \sum_{n=0}^{\infty} \frac{(-i)^n}{\hbar^n} \int_{t_0}^{t} dt_1 \hat{H}_I(t_1) \int_{t_0}^{t_1} dt_2 \hat{H}_I(t_2) \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{H}_I(t_n). \quad (5.42)$$
The $S$ operator is the unitary operator that transforms states prepared at times in the remote past ($t = -\infty$), when the interaction $H_I(t)$ is assumed to vanish, into states in the remote future ($t = \infty$), when $H_I(t)$ is also assumed to vanish. Thus

$$S = U(\infty, -\infty).$$

Expanding $S$ in powers of $H_I$, we have

$$S = I + \sum_{n=1}^{\infty} S^{(n)},$$

where

$$S^{(n)} = \frac{(-i)^n}{\hbar^n} \int_{-\infty}^{\infty} dt_1 \hat{H}_I(t_1) \int_{-\infty}^{t_1} dt_2 \hat{H}_I(t_2) \cdots \int_{-\infty}^{t_{n-1}} dt_n \hat{H}_I(t_n).$$

To first order in $H_I$ we have

$$S \approx I - \frac{i}{\hbar} \int_{-\infty}^{\infty} dt \hat{H}_I(t). \quad (5.40)$$

The first-order transition amplitude for a state $\Phi_i$ prepared in the remote past to evolve into a state $\Phi_f$ in the remote future is

$$S^{(1)}_{fi} = \langle \Phi_f|S^{(1)}|\Phi_i \rangle = -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt \langle \Phi_f|e^{iHt/\hbar}H_Ie^{-iHt/\hbar}|\Phi_i \rangle. \quad (5.41)$$

### 5.2.4 Transition Matrix Elements

Let us consider an atom in an initial state $\Psi_i$ interacting with $n_i$ photons. The initial state is

$$\Phi_i = \Psi_i |n_i \rangle.$$

The operator $c_i$ in $H_I(t)$ will cause transitions to states with $n_i - 1$ photons, while the operator $c_i^\dagger$ will lead to states with $n_i + 1$ photons. Thus, we must consider two possibilities:

1. photon absorption, leading to a final state

   $$\Phi_f = \Psi_f |n_i - 1 \rangle,$$

2. photon emission, leading to a final state

   $$\Phi_f = \Psi_f |n_i + 1 \rangle.$$

For the case of photon absorption, using the fact that

$$\langle n_i - 1|c_i|n_i \rangle = \sqrt{n_i},$$
we may write
\[
S_{fi}^{(1)} = -\frac{i}{\hbar} \sqrt{n_i} \int_{-\infty}^{\infty} dt \ e^{i(E_f - E_i - \hbar\omega)t/\hbar} \langle \Psi_f | H_I | \Psi_i \rangle
\]
\[
= -2\pi i \delta(E_f - E_i - \hbar\omega) \sqrt{n_i} \langle \Psi_f | H_I | \Psi_i \rangle.
\]
(5.42)

Similarly, for the case of photon emission, we find
\[
S_{fi}^{(1)} = -\frac{i}{\hbar} \sqrt{n_i + 1} \int_{-\infty}^{\infty} dt \ e^{i(E_f - E_i + \hbar\omega)t/\hbar} \langle \Psi_f | H_I^\dagger | \Psi_i \rangle
\]
\[
= -2\pi i \delta(E_f - E_i + \hbar\omega) \sqrt{n_i + 1} \langle \Psi_f | H_I^\dagger | \Psi_i \rangle.
\]
(5.43)

We introduce the transition amplitude
\[
T_{fi} = \begin{cases} 
\langle \Psi_f | H_I | \Psi_i \rangle, & \text{for absorption of radiation,} \\
\langle \Psi_f | H_I^\dagger | \Psi_i \rangle, & \text{for emission of radiation.}
\end{cases}
\]

We treat the two cases simultaneously using
\[
S_{fi} = -2\pi \delta(E_f - E_i \mp \hbar\omega) T_{fi} \left( \frac{\sqrt{n_i}}{\sqrt{n_i + 1}} \right),
\]
(5.45)

where the upper contribution refers to absorption and the lower refers to emission. The probability of a transition from state $\Psi_i$ to state $\Psi_f$ is just the square of $S_{fi}$. In evaluating the square, we replace one factor of $2\pi \delta(E_f - E_i \mp \hbar\omega)$ by $T/\hbar$, where $T$ is the total interaction time. Thus, we find that the transition probability per unit time $W_{fi}$ is given by
\[
W_{fi} = \frac{2\pi}{\hbar} \delta(E_f - E_i \mp \hbar\omega) |T_{fi}|^2 \left( \frac{n_i}{n_i + 1} \right).
\]
(5.46)

In an interval of wave numbers $d^3k$, there are
\[
d^3n_i = \frac{V}{(2\pi)^3} d^3k = \frac{V}{(2\pi c)^3} \omega^2 d\omega d\Omega_k
\]
(5.47)

photon states of a given polarization. The corresponding number of transitions per second $d^3w_{fi}$ is thus given by
\[
d^3w_{fi} = W_{fi} d^3n_i = \frac{V}{(2\pi)^3 c^3 \hbar} \delta(E_f - E_i \mp \hbar\omega) \omega^2 d\omega d\Omega_k |T_{fi}|^2 \left( \frac{n_i}{n_i + 1} \right).
\]

Integrating over $\omega$, we obtain
\[
d^2w_{fi} = \frac{V}{(2\pi \hbar)^2 c^3} \omega^2 d\Omega_k |T_{fi}|^2 \left( \frac{n_i}{n_i + 1} \right),
\]

where $n_i$ is now the number of photons with energy $\hbar\omega = E_f - E_i$ for absorption and $\hbar\omega = E_i - E_f$ for emission. Factoring $-\alpha c \sqrt{\hbar/2\epsilon_0\omega V}$ from the interaction Hamiltonian, we obtain
\[
d^2w_{fi} = \frac{\alpha}{2\pi} \omega d\Omega_k |T_{fi}|^2 \left( \frac{n_i}{n_i + 1} \right),
\]
(5.48)
where the single-particle interaction Hamiltonian is now replaced by
\[ h_I(r, \omega) \rightarrow \alpha \cdot \hat{\epsilon}_\lambda e^{i\mathbf{k} \cdot \mathbf{r}}. \] (5.49)

Let us assume that we have a collection of atoms in equilibrium with a radiation field. Further, let us assume that the photons of frequency \( \omega \) in the radiation field are distributed isotropically and that the number of photons in each of the two polarization states is equal. In this case, the photon number \( n \) can be related to the spectral density function \( \rho(\omega) \) which is defined as the photon energy per unit volume in the frequency interval \( d\omega \). One finds from (5.47) that
\[ \rho(\omega) = 2 \times n \hbar \omega \times \frac{4\pi \omega^2}{(2\pi c)^3} = \frac{\hbar \omega^3}{\pi^2 c^3} n. \] (5.50)

For isotropic, unpolarized radiation, we can integrate Eq.(5.23) over angles \( \Omega_k \) and sum over polarization states \( \hat{\epsilon}_\lambda \), treating \( n \) as a multiplicative factor. The resulting absorption probability per second, \( w_{b\rightarrow a} \), leading from an initial (lower energy) state \( a \) to final (higher energy) state \( b \) in presence of \( n \) photons of energy \( \hbar \omega \) is given in terms of the spectral density function \( \rho(\omega) \) as
\[ w_{ab} = \frac{\pi^2 c^3}{\hbar \omega^3} \rho(\omega) \frac{\alpha}{2\pi} \omega \sum_\lambda \int d\Omega_k |T_{ba}|^2. \] (5.51)

Similarly, the emission probability per second leading from state \( b \) to state \( a \) in the presence of \( n \) photons of energy \( \hbar \omega \) is given in terms of \( \rho(\omega) \) by
\[ w_{em}^{ba} = \left( 1 + \frac{\pi^2 c^3}{\hbar \omega^3} \rho(\omega) \right) \frac{\alpha}{2\pi} \omega \sum_\lambda \int d\Omega_k |T_{ab}|^2. \] (5.52)

The emission probability consists of two parts, a spontaneous emission contribution, \( w_{sp}^{ba} \), that is independent of \( \rho(\omega) \), and an induced or stimulated emission contribution, \( w_{ie}^{ba} \), that is proportional to \( \rho(\omega) \).

Let the state \( a \) be a member of a \( g \)-fold degenerate group of levels \( \gamma \), and \( b \) be a member of a \( g' \)-fold degenerate group of levels \( \gamma' \). If we assume that the atom can be in any of the degenerate initial levels with equal probability, then the average transition probability from \( \gamma \rightarrow \gamma' \) is found by summing over sublevels \( a \) and \( b \) and dividing by \( g \), whereas the average transition probability from \( \gamma' \rightarrow \gamma \) is given by the sum over \( a \) and \( b \) divided by \( g' \). The Einstein \( A \) - and \( B \)-coefficients are defined in terms of average transition probabilities per second between degenerate levels through the relations
\[ B_{\gamma\gamma'} \rho(\omega) = w_{\gamma\gamma'}^{ab} = \frac{1}{g} \sum_{ab} w_{a\rightarrow b}^{ab}, \] (5.53)
\[ A_{\gamma'\gamma} = w_{sp}^{ab} = \frac{1}{g} \sum_{ab} w_{b\rightarrow a}^{sp}, \] (5.54)
\[ B_{\gamma'\gamma} \rho(\omega) = w_{sp}^{ab} = \frac{1}{g} \sum_{ab} w_{sp}^{ab}. \] (5.55)
\[ N_{\gamma'} \propto g'e^{-E_{\gamma'}/kT} \]

\[
\begin{array}{c|c}
N_{\gamma} & B_{\gamma'\gamma} \rho(\omega) \\
\hline
N_{\gamma'} & N_{\gamma}[B_{\gamma'\gamma} \rho(\omega) + A_{\gamma'\gamma}] \\
\end{array}
\]

\[ N_{\gamma} \propto ge^{-E_{\gamma}/kT} \]

Figure 5.1: Detailed balance for radiative transitions between two levels.

It follows from Eqs. (5.51-5.52), that the three Einstein coefficients are related by equations

\[ g'B_{\gamma'\gamma} = gB_{\gamma'\gamma}, \quad (5.56) \]

\[ A_{\gamma'\gamma'} = \frac{\hbar\omega^3}{\pi^2c^3}B_{\gamma'\gamma}. \quad (5.57) \]

If we suppose that there are \( N_{\gamma} \) atoms in the lower level \( \gamma \), and \( N_{\gamma'} \) atoms in the upper level \( \gamma' \), then, on average, there will be \( N_{\gamma}B_{\gamma'\gamma} \rho(\omega) \) upward transitions to level \( \gamma' \) per second, and \( N_{\gamma'}[B_{\gamma'\gamma} \rho(\omega) + A_{\gamma'\gamma}] \) downward transitions from \( \gamma' \) to \( \gamma \) per second. The principle of detailed balance requires that, in equilibrium, the number of upward transitions per second between the two levels equals the number of downward transitions per second. This, in turn, leads to the relation

\[ \frac{N_{\gamma'}}{N_{\gamma}} = \frac{B_{\gamma'\gamma} \rho(\omega)}{A_{\gamma'\gamma} + B_{\gamma'\gamma} \rho(\omega)}. \quad (5.58) \]

Assuming that the number of atomic states of energy \( E_{\gamma} \) in the equilibrium distribution at temperature \( T \) is proportional to \( \exp(-E_{\gamma}/kT) \), where \( k \) is Boltzmann’s constant, we have

\[ \frac{N_{\gamma'}}{N_{\gamma}} = \frac{g'e^{-E_{\gamma'}/kT}}{ge^{-E_{\gamma}/kT}} = \frac{g'e^{-\hbar\omega/kT}}{g}. \]

Substituting this relation into (5.58), and making use of the symmetry relations between the Einstein coefficients, (5.56-5.57), leads to Planck’s formula for the spectral energy density,

\[ \rho(\omega) = \frac{1}{\pi^2c^3} \frac{\hbar\omega^3}{\epsilon\hbar\omega/kT - 1}. \quad (5.59) \]

In the low-energy limit, this reduces to the classical Rayleigh-Jeans formula

\[ \lim_{\omega \to 0} \rho(\omega) = \frac{\omega^2}{\pi^2c^3} kT. \]

The Planck formula is a direct consequence of the fact that the photon creation and annihilation operators satisfy the commutation relations (5.22). Conversely,
the fact that radiation in equilibrium with matter is found to satisfy the Planck formula experimentally is strong evidence for the quantum mechanical nature of the electromagnetic field.

5.2.5 Gauge Invariance

Let us consider the interaction of an electron with a field described by potentials

$$A(r,\omega)e^{-i\omega t} \text{ and } \phi(r,\omega)e^{-i\omega t},$$

such as those associated with absorption of a photon with frequency $\omega$. The corresponding interaction Hamiltonian can be written

$$h(r,t) = h(r,\omega)e^{-i\omega t},$$

with

$$h_I(r,\omega) = e\{-c\alpha \cdot A(r,\omega) + \phi(r,\omega)\}. \quad (5.60)$$

A gauge transformation induces the following change in $h_I(r,\omega)$:

$$\Delta h_I(r,\omega) = e\{-c\alpha \cdot \nabla \chi(r,\omega) + i\omega \chi(r,\omega)\}. \quad (5.61)$$

This equation can be rewritten in terms of the momentum operator $p$ in the form

$$\Delta h_I = e\{-ic\hbar \alpha \cdot p \chi + i\omega \chi\}. \quad (5.62)$$

The first term in braces can be reexpressed in terms of the commutator of the single-particle Dirac Hamiltonian,

$$h_0 = c\alpha \cdot p + \beta mc^2 + V_{\text{nuc}}(r) + U(r), \quad (5.63)$$

with the gauge function $\chi(r,\omega)$, leading to

$$\Delta h_I = -ie\hbar \{[h_0, \chi] - \hbar \omega \chi\}. \quad (5.64)$$

It is important to note that the expressions (5.62) and (5.64) for $\Delta h_I$ are equivalent for local potentials but not for the non-local Hartree-Fock potential.

The transition amplitude from an initial state $|a\rangle$ to a final state $|b\rangle$, both assumed to be eigenstates of $h_0$, is proportional to the matrix element $\langle b| h_I |a\rangle$. The change in this matrix element induced by a gauge transformation is given by

$$\langle b|\Delta h_I|a\rangle = -ie\hbar \langle b|[h_0, \chi] - \hbar \omega \chi|a\rangle = -ie\hbar (\epsilon_b - \epsilon_a - \hbar \omega) \langle b|\chi|a\rangle. \quad (5.65)$$

It follows that, for states $|a\rangle$ and $|b\rangle$ that satisfy $\hbar \omega = \epsilon_b - \epsilon_a$, transition amplitudes calculated using single-particle orbitals in a local potential are gauge invariant.
Later, we will encounter the expression
\[ \langle b | \frac{d\Delta I}{d\omega} | a \rangle. \]
This can be rewritten with the aid of the above identities as
\[ \langle b | \frac{d\Delta I}{d\omega} | a \rangle = -ie\bar{\hbar}\langle b | [h_0, \frac{d\chi}{d\omega}] - \hbar\omega \frac{d\chi}{d\omega} - \hbar\chi | a \rangle = ie \langle b | \chi | a \rangle, \]
where the identity on the right-hand side is valid only for states satisfying \( \hbar\omega = \epsilon_b - \epsilon_a \).

### 5.2.6 Electric Dipole Transitions

Let us consider a one-electron atom and examine the transition amplitude
\[ T_{ba} = \int d^3r \psi_b^\dagger(r) \alpha \cdot \hat{\epsilon} e^{ik \cdot r} \psi_a(r). \]  
(5.67)

The values of \( r \) for which there are significant contributions to this integral are those less than a few atomic radii, which, for an ion with charge \( Z \), is of order \( 1/Z \) a.u. The photon energy for transitions between states having different principal quantum numbers in such an ion is of order \( Z^2 \) a.u. For transitions between states with the same principal quantum number, the photon energy is of order \( Z \) a.u. Using the fact that \( k = \omega/c \), the factor \( kr \) in the exponent is, therefore, of order \( \alpha Z \) for transitions between states with different principal quantum numbers and of order \( \alpha \) for transitions between states having the same principal quantum number. In either case, for neutral atoms or ions with small ionic charge \( Z \), the quantity \( |k \cdot r| \leq kr \ll 1 \), so one can accurately approximate the exponential factor in Eq. (5.67) by 1. In this approximation, the transition amplitude \( T_{ba} \) is just the matrix element of \( \alpha \cdot \hat{\epsilon} \).

We will first examine the transition amplitude in the nonrelativistic limit. To obtain a nonrelativistic expression for the transition amplitude, we turn to the Pauli approximation. We write the Dirac wave function \( \psi_a(r) \) in terms of two-component functions \( \phi_a(r) \) and \( \chi_a(r) \),
\[ \psi_a(r) \approx \begin{pmatrix} \phi_a(r) \\ \chi_a(r) \end{pmatrix}. \]
(5.68)

In the Pauli approximation, the large-component \( \phi_a \) is the nonrelativistic wave function,
\[ \left( \frac{\hbar^2}{2m} + V(r) \right) \phi_a(r) = W_a \phi_a(r), \]
(5.69)
and the small component \( \chi_a(r) \) is given in terms of \( \phi_a(r) \) by
\[ \chi_a(r) = \frac{\sigma \cdot p}{2mc} \phi_a(r). \]
(5.70)
The transition amplitude reduces to

\[
T_{ba} = \frac{1}{2mc} \int d^3r \phi_b^\dagger(r) \left[ \sigma \cdot p \sigma \cdot \hat{\epsilon} + \sigma \cdot \hat{r} \sigma \cdot \epsilon \right] \phi_a(r) \tag{5.71}
\]

\[
= \frac{1}{mc} \int d^3r \phi_b^\dagger(r) \hat{p} \cdot \hat{\epsilon} \phi_a(r) = \frac{1}{c} \langle b|\hat{v}|a \rangle \cdot \hat{\epsilon} \tag{5.72}
\]

This is known as the velocity-form of the transition matrix element. Now, the commutator of the single-particle Schrödinger Hamiltonian \( h_{nr} = \frac{p^2}{2m} + V(r) \) with the vector \( r \) can be written

\[
[h_{nr}, r] = -i \frac{\hbar}{m} p = -i \hbar \, v,
\]

so one can rewrite matrix elements of \( v \) in terms of matrix elements of the vector \( r \). Using the commutator relation, we find

\[
\langle b|v|a \rangle = i \omega_{ba} \langle b|r|a \rangle, \tag{5.74}
\]

where \( \omega_{ba} = (W_b - W_a)/\hbar \). This allows us to express the transition amplitude in length-form as

\[
T_{ba} = ik_{ba} \langle b|r|a \rangle \cdot \hat{\epsilon}. \tag{5.75}
\]

where \( k_{ba} = \omega_{ab}/c \).

The electric dipole operator is \( d = e \hat{r} \) so the transition amplitude in length form is proportional to the matrix element of the electric dipole operator. The amplitudes are therefore referred to as electric dipole transition amplitudes. In a spherical basis, the electric dipole operator is an odd-parity irreducible tensor operator of rank one. It follows that \( T_{ba} \) is nonvanishing only between states \( a \) and \( b \) that have different parity and that satisfy the angular momentum triangle relations \( |l_a - 1| \leq l_b \leq l_a + 1 \). From parity considerations, it follows that only states satisfying \( l_b = l_a \pm 1 \) contribute nonvanishing matrix elements. Transitions forbidden by the dipole selection rules can give finite but small contributions to \( T_{ba} \) when higher-order terms are included in the expansion of the exponential in Eq.(5.67). These higher-order multipole contributions will be discussed further in the following section.

Let us now consider a transition from a particular atomic substate \( a \) to a substate \( b \) by spontaneous emission. The spontaneous emission probability is

\[
w^{sp}_{ab} = \frac{\alpha}{2\pi} \omega \sum_\lambda d \Omega_k |\langle a|v|b \rangle \cdot \hat{\epsilon}_\lambda|^2. \tag{5.76}
\]

We first examine the dependence of this expression on the photon polarization vector \( \epsilon_\lambda \). For this purpose, consider the quantity \( I_\lambda = (\hat{\epsilon}_\lambda \cdot \hat{A}) (\hat{\epsilon}_\lambda \cdot \hat{A}^*) \), where \( \hat{A} = \langle a|v|b \rangle \). To carry out the sum over polarization states, we must sum \( I_\lambda \) over both states of polarization. Taking \( \hat{k} \) to be along the \( z \) axis, this leads to

\[
I_1 + I_{-1} = A_x A_x^* + A_y A_y^* = \hat{A} \cdot \hat{A}^* - \hat{A} \cdot \hat{k} \hat{A}^* \cdot \hat{k} = |\hat{A}|^2 \sin^2 \theta. \tag{5.77}
\]
5.2. QUANTIZED ELECTROMAGNETIC FIELD

Here, \( \theta \) is the angle between the emitted photon and the vector \( \mathbf{A} \).

The integration over photon angles is carried out next. Choosing \( \mathbf{A} \) as an axis, we have

\[
\int d\Omega_k \sin^2 \theta = 2\pi \int_{-1}^{1} d\mu (1 - \mu^2) = \frac{8\pi}{3}.
\]

Thus, after summing over photon polarization states and integrating over photon emission angles, we obtain the spontaneous emission probability per second,

\[
w_{sp}^{ba} = \frac{4\alpha \omega}{3 \epsilon^2} |\langle a||r||b \rangle|^2 = \frac{4\alpha \omega^3}{3 \epsilon^2} |\langle a||r||b \rangle|^2.
\]

We write the components of \( \mathbf{r} \) in a spherical basis as \( r_\nu \) and find

\[
\langle a||r_\nu||b \rangle = -\frac{1}{l_b m_b} \langle a||r||b \rangle \delta_{\sigma_a \sigma_b},
\]

where \( \sigma_a \) and \( \sigma_b \) are spin projections, and where the reduced matrix element of \( \mathbf{r} \) is given by

\[
\langle a||r||b \rangle = \langle la||C_1||lb \rangle \int_0^\infty r P_a(r) P_b(r) \, dr.
\]

The velocity-form of this reduced matrix element is obtained with the aid of Eq.(5.74),

\[
\langle b||r||a \rangle = -i \frac{\hbar}{m \omega_{ba}} \langle b||p||a \rangle = -\frac{\hbar}{m \omega_{ba}} \langle b||\nabla||a \rangle,
\]

together with the expression for the reduced matrix element of \( \nabla \),

\[
\langle a||\nabla||b \rangle = \langle la||C_1||lb \rangle \left\{ \begin{array}{ll}
\int_0^\infty dr P_b \left( \frac{d}{dr} \frac{\omega}{r} \right) P_a, & \text{for } l_b = l_a - 1, \\
\int_0^\infty dr P_a \left( \frac{d}{dr} \frac{\omega + 1}{r} \right) P_b, & \text{for } l_b = l_a + 1.
\end{array} \right.
\]

In evaluating the reduced matrix elements, the formula

\[
\langle la||C_1||lb \rangle = \left\{ \begin{array}{ll}
-\sqrt{l_a} & \text{for } l_b = l_a - 1, \\
\sqrt{l_a + 1} & \text{for } l_b = l_a + 1,
\end{array} \right.
\]

is useful.

Summing \( w_{sp}^{ba} \) over the magnetic substates \( m_b \) and \( \sigma_b \) of the final state, and \( m_a \) and \( \sigma_a \) of the initial state, we obtain the Einstein A-coefficient for spontaneous emission:

\[
A_{ab} = \frac{1}{2l_a} \sum_{m_a \sigma_a} w_{sp}^{ba} = \frac{4\alpha \omega^3}{3 \epsilon^2} \frac{1}{l_a} \sum_{m_a \nu} (-1)^\nu \frac{1}{l_b m_b} - \frac{1}{l_a m_a} \langle a||r||b \rangle \langle b||r||a \rangle
\]

\[
= \frac{4\alpha \omega^3}{3 \epsilon^2} \frac{1}{l_a} |\langle a||r||b \rangle|^2.
\]
The Einstein $A$-coefficient is often expressed in terms of the line strength $S_{E1}$ which is defined as

$$S_{E1} = |\langle a | r | b \rangle|^2.$$  

We can write

$$A_{ab} = \frac{4\alpha}{3} \frac{\omega^3}{c^2} \frac{S_{E1}}{|l_a|} = \frac{16\pi k}{3} \frac{k^3 S_{E1}}{|l_a|} R_\infty c = \frac{2.02613 \times 10^{18} S_{E1}}{|l_a|} s^{-1}. \quad (5.83)$$

In the third term, $R_\infty$ is the Rydberg constant, and in the last term, the wavelength $\lambda$ is expressed in Å. The line strength in the above equation is in atomic units. In these equations, we have used the fact that the atomic unit of frequency is $4\pi R_\infty c$, where $R_\infty c = 3.28984 \times 10^{15} s^{-1}$.

The oscillator strength $f_{kn}$ for a transition $k \rightarrow n$ is defined by

$$f_{kn} = \frac{2m\omega_{nk}}{3\hbar} |\langle k | r | n \rangle|^2, \quad (5.84)$$

where $\omega_{nk} = (W_n - W_k)/\hbar$. If the transition is from a lower state to an upper state (absorption), then the oscillator strength is positive. The oscillator strength is a dimensionless quantity. Oscillator strengths satisfies the following important identity, known as the Thomas-Reiche-Kuhn (TRK) sum rule

$$\sum_n f_{kn} = N, \quad (5.85)$$

where $N$ is the total number of atomic electrons. In this equation, $n$ ranges over all states permitted by the dipole selection rules. To prove the TRK sum rule for a one electron atom, we recall that

$$\omega_{kn} \langle k | r | n \rangle = \frac{i}{m} \langle k | p | n \rangle,$$

and write

$$f_{kn} = \frac{m}{3\hbar} \left\{ \frac{i}{m} \langle k | p | n \rangle \cdot \langle n | r | k \rangle - \frac{i}{m} \langle k | r | n \rangle \cdot \langle n | p | k \rangle \right\}.$$ 

Summing over $n$, we obtain

$$\sum_n f_{kn} = \frac{i}{3\hbar} \langle k | [p_x, x] + [p_y, y] + [p_z, z] | k \rangle = 1. \quad (5.86)$$

The reduced oscillator strength for a transition between degenerate levels is defined as the average over initial substates and the sum over final substates of the oscillator strength. For spontaneous emission in a one-electron atom, this gives

$$\tilde{f}_{ab} = \frac{-2m}{3\hbar} \frac{\omega}{2|l_a|} \sum_{m_a, m_b} |\langle a | r | b \rangle|^2$$

$$= \frac{-2m}{3\hbar} \frac{\omega}{|l_a|} S_{E1}$$

$$= \frac{-303.756}{|l_a|\lambda} S_{E1}. \quad (5.87)$$
Table 5.1: Reduced oscillator strengths for transitions in hydrogen

<table>
<thead>
<tr>
<th>n</th>
<th>1s → np</th>
<th>2s → np</th>
<th>2p → ns</th>
<th>2p → nd</th>
<th>3s → np</th>
<th>3p → ns</th>
<th>3p → nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>...</td>
<td>...</td>
<td>-0.1387</td>
<td>...</td>
<td>...</td>
<td>-0.0264</td>
<td>...</td>
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<tr>
<td>2</td>
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<td>...</td>
<td>...</td>
<td>-0.0408</td>
<td>-0.1450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0791</td>
<td>0.4349</td>
<td>0.0136</td>
<td>0.6958</td>
<td>...</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.0290</td>
<td>0.1028</td>
<td>0.0030</td>
<td>0.1218</td>
<td>0.4847</td>
<td>0.0322</td>
<td>0.1392</td>
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<td>0.0444</td>
<td>0.1210</td>
<td>0.0074</td>
<td>0.0655</td>
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<td>6</td>
<td>0.0078</td>
<td>0.0216</td>
<td>0.0006</td>
<td>0.0216</td>
<td>0.0514</td>
<td>0.0030</td>
<td>0.0561</td>
</tr>
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<td>7</td>
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<td>0.0127</td>
<td>0.0004</td>
<td>0.0123</td>
<td>0.0274</td>
<td>0.0016</td>
<td>0.0290</td>
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<td>8</td>
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<td>0.0082</td>
<td>0.0002</td>
<td>0.0078</td>
<td>0.0165</td>
<td>0.0009</td>
<td>0.0172</td>
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<td>0.0056</td>
<td>0.0002</td>
<td>0.0052</td>
<td>0.0109</td>
<td>0.0006</td>
<td>0.0112</td>
</tr>
<tr>
<td>10</td>
<td>0.0016</td>
<td>0.0040</td>
<td>0.0001</td>
<td>0.0037</td>
<td>0.0076</td>
<td>0.0004</td>
<td>0.0077</td>
</tr>
<tr>
<td>11</td>
<td>0.0012</td>
<td>0.0030</td>
<td>0.0001</td>
<td>0.0027</td>
<td>0.0055</td>
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<td>0.0055</td>
</tr>
<tr>
<td>12</td>
<td>0.0009</td>
<td>0.0022</td>
<td>0.0001</td>
<td>0.0021</td>
<td>0.0041</td>
<td>0.0002</td>
<td>0.0041</td>
</tr>
<tr>
<td>13-∞</td>
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<td>0.0120</td>
<td>0.0003</td>
<td>0.0108</td>
<td>0.0212</td>
<td>0.0012</td>
<td>0.0210</td>
</tr>
</tbody>
</table>

Discrete 0.5650 0.6489 -0.1189 0.9282 0.7095 -0.1233 0.9094
Cont. 0.4350 0.3511 0.0078 0.1829 0.2905 0.0122 0.2017
Total 1.0000 1.0000 -0.1111 1.1111 1.0000 -0.1111 1.1111

The wavelength λ on the last line is expressed in Å.

Reduced oscillator strengths for transitions between levels in helium are given in Table 5.1. For transitions from s states, the only possible final states are np states. The sum of reduced oscillator strengths over all p states saturates the TRK sum rule

\[ \sum_n \tilde{f}_{ks \rightarrow np} = 1. \]

This sum includes an infinite sum over discrete states and an integral over the p-wave continuum. For the s → p transitions shown in the table, 30-40% of the oscillator strength is in the continuum. For states of angular momentum \( l \neq 0 \), the selection rules permit transitions to either \( n l - 1 \) or \( n l + 1 \) final states. The reduced oscillator strengths for such transitions satisfy the following partial sum rules

\[ \sum_n \tilde{f}_{kl \rightarrow nl-1} = -\frac{l(2l-1)}{3(2l+1)}, \]

\[ \sum_n \tilde{f}_{kl \rightarrow nl+1} = \frac{(l+1)(2l+3)}{3(2l+1)}. \]

The sum of the two partial contributions is 1, as expected from the TRK sum rule. These \( l \neq 0 \) transitions are tabulated for 2p → ns, nd and 3p → ns, nd transitions in Table 5.1. Again, these oscillator strengths are seen to have substantial contributions from the continuum.
Table 5.2: Hartree-Fock calculations of transition rates $A_{if} \, [s^{-1}]$ and lifetimes $\tau \, [s]$ for levels in lithium. Numbers in parentheses represent powers of ten.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$A_{if} , [s^{-1}]$</th>
<th>Transition</th>
<th>$A_{if} , [s^{-1}]$</th>
<th>Transition</th>
<th>$A_{if} , [s^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5s → 4p</td>
<td>2.22(6)</td>
<td>5p → 5s</td>
<td>2.41(5)</td>
<td>5d → 5p</td>
<td>2.08(2)</td>
</tr>
<tr>
<td>5s → 3p</td>
<td>2.76(6)</td>
<td>5p → 4s</td>
<td>6.10(3)</td>
<td>5d → 4p</td>
<td>1.39(6)</td>
</tr>
<tr>
<td>5s → 2p</td>
<td>4.59(6)</td>
<td>5p → 3s</td>
<td>2.82(4)</td>
<td>5d → 3p</td>
<td>3.45(6)</td>
</tr>
<tr>
<td>5s → all</td>
<td>9.58(6)</td>
<td>5p → 2s</td>
<td>7.15(5)</td>
<td>5d → 2p</td>
<td>1.04(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5p → 4d</td>
<td>2.57(5)</td>
<td>5d → 4f</td>
<td>5.07(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5p → 3d</td>
<td>2.10(5)</td>
<td>5d → all</td>
<td>1.53(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5p → all</td>
<td>1.46(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_{5s} , [s]$</td>
<td>1.04(-7)</td>
<td>$\tau_{5p} , [s]$</td>
<td>6.86(-7)</td>
<td>$\tau_{5d} , [s]$</td>
<td>6.52(-8)</td>
</tr>
<tr>
<td>4s → 3p</td>
<td>7.34(6)</td>
<td>4p → 4s</td>
<td>7.96(5)</td>
<td>4d → 4p</td>
<td>5.46(2)</td>
</tr>
<tr>
<td>4s → 2p</td>
<td>1.01(7)</td>
<td>4p → 3s</td>
<td>1.73(2)</td>
<td>4d → 3p</td>
<td>6.85(6)</td>
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<tr>
<td>4s → all</td>
<td>1.74(7)</td>
<td>4p → 2s</td>
<td>1.02(6)</td>
<td>4d → 2p</td>
<td>2.25(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4p → 3d</td>
<td>4.91(5)</td>
<td>4d → all</td>
<td>2.93(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4p → all</td>
<td>2.30(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_{4s} , [s]$</td>
<td>5.73(-8)</td>
<td>$\tau_{4p} , [s]$</td>
<td>4.34(-7)</td>
<td>$\tau_{4d} , [s]$</td>
<td>3.41(-8)</td>
</tr>
<tr>
<td>3s → 2p</td>
<td>3.28(7)</td>
<td>3p → 3s</td>
<td>3.82(6)</td>
<td>3d → 3p</td>
<td>1.56(3)</td>
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<tr>
<td></td>
<td></td>
<td>3p → 2s</td>
<td>7.02(5)</td>
<td>3d → 2p</td>
<td>6.73(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3p → all</td>
<td>4.52(6)</td>
<td>3d → all</td>
<td>6.73(7)</td>
</tr>
<tr>
<td>$\tau_{3s} , [s]$</td>
<td>3.05(-8)</td>
<td>$\tau_{3p} , [s]$</td>
<td>2.21(-7)</td>
<td>$\tau_{3d} , [s]$</td>
<td>1.48(-8)</td>
</tr>
<tr>
<td>2p → 2s</td>
<td>3.76(7)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$\tau_{2p} , [s]$</td>
<td>2.66(-8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.2. QUANTIZED ELECTROMAGNETIC FIELD

In Table 5.2, we present the results of Hartree-Fock calculations for transitions in lithium. We consider spontaneous transitions from all \( s \), \( p \), and \( d \) levels with \( n \leq 5 \). Both branches \( l \rightarrow l \pm 1 \) are considered, and the \( A \) coefficients for all allowed lower states are evaluated. The reciprocal of the resulting sum is the mean lifetime of the state,

\[
\tau_a = \frac{1}{\sum_{b \leq a} A_{ab}}. \tag{5.88}
\]

The \( 2p \) lifetime in lithium, for example, is calculated to be \( \tau_{2p}^{\text{theory}} = 26.6 \text{ ns} \) compared to the measured lifetime \( \tau_{2p}^{\exp} = 27.2 \text{ ns} \). Similarly, a Hartree-Fock calculation for sodium gives a value \( \tau_{3p}^{\text{theory}} = 18.0 \text{ ns} \) compared with the experimental value \( \tau_{3p}^{\exp} = 16.9 \text{ ns} \).

5.2.7 Magnetic Dipole and Electric Quadrupole Transitions

Including higher-order terms in the expansion of the exponential factor \( \exp(ik \cdot r) \) in the theory presented above leads to higher-order multipole contributions to the transition amplitude. In this section, we consider the contributions obtained by retaining only the first-order terms in the expansion of the exponential \( \exp(ik \cdot r) \approx 1 + ik \cdot r \). Using the Pauli approximation, the transition amplitude becomes

\[
T_{ba} = \frac{1}{2mc} \int d^3r \phi_b^\dagger(r) \left[ 2p \hat{\epsilon} (1 + ik \cdot r) + \hbar \sigma \cdot k \sigma \cdot \hat{\epsilon} \right] \phi_a(r). \tag{5.89}
\]

We write \( T_{ba} = T_{ba}^{(0)} + T_{ba}^{(1)} \), where \( T_{ba}^{(0)} \) is the electric dipole amplitude discussed previously, and where the contributions of interest here are given by

\[
T_{ba}^{(1)} = \frac{i k}{2mc} \int d^3r \phi_b^\dagger(r) \left( 2\hat{k} \cdot r p \hat{\epsilon} + \hbar \sigma \cdot (\hat{k} \times \hat{\epsilon}) \right) \phi_a(r). \tag{5.90}
\]

Let us assume that \( \hat{k} \) is directed along \( z \) and that \( \hat{\epsilon} \) is in the \( xy \) plane. It follows that

\[
2\hat{k} \cdot r p \hat{\epsilon} = 2zp_x \epsilon_x + 2zp_y \epsilon_y.
\]

We write

\[
2zp_x = (zp_x - xp_z) + (zp_x + xp_z),
\]

and use the fact that

\[
(zp_x + xp_z) = \frac{im}{\hbar} [h, zx],
\]

to obtain

\[
2zp_x \epsilon_x = \left( L_y + \frac{im}{\hbar} [h, zx] \right) \epsilon_x.
\]

Similarly, we find

\[
2zp_y \epsilon_y = \left( -L_x + \frac{im}{\hbar} [h, zy] \right) \epsilon_y.
\]
These terms can be recombined in vector form to give
\[ 2\hat{k} \cdot \mathbf{p} \cdot \hat{\epsilon} = L \cdot [\hat{k} \times \hat{\epsilon}] + \frac{im}{3\hbar} \sum_{ij} \hat{k}_i \hat{\epsilon}_j [h, Q_{ij}], \tag{5.91} \]
where \( Q_{ij} = 3x_ix_j - r^2 \delta_{ij} \) is the quadrupole-moment operator. Using the identity (5.91), we find
\[ T_{ba}^{(1)} = i\hbar \langle b|M|a \rangle \cdot [\hat{k} \times \hat{\epsilon}] - \frac{k\omega_{ba}}{6c} \sum_{ij} \langle b|Q_{ij}|a \rangle \hat{k}_i \hat{\epsilon}_j, \tag{5.92} \]
where \( M \) is the magnetic moment operator
\[ M = \frac{1}{2mc} [L + 2S], \tag{5.93} \]
with \( S = \frac{1}{2} \sigma \). As in the definition of the electric dipole moment, we have factored the electric charge \( e \) in our definition of the magnetic dipole moment. It follows that our magnetic moment has the dimension of a length. Indeed, the coefficient \( \hbar/mc = \alpha a_0 \) in (5.93) is the electron Compton wavelength.

The first of the contributions in (5.92) is referred to as the magnetic dipole amplitude and the second as the electric quadrupole amplitude. As we will prove later, in the general discussion of multipole radiation, these two amplitudes contribute to the decay rate incoherently. That is to say, we may square each amplitude independently, sum over the photon polarization and integrate over photon angles to determine the corresponding contribution to the transition rate, without concern for possible interference terms.

**Magnetic Dipole**  Let us consider first the spontaneous magnetic-dipole decay \( a \rightarrow b \)
\[ w_{ba}^{\text{sp}} = \frac{\alpha}{2\pi} \omega k^2 \sum_{\lambda} \int d\Omega_k \, |\langle b|M|a \rangle \cdot [\hat{k} \times \hat{\epsilon}_\lambda]|^2. \]
The sum over photon polarization states can easily be carried out to give
\[ \sum_{\lambda} |\langle b|M|a \rangle \cdot [\hat{k} \times \hat{\epsilon}_\lambda]|^2 = |\langle b|M|a \rangle|^2 \sin^2 \theta, \]
where \( \theta \) is the angle between \( \hat{k} \) and the vector matrix element. Integrating \( \sin^2 \theta \) over angles gives a factor of \( 8\pi/3 \). We therefore obtain for the Einstein \( A \)-coefficient
\[ A_{ab} = \frac{4}{3} \frac{\omega^3}{\epsilon^3} \frac{1}{g_a} \sum_m |\langle b|M|a \rangle|^2, \tag{5.94} \]
where \( g_a \) is the degeneracy of the initial state and where the sum is over all magnetic substates of \( a \) and \( b \). The sums can be carried out just as in the electric dipole case. Defining a magnetic dipole line strength as
\[ S_{M1} = |\langle b|L + 2S|a \rangle|^2, \]
we obtain
\[ A_{ab} = \frac{1}{3} \frac{\omega^3 S_{M1}}{c} \frac{g_a}{g_a} = \frac{2.69735 \times 10^{13} S_{M1}}{\lambda^3} \frac{g_a}{g_a} \text{s}^{-1}, \] (5.95)
where the wavelength \( \lambda \) is expressed in Å units and \( S_{M1} \) is dimensionless.

The magnetic-dipole selection rules require that \( j_b = j_a \) or \( j_b = j_a \pm 1 \) and that the parity of the initial and final states be the same. For nonrelativistic single-electron states, this implies that \( l_b = l_a \). Magnetic dipole transitions of the type \( n_a l_a \rightarrow n_b l_b \), with \( l_b = l_a \) between states with \( n_b \neq n_a \), however, vanish because radial wave functions with the same value of \( l \) but different principal quantum numbers are orthogonal. It should be mentioned that the amplitudes for such transitions is nonvanishing (but small) in a relativistic calculation.

Let us consider, as an example, the magnetic dipole transition between the two ground-state hyperfine levels in hydrogen. The initial and final states are obtained by coupling the \( s = 1/2 \) electron to the \( s = 1/2 \) proton to form states with, \( F_a = 1 \) and \( F_b = 0 \), respectively. Since both initial and final states have \( l = 0 \), the magnetic-dipole matrix element becomes
\[ \langle a | L_{\nu} + 2S_{\nu} | b \rangle = \langle 1/2, 1/2, F_a | 2S_{\nu} | 1/2, 1/2, F_b \rangle. \]

The corresponding reduced matrix element is easily found to be
\[ \langle a | 2S_{\nu} | b \rangle = (-1)^{F_a} \sqrt{|F_a|} \frac{F_b}{1/2} \langle F_a | F_b | 1/2 \rangle \langle 1/2 | \sigma | 1/2 \rangle. \]

The one-electron reduced matrix element of \( \sigma \) is \( \langle 1/2 | \sigma | 1/2 \rangle = \sqrt{3} \), and the six-\( j \) symbol above has the value \( 1/\sqrt{6} \), from which it follows
\[ \langle a | 2S_{\nu} | b \rangle = \sqrt{|F_a|} = \sqrt{3}. \]

Since the initial state degeneracy is \( g_a = 3 \), it follows that
\[ A_{ab} = \frac{2.69735 \times 10^{13}}{(2.1106)^3} \times 10^{27} = 2.87 \times 10^{-15} \text{s}^{-1}. \]

Here, we have used the fact that the wavelength of the hyperfine transition is 21,106 cm. The mean lifetime of the \( F = 1 \) state is \( \tau = 11 \times 10^9 \) years!

**Electric Quadrupole** From Eq.(5.92), the electric quadrupole transition amplitude is
\[ T^{(1)}_{ba} = -\frac{k^2}{6} \sum_{ij} \langle b | Q_{ij} | a \rangle \hat{k}_i \hat{\epsilon}_j, \] (5.96)
where we assume \( \omega_{ba} = \omega > 0 \) and set \( k = \omega/c \). This amplitude must be squared, summed over photon polarization states, and integrated over photon angles. The sum over polarization states of the squared amplitude is easy to
evaluate in a coordinate system with \( k \) along the \( z' \) axis and \( \epsilon_\lambda \) in the \( x'y' \) plane. In this coordinate system, one obtains

\[
\sum_\lambda \left| \sum_{ij} \langle b | Q_{ij} | a \rangle \hat{k}_i \hat{\epsilon}_j \right|^2 = |\langle b | Q_{z'x'} | a \rangle|^2 + |\langle b | Q_{z'y'} | a \rangle|^2,
\]

where \( \hat{\epsilon}_j \) is the \( j \)th component of \( \hat{\epsilon}_\lambda \). To carry out the integral over photon angles, we transform this expression to a fixed coordinate system. This is done with the aid of Euler angles. We suppose that the \( z' \) axis is at an angle \( \theta \) with the fixed \( z \) axis and that the \( x' \) axis is along the intersection of the plane perpendicular to \( z' \) and the \( xy \) plane. The variable \( x' \) axis, makes an angle \( \phi \) with the fixed \( x \) axis. The two coordinate systems are shown in Fig. 5.2. The transformation equations from \((x, y, z)\) to \((x', y', z')\) are

\[
\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\cos \theta \sin \phi & \cos \theta \cos \phi & \sin \theta \\ \sin \theta \sin \phi & -\sin \theta \cos \phi & \cos \theta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}. \tag{5.97}
\]

It follows that

\[
Q_{z'x'} = \sin \theta \sin 2\phi (Q_{xx} - Q_{yy})/2 - \sin \theta \cos 2\phi Q_{xy} + \cos \theta \cos \phi Q_{zx} + \cos \theta \sin \phi Q_{zy}.
\]

\[
Q_{z'y'} = -\sin \theta \cos \phi (1 - \cos 2\phi) Q_{xx}/2 - \sin \theta \cos \theta (1 + \cos 2\phi) Q_{yy}/2 + \sin \theta \cos \theta (1 - 2\cos^2 \theta) \sin \phi Q_{zx} - (1 - 2\cos^2 \theta) \cos \phi Q_{yz} + \cos \theta \sin \theta Q_{zz}.
\]
Here, we use $Q_{xy}$ as shorthand for $\langle b | Q_{xy} | a \rangle$. Squaring and integrating over $\phi$, we obtain
\[
\int_0^{2\pi} d\phi |Q_{z'x'}|^2 = \pi \left[ \sin^2 \theta |Q_{xx} - Q_{yy}|^2 / 4 + \sin^2 \theta |Q_{xy}|^2 + \cos^2 \theta |Q_{zz}|^2 + \cos^2 \theta |Q_{zy}|^2 \right],
\]
and conversely
\[
\int_0^{2\pi} d\phi |Q_{z'y'}|^2 = \pi \left[ \sin^2 \theta \cos^2 \theta |Q_{xx} + Q_{yy} - 2Q_{zz}|^2 / 2 + \sin^2 \theta \cos^2 \theta |Q_{xx} - Q_{yy}|^2 / 4
+ \sin^2 \theta \cos^2 \theta |Q_{xy}|^2 + (1 - 2 \cos^2 \theta)^2 |Q_{xz}|^2 + (1 - 2 \cos^2 \theta)^2 |Q_{yz}|^2 \right].
\]
Integrating the sum of the two terms above over $\theta$ gives
\[
\int \left[ |Q_{z'x'}|^2 + |Q_{z'y'}|^2 \right] d\Omega = \frac{8\pi}{5} \left[ |Q_{xx}|^2 + |Q_{yy}|^2 + |Q_{xy}|^2 + |Q_{xz}|^2 + |Q_{yz}|^2 + \Re(Q_{xx}Q_{yy}^*) \right].
\]
The terms in square brackets on the right hand side of this expression can be rewritten in terms of the spherical components of the quadrupole tensor $Q_{\nu}^{(2)}$ as
\[
[\cdots] = 3 \sum_\nu |Q_{\nu}^{(2)}|^2.
\]
To prove this relation, we use the fact that the components of the quadrupole moment tensor in a spherical basis are
\[
Q^{(2)}_{\nu} = r^2 C^{(2)}_\nu (\hat{r}).
\]  
(5.98)

From the definition, we infer the following relations between rectangular and spherical components:
\[
Q^{(2)}_0 = \frac{1}{2} Q_{xx},
Q^{(2)}_{\pm 1} = \mp \frac{1}{\sqrt{6}} (Q_{xz} \pm iQ_{yz}),
Q^{(2)}_{\pm 2} = \frac{1}{\sqrt{24}} (Q_{xx} - Q_{yy} \pm 2iQ_{xy}),
\]
and conversely
\[
Q_{xx} = \sqrt{\frac{3}{2}} \left( Q^{(2)}_2 + Q^{(2)}_{-2} \right) - Q^{(2)}_0,
Q_{yy} = -\sqrt{\frac{3}{2}} \left( Q^{(2)}_2 + Q^{(2)}_{-2} \right) - Q^{(2)}_0,
Q_{xy} = -i \sqrt{\frac{3}{2}} \left( Q^{(2)}_2 - Q^{(2)}_{-2} \right),
Q_{xz} = 2Q_0^{(2)},
Q_{yz} = i \sqrt{\frac{3}{2}} \left( Q^{(2)}_1 - Q^{(2)}_{-1} \right),
\]
and
\[
Q_{xx} = \sqrt{\frac{3}{2}} \left( Q^{(2)}_2 + Q^{(2)}_{-2} \right) - Q^{(2)}_0,
Q_{yy} = -\sqrt{\frac{3}{2}} \left( Q^{(2)}_2 + Q^{(2)}_{-2} \right) - Q^{(2)}_0,
Q_{xy} = i \sqrt{\frac{3}{2}} \left( Q^{(2)}_2 - Q^{(2)}_{-2} \right),
Q_{xz} = 2Q_0^{(2)},
Q_{yz} = i \sqrt{\frac{3}{2}} \left( Q^{(2)}_1 - Q^{(2)}_{-1} \right).
\]
Summing $|\langle a | Q_{\nu}^{(2)} | b \rangle|^2$ over $\nu$ and magnetic substates of $a$ and $b$ leads to the expression for the Einstein $A$-coefficient for quadrupole radiation,
\[
A_{ab} = \frac{24\pi \alpha}{5} \frac{k^4}{2\pi} \frac{1}{300 g_a} |\langle a | Q^{(2)} | b \rangle|^2 = \frac{1}{15} k^5 \frac{S_{E2}}{g_a} = \frac{1.1198 \times 10^{18}}{\lambda^5} \frac{S_{E2}}{g_a} \text{ s}^{-1},
\]  
(5.99)
where the quadrupole line strength, which is given by
\[ S_{E2} = |\langle a|Q^{(2)}||b\rangle|^2, \]
is expressed in atomic units and \( \lambda \) is in Å.

For a one-electron atom, the quadrupole reduced matrix element can be written
\[ \langle a|Q^{(2)}||b\rangle = \sqrt{2} \langle l_a||C^{(2)}||l_b\rangle \int_0^\infty P_a(r) r^2 P_b(r) \, dr. \tag{5.100} \]
The factor of \( \sqrt{2} \) here arises from consideration of the electron spin. It can be omitted from the reduced matrix element, in which case the initial state degeneracy \( g_a \) must be replaced by \( g_a \rightarrow |l_a|. \) The quadrupole selection rules require that \( |j_a - 2| \leq j_b \leq j_a + 2 \) and that the parity of initial and final states be the same. For the nonrelativistic single-electron case, the selection rules imply that \( l_b = l_a \pm 2, l_a. \)

Electric quadrupole transitions are important in ions such as Ca\(^+\), which has a 4\( s \) ground state and a 3\( d \) first excited state. Since the angular momentum of the excited state differs from that of the ground state by 2, the excited state cannot decay to the ground state by electric or magnetic dipole radiation. The decay is permitted, however, by the electric quadrupole selection rules. The angular reduced matrix element in (5.100) with \( l_a = 2 \) and \( l_b = 0 \) has the value
\[ \langle 2|C^{(2)}||0 \rangle = 1. \]
The radial integral in Eq.(5.100) can be evaluated numerically. We obtain for Ca\(^+\) (and the analogous case Sr\(^+\)) from Hartree-Fock calculations the values
\[ \int_0^\infty dr P_{4s}(r) r^2 P_{3d}(r) = -10.8304, \quad \text{for Ca}^+; \]
\[ \int_0^\infty dr P_{5s}(r) r^2 P_{4d}(r) = -14.2773, \quad \text{for Sr}^+. \]
The decay rate for the 3\( d \) state of Ca\(^+\) is
\[ A(3d) = \frac{1.1198 \times 10^{18} \times (10.8304)^2}{(7310)^5 \times 5} = 1.259 \text{s}^{-1}, \]
and the corresponding decay rate for the 4\( d \) state of Sr\(^+\) is
\[ A(4d) = \frac{1.1198 \times 10^{18} \times (14.2773)^2}{(6805)^5 \times 5} = 3.128 \text{s}^{-1}. \]
The lifetime of the 4\( d \) state in Sr\(^+\) has been measured experimentally and found to be 0.40 ± 0.04 sec for the 4\( d_{3/2} \) state and 0.34 ± 0.03 sec for the 4\( d_{5/2} \) state, in fair agreement with the value \( \tau = 0.320 \) sec predicted by the HF calculation.

### 5.2.8 Nonrelativistic Many-Body Amplitudes

The nonrelativistic theory of electric-dipole transitions can be generalized to many-electron atoms by simply replacing the single-particle transition operator
5.2. QUANTIZED ELECTROMAGNETIC FIELD

\( t = \frac{1}{c} \mathbf{v} \cdot \hat{\mathbf{c}} \) by its many-electron counterpart, \( T = \sum_i t_i \). In velocity form, we write

\[
T = \frac{1}{c} \mathbf{V} \cdot \hat{\mathbf{c}},
\]

where,

\[
\mathbf{V} = \sum_{i=1}^{N} \mathbf{v}_i, \quad \text{first quantization,}
\]

\[
= \sum_{ij} \langle i| \mathbf{v} |j \rangle a_i^\dagger a_j, \quad \text{second quantization.}
\]

It is elementary to prove that

\[
\mathbf{V} = \frac{i}{\hbar} [\mathbf{H}, \mathbf{R}],
\]

where \( \mathbf{R} = \sum_i \mathbf{r}_i \) and where \( \mathbf{H} = H_0 + V_I \) is the nonrelativistic many-body Hamiltonian. This relation is used to show that the equivalent length-form of the transition operator is obtained through the substitution

\[
\langle F|\mathbf{V}|I \rangle \rightarrow i\omega_{FI} \langle F|\mathbf{R}|I \rangle,
\]

with \( \omega_{FI} = (E_F - E_I)/\hbar \). It should be carefully noted that the length - velocity equivalence in the many-body case is true for exact many-body wave functions, but is not, in general, valid for approximate wave functions. Indeed, one can use the difference in length-form and velocity-form amplitudes, in certain cases, as a measure of the quality of the many-body wave functions \( \Psi_I \) and \( \Psi_F \).

It follows from the analysis given earlier in this section that the Einstein A-coefficient is

\[
A_{IF} = \frac{4}{3} \frac{\omega^3 S_{E1}}{c^2 g_i}, \quad (5.101)
\]

where \( g_i \) is the initial state degeneracy and where \( S_{E1} = |\langle F||R||I \rangle|^2 \) is the line strength. The line strength can be evaluated in velocity-form by making the replacement

\[
\langle F||R||I \rangle \rightarrow - \frac{\hbar}{m\omega_{FI}} \langle F||\nabla||I \rangle.
\]

Let us apply this formalism to study transitions in two-electron atoms. We proceed in two steps. First, we evaluate the matrix element of the dipole operator between two uncoupled states,

\[
|I \rangle = a_a^\dagger a_b^\dagger |0 \rangle, \quad (5.102)
\]

\[
|F \rangle = a_c^\dagger a_d^\dagger |0 \rangle. \quad (5.103)
\]

We easily find

\[
\langle F|R_{\nu}|I \rangle = (r_{\nu})_{ca}\delta_{db} - (r_{\nu})_{da}\delta_{cb} - (r_{\nu})_{cb}\delta_{da} + (r_{\nu})_{db}\delta_{ca}.
\]
Next, we couple the atomic states in the \(LS\) scheme and find
\[
\langle L' M'_L S' M'_S | R_\nu | L M_L S M_S \rangle = \eta \eta' \sum_{m' s' \mu' s} \frac{1}{2 \mu_c} \left\{ - \frac{1}{2 \mu_d} \langle c || r || a \rangle \delta_{db} - \frac{1}{1/2 \mu_d} \langle d || r || a \rangle \delta_{cb} ight\}.
\]
\[
= \eta \eta' \left\{ - \frac{1}{2 \mu_c} \langle c || r || a \rangle \delta_{db} - \frac{1}{1/2 \mu_c} \langle d || r || a \rangle \delta_{cb} \right\}.
\]

The spin sums in this equation can be easily carried out leading to a factor of \(\delta_{S' S} \delta_{M'_S M_S}\) in the two direct terms and a factor of \((-1)^{S+1} \delta_{S' S} \delta_{M'_S M_S}\) in the two exchange terms. The orbital angular momentum sums are a bit more difficult. From the Wigner-Eckart theorem, it follows that each of the four terms in the sum must be proportional to
\[
\langle L' S' | R || L S \rangle = \eta \eta' \sqrt{\frac{|S'|}{|S|}} \left[ (-1)^{L+L_c+L_a+1} \left\{ \frac{L'}{l_a} \frac{L}{l_{c,b}} \frac{1}{l_b} \right\} \langle c || r || a \rangle \delta_{db} 
+ (-1)^{L'+L+S+1} \left\{ \frac{L'}{l_a} \frac{L}{l_{d,b}} \frac{1}{l_b} \right\} \langle d || r || a \rangle \delta_{cb} 
+ (-1)^{S+L_b+L_c+1} \left\{ \frac{L'}{l_b} \frac{L}{l_{c,a}} \frac{1}{l_a} \right\} \langle c || r || b \rangle \delta_{da} 
+ (-1)^{L'+L_b+L_c+1} \left\{ \frac{L'}{l_b} \frac{L}{l_{d,a}} \frac{1}{l_a} \right\} \langle d || r || b \rangle \delta_{ca} \right].
\]

where we have used the fact that
\[
\frac{00}{S M_S} = \frac{1}{\sqrt{|S|}} \delta_{S' S} \delta_{M'_S M_S}.
\]

Let us consider, as specific examples, transitions from excited \((nl_1 s)\) states to either the \((1s)^2 \, ^1S\) ground state or to a \((2s_1 s) \, ^1S\) excited state. Since \(L' = 0\)
for the final states, the dipole selection rules lead to \( L = 1 \) for the initial states. There are the three possible cases:

1. \((np1s)^1P \rightarrow (1s)^21S\). In this case \( S = 0, \eta = 1, \eta' = 1/\sqrt{2}, a = np \) and \( b = c = d = 1s \). The reduced matrix element in Eq.(5.105) becomes

\[
\langle 2^1S || R || n^1P \rangle = \sqrt{2} \langle 1s || r || np \rangle.
\]

2. \((np1s)^1P \rightarrow (2s1s)^1S\). Here, \( S = 0, \eta = \eta' = 1, \eta = np, c = 2s \) and \( b = d = 1s \). The reduced matrix element is

\[
\langle 2^1S || R || n^1P \rangle = \langle 2s || r || np \rangle.
\]

3. \((np1s)^3P \rightarrow (2s1s)^3S\). This case is the same as the previous except \( S = 1 \). The reduced matrix element is

\[
\langle 2^3S || R || n^3P \rangle = \sqrt{3} \langle 2s || r || np \rangle.
\]

The evaluation of the two-particle reduced matrix element thus reduces to the evaluation of a single-particle matrix element between “active” electrons. We describe the helium ground-state in the Hartree-Fock approximation. The ground-state HF potential \( v_0(1s, r) \) is then used as a screening potential \([U(r) = v_0(1s, r)]\) in calculating excited-state orbitals. We find that the lowest-order \( 2^1P - 1^1S \) energy difference is \( \hbar \omega_0 = 0.7905 \), and the first-order energy difference is \( \hbar \omega_1 = 0.0081 \), leading to a predicted wavelength \( \lambda = 570.51 \text{ Å} \) for the transition, in reasonably good agreement with the measured wavelength \( \lambda_{\text{exp}} = 584.33 \text{ Å} \). The calculated matrix elements in length- and velocity-form are identical if the lowest-order energy is used in the calculation, but differ if the more accurate energy \( \hbar (\omega_0 + \omega_1) = 0.7986 \) is used. We find that \( \langle 1s || r || 2p \rangle_I = 0.561 \) compared with \( \langle 1s || r || 2p \rangle_v = 0.555 \). The calculated line strength is \( S_{E1} = 0.629 \) compared to the exact value \( S_{E1}^{\text{exact}} = 0.5313 \), while the oscillator strength is \( f = 0.335 \) compared to the exact result \( f^{\text{exact}} = 0.2762 \). Finally, the value of the Einstein A-coefficient from the approximate calculation is \( A = 22.9 \times 10^8 \text{ s}^{-1} \) compared to the exact value \( A^{\text{exact}} = 17.99 \times 10^8 \text{ s}^{-1} \). The exact values given here are from a recent relativistic all-order calculation by Plante. Generally, a simpler nonrelativistic calculation suffices to give an understanding of the transition probabilities in two-electron systems at the level of 10-20%. In Table 5.3, we give results of calculations of wavelengths and oscillator strengths for transitions from \( n^1P \) states to the \( 1^1S \) ground state and the \( 2^1S \) excited states in two-electron ions with \( Z \) ranging from 2 to 10. The calculations are of the type described above. The accuracy of the approximate calculations gradually improves along the isoelectronic sequence. At \( Z = 10 \) the tabulated values are accurate at the 1-2% level. The oscillator strengths are plotted against \( Z \) in Fig 5.3.
Table 5.3: Wavelengths and oscillator strengths for transitions in heliumlike ions calculated in a central potential $v_0(1s, r)$. Wavelengths are determined using first-order energies.

<table>
<thead>
<tr>
<th>Z</th>
<th>$\lambda$(Å)</th>
<th>f</th>
<th>$\lambda$(Å)</th>
<th>f</th>
<th>$\lambda$(Å)</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>570.5</td>
<td>0.335</td>
<td>527.3</td>
<td>0.086</td>
<td>513.5</td>
<td>0.035</td>
</tr>
<tr>
<td>3</td>
<td>197.4</td>
<td>0.528</td>
<td>177.0</td>
<td>0.121</td>
<td>170.7</td>
<td>0.047</td>
</tr>
<tr>
<td>4</td>
<td>99.8</td>
<td>0.615</td>
<td>88.1</td>
<td>0.134</td>
<td>84.6</td>
<td>0.051</td>
</tr>
<tr>
<td>5</td>
<td>60.1</td>
<td>0.664</td>
<td>52.6</td>
<td>0.140</td>
<td>50.4</td>
<td>0.053</td>
</tr>
<tr>
<td>6</td>
<td>40.2</td>
<td>0.695</td>
<td>34.9</td>
<td>0.144</td>
<td>33.4</td>
<td>0.054</td>
</tr>
<tr>
<td>7</td>
<td>28.8</td>
<td>0.717</td>
<td>24.9</td>
<td>0.147</td>
<td>23.8</td>
<td>0.055</td>
</tr>
<tr>
<td>8</td>
<td>21.6</td>
<td>0.732</td>
<td>18.6</td>
<td>0.148</td>
<td>17.8</td>
<td>0.055</td>
</tr>
<tr>
<td>9</td>
<td>16.8</td>
<td>0.744</td>
<td>14.5</td>
<td>0.150</td>
<td>13.8</td>
<td>0.056</td>
</tr>
<tr>
<td>10</td>
<td>13.4</td>
<td>0.754</td>
<td>11.6</td>
<td>0.151</td>
<td>11.0</td>
<td>0.056</td>
</tr>
</tbody>
</table>

| 2  | 27744.0       | 0.248 | 3731.2        | 0.121 | 3072.5        | 0.042 |
| 3  | 10651.8       | 0.176 | 1473.7        | 0.194 | 1128.0        | 0.058 |
| 4  | 6483.9        | 0.133 | 673.7         | 0.255 | 511.3         | 0.071 |
| 5  | 4646.6        | 0.106 | 385.3         | 0.292 | 291.0         | 0.078 |
| 6  | 3617.4        | 0.088 | 249.3         | 0.316 | 187.6         | 0.083 |
| 7  | 2960.5        | 0.075 | 174.4         | 0.334 | 131.0         | 0.086 |
| 8  | 2505.1        | 0.065 | 128.9         | 0.347 | 96.6          | 0.088 |
| 9  | 2170.9        | 0.058 | 99.1          | 0.357 | 74.2          | 0.090 |
| 10 | 1915.3        | 0.052 | 78.6          | 0.365 | 58.8          | 0.092 |

| 2  | 10039.4       | 0.685 | 5568.2        | 0.081 | 4332.4        | 0.030 |
| 3  | 5292.1        | 0.355 | 1179.9        | 0.242 | 932.1         | 0.070 |
| 4  | 3642.8        | 0.236 | 577.6         | 0.297 | 448.1         | 0.081 |
| 5  | 2786.5        | 0.176 | 342.5         | 0.328 | 263.1         | 0.087 |
| 6  | 2258.9        | 0.140 | 226.6         | 0.348 | 172.9         | 0.090 |
| 7  | 1900.2        | 0.116 | 161.0         | 0.362 | 122.3         | 0.092 |
| 8  | 1640.3        | 0.100 | 120.3         | 0.372 | 91.1          | 0.094 |
| 9  | 1443.2        | 0.087 | 93.3          | 0.379 | 70.4          | 0.095 |
| 10 | 1288.4        | 0.077 | 74.4          | 0.385 | 56.1          | 0.096 |
5.3 Theory of Multipole Transitions

In the following paragraphs, we extend and systematize the decomposition of the transition amplitude into electric dipole, magnetic dipole and electric quadrupole components started the previous sections. The transition amplitude for a one-electron atom is

$$T_{ba} = \int d^3 r \psi^\dagger_b \alpha \cdot A(r, \omega) \psi_a,$$  \hspace{1cm} (5.106)

where $A(r, \omega)$ is the transverse-gauge vector potential

$$A(r, \omega) = \hat{\epsilon} e^{i k \cdot r}.$$  \hspace{1cm} (5.107)

As a first step in the multipole decomposition, we expand the vector potential $A(r, \omega)$ in a series of vector spherical harmonics

$$A(r, \omega) = \sum_{JLM} A_{JLM} Y_{JLM}(\hat{r}).$$  \hspace{1cm} (5.107)

The expansion coefficients are, of course, given by

$$A_{JLM} = \int d\Omega (Y_{JLM}(\hat{r}) \cdot \hat{\epsilon}) e^{i k \cdot r}.$$  \hspace{1cm} (5.108)
In this equation and below, vector operators on the left-hand side are understood to be adjoint operators. Using the well-known expansion of a plane wave in terms of spherical Bessel functions \( j_l(\hat{k}r) \),

\[
e^{i\mathbf{k} \cdot \mathbf{r}} = 4\pi \sum_{lm} i^l j_l(\hat{k}r) Y_{lm}^*(\hat{k}) Y_{lm}(\hat{r}),
\]

and carrying out the angular integration in Eq. (5.108), we can rewrite the expansion of the vector potential (5.107) in the form

\[
A(\mathbf{r}, \omega) = 4\pi \sum_{JLM} i^J (\mathbf{Y}_{JLM}(\hat{k}) \cdot \hat{\epsilon}) a_{JLM}(\mathbf{r}), \tag{5.109}
\]

where

\[
a_{JLM}(\mathbf{r}) = j_J(\hat{k}r) Y_{JLM}(\hat{r}). \tag{5.110}
\]

It is more convenient to express this expansion in terms of the vector spherical harmonics \( Y^{(\lambda)}_{JM}(\hat{r}) \) rather than \( Y_{JLM}(\hat{r}) \). This can be accomplished with the aid of the relations

\[
Y_{JJ-1M}(\hat{r}) = \sqrt{\frac{J}{2J+1}} Y_{JM}^{(-1)}(\hat{r}) + \sqrt{\frac{J+1}{2J+1}} Y_{JM}^{(1)}(\hat{r}), \tag{5.111}
\]

\[
Y_{JJM}(\hat{r}) = Y_{JM}^{(0)}(\hat{r}), \tag{5.112}
\]

\[
Y_{JJ+1M}(\hat{r}) = -\sqrt{\frac{J+1}{2J+1}} Y_{JM}^{(-1)}(\hat{r}) + \sqrt{\frac{J}{2J+1}} Y_{JM}^{(1)}(\hat{r}). \tag{5.113}
\]

This transformation leads immediately to the multipole expansion of the vector potential,

\[
A(\mathbf{r}, \omega) = 4\pi \sum_{JLM\lambda} i^{J-\lambda} (\mathbf{Y}^{(\lambda)}_{JM}(\hat{k}) \cdot \hat{\epsilon}) a_{JLM}^{(\lambda)}(\mathbf{r}). \tag{5.114}
\]

The vector functions \( a_{JLM}^{(\lambda)}(\mathbf{r}) \) are referred to as multipole potentials. They are given by

\[
a_{JM}^{(0)}(\mathbf{r}) = a_{JLM}(\mathbf{r}), \tag{5.115}
\]

\[
a_{JM}^{(1)}(\mathbf{r}) = \sqrt{\frac{J+1}{2J+1}} a_{JJ-1M}(\mathbf{r}) - \sqrt{\frac{J}{2J+1}} a_{JJ+1M}(\mathbf{r}). \tag{5.116}
\]

Only terms with \( \lambda = 0 \) and \( \lambda = 1 \) contribute to the multipole expansion (5.114), since \( Y_{JM}^{(-1)}(\hat{k}) = \hat{k} Y_{JM}(\hat{k}) \) is orthogonal to \( \hat{\epsilon} \). The multipole potentials satisfy the Helmholtz equation

\[
\nabla^2 a_{JM}^{(\lambda)} + k^2 a_{JM}^{(\lambda)} = 0, \tag{5.117}
\]

and the transversality condition

\[
\nabla \cdot a_{JM}^{(\lambda)} = 0. \tag{5.118}
\]
The multipole potentials with $\lambda = 0$ are the *magnetic* multipole potentials and those with $\lambda = 1$ are the *electric* multipole potentials. The interaction $\alpha \cdot a^{(\lambda)}_{J M}$ is an irreducible tensor operator of rank $J$. The parity of the multipole potential $a^{(\lambda)}_{J M}(r)$ is $(-1)^{J+1-\lambda}$. It should be noted that in the multipole expansion, all information concerning the photon’s polarization and its propagation direction is contained in the expansion coefficient.

With the aid of Eqs.(5.111-5.113), and the following well-known identities among spherical Bessel functions,

$$j_{n-1}(z) = \frac{n+1}{z} j_n(z) + j'_n(z), \quad (5.119)$$

$$j_{n+1}(z) = \frac{n}{z} j_n(z) - j'_n(z), \quad (5.120)$$

where

$$j'_n(z) = \frac{d}{dz} j_n(z),$$

the multipole potentials $a^{(\lambda)}_{J M}(r)$ can be put in the form

$$a^{(0)}_{J M}(r) = j_J(kr) Y^{(0)}_{J M}(\hat{r}), \quad (5.121)$$

$$a^{(1)}_{J M}(r) = \left[ j'_J(kr) + \frac{j_J(kr)}{kr} \right] Y^{(1)}_{J M}(\hat{r})$$

$$+ \sqrt{J(J+1)} \frac{j_J(kr)}{kr} Y^{(-1)}_{J M}(\hat{r}). \quad (5.122)$$

Let us examine the small $k$ limit in Eqs.(5.121,5.122) for the special case $J = 1$. We find on expanding $j_1(kr) \approx kr/3$,

$$\lim_{k \to 0} a^{(0)}_{1 m}(r) = \frac{kr}{3} Y^{(0)}_{1 m}(\hat{r}) = -i \sqrt{\frac{3}{8\pi}} \frac{k}{3} [r \times \xi_m]$$

$$\lim_{k \to 0} a^{(1)}_{1 m}(r) = \frac{2}{3} Y^{(1)}_{1 m}(\hat{r}) + \sqrt{\frac{3}{8\pi}} \frac{2}{3} Y^{(-1)}_{1 m}(\hat{r}) = \frac{2}{3} \frac{2}{3 \xi_m},$$

where $\xi_m$ are the three unit spherical basis vectors. With the aid of the Pauli approximation, we can easily show that nonrelativistically the $J = 1$ transition operators take the limiting forms

$$\alpha \cdot a^{(0)}_{1 m}(r) \to \frac{2}{3} \sqrt{\frac{3}{8\pi}} \frac{ik}{2mc} (L + 2S) \cdot \xi_m$$

$$\alpha \cdot a^{(1)}_{1 m}(r) \to \frac{2}{3} \sqrt{\frac{3}{8\pi}} \frac{1}{c} (v \cdot \xi_m).$$

Thus, the $J = 1$ components of relativistic multipole operators introduced here are, up to a factor, the *velocity form* of the magnetic and electric dipole operators. We therefore refer to the transverse-gauge operators as velocity-form operators. Later, we will show how to recover the corresponding length-form operators.
The multipole expansion of the vector potential (5.114) leads to a corresponding multipole expansion of the transition operator

\[ T_{ba} = 4\pi \sum_{J M \lambda} i^{J-\lambda} |Y^{(\lambda)}_{J M}(\hat{k}) \cdot \hat{\epsilon}| [T^{(\lambda)}_{J M}]_{ba}, \tag{5.123} \]

where

\[ [T^{(\lambda)}_{J M}]_{ba} = \int d^3r \psi^\dagger_b \mathbf{a}_{J M}(r) \psi_a. \tag{5.124} \]

To obtain the transition probability, we must square the amplitude, sum over polarization states, and integrate over photon directions. On squaring the amplitude, we encounter terms of the form

\[ [Y^{(\lambda)}_{J M}(\hat{k}) \cdot \hat{\epsilon}_\nu] [\hat{\epsilon}_\nu \cdot Y^{(\lambda')}_{J M'}(\hat{k})], \tag{5.125} \]

to be summed over polarization directions \( \hat{\epsilon}_\nu \). Using the fact that the vector spherical harmonics with \( \lambda = 0, 1 \) are orthogonal to \( \hat{k} \), the polarization sum becomes

\[ \sum_\nu [Y^{(\lambda)}_{J M}(\hat{k}) \cdot \hat{\epsilon}_\nu] [\hat{\epsilon}_\nu \cdot Y^{(\lambda')}_{J M'}(\hat{k})] = [Y^{(\lambda)}_{J M}(\hat{k}) \cdot Y^{(\lambda')}_{J M'}(\hat{k})]. \tag{5.126} \]

This expression is easily integrated over photon directions leading to

\[ \int d\Omega_k [Y^{(\lambda)}_{J M}(\hat{k}) \cdot Y^{(\lambda')}_{J M'}(\hat{k})] = \delta_{J J'} \delta_{M M'} \delta_{\lambda \lambda'}. \tag{5.127} \]

We therefore obtain for the transition rate

\[ w_{ba} = \frac{\alpha}{2\pi} \omega \sum_\nu \int d\Omega_k |T^{(\lambda)}_{ba}|^2 = 8\pi \alpha \omega \sum_{J M \lambda} |[T^{(\lambda)}_{J M}]_{ba}|^2. \tag{5.128} \]

We see that the rate is an incoherent sum of all possible multipoles. Angular momentum selection rules, of course, limit the type and number of multipoles that contribute to the sum.

As shown previously in Sec. 5.2.5, a gauge transformation leaves single-particle amplitudes invariant, provided the energy difference between the initial and final states equals the energy carried off by the photon. The transformed multipole potential can be written

\[ \mathbf{a}^{(\lambda)}_{J M}(r) \rightarrow \mathbf{a}^{(\lambda)}_{J M}(r) + \nabla \chi_{J M}(r), \]

\[ \phi_{J M}(r) \rightarrow i\omega \chi_{J M}(r), \]

where the gauge function \( \chi_{J M}(r) \) is a solution to the Helmholtz equation. We choose the gauge function to be

\[ \chi_{J M}(r) = -\frac{1}{k} \sqrt{\frac{J+1}{J}} j_J(kr) Y_{J M}(\hat{r}), \]
to cancel the lowest-order (in powers of \(kr\)) contribution to the interaction. The resulting transformation has no effect on the magnetic multipoles, but transforms electric multipole potentials to the form

\[
\mathbf{a}^{(1)}_{JM}(r) = -j_{J+1}(kr) \left[ Y_{JM}(\hat{r}) - \sqrt{\frac{J+1}{J}} Y_{J-1}(\hat{r}) \right],
\]

\[
\phi^{(1)}_{JM}(kr) = -ic \sqrt{\frac{J+1}{J}} j_J(kr) Y_{JM}(\hat{r}).
\] (5.129)

The resulting potentials reduce to the length-form multipole potentials in the nonrelativistic limit. We refer to this choice of gauge as the length-gauge in the sequel. Let us examine the nonrelativistic limit of the length-gauge transition operator

\[
\mathbf{\alpha} \cdot \mathbf{a}^{(1)}_{JM}(r) - \frac{1}{c} \phi_{JM}(r).
\]

Since the vector potential contribution is smaller than the scalar potential by terms of order \(kr\), the interaction can be approximated for small values of \(kr\) by

\[
\lim_{k \to 0} \left[ \mathbf{\alpha} \cdot \mathbf{a}^{(1)}_{JM}(r) - \frac{1}{c} \phi_{JM}(r) \right] = i \sqrt{\frac{(2J+1)(J+1)}{4\pi J}} \frac{k'^J}{(2J+1)!!} Q_{JM}(r),
\]

where

\[
Q_{JM}(r) = r^J C_{JM}(\hat{r})
\]

is the electric \(J\)-pole moment operator in a spherical basis.

In either gauge, the multipole-interaction can be written in terms of a dimensionless multipole-transition operator \(t_{JM}^{(\lambda)}(r)\) defined by

\[
\left[ \mathbf{\alpha} \cdot \mathbf{a}^{(\lambda)}_{JM}(r) - \frac{1}{c} \phi_{JM}(r) \right] = i \sqrt{\frac{(2J+1)(J+1)}{4\pi J}} t_{JM}^{(\lambda)}(r).
\] (5.130)

The one-electron reduced matrix elements \(\langle i || t_{JM}^{(\lambda)} || j \rangle\) are given by **Transverse Gauge:**

\[
\langle \kappa_i || t_{JM}^{(0)} || \kappa_j \rangle = \langle -\kappa_i || C_{JM} || \kappa_j \rangle \int_0^\infty dr \frac{\kappa_i + \kappa_j}{J+1} [P_i(r)Q_j(r) + Q_i(r)P_j(r)],
\]

\[
\langle \kappa_i || t_{JM}^{(1)} || \kappa_j \rangle = \langle \kappa_i || C_{JM} || \kappa_j \rangle \int_0^\infty dr \left\{ -\frac{\kappa_i - \kappa_j}{J+1} \left[ j'_j(kr) + \frac{j_J(kr)}{kr} \right] \times \right.
\]

\[
\left. [P_i(r)Q_j(r) + Q_i(r)P_j(r)] + J \frac{j_J(kr)}{kr} [P_i(r)Q_j(r) - Q_i(r)P_j(r)] \right\},
\]

and
Length Gauge:

\[
\langle \kappa_i | t_j^{(1)} | \kappa_j \rangle = \langle \kappa_i | C_J | \kappa_j \rangle \int_0^\infty \, dr \left\{ j_j (kr) [P_i (r) P_j (r) + Q_i (r) Q_j (r)] + j_{j+1} (kr) \left[ \frac{\kappa_i - \kappa_j}{J+1} [P_i (r) Q_j (r) + Q_i (r) P_j (r)] + [P_i (r) Q_j (r) - Q_i (r) P_j (r)] \right] \right\}.
\]

The functions \( P_i (r) \) and \( Q_i (r) \) in the above equations are the large and small components, respectively, of the radial Dirac wave functions for the orbital with quantum numbers \((n_i, \kappa_i)\).

The multipole-transition operators \( t_j^{(\lambda)} (r) \) are related to the frequency-dependent multipole-moment operators \( q_j^{(\lambda)} (r, \omega) \) by

\[
q_j^{(\lambda)} (r, \omega) = \frac{(2J + 1)!!}{k^J} t_j^{(\lambda)} (r).
\]

Both the transition operators and the multipole-moment operators are irreducible tensor operators. For a many-body system, the multipole-transition operators are given by

\[
T_{jM}^{(\lambda)} = \sum_{ij} (t_{jM})_{ij} a_i^\dagger a_j,
\]

\[
Q_{jM}^{(\lambda)} = \sum_{ij} (q_{jM})_{ij} a_i^\dagger a_j,
\]

where \((t_{jM})_{ij} = \langle i | t_j^{(\lambda)} (r) | j \rangle\) and \((q_{jM})_{ij} = \langle i | q_j^{(\lambda)} (r, \omega) | j \rangle\).

The Einstein \( A \)-coefficient, giving the probability per unit time for emission of a photon with multipolarity \((J\lambda)\) from a state \( I \) with angular momentum \( J_I \), to a state \( F \) with angular momentum \( J_F \), is

\[
A_j^{(\lambda)} = 2\alpha \omega \frac{[J]}{[J_I]} \frac{J + 1}{J} |\langle F | T_j^{(\lambda)} | I \rangle|^2 = \frac{(2J + 2)(2J + 1) k^{2J+1}}{J [(2J + 1)!!]^2} \frac{|\langle F | Q_j^{(\lambda)} | I \rangle|^2}{[J_I]},
\]

where \([J_I] = 2J_I + 1\). This equation leads to the familiar expressions

\[
A_1^{(1)} = \frac{4k^3 |\langle F | Q_1 | I \rangle|^2}{3 [J_I]},
\]

\[
A_2^{(2)} = \frac{k^5 |\langle F | Q_2 | I \rangle|^2}{15 [J_I]},
\]

for electric dipole and quadrupole transitions, where

\[
Q_{jM} = Q_{jM}^{(1)}.
\]

For magnetic multipole transitions, we factor an additional \( \alpha / 2 \) from the frequency-dependent multipole moment operator \( Q_j^{(0)} \) and define

\[
M_{jM} = 2\alpha Q_{jM}^{(0)},
\]
to facilitate comparison with the previous nonrelativistic theory. The Einstein $A$-coefficient for magnetic-dipole radiation may thus be written

$$A_1^{(0)} = \frac{k^3}{3c^2} \frac{|\langle F||M_1||I \rangle|^2}{|J_I|}.$$ 

(5.133)
Chapter 6

Introduction to MBPT

In this chapter, we take the first step beyond the independent-particle approximation and study the effects of electron correlation in atoms. One of the simplest and most direct methods for treating correlation is many-body perturbation theory (MBPT). In this chapter, we consider first-order MBPT corrections to the many-body wave functions and second-order corrections to the energy, where the terms first-order and second-order refer to powers of the interaction potential.

We retain the notation of Chap. 4 and write the many-electron Hamiltonian $H = H_0 + V_I$ in normally-ordered form,

\begin{align*}
H_0 &= \sum_i \epsilon_i a_i^\dagger a_i, \\
V_I &= V_0 + V_1 + V_2, \\
V_0 &= \sum_a \left( \frac{1}{2} V_{HF} - U \right)_{aa}, \\
V_1 &= \sum_{ij} (\Delta V)_{ij} \ : a_i^\dagger a_j : , \\
V_2 &= \frac{1}{2} \sum_{ijkl} g_{ijkl} \ : a_i^\dagger a_j^\dagger a_k a_l : ,
\end{align*}

where $(\Delta V)_{ij} = (V_{HF} - U)_{ij}$ with $(V_{HF})_{ij} = \sum_b (g_{ibjb} - g_{ibbj})$. The normal ordering here is with respect to a suitably chosen closed-shell reference state $|O_c\rangle = a_n^\dagger a_{n-1}^\dagger \cdots a_0^\dagger |0\rangle$. If we are considering correlation corrections to a closed-shell atom, then the reference state is chosen to be the ground-state wave function for the closed-shell atom. Similarly, if we wish to treat correlation corrections to states in atoms with one- or two-electrons beyond a closed-shell ion, the reference state is chosen to be the ground-state of that ion.

We let $\Psi$ be an exact eigenstate of the many-body Hamiltonian $H$ and let $E$ be the corresponding eigenvalue. We decompose $\Psi$ into an unperturbed wave function $\Psi_0$ satisfying

\[ H_0 \Psi_0 = E_0 \Psi_0 , \]
CHAPTER 6. INTRODUCTION TO MBPT

and a perturbation $\Delta \Psi$. For those examples considered in this chapter, the state $\Psi_0$ is nondegenerate. The wave function $\Psi$ is normalized using the intermediate normalization condition $\langle \Psi_0 | \Psi \rangle = 1$. Setting $\Psi = \Psi_0 + \Delta \Psi$ and $E = E_0 + \Delta E$, we may rewrite the Schrödinger equation in the form

$$ (H_0 - E_0) \Delta \Psi = (\Delta E - V_I) \Psi. \quad (6.7) $$

From this equation, it follows (with the aid of the intermediate normalization condition) that

$$ \Delta E = \langle \Psi_0 | V_I | \Psi_0 \rangle. \quad (6.8) $$

It is often convenient to work with operators that map the unperturbed wave function $\Psi_0$ onto $\Psi$ or $\Delta \Psi$ rather than the wave functions $\Psi$ or $\Delta \Psi$ themselves. The wave operator $\Omega$ is the operator that maps the unperturbed wave function onto the exact wave function

$$ \Psi = \Omega \Psi_0, \quad (6.9) $$

and the correlation operator $\chi = \Omega^2 - 1$ is the operator that maps $\Psi_0$ onto $\Delta \Psi$,

$$ \Delta \Psi = \chi \Psi_0. \quad (6.10) $$

It follows from (6.8) that

$$ \Delta E = \langle \Psi_0 | V_I \Omega | \Psi_0 \rangle = \langle \Psi_0 | V_I | \Psi_0 \rangle + \langle \Psi_0 | V_I \chi | \Psi_0 \rangle. \quad (6.11) $$

The operator $V_{\text{eff}} = V_I \Omega$ is an effective potential, in the sense that

$$ \Delta E = \langle \Psi_0 | V_{\text{eff}} | \Psi_0 \rangle. \quad (6.12) $$

We expand both $\Delta \Psi$ and $\Delta E$ in powers of $V_I$,

$$ \Delta \Psi = \Psi^{(1)} + \Psi^{(2)} + \cdots, \quad (6.13) $$

$$ \Delta E = E^{(1)} + E^{(2)} + \cdots. \quad (6.14) $$

The Schrödinger equation (6.7) then leads to an hierarchy of inhomogeneous equations

$$ (H_0 - E_0) \Psi^{(1)} = (E^{(1)} - V_I) \Psi_0, \quad (6.15) $$

$$ (H_0 - E_0) \Psi^{(2)} = (E^{(1)} - V_I) \Psi^{(1)} + E^{(1)} \Psi_0, \quad (6.16) $$

$$ (H_0 - E_0) \Psi^{(3)} = (E^{(1)} - V_I) \Psi^{(2)} + E^{(2)} \Psi^{(1)} + E^{(3)} \Psi_0, \quad \cdots \quad (6.17) $$

We consider the solution to these equations for several simple cases in the following sections.

### 6.1 Closed-Shell Atoms

In this section, we work out the lowest-order correlation corrections to the wave function and energy for a closed-shell atom. We take the lowest-order wave
function $\Psi_0$ to be the reference wave function $|O_c\rangle$. The lowest-order energy is then $E_0 = \sum_a \epsilon_a$, where the sum extends over all occupied core states. For a closed-shell atom, the reference state is the unique solution to Eq.(6.6).

Equation (6.15) has a non-trivial solution only if the right-hand side is orthogonal to the solution to the homogeneous equation. This implies that

$$E^{(1)} = \langle \Psi_0 | V_I | \Psi_0 \rangle = \langle O_c | V_I | O_c \rangle = V_0.$$  

(6.18)

Thus, the solvability condition leads to the previously derived expression for the sum of the lowest- and first-order energy,

$$E_0 + E^{(1)} = \sum_a \left( \epsilon_a + \frac{1}{2} (V_{HF})_{aa} - U_{aa} \right) = \sum_a I_a + \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}),$$  

(6.19)

where $I_a = \langle a | h - U | a \rangle$ is the one-particle matrix element of the sum of single-particle kinetic energy and electron-nucleus potential energy. We see that the sum of the lowest- and first-order energies is just the expectation value of the many-body Hamiltonian evaluated using the independent-particle many-body wave function. Indeed, to obtain Hartree-Fock wave functions in Chapter III, we minimized this sum treated as a functional of single-particle orbitals $\phi_a(r)$.

Since $E^{(1)} = V_0$, the right-hand side of Eq.(6.15) can be simplified, leading to

$$(H_0 - E_0) \Psi^{(1)} = -V_1 \Psi_0 - V_2 \Psi_0$$

$$= \left[ -\sum_{na} (\Delta V)_{na} a_n^\dagger a_a - \frac{1}{2} \sum_{mnab} g_{mnab} a_m^\dagger a_n^\dagger a_b a_a \right] |O_c\rangle.$$  

(6.20)

Here we have taken advantage of the normal ordering in $V_1$ and $V_2$ and retained only the nonvanishing core ($a_a$ or $a_b$) annihilation operators and excited state ($a_n$ or $a_n^\dagger$) creation operators in the sums. (As in previous chapters, we denote core orbitals by subscripts $a, b, \ldots$ at the beginning of the alphabet and designate excited orbitals by letters $m, n, \ldots$ in the middle of the alphabet.) The general solution to Eq.(6.15) is the sum of a particular solution to the inhomogeneous equation and the general solution to the homogeneous equation. The intermediate normalization condition implies that the perturbed wave function $\Psi^{(1)}$ is orthogonal to $\Psi_0$. We therefore seek a solution to (6.15) that is orthogonal to $\Psi_0$. From an examination of the right-hand side of the inhomogeneous equation, we are led to write $\Psi^{(1)} = \chi^{(1)} \Psi_0$, where the first-order correlation operator $\chi^{(1)}$ is a linear combination of one-particle–one-hole operators $a_n^\dagger a_a$ and two-particle–two-hole operators $a_m^\dagger a_n^\dagger a_b a_a$,

$$\chi^{(1)} = \sum_{an} \chi_{na}^{(1)} a_n^\dagger a_a + \sum_{mnab} \chi_{mnab}^{(1)} a_m^\dagger a_n^\dagger a_b a_a.$$  

(6.21)

The first-order wave function is, in other words, constructed as a linear combination of particle-hole excited states and two-particle–two-hole excited states.
Substituting this ansatz into Eq.(6.20), we obtain

$$\left[ \sum_{an} (\epsilon_n - \epsilon_a) \chi_{na}^{(1)} a_n^\dagger a_a + \sum_{mnab} (\epsilon_m + \epsilon_n - \epsilon_a - \epsilon_b) \chi_{mnab}^{(1)} a_m^\dagger a_n^\dagger a_b a_a \right] |O_c\rangle$$

$$= \left[ - \sum_{na} (\Delta V)_{na} a_n^\dagger a_a - \frac{1}{2} \sum_{mnab} g_{mnab} a_m^\dagger a_n^\dagger a_b a_a \right] |O_c\rangle .$$  \hspace{1cm} (6.22)

Identifying coefficients of the particle-hole and two-particle–two-hole operators on the left and right of this equation, we find

$$\chi_{na}^{(1)} = - \frac{(\Delta V)_{na}}{\epsilon_n - \epsilon_a} ,$$  \hspace{1cm} (6.23)

$$\chi_{mnab}^{(1)} = - \frac{1}{2} \frac{g_{mnab}}{\epsilon_m + \epsilon_n - \epsilon_a - \epsilon_b} .$$  \hspace{1cm} (6.24)

Using these expansion coefficients, we can reconstruct the first-order correlation operator \( \chi^{(1)} \) from Eq.(6.21). Then, using \( \Psi^{(1)} = \chi^{(1)} \Psi_0 \), we have the first-order wave function.

According to Eq.(6.8), the second-order energy is

$$E^{(2)} = \langle \Psi_0 | V_I | \Psi^{(1)} \rangle = \langle \Psi_0 | V_I \chi^{(1)} | \Psi_0 \rangle .$$ \hspace{1cm} (6.25)

Substituting the expansion for \( \chi^{(1)} \), we find

$$E^{(2)} = \langle O_c | \left[ V_0 + \sum_{ij} (\Delta V)_{ij} : a_i^\dagger a_j : + \frac{1}{2} \sum_{ijkl} g_{ijkl} : a_i^\dagger a_j^\dagger a_l^\dagger a_k : \right] \times$$

$$\left[ \sum_{na} \chi_{na}^{(1)} a_n^\dagger a_a + \sum_{mnab} \chi_{mnab}^{(1)} a_m^\dagger a_n^\dagger a_b a_a \right] |O_c\rangle .$$ \hspace{1cm} (6.26)

Using Wick’s theorem to evaluate the matrix elements of products of creation and annihilation operators, we obtain

$$E^{(2)} = \sum_{na} (\Delta V)_{an} \chi_{na}^{(1)} + \sum_{mnab} \tilde{g}_{abmn} \chi_{mnab}^{(1)}$$

$$= - \sum_{na} \frac{(\Delta V)_{an}(\Delta V)_{na}}{\epsilon_n - \epsilon_a} - \frac{1}{2} \sum_{mnab} \tilde{g}_{abmn} g_{mnab} .$$ \hspace{1cm} (6.27)

To evaluate the second-order correction to the energy, it is necessary to carry out the sum over magnetic substates and evaluate the resulting multiple sums over the remaining quantum numbers numerically.

### 6.1.1 Angular Momentum Reduction

The sum over magnetic quantum numbers for the one-particle–one-hole contribution to the correlation energy is elementary. Since \( \Delta V \) in Eq. (6.27) is a
6.1. CLOSED-SHELL ATOMS

Scalar, it follows that \( l_n = l_a, m_n = m_a, \) and \( \mu_n = \mu_a. \) The sum over magnetic substates can be carried out leaving a sum over all occupied subshells \( a = (n_a, l_a) \) and those excited orbitals \( n = (n_n, l_n) \) having \( l_n = l_a, \)

\[
E_1^{(2)} = - \sum_{n_a} 2[l_a] \frac{(\Delta V)_{an}(\Delta V)_{na}}{\epsilon_n - \epsilon_a},
\]

(6.28)

with

\[
(\Delta V)_{an} = \sum_b 2[l_b] \left[ R_0(a, b, n, b) - \sum_k \Lambda_{l_b k} R_k(a, b, b, n) \right] - U_{an}.
\]

The corresponding formulas in the relativistic case are the same with \( 2[l_a] \) replaced by \( [j_a] \) and \( \Lambda_{l_b k} \) replaced by \( \Lambda_{\kappa_a \kappa_b} \).

The sum over magnetic substates is more difficult for the \( g_{abmn} \tilde{g}_{mnab} \) term. As a first step, we separate out the dependence on magnetic quantum numbers of the Coulomb matrix element using

\[
g_{mnab} = \sum_k \frac{l_m m_n}{l_m b_a} + \delta_{\mu_a \mu_m} \delta_{\mu_b \mu_n} X_k(mnab),
\]

(6.29)

where

\[
X_k(mnab) = (-1)^k \langle t_m || C_k || l_a \rangle \langle l_n || C_l || l_b \rangle R_k(mnab).
\]

(6.30)

Next, we consider the sum over magnetic quantum numbers of the product,

\[
\sum_{m'} \frac{l_{m'} m_a}{l_{m'} m_n} - \frac{l_{m'} m_n}{l_{m'} m_b} + \frac{l_{m'} m_m}{l_{m'} l_b} = (-1)^{l_m - l_a + l_n - l_b} \frac{1}{[k]} \delta_{k' k},
\]

(6.31)

and the sum of the exchange product,

\[
\sum_{m'} \frac{l_{m'} m_a}{l_{m'} m_n} - \frac{l_{m'} m_n}{l_{m'} m_b} + \frac{l_{m'} m_m}{l_{m'} l_b} = (-1)^{l_m - l_a + l_n - l_b} \left\{ \frac{l_a}{l_b} \frac{l_m}{l_n} \frac{k}{k'} \right\}.
\]

(6.32)

These two terms are combined to give an expression for the two-particle–two-hole contribution to the correlation energy,

\[
E_2^{(2)} = - \sum_k \frac{2}{[k]} \sum_{abmn} \frac{Z_k(mnab)X_k(mnab)}{\epsilon_m + \epsilon_n - \epsilon_b - \epsilon_a},
\]

(6.33)

where

\[
Z_k(mnab) = X_k(mnab) - \frac{1}{2} \sum_{k'} [k] \left\{ \frac{l_a}{l_b} \frac{l_m}{l_n} \frac{k}{k'} \right\} X_k(mnab).
\]

(6.34)
In the relativistic case, the coefficient $2/|k|$ in Eq. (6.33) must be replaced by $1/(2|k|)$ and the coefficient $-1/2$ in the second term of Eq. (6.34) must be replaced by $+1$.

In summary, the (non-relativistic) second-order correlation energy for a closed-shell atom or ion is

$$E^{(2)} = E_1^{(2)} + E_2^{(2)} = -\sum_{l_m=l_n} 2|l_m| \frac{(\Delta V)_{an}(\Delta V)_{na}}{\epsilon_n - \epsilon_a}$$

$$-\sum_k \frac{2}{|k|} \sum_{amnu} Z_k(mnab)X_k(mnab) \frac{\epsilon_m + \epsilon_n - \epsilon_b - \epsilon_a}{\epsilon_{1s}}.$$

(6.35)

If we assume that our basic orbitals $\phi_m$ are obtained in the HF potential of the core, then $(\Delta V)_{aa} = (V_{HF} - U)_{aa} = 0$, and the first term in Eq. (6.35) vanishes. This is an example of a general rule: formulas of MBPT take their simplest form starting from a HF potential.

### 6.1.2 Example: 2nd-order Correlation Energy in Helium

As a simple example, let us evaluate the ground-state correlation energy for helium, starting from the Hartree-Fock approximation. Since the core orbitals $a$ and $b$ are both $1s$ orbitals, one easily shows that the quantities $X_k(abmn)$ vanish unless $l_m = l_n = k$. Furthermore, using the fact that $\langle l || C_l || 0 \rangle = 1$, we find,

$$X_l(1s, 1s, nl, ml) = (-1)^{l} R_l(1s, 1s, nl, ml).$$

Moreover,

$$\left\{ \begin{array}{c} 0 \\ l \\ k \end{array}, \begin{array}{c} 0 \\ l \\ k' \end{array} \right\} = \frac{1}{|l|} \delta_{kl} \delta k' l.$$

Combining these facts, we can rewrite the equation for the second-order correlation energy (6.35) as

$$E^{(2)} = -\sum_{l=0}^{\infty} \frac{1}{|l|} \sum_{mn} \frac{|R_l(1s, 1s, nl, ml)|^2}{\epsilon_{1s} + \epsilon_{ml} - 2\epsilon_{1s}}.$$

(6.36)

We are, therefore, faced with the problem of evaluating an infinite sum over angular momentum states $l$ of terms that are represented here as double sums over principal quantum numbers $m$ and $n$ of squares of Slater integrals divided by energy differences. The formalism is a bit misleading in the sense that, except for the $1s$ state, there are no bound states in the HF potential for helium. The double sums in this case represent double integrals over the continuum. In the following two subsections, we describe a method for evaluating expressions such as this numerically. We will return to this example later in the chapter.
6.2 B-Spline Basis Sets

As an aid to evaluating MBPT expressions for the correlation energy, we introduce discrete basis sets and, thereby, reduce the infinite sums and integrals over the real spectrum to finite sums over a pseudospectrum.

Since correlation corrections in atoms have finite range, we restrict our attention to a finite (but large) cavity of radius $R$. To study the ground-state or low-lying excited states of ions, the radius of this cavity is chosen to be $R \approx 40/Z_{\text{ion}}$ a.u., where $Z_{\text{ion}}$ is the ionic charge. For large cavities, the results of correlation calculations are independent of the cavity radius. We require that the radial wave functions vanish at the origin and at the cavity boundary. The spectrum in the cavity is discrete but infinite.

Next, we expand the solutions to the radial Schrödinger equation in a finite basis. This basis is chosen to be a set of $n$ B-splines of order $k$. Following deBoor (1978), we divide the interval $[0, R]$ into segments. The endpoints of these segments are given by the knot sequence $\{t_i\}, i = 1, 2, \cdots, n + k$. The B-splines of order $k$, $B_{i,k}(r)$, on this knot sequence are defined recursively by

$$B_{i,1}(r) = \begin{cases} 1, & t_i \leq r < t_{i+1}, \\ 0, & \text{otherwise} \end{cases} \quad (6.37)$$

and

$$B_{i,k}(r) = \frac{r - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(r) + \frac{t_{i+k} - r}{t_{i+k} - t_{i+1}} B_{i+1,k-1}(r). \quad (6.38)$$

The function $B_{i,k}(r)$ is a piecewise polynomial of degree $k - 1$ inside the interval $t_i \leq r < t_{i+k}$ and $B_{i,k}(r)$ vanishes outside this interval. The knots defining our grid have k-fold multiplicity at the endpoints 0 and $R$; i.e. $t_1 = t_2 = \cdots = t_k = 0$ and $t_{n+1} = t_{n+2} = \cdots = t_{n+k} = R$. The knots $t_{k+1}, t_{k+2}, \cdots, t_n$ are distributed on an exponential scale between 0 and $R$. In Fig. 6.1, we show 30 B-splines of order $k$ covering the interval $r = 0 - 40$ a.u. This set of B-splines could be used as a basis set for expanding radial wave functions.

The set of B-splines of order $k$ on the knot sequence $\{t_i\}$ forms a complete basis for piecewise polynomials of degree $k - 1$ on the interval spanned by the knot sequence. We represent the solution to the radial Schrödinger equation as a linear combination of these B-splines and we work with the B-spline representation of the wave functions rather than the wave functions themselves.

The radial Schrödinger wave function $P_l(r)$ satisfies the variational equation

$$\delta S = 0,$$

where

$$S = \int_0^R \left\{ \frac{1}{2} \left( \frac{dP_l}{dr} \right)^2 + \left( \frac{1}{2} \frac{l(l+1)}{r^2} \right) P_l(r)^2 \right\} - \frac{1}{2} \epsilon \int_0^R P_l(r)^2 dr. \quad (6.39)$$

The parameter $\epsilon$ is a Lagrange multiplier introduced to insure that the normalization constraint

$$\int_0^R P_l(r)^2 dr = 1, \quad (6.40)$$
is satisfied. The variational principle $\delta S = 0$, together with the constraints $\delta P_{\kappa}(0) = 0$ and $\delta P_{\kappa}(R) = 0$, leads to the radial Schrödinger equation for $P_l(r)$.

We expand $P_l(r)$ in terms of B-splines of order $k$ as

$$P_l(r) = \sum_{i=1}^{n} p_i B_i(r). \quad (6.41)$$

The subscript $k$ has been omitted from $B_{i,k}(r)$ for notational simplicity. The action $S$ becomes a quadratic function of the expansion coefficients $p_i$ when the expansions are substituted into the action integral. The variational principle then leads to a system of linear equations for the expansion coefficients,

$$\frac{\partial S}{\partial p_i} = 0, \quad i = 1, \cdots, n. \quad (6.42)$$

The resulting equations can be written in the form of an $n \times n$ symmetric generalized eigenvalue equation,

$$Av = \epsilon Bv, \quad (6.43)$$

where $v$ is the vector of expansion coefficients,

$$v = (p_1, p_2, \cdots, p_n). \quad (6.44)$$
6.2. B-SPLINE BASIS SETS

Table 6.1: Eigenvalues of the generalized eigenvalue problem for the B-spline approximation of the radial Schrödinger equation with \( l = 0 \) in a Coulomb potential with \( Z = 2 \). Cavity radius is \( R = 30 \) a.u. We use 40 splines with \( k = 7 \).

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \epsilon_n )</th>
<th>( n )</th>
<th>( \epsilon_n )</th>
<th>( n )</th>
<th>( \epsilon_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2.00000000</td>
<td>11</td>
<td>0.5470886</td>
<td>34</td>
<td>300779.9846480</td>
</tr>
<tr>
<td>2</td>
<td>-0.50000000</td>
<td>12</td>
<td>0.7951813</td>
<td>35</td>
<td>616576.9524036</td>
</tr>
<tr>
<td>3</td>
<td>-0.22222222</td>
<td>13</td>
<td>1.2210506</td>
<td>36</td>
<td>1414036.2030934</td>
</tr>
<tr>
<td>4</td>
<td>-0.1249925</td>
<td>14</td>
<td>2.5121874</td>
<td>37</td>
<td>4074016.5630432</td>
</tr>
<tr>
<td>5</td>
<td>-0.0783858</td>
<td>15</td>
<td>4.9347168</td>
<td>38</td>
<td>20369175.6484520</td>
</tr>
<tr>
<td>6</td>
<td>-0.0379157</td>
<td>16</td>
<td>9.3411933</td>
<td>39</td>
<td>554833327</td>
</tr>
<tr>
<td>7</td>
<td>0.0161116</td>
<td>17</td>
<td>17.2134844</td>
<td>40</td>
<td>973454446</td>
</tr>
</tbody>
</table>

The matrices \( A \) and \( B \) are given by

\[
A_{ij} = \int_0^R \left\{ \frac{1}{2} \frac{dB_i}{dr} \frac{dB_j}{dr} + B_i(r) \left( V(r) + \frac{l(l+1)}{2r^2} \right) B_j(r) \right\} dr, \quad (6.45)
\]

\[
B_{ij} = \int_0^R B_i(r)B_j(r)dr. \quad (6.46)
\]

It should be mentioned that the matrices \( A \) and \( B \) are diagonally dominant banded matrices. The solution to the eigenvalue problem for such matrices is numerically stable. Routines from the LAPACK library (Anderson et al., 1999) can be used to obtain the eigenvalues and eigenvectors numerically.

Solving the generalized eigenvalue equation, one obtains \( n \) real eigenvalues \( \epsilon^\lambda \) and \( n \) eigenvectors \( v^\lambda \). The eigenvectors satisfy the orthogonality relations,

\[
\sum_{i,j} v_i^\lambda B_{ij} v_j^\mu = \delta_{\lambda\mu}, \quad (6.47)
\]

which leads to the orthogonality relations

\[
\int_0^R P^\lambda_l(r)P^\mu_l(r)dr = \delta_{\lambda\mu}, \quad (6.48)
\]

for the corresponding radial wave functions.

The first few eigenvalues and eigenvectors in the cavity agree precisely with the first few bound-state eigenvalues and eigenvectors obtained by numerically integrating the radial Schrödinger equations; but, as the principal quantum number increases, the cavity spectrum departs more and more from the real spectrum. This is illustrated in Table 6.1, where we list the eigenvalues obtained
for $l = 0$ states in a Coulomb potential with $Z = 2$. In this example we use $n = 40$ splines with $k = 7$. In Fig. 6.2, we show the B-spline components of the $2s$ state in a Coulomb potential with $Z = 2$ obtained using $n = 30$ splines of order $k = 6$.

The cavity spectrum is complete in the space of piecewise polynomials of degree $k - 1$ and, therefore, can be used instead of the real spectrum to evaluate correlation corrections to states confined to the cavity. The quality of the numerically generated B-spline spectrum can be tested by using it to evaluate various energy-weighted sum rules, such as the Thomas-Reiche-Kuhn sum rule. It is found (Johnson et al., 1988) that the generalized TRK sum rule is satisfied to parts in $10^7$ using 40 splines of order 7 for a given $l$ and to parts in $10^9$ using 50 splines of order 9.

### 6.3 Hartree-Fock Equation and B-splines

While it is useful to have a finite basis set for the Schrödinger equation in a local potential, it is even more useful to have a basis set for the Hartree-Fock (HF) potential, since in MBPT takes its simplest form when expressed in terms of HF orbitals. One supposes that the HF equations for the occupied orbitals of a closed-shell system have been solved and uses the resulting orbitals to construct the HF potential. Once this potential has been determined, a complete set of single particle orbitals can be constructed. To determine these orbitals using B-splines, it is necessary to modify the potential term in the action integral $S$ and the matrix $A$ in the generalized eigenvalue problem. If we let $V_{HF}$ represent the HF potential, then its contribution to the action integral $S$ for an orbital $a$
6.3. HARTREE-FOCK EQUATION AND B-SPLINES

will be

\[
\int_0^R P_a(r)V_{HF}P_a(r)dr = \sum_b 2[l_b] \left( R_0(abab) - \sum_k \Lambda_{a,k_l b} R_k(abb) \right),
\]

(6.49)

where the sum is over all occupied shells. This contribution to \( S \) leads to the following modification of the potential contribution in the matrix element \( A_{ij} \),

\[
\int_0^R dr B_i(r)V_{HF}B_j(r)
\]

\[
= \int_0^R dr B_i(r) \sum_b 2[l_b] \left\{ v_0(b, b, r)B_j(r)dr - \sum_k \Lambda_{a,k_l b} v_k(b, B_j, r)P_b(r) \right\},
\]

(6.50)

where \( v_l(a, b, r) \) is the usual Hartree screening potential.

To solve the generalized eigenvalue problem in the HF case, we do a preliminary numerical solution of the nonlinear HF equations to determine the occupied orbitals \( P_b(r) \). With the aid of these orbitals, we construct the matrix \( A \) using the above formula. The linear eigenvalue problem can then be solved to give the complete spectrum (occupied and unoccupied) of HF states. With this procedure, the states \( P_b(r) \) are both input to and output from the routine to solve the eigenvalue equation. By comparing the the eigenfunctions of occupied levels obtained as output with the corresponding input levels, one can monitor the accuracy of the solutions to the eigenvalue problem. It should be noted that this consistency check will work only if the cavity radius is large enough so that boundary effects do not influence the occupied levels in the spline spectrum at the desired level of accuracy.

In Table 6.2, we compare low-lying levels for the sodium atom (\( Z = 11 \)) obtained by solving the generalized eigenvalue problem with values obtained by solving the HF equations numerically. The potential used in this calculation is the HF potential of the closed Na\(^+\) core. It is seen that the B-spline eigenvalues of the occupied 1\( s \), 2\( s \) and 2\( p \) levels agree precisely with the corresponding numerical eigenvalues. The B-spline eigenvalues of higher levels depart from the numerical eigenvalues because of cavity boundary effects.

**Example: correlation energy for helium**  
Let us now return to our discussion of the correlation energy of helium. We introduce a cavity of radius \( R = 40 \) a.u. and evaluate the B-spline basis functions for \( l = 1, 10 \). For each value of \( l \), we use \( n = 40 \) splines of order \( k = 6 \) and obtain 38 basis functions. These basis functions can be used to replace the exact spectrum to a high degree of accuracy. We evaluate the partial-wave contributions to the correlation energy,

\[
E_l^{(2)} = -\frac{1}{[l]} \sum_{mn} \left| R_l(1s, 1s, nl, ml) \right|^2 \epsilon_{nl} + \epsilon_{ml} - 2\epsilon_{1s},
\]

(6.51)
CHAPTER 6. INTRODUCTION TO MBPT

Table 6.2: Comparison of the HF eigenvalues from numerical integration of the
HF equations (HF) with those found by solving the HF eigenvalue equation in
a cavity using B-splines (spline). Sodium, Z = 11, in a cavity of radius R = 40
a.u..

<table>
<thead>
<tr>
<th>nl</th>
<th>HF</th>
<th>spline</th>
<th>nl</th>
<th>HF</th>
<th>spline</th>
<th>nl</th>
<th>HF</th>
<th>spline</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>-40.759750</td>
<td>-40.759750</td>
<td>2s</td>
<td>-3.073688</td>
<td>-3.073688</td>
<td>2p</td>
<td>-1.797192</td>
<td>-1.797192</td>
</tr>
<tr>
<td>3s</td>
<td>-0.181801</td>
<td>-0.181801</td>
<td>3p</td>
<td>-0.109438</td>
<td>-0.109438</td>
<td>3d</td>
<td>-0.055667</td>
<td>-0.055667</td>
</tr>
<tr>
<td>4s</td>
<td>-0.070106</td>
<td>-0.070106</td>
<td>4p</td>
<td>-0.050321</td>
<td>-0.050318</td>
<td>4d</td>
<td>-0.031315</td>
<td>-0.031021</td>
</tr>
<tr>
<td>5s</td>
<td>-0.037039</td>
<td>-0.036876</td>
<td>5p</td>
<td>-0.028932</td>
<td>-0.027955</td>
<td>5d</td>
<td>-0.020038</td>
<td>-0.014308</td>
</tr>
<tr>
<td>6s</td>
<td>-0.022871</td>
<td>-0.017983</td>
<td>6p</td>
<td>-0.018783</td>
<td>-0.008656</td>
<td>6d</td>
<td>-0.013912</td>
<td>0.008226</td>
</tr>
<tr>
<td>4f</td>
<td>-0.031250</td>
<td>-0.031157</td>
<td>5f</td>
<td>-0.020000</td>
<td>-0.016573</td>
<td>5g</td>
<td>-0.018710</td>
<td>-0.018710</td>
</tr>
<tr>
<td>6f</td>
<td>-0.013889</td>
<td>0.002628</td>
<td>6g</td>
<td>-0.013889</td>
<td>0.003477</td>
<td>6h</td>
<td>-0.013889</td>
<td>-0.009268</td>
</tr>
</tbody>
</table>

in Eq.(6.36) by summing over the $38 \times 38$ possible basis functions. The resulting
contributions to the correlation energy are tabulated for $l = 0$ to 9 in Table 6.3.
As $l \to \infty$, the partial-wave contributions are known to fall off as

$$E_l^{(2)} \to -\frac{a}{(l+1/2)^2}.$$  

We use this known asymptotic behavior to estimate the remainder from $l = 10$ to $\infty$. The resulting second-order correlation energy for helium is $E^{(2)} = -0.03738$ a.u.. Adding this value to the HF energy $E_{HF} = -2.86168$ a.u., we obtain $E_0 + E^{(1)} + E^{(2)} = -2.89906$ a.u., compared to the experimental value $E_{exp} = -2.903\ldots$ a.u.. The 0.13% difference between the second-order energy and experiment is accounted for by third- and higher-order perturbation theory.

6.4 Atoms with One Valence Electron

Let us now turn to the problem of determining the second-order correlation energy for an atom with one valence electron. For simplicity, we start with a “frozen-core” Hartree-Fock formulation. The unperturbed state of the atom is

$$\Psi_0 = a_v^{|0_v},$$

where $|0_v>$ is the HF core state and the corresponding unperturbed
energy is $E_0 = \sum_a \epsilon_a + \epsilon_v$.

Since $V_1 = \sum_i (\Delta V)_{ij} : a_i^|a_j := 0$ for a HF potential, it follows that the first-order correction to the energy is $E^{(1)} = V_0$. Thus, $E_0 + E^{(1)} = (E_0 + V_0)_{\text{core}} + \epsilon_v$. In other words, there is no first-order correction to the valence removal energy!

This result, of course, depends on the fact that the calculation starts from a
Table 6.3: Contributions to the second-order correlation energy for helium.

<table>
<thead>
<tr>
<th>l</th>
<th>( E_l )</th>
<th>( l )</th>
<th>( E_l )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.013498</td>
<td>5</td>
<td>-0.000168</td>
</tr>
<tr>
<td>1</td>
<td>-0.018980</td>
<td>6</td>
<td>-0.000088</td>
</tr>
<tr>
<td>2</td>
<td>-0.003194</td>
<td>7</td>
<td>-0.000050</td>
</tr>
<tr>
<td>3</td>
<td>-0.000933</td>
<td>8</td>
<td>-0.000031</td>
</tr>
<tr>
<td>4</td>
<td>-0.000362</td>
<td>9</td>
<td>-0.000020</td>
</tr>
<tr>
<td>10</td>
<td>-∞</td>
<td>-∞</td>
<td>-0.000053</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td></td>
<td><strong>-0.037376</strong></td>
</tr>
</tbody>
</table>

frozen-core HF potential. In any other potential, there will be a first-order correction to the energy.

### 6.4.1 Second-Order Energy

Again, since \( V_1 = 0 \), the first-order wave function will contain only double excitations! There are two possibilities, either two core electrons are excited or one core electron and the valence electron are excited. We correspondingly decompose the first-order correlation operator as

\[
\chi^{(1)} = \sum_{abmn} \chi_{mnab}^{(1)} a_m^\dagger a_n^\dagger a_b a_a + \sum_{bmn} \chi_{mnvb}^{(1)} a_m^\dagger a_n^\dagger a_b a_v.
\]

Substituting into Eq. (6.15) and matching terms, we find

\[
\chi_{mnab}^{(1)} = -\frac{1}{2} \frac{g_{mnab}}{\epsilon_m + \epsilon_n - \epsilon_a - \epsilon_b}
\]

\[
\chi_{mnvb}^{(1)} = -\frac{1}{2} \frac{\tilde{g}_{mnvb}}{\epsilon_m + \epsilon_n - \epsilon_v - \epsilon_b}.
\]

The second-order energy is obtained from

\[
E^{(2)} = \langle \Psi_0 | V_2 \chi^{(1)} | \Psi_0 \rangle = \langle 0_c | a_v V_2 \chi^{(1)} a_v^\dagger | 0_c \rangle
\]

\[
= \frac{1}{2} \sum_{ijkl} g_{ijkl} \chi_{mnab}^{(1)} \langle 0_c | a_v : a_i^\dagger a_j^\dagger a_k : a_m^\dagger a_n^\dagger a_a : a_v^\dagger | 0_c \rangle
\]

\[
+ \frac{1}{2} \sum_{ijkl} g_{ijkl} \chi_{mnvb}^{(1)} \langle 0_c | a_v : a_i^\dagger a_j^\dagger a_k : a_m^\dagger a_n^\dagger a_b : | 0_c \rangle.
\]

With the aid of Wick’s theorem, this reduces to

\[
E^{(2)} = \sum_{mnab} \tilde{g}_{mnab} \chi_{mnab}^{(1)} + 2 \sum_{nab} \tilde{g}_{abvn} \chi_{abvn}^{(1)} + \sum_{mnab} \tilde{g}_{vbmn} \chi_{vbmn}^{(1)}.
\]
The first term in this equation is just the second-order correction to the core energy $E^{(2)}_{\text{core}}$, which is the same for all valence states, and which reduces to

$$E^{(2)}_{\text{core}} = -\frac{1}{2} \sum_{mnab} \tilde{g}_{abmn} g_{mnab}. \quad (6.55)$$

This term can be evaluated using the methods given the previous section. The remaining two terms in second-order correlation energy $E^{(2)}_{\text{v}}$ vary from state to state and represent the correlation correction to the energy relative to the core (the negative of the valence-electron removal energy). The valence correlation energy reduces to

$$E^{(2)}_{\text{v}} = \sum_{nab} \tilde{g}_{abvn} g_{vnab} - \sum_{mnb} \tilde{g}_{vbmn} g_{mnvb}. \quad (6.56)$$

### 6.4.2 Angular Momentum Decomposition

To aid in the angular momentum decomposition, we start with an easily proved graphical identity:

$$-\frac{k}{j_a m_a} \frac{j_b m_b}{j_n m_n} = \sum_l [l] \left\{ \begin{array}{ccc} a & m & l \\ b & n & k \end{array} \right\} - \frac{1}{2} \sum_k \left[ k \right] \left\{ \begin{array}{ccc} a & m & l \\ b & n & k \end{array} \right\} X_k(abmn) \delta_{\sigma_m \sigma_a} \delta_{\sigma_n \sigma_b} \right). \quad (6.57)$$

With the aid of this identity, the sum over magnetic quantum numbers in the first term of Eq. (6.56) can be easily carried out giving:

$$\sum_{mnab} \tilde{g}_{abvn} g_{vnab} = \sum_k \frac{2}{[k][v]} Z_k(abvn) X_k(abv), \quad (6.58)$$

where

$$Z_k(abcd) = X_k(abcd) - \frac{1}{2} \sum_l \left[ k \right] \left\{ \begin{array}{ccc} a & c & k \\ b & d & l \end{array} \right\} X_l(abde). \quad (6.59)$$
Table 6.4: Hartree-Fock eigenvalues $\epsilon_v$ with second-order energy corrections $E_v^{(2)}$ are compared with experimental binding energies for a few low-lying states in atoms with one valence electron.

<table>
<thead>
<tr>
<th>Atom</th>
<th>State</th>
<th>$\epsilon_v$</th>
<th>$E_v^{(2)}$</th>
<th>Sum</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2s</td>
<td>-0.19630</td>
<td>-0.00165</td>
<td>-0.19795</td>
<td>-0.19814</td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>-0.12864</td>
<td>-0.00138</td>
<td>-0.13001</td>
<td>-0.13024</td>
</tr>
<tr>
<td>Na</td>
<td>3s</td>
<td>-0.18180</td>
<td>-0.00586</td>
<td>-0.18766</td>
<td>-0.18886</td>
</tr>
<tr>
<td></td>
<td>3p</td>
<td>-0.10944</td>
<td>-0.00178</td>
<td>-0.11122</td>
<td>-0.11155</td>
</tr>
<tr>
<td></td>
<td>3d</td>
<td>-0.05567</td>
<td>-0.00023</td>
<td>-0.05589</td>
<td>-0.05594</td>
</tr>
<tr>
<td>K</td>
<td>4s</td>
<td>-0.14695</td>
<td>-0.01233</td>
<td>-0.15928</td>
<td>-0.15952</td>
</tr>
<tr>
<td></td>
<td>4p</td>
<td>-0.09555</td>
<td>-0.00459</td>
<td>-0.10014</td>
<td>-0.10018</td>
</tr>
<tr>
<td></td>
<td>3d</td>
<td>-0.05812</td>
<td>-0.00282</td>
<td>-0.06093</td>
<td>-0.06139</td>
</tr>
<tr>
<td>Cu</td>
<td>4s</td>
<td>-0.23285</td>
<td>-0.03310</td>
<td>-0.26595</td>
<td>-0.28394</td>
</tr>
<tr>
<td></td>
<td>4p</td>
<td>-0.12286</td>
<td>-0.01154</td>
<td>-0.13441</td>
<td>-0.14406</td>
</tr>
<tr>
<td></td>
<td>4d</td>
<td>-0.05508</td>
<td>-0.00070</td>
<td>-0.05578</td>
<td>-0.05640</td>
</tr>
<tr>
<td>Rb</td>
<td>5s</td>
<td>-0.13720</td>
<td>-0.01454</td>
<td>-0.15174</td>
<td>-0.15351</td>
</tr>
<tr>
<td></td>
<td>5p</td>
<td>-0.09013</td>
<td>-0.00533</td>
<td>-0.09546</td>
<td>-0.09547</td>
</tr>
<tr>
<td></td>
<td>4d</td>
<td>-0.06007</td>
<td>-0.00515</td>
<td>-0.06522</td>
<td>-0.06532</td>
</tr>
</tbody>
</table>

The second term in Eq. (6.56) can be treated similarly leading to the following expression for the second-order energy:

$$E_v^{(2)} = \sum_k \frac{2}{|k||v|} \sum_{abn} Z_k(vnab) X_k(vnab) \frac{\epsilon_v + \epsilon_n - \epsilon_a - \epsilon_b}{\epsilon_v + \epsilon_n - \epsilon_v - \epsilon_b}$$

In Table 6.4, we list the Hartree-Fock eigenvalues and the corresponding second-order corrections obtained from Eq. (6.60) for a few low lying states in light mono-valent atoms. It is seen in every case that the second-order correlation corrections substantially improve the agreement with experiment. For light atoms, second-order MBPT underestimates the correlation corrections. This trend is reversed for heavy alkali-metal atoms such as cesium, where second-order MBPT substantially overestimates the correlation energy.

### 6.4.3 Quasi-Particle Equation and Brueckner-Orbitals

As mentioned earlier, there is no first-order correction to the valence-electron energy $\epsilon_v$. There are, however, second- and higher-order corrections. The second-order correction $E_v^{(2)}$ can be written, according to Eq. (6.56), as the diagonal
matrix element of a non-local operator $\Sigma^{(2)}(\epsilon_v)$, whose matrix elements are given by
\[
\left[\Sigma^{(2)}(\epsilon_v)\right]_{ij} = \sum_{nab} \tilde{g}_{abjn} g_{inab} - \sum_{mnab} \tilde{g}_{bmn} g_{mnb} \epsilon_n + \epsilon_n - \epsilon_b.
\] (6.61)
The operator $\Sigma(\epsilon)$ is referred to as the self-energy operator; the operator $\Sigma^{(2)}(\epsilon)$ is its second-order approximation. The sum of the zeroth- and second-order energy is the diagonal matrix element of $h_0 + V_{HF} + \Sigma^{(2)}(\epsilon_v)$. We are, therefore, led to consider the generalization of the valence-electron Hartree-Fock equation
\[
\left(h_0 + V_{HF} + \Sigma^{(2)}(\epsilon)\right) \psi = \epsilon \psi.
\] (6.62)

This equation is referred to as the quasi-particle equation and its solutions are referred to as (second-order) Brueckner orbitals. The quasi-particle equation describes how the valence orbital is modified by correlation corrections.

One can develop an approximation for $\Sigma^{(2)}(\epsilon)$ in the coordinate representation valid for states large distances. The dominant contribution to the operator arises from the “direct” integral in the second term of Eq. (6.61); the remaining terms are small at large distance. Moreover, the largest contributions are from states $m$ with energies near $\epsilon_v$. Thus,
\[
\Sigma^{(2)}(\epsilon, r, r') \approx -\frac{1}{2} \frac{\alpha_c}{r^4} \delta(r - r'),
\] (6.63)
where we have made use of the completeness of orbitals $\phi_m$. This expression can be expanded for large $r$ to give
\[
\Sigma^{(2)}(\epsilon, r, r') \rightarrow -\frac{1}{2} \frac{\alpha_c}{r^4} \delta(r - r'),
\] (6.63)
where
\[
\alpha_c = \frac{2}{3} \sum_{lnb} \frac{\langle b | r | n \rangle \cdot \langle n | r | b \rangle}{\epsilon_n - \epsilon_b}
\] (6.64)
is the core polarizability. The interpretation of this equation is simple: the valence electron induces a dipole moment in the core and interacts with this induced moment; thus the name self-energy. As an alternative to MBPT, it is possible to describe the effects of the self-energy approximately by adding a phenomenological potential $-\alpha_c/2r^4$ to the HF potential and solving the modified Schrödinger equation. It is worth mentioning that the approximate interaction given in Eq. (6.64) is singular for $ns$ states, so it is necessary to return to the more exact formulation for such states.
6.4. ATOMS WITH ONE VALENCE ELECTRON

Let us now solve Eq. (6.62) perturbatively; neglecting \( \Sigma \) in lowest order. We write \( \psi = \phi_v + \delta \phi_v \) and \( \epsilon = \epsilon_v + \delta \epsilon_v \), where \( \phi_v \) and \( \epsilon_v \) are the HF orbital and eigenvalue for state \( v \). We find that the perturbation \( \delta \phi_v \) satisfies the inhomogeneous equation

\[
(h_0 + V_{HF} - \epsilon_v) \delta \phi_v = \left( \delta \epsilon_v - \Sigma^{(2)}(\epsilon_v) \right) \phi_v.
\]

Since \( \epsilon_v \) is an eigenvalue of the homogeneous equation, the inhomogeneous equation has a solution if, and only if, the right-hand side is orthogonal \( \phi_v \). The solvability condition can be written

\[
\delta \epsilon_v = \langle \phi_v | \Sigma^{(2)}(\epsilon_v) | \phi_v \rangle = \left[ \Sigma^{(2)}(\epsilon_v) \right]_{vv},
\]

which is just the condition that \( \delta \epsilon_v \) be the second-order correlation energy. The solution to (6.65) is then given by

\[
\delta \phi_v(r) = -\sum_{i \neq v} \frac{\delta \epsilon_i \epsilon_v}{\epsilon_i - \epsilon_v} \phi_i(r).
\]

If we let \( P_v(r) \) and \( \delta P_v(r) \) be radial functions associated with \( \phi_v \) and \( \delta \phi_v \), respectively, then the radial probability density is \( \rho_v(r) = P_v^2(r) \) and the perturbed radial probability density is \( \delta \rho_v(r) = 2P_v(r) \delta P_v(r) \). We illustrate these radial densities for the 3s state of sodium in Fig. 6.3. One sees from this figure that the Brueckner correction draws the valence wave function in toward the atomic core, in harmony with the attractive nature of \( \Sigma^{(2)} \).

6.4.4 Monovalent Negative Ions

One interesting application of the quasi-particle equation is the study of negative ions. Consider, for example, a neutral closed-shell atom. The HF potential for
Table 6.5: Expansion coefficients $c_n$, $n = 1 \cdots 20$ of the 5s state of Pd$^-$ in a basis of HF orbitals for neutral Pd confined to a cavity of radius $R = 50$ a.u..

<table>
<thead>
<tr>
<th>$n$</th>
<th>$c_n$</th>
<th>$n$</th>
<th>$c_n$</th>
<th>$n$</th>
<th>$c_n$</th>
<th>$n$</th>
<th>$c_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000001</td>
<td>6</td>
<td>0.556972</td>
<td>11</td>
<td>-0.163415</td>
<td>16</td>
<td>-0.099651</td>
</tr>
<tr>
<td>2</td>
<td>0.000028</td>
<td>7</td>
<td>0.461970</td>
<td>12</td>
<td>-0.132544</td>
<td>17</td>
<td>-0.002016</td>
</tr>
<tr>
<td>3</td>
<td>-0.000294</td>
<td>8</td>
<td>0.344215</td>
<td>13</td>
<td>-0.031214</td>
<td>18</td>
<td>0.000242</td>
</tr>
<tr>
<td>4</td>
<td>-0.003225</td>
<td>9</td>
<td>0.254265</td>
<td>14</td>
<td>-0.074083</td>
<td>19</td>
<td>-0.000009</td>
</tr>
<tr>
<td>5</td>
<td>0.458841</td>
<td>10</td>
<td>-0.175688</td>
<td>15</td>
<td>-0.031380</td>
<td>20</td>
<td>-0.000000</td>
</tr>
</tbody>
</table>

such an atom has no bound states other than the occupied core states. Excited states see the neutral potential of the completely shielded nucleus. It is known experimentally, however, that various neutral closed-shell atoms support bound states; the electron binds to the closed core to form a one-electron negative ion. The binding force is provided by the polarization potential of the core $-\alpha / 2 r^4$.

There is an obvious difficulty in describing such an atom within the framework of MBPT; the bound state does not exist in the HF approximation. Indeed, the force responsible for binding appears shows up first in second-order MBPT! One approach that can be used in this case is to solve the quasi-particle equation exactly, without recourse to perturbation theory. To this end, we expand the Brueckner orbital $\psi$ as a linear combination of HF basis orbitals $\phi_k$:

$$\psi(r) = \sum_k c_k \phi_k(r).$$

Substituting into Eq. (6.62), we find that the expansion coefficients satisfy the eigenvalue equation

$$\epsilon c_i = \sum_j \left[ \epsilon_i \delta_{ij} + \left[ \Sigma^{(2)}(\epsilon) \right]_{ij} \right] c_j.$$  \hspace{1cm} (6.66)

For neutral atoms, this equation has solutions that corresponds HF core orbitals modified by the self-energy operator. Other solutions with $\epsilon < 0$ also exist in some cases; the new bound-state solutions being associated with the negative ion. To obtain the solution corresponding to a loosely-bound electron, it is usually sufficient to set $\epsilon = 0$ in the expression for $\Sigma^{(2)}(\epsilon)$.

As a specific example, we consider the case of palladium (Pd), $Z=46$. This atom has closed $n = 1, 2, 3$ shells and closed $4s, 4p, 4d$ subshells. The Pd negative ion is found experimentally (Scheer et al., 1998) to have a 5s bound state with binding energy, (or affinity) 562.13 meV. The expansion coefficients $c_i$ in Eq. (6.66) for the 5s eigenstate are given in Table 6.5. The 5s eigen energy is found to be $\epsilon_{5s} = -0.01957$ a.u., corresponding to an electron affinity of 532.5 meV. The radial density of neutral Pd is shown in the lower panel of Fig. 6.4 and the 5s Brueckner orbital of Pd$^-$ is shown in the upper panel.
Figure 6.4: Lower panel: radial density of neutral Pd ($Z=46$). The peaks corresponding to closed $n = 1, 2, \cdots$ shells are labeled. Upper panel: radial density of the $5s$ ground-state orbital of Pd$. The $5s$ orbital is obtained by solving the quasi-particle equation.
6.5 CI Calculations

An alternative to MBPT that has some advantages for simple atomic systems is the configuration-interaction (CI) method, which we here describe for the case of helium.

As a first step, we introduce the configuration state function

\[ \Phi_{kl}(LS) = \frac{1}{\sqrt{2}} a_k^+ a_l^+ |0\rangle, \]

(6.67)

where \( \eta_{kl} \) is a symmetry factor defined by

\[ \eta_{kl} = \begin{cases} \frac{1}{\sqrt{2}}, & \text{for } k = l, \\ 1, & \text{for } k \neq l. \end{cases} \]

This function is an \( LS \) eigenstate of \( H_0 \) with energy \( E_0 = \epsilon_k + \epsilon_l \). An \( LS \) eigenstate of the exact Hamiltonian \( H_0 + V \), referred to as the CI wave function, is expanded as a linear combination of such configuration-state functions

\[ \Psi(LS) = \sum_{k \leq l} C_{kl} \Phi_{kl}(LS), \]

(6.68)

where the expansion coefficients \( C_{kl} \) are to be determined. The normalization condition

\[ \langle \Psi(LS) | \Psi(LS) \rangle = 1 \]

reduces to

\[ \sum_{k \leq l} C_{kl}^2 = 1. \]

We designate the interaction matrix \( \langle \Phi_{vw}(LS)|V|\Phi_{xy}(LS) \rangle \) by \( V_{vw,xy} \) and find

\[ V_{vw,xy} = \eta_{vw} \eta_{xy} \sum_k (-1)^{L+k+l_w+l_x} \left[ \begin{array}{c} l_v \cr \cr l_y \cr \cr l_x \cr \cr k \end{array} \right] \left[ \begin{array}{ccc} l_v & l_w & L \\ l_y & l_x & k \end{array} \right] X_k(vwxy) \]

\[ + (-1)^{S+k+l_w+l_x} \left[ \begin{array}{c} l_v \cr \cr l_x \cr \cr l_y \cr \cr k \end{array} \right] \left[ \begin{array}{ccc} l_x & l_y & L \\ l_x & l_y & k \end{array} \right] X_k(vyxw) \].

(6.69)

The expectation value of the Hamiltonian with the CI wave function becomes a quadratic function of the expansion coefficients

\[ \langle \Psi(LS) | H | \Psi(LS) \rangle = \sum_{v \leq w, x \leq y} \left[ (\epsilon_v + \epsilon_w) \delta_{vx} \delta_{yw} + V_{vw,xy} \right] C_{xy} C_{vw}. \]

To obtain the expansion coefficients, we minimize the expectation of the Hamiltonian subject to the normalization condition. This leads to the eigenvalue equation

\[ \sum_{x \leq y} \left[ (\epsilon_v + \epsilon_w) \delta_{vx} \delta_{yw} + V_{vw,xy} \right] C_{xy} = E C_{vw}. \]

(6.70)
Table 6.6: Contribution $\delta E$ of $(nlml)$ configurations to the CI energy of the helium ground state. The dominant contributions are from the $l = 0$ $nsms$ configurations. Contributions of configurations with $l \geq 7$ are estimated by extrapolation.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$mlnl$</th>
<th>$\delta E$</th>
<th>$E_i$</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>$msns$</td>
<td>-2.8790278</td>
<td>-2.8790278</td>
</tr>
<tr>
<td>1</td>
<td>$mpnp$</td>
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<td>-2.9005139</td>
</tr>
<tr>
<td>2</td>
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<td>-0.0022505</td>
<td>-2.9027644</td>
</tr>
<tr>
<td>3</td>
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<td>-2.9033182</td>
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<tr>
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<td>-2.9036275</td>
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<tr>
<td>7 ... $\infty$</td>
<td></td>
<td>-0.0000692</td>
<td>-2.9036967</td>
</tr>
</tbody>
</table>

Expt. -2.9036778

Let us consider as a specific example the $^1S_0$ ground state of helium. Angular momentum selection rules limit the possible configurations $(vw)$ to those with $l_v = l_w$. Thus, we have contributions from states of the form $(msns)$, $(mpnp)$, $(mdnd)$, $\cdots$. In a basis with $N$ basis functions, there are $N(N + 1)/2$ pairs $(mlnl)$ with $m \leq n$. If we include, for example, 20 basis orbitals of type $nl$ in our expansion, then we would have 210 expansion coefficients for each $l$.

In Table 6.6, we show the results of a sequence of CI calculations of the helium ground-state energy including configurations with successively larger values of the orbital angular momentum. The major contributions are from $(msns)$ configurations, and contributions from higher-partial waves are seen to converge rapidly. The final extrapolated value of the CI energy differs from the experimental energy by 1 part in $10^6$ owing to omitted relativistic and quantum-electrodynamic corrections.
Appendix A

A.1 Problems

Problem Set 1

1. Derive the relations

\[ J^2 = J_+ J_- + J_x^2 - J_z, \]
\[ J^2 = J_+ J_- + J_x^2 + J_z. \]

2. Show that the normalization factor \( c \) in the equation \( \Theta_{l,-l}(\theta) = c \sin^l \theta \) is

\[ c = \frac{1}{2^l l!} \sqrt{\frac{(2l+1)!}{2}}, \]

and thereby verify that Eq. (1.30) is correct.

3. Write a MAPLE program to obtain the first 10 Legendre polynomials using Rodrigues’ formula.

4. Legendre polynomials satisfy the recurrence relation

\[ lP_l(x) = (2l - 1)xP_{l-1}(x) - (l - 1)P_{l-2}(x). \]

Write a MAPLE program to determine \( P_2(x), P_3(x), \ldots, P_{10}(x) \) (starting with \( P_0(x) = 1 \) and \( P_1(x) = x \)) using the above recurrence relation.

5. Write a MAPLE program to generate the associated Legendre functions \( P_l^m(x) \). Determine all \( P_l^m(x) \) with \( l \leq 4 \) and \( 1 \leq m \leq l \).

Problem Set 2

1. Use the MAPLE routine cgc.map to evaluate \( C(1, 3/2, J; m_1, m_2, M) \) for all possible values of \( (m_1, m_2, J, M) \). Show that the resulting values satisfy the two orthogonality relations.
2. Prove
\[ \langle l_1 || C^k || l_2 \rangle = (-1)^{l_1 - l_2} \langle l_2 || C^k || l_1 \rangle, \]
where \( C^k_q \) is the tensor operator
\[ C^k_q \overset{\text{def}}{=} \sqrt{\frac{4\pi}{2k + 1}} Y_{kq}(\theta, \phi). \]

3. Prove
\[ [J^2, \sigma \cdot r] = 0, \quad [J_z, \sigma \cdot r] = 0, \]
where \( J = L + \frac{1}{2} \sigma \)

4. Prove
\[ Y_{J,JM}(\hat{r}) = \frac{L}{\sqrt{J(J+1)}} Y_{JM}(\hat{r}) \]

**Problem Set 3**

1. Write a MAPLE procedure to generate the formula for the radial Coulomb wave function \( P_{nl}(r) \).

2. Use your procedure to evaluate
   (a) \( \int_0^\infty P_{31}^2(r) \, dr \)
   (b) \( \int_0^\infty P_{31}(r) P_{21}(r) \, dr \)

3. Use your procedure to generate formulas for all 5 of the \( n = 5 \) radial wave functions. Plot each of the 5 wave functions.

**Problem Set 4**

1. Use the FORTRAN program MOD_POT.F to determine the value of \( b \) in the parametric potential
\[ V(r) = -\frac{Z}{r} + \frac{Z - 1}{r} (1 - e^{-br}), \]
that gives the best least-squares fit to the 4s, 5s, 6s, 4p, 5p, 3d and 4d levels in potassium. Use the resulting potential to predict the value of the 1s binding energy in potassium. How does your prediction compare with experiment? The data for the energy levels are found in C.E. Moore, NSRDS-NBS 35, Vol. 1. You should average over the fine structure of the \( p \) and \( d \) levels.

- The routine GOLDEN from the NUMERICAL RECIPES library is used to minimize the sum of squares of energy differences.
• The linear algebra routines used in outsch.f are from the LINPACK library.

2. Use the FORTRAN program thomas.f to determine the Thomas-Fermi potential for potassium, Z=19.

3. Find the K\(^+\) core radius \(R\).

4. Plot the effective charge \(Z_{\text{eff}}(r)\), defined by the relation:
   \[
   V(r) = -\frac{Z_{\text{eff}}(r)}{r} = -\frac{Z - N}{R} - \frac{Z\phi(r)}{r}
   \]

**Problem Set 5**

(a) Write out specific formulas for the radial Dirac functions \(P_{n\kappa}(r)\) and \(Q_{n\kappa}(r)\) of the \(n = 2\) states of a hydrogenlike ion with nuclear charge \(Z\). You may use MAPLE if you wish, however, you may find it simpler to expand the hypergeometric functions by hand.

(b) Verify that the \(n = 2\) radial functions determined in the previous problem are properly normalized for each of the three states.

(c) Plot the radial density function \(P_{n\kappa}(r)^2 + Q_{n\kappa}(r)^2\) for each of the \(n = 2\) states assuming \(Z = 20\).

(d) Give formulas for \(\langle r \rangle\) and \(\langle 1/r \rangle\) for each state in problem 1. Verify that the relativistic formulas approach the proper nonrelativistic limits.

(e) Suppose the nucleus is represented by a uniformly charged ball of radius \(R\):
   i. Show that the nuclear potential (in atomic units) is given by
   \[
   V_{\text{nuc}}(r) = \begin{cases} 
   -\frac{Z}{R} \left(\frac{3}{2} - \frac{r^2}{2R^2}\right), & r < R, \\
   -\frac{Z}{R}, & r \geq R.
   \end{cases}
   \]
   ii. Determine the nuclear finite-size correction to the \(n = 1\) and \(n = 2\) Dirac energy levels using first-order perturbation theory. How large are these corrections for hydrogen? (Assume \(R = 1.04\) fm for H and give your answer in cm\(^{-1}\).) How large are they for hydrogenlike uranium? (Assume \(R = 7.25\) fm for U and give your answer in eV.)

**Problem Set 6**

(a) Show that the exchange contribution to the interaction energy for the state \(|ab, LS\rangle\) is
   \[
   \eta^2 \sum_k (-1)^{l_a + l_b + S + k} \begin{pmatrix} l_a & l_b & L & k \\ l_a & l_b & \end{pmatrix} X_k(ab a). 
   \]
(b) \textit{LS to jj transformation matrix:}

i. Each nonrelativistic LS-coupled state belonging to a given $J$,

\[ |[(l_1 l_2) L, (s_1 s_2) S] J \rangle, \]

can be expanded as a linear combination of the nonrelativistic

\[ jj \]-coupled states

\[ |[(l_1 s_1) j_1, (l_2 s_2) j_2] J \rangle, \]

belonging to the same $J$. Write the matrix of expansion coefficients in terms of six-j symbols. (The expansion coefficients are related to 9-j symbols.)

ii. Prove that this transformation matrix is symmetric.

iii. Give numerical values for the elements of the $2 \times 2$ matrix that gives the two \((sp)\) states $^1P_1$ and $^3P_1$ in terms of the two states \((s_1/2p_{1/2})_1^1 \) and \((s_1/2p_{3/2})_1^1 \).

iv. Give numerical values for the elements of the $3 \times 3$ matrix that gives the three \((pd)\) states $^1P_1$, $^3P_1$ and $^3D_1$ in terms of the three states \((p_{1/2}d_{3/2})_1 \), \((p_{3/2}d_{3/2})_1 \) and \((p_{3/2}d_{5/2})_1 \).

\textbf{Problem Set 7}

1. For an atom with two valence electrons above a closed core, determine the number of states in the configuration \((nsn')l\) and give \(LS\) and \(jj\) designations of the states. Determine the number of states in an \((nd)^2\) configuration and give \(LS\) and \(jj\) designations of the states.

2. Which of the following products are normally ordered?

(a) $a_d^\dagger a^\dagger$ (d) $a_n^\dagger a_d^\dagger a^\dagger a_b$

(b) $a_d a_n^\dagger$ (e) $a_d^\dagger a_d^\dagger a^\dagger a_b$

(c) $a_n a_b^\dagger$ (f) $a_d^\dagger a_b^\dagger a_c^\dagger$

Determine the expectation of each of these products in the core state.

3. In the Auger process, an initial state $|I\rangle = a_a|O_c\rangle$ with a hole in state $a$ makes a transition to a final state $|F\rangle$ with holes in states $b$ and $c$ and an excited electron in state $m$. The transition probability is proportional to the square of the matrix element $\langle F|V|I\rangle$. Express this matrix element in terms of the two-particle Coulomb integrals $g_{ijkl}$.

4. In the relativistic case, show that the energy in the relativistic particle-hole state obtained by coupling states $\langle(-1)^{j_v-2s_a}a_v^\dagger a_a|O_c\rangle$ to angular momentum $JM$ is

\[
E^{(1)}(j_\alpha j_\alpha J) = \frac{(-1)^{j_v^+ j_a^+ - j_a}}{[J]} X_f(vaav) + [J] \sum_k \left\{ \begin{array}{ccc} j_v & j_a & J \\ j_a & j_v & k \end{array} \right\} X_k(vava) \]
provided the orbitals are evaluated in a $V^{N-1}$ HF potential. Express this matrix element in terms of Slater integrals for the case: $a = 2p_{1/2}$, $v = 3s_{1/2}$, and $J = 0$. What is the $LS$ designation of this state?

Problem Set 8

1. Verify the relation:

$$\langle b||\nabla||a \rangle = \langle l_b||C_1||l_a \rangle \left\{ \int_0^\infty dr P_b^L \left( \frac{d}{dr} + \frac{l_a}{r} \right) P_a^L, \quad \text{for} \ l_b = l_a - 1, \right.$$  
$$\left. \int_0^\infty dr P_b^L \left( \frac{d}{dr} - \frac{l + 1}{r} \right) P_a^L, \quad \text{for} \ l_b = l_a + 1. \right.$$  

Hint: Use vector spherical harmonics. at the first step.

2. Verify

$$\sum_n \tilde{f}_{ks\rightarrow np} = 1$$  
and

$$\sum_n \tilde{f}_{kl\rightarrow nlt-1} = -\frac{l(2l-1)}{3(2l+1)},$$  
$$\sum_n \tilde{f}_{kl\rightarrow nlt+1} = \frac{(l+1)(2l+3)}{3(2l+1)}.$$

3. Determine the lifetime of the $3p_{3/2}$ excited state in Al. Hint: This state decays to the ground state by an M1 transition. The transition energy is found in the spectroscopic tables.

A.2 Examinations

Exam I

1. Show that the state

$$|J, M \rangle = \sum_{m_1 m_2}^{j_1 m_1} \frac{J^M}{j_2 m_2} |j_1, m_1 \rangle |j_2, m_2 \rangle,$$

is an eigenstate of $J_1 \cdot J_2$. What is the corresponding eigenvalue.

2. The interaction Hamiltonian for a one-electron atom in an external magnetic field directed along the $z$-axis is $H_I = -\mu_0 \sigma_z B$,

(a) Express the energy shift of the state $|n, j, j \rangle$ in terms of a reduced matrix element of $\sigma$.

(b) Show that the energy shift of the states $|n, j, m \rangle$ and $|n, j, j \rangle$ are related by

$$\Delta E_{njm} = \frac{m}{j} \Delta E_{njj}.$$
3. Hartree-Fock:

(a) Write down in detail the Hartree-Fock equations for the 3 closed subshells of the neon atom. (Give numerical values for the occupation numbers and exchange factors).

(b) Write down in detail the Dirac-Fock equations for the 4 closed subshells of the neon atom. (Give numerical values for the occupation numbers and exchange factors).

4. Compile and run the program NRHF.F for Li using the data set LI.IN as input. How do the HF eigenvalues compare with experiment? Modify the data set to determine the 2p and 3s energies for boron, assuming a "frozen" Be-like core and a single valence electron. How do these energies compare with experiment. (A description of the input data file is given at the beginning of the program)

Final Exam

1. Consider a transition from the (1s3d) \(^3\)D state to the (1s2p) \(^3\)P state in a helium-like ion:

(a) Show that, in the independent-particle approximation, 
\[
\langle (1s2p) \(^3\)P || r || (1s3d) \(^3\)D \rangle = \langle 2p || r || 3d \rangle
\]

(b) Suppose that one can resolve the fine-structure of the initial and final states. Express the matrix elements \(\langle (1s2p) \(^3\)P \(_{J_F}\) || r || (1s3d) \(^3\)D \(_{I}\) \rangle\) in terms of \(\langle (1s2p) \(^3\)P || r || (1s3d) \(^3\)D \rangle\) or \(\langle 2p || r || 3d \rangle\).

(c) The intensity of the lines from \((1s3d) \(^3\)D\(_{I}\)\) to \((1s2p) \(^3\)P\(_{J_F}\)\) is

\[
A_{I \rightarrow F} \propto \frac{S_{FI}}{[J_I]} = \frac{|\langle (1s2p) \(^3\)P \(_{J_F}\) || r || (1s3d) \(^3\)D\(_{I}\) \rangle|^2}{[J_I]}
\]

By explicitly evaluating the relevant 6j symbols (using MAPLE, for example), show that the ratios of intensities for transitions \(J_I \rightarrow J_F:\)

\[
1 \rightarrow 0 : 1 \rightarrow 1 : 2 \rightarrow 1 : 1 \rightarrow 2 : 2 \rightarrow 2 : 3 \rightarrow 2
\]

are

\[
\]

2. Suppose we choose to describe an atom in lowest order using a potential \(U(r)\) other than the HF potential.
(a) Show that the correction to the first-order energy from the single-particle part of the potential \((V_1)\) for a one electron atom in a state \(v\) is
\[
E^{(1)}_v = \Delta v\v
\]
where \(\Delta = V_{HF} - U\).
(b) Show that the corresponding second-order correction is
\[
E^{(2)}_v = -\sum_{na} \Delta_{na} g_{ave} \Delta_{an} - \sum_{i \neq v} \frac{\Delta_{vi} \Delta_{iv}}{\epsilon_i - \epsilon_v}.
\]
Here, \(i\) runs over \(a\) and \(n\).

A.3 Answers to Problems

Answers to Problem Set 1

1. Derive the relations
\[
J^2 = J_+ J_- + J_+^2 - J_z, \\
J^2 = J_- J_+ + J_-^2 + J_z.
\]

Solution:
Consider the product \(J_+ J_-\)
\[
J_+ J_- = (J_x + iJ_y)(J_x - iJ_y) = J_x^2 + J_y^2 - i[J_x, J_y] = J^2 - J_z,
J_- J_+ = (J_x - iJ_y)(J_x + iJ_y) = J_x^2 + J_y^2 + i[J_x, J_y] = J^2 - J_z,
\]
where we have used \([J_x, J_y] = iJ_z\). Rearranging these expressions leads to
\[
J^2 = J_+ J_- + J_+^2 - J_z, \\
J^2 = J_- J_+ + J_-^2 + J_z.
\]

2. Show that the normalization factor \(c\) in the equation \(\Theta_{l,-l}(\theta) = c \sin^l \theta\) is
\[
c = \frac{1}{2^{l!}} \sqrt{\frac{(2l+1)!}{2}},
\]
and thereby verify that Eq. (1.30) is correct.

Solution:
\[
\int_0^\pi |\Theta_{l,-l}(\theta)|^2 \sin \theta d\theta = c^2 \int_0^\pi \sin^{2l+1}(\theta) d\theta = c^2 \int_{-1}^1 (1-x^2)^l dx = 1.
\]
Evaluate \(I_l = \int_{-1}^1 (1-x^2)^l dx\) by parts:
\[
\begin{align*}
  u &= (1-x^2)^l, & dv &= dx, \\
  du &= -2l x (1-x^2)^{l-1}, & v &= x
\end{align*}
\]
From this, it follows

\[ \int_1^l = x(1 - x^2)^l \bigg|_{-1}^1 + 2l \int_{-1}^1 x^2(1 - x^2)^{l-1} dx \]

\[ = 2l \int_{-1}^1 \left[ -(1 - x^2) + 1 \right] (1 - x^2)^{l-1} dx = 2l \left[ -I_l + I_{l-1} \right]. \]

This may be rewritten as the induction relation \( I_l = 2l I_l/(2l + 1) \). Using the fact that \( I_0 = 2 \), one finds

\[
\begin{align*}
I_1 & = \frac{2 \cdot 1}{3} \cdot 2 \\
I_2 & = \frac{2 \cdot 2 \cdot 2}{5} \cdot 1 \cdot 2 \\
\vdots & = \ldots \\
I_l & = \frac{2 \cdot l \cdots 2 \cdot 1}{(2l + 1) \cdots 5 \cdot 3} \cdot 2 = \frac{2^l \cdot l!}{3 \cdot 5 \cdots (2l + 1) \cdot 2} \\
& = \frac{(2^l \cdot l!)^2}{(2l + 1)!} \cdot 2
\end{align*}
\]

It follows that

\[ c = \sqrt{T I_l} = \frac{1}{2^l l!} \sqrt{(2l + 1)!} \cdot 2 \]

3. Write a MAPLE program to obtain the first 10 Legendre polynomials using Rodrigues’ formula.

**Solution:**

\[
\begin{align*}
\text{for } l & \text{ from } 1 \text{ to } 10 \text{ do} \\
P[0] & := 1; \\
P[1] & := x; \\
\text{for } l & \text{ from } 2 \text{ to } 10 \text{ do} \\
P[l] & := \text{expand}((2^l-1)*x*P[l-1]-(l-1)*P[l-1])/2; \\
\text{od};
\end{align*}
\]

4. Legendre polynomials satisfy the recurrence relation

\[ lP_l(x) = (2l - 1)XP_{l-1}(x) - (l - 1)P_{l-2}(x). \]

Write a MAPLE program to determine \( P_2(x), P_3(x), \ldots, P_{10}(x) \) (starting with \( P_0(x) = 1 \) and \( P_1(x) = x \)) using the above recurrence relation.

**Solution:**

\[
\begin{align*}
P[0] & := 1; \\
P[1] & := x; \\
\text{for } l & \text{ from } 2 \text{ to } 10 \text{ do} \\
P[l] & := \text{expand}(((2^l-1)*x*P[l-1]-(l-1)*P[l-1])/2); \\
\text{od};
\end{align*}
\]
5. Write a MAPLE program to generate the associated Legendre functions and $P_l^m(x)$. Determine all $P_l^m(x)$ with $l \leq 4$ and $1 \leq m \leq l$.

Solution:

```maple
for l from 1 to 4 do
    P[l,0] := expand(diff((x^2-1)^l,x$1)/(2^l*l!));
    for m from 1 to l do
        p[l,m] := (1-x^2)^((m/2)) * expand(diff(P[l,0],x$m));
        print(P[l,m]= p[l,m]);
    od;
od;
```

$P[1,0] := x$  \quad $P[1,1] = \sqrt{1-x^2}$

$P[2,0] := 3/2 x^2 - 1/2$  \quad $P[2,1] = 3\sqrt{1-x^2}x$  \quad $P[2,2] = 3 - 3x^2$

$P[3,0] := 5/2 x^3 - 3/2x$  \quad \ldots

---

Answers to Problem Set 2

1. Program to test orthogonality relations:

```maple
read 'cgc.map';
j1:= 1;
j2:= 3/2;
jmin:=abs(j1-j2);
jmax:=j1+j2;
for J from jmin to jmax do
    for M from -J to J do
        for K from jmin to jmax do
            for N from -K to K do
                sp := 0;
                for m1 from -j1 to j1 do
                    for m2 from -j2 to j2 do
                        sp := sp + cgc(j1,j2,J,m1,m2,M)*cgc(j1,j2,K,m1,m2,N);
                    od;
                od;
                if simplify(sp) <> 0 then print(ScPr(J,K,M,N) = simplify(sp)) fi;
            od;
        od;
    od;
```

Result:

\[ \text{ScPr}(1/2, 1/2, -1/2, -1/2) = 1 \]
\[ \text{ScPr}(1/2, 1/2, 1/2, 1/2) = 1 \]
\[ \text{ScPr}(3/2, 3/2, -3/2, -3/2) = 1 \]
\[ \text{ScPr}(3/2, 3/2, -1/2, -1/2) = 1 \]
\[ \text{ScPr}(3/2, 3/2, 1/2, 1/2) = 1 \]
\[ \text{ScPr}(3/2, 3/2, 3/2, 3/2) = 1 \]
\[ \text{ScPr}(5/2, 5/2, -5/2, -5/2) = 1 \]
\[ \text{ScPr}(5/2, 5/2, -3/2, -3/2) = 1 \]
\[ \text{ScPr}(5/2, 5/2, -1/2, -1/2) = 1 \]
\[ \text{ScPr}(5/2, 5/2, 1/2, 1/2) = 1 \]
\[ \text{ScPr}(5/2, 5/2, 3/2, 3/2) = 1 \]
\[ \text{ScPr}(5/2, 5/2, 5/2, 5/2) = 1 \]

The program to test the second orthogonality relation is similar.

2. Reduced matrix element of a normalized spherical harmonic:

\[ \langle l_1 || C^k || l_2 \rangle = (-1)^{l_1} \sqrt{(2l_1 + 1)(2l_2 + 1)} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \]
\[ = (-1)^{l_1} \sqrt{(2l_1 + 1)(2l_2 + 1)} \begin{pmatrix} l_2 & k & l_1 \\ 0 & 0 & 0 \end{pmatrix} \]
\[ = (-1)^{l_1-l_2} (-1)^{l_2} \sqrt{(2l_1 + 1)(2l_2 + 1)} \begin{pmatrix} l_2 & k & l_1 \\ 0 & 0 & 0 \end{pmatrix} \]
\[ = (-1)^{l_1-l_2} (l_2 || C^k || l_1) \]

The factor \((-1)^{l_1+k+l_2}\) from the interchange of \(l_1\) and \(l_2\) on the second line is just 1, since \(l_1 + l_2 + k\) is even.

3. Consider \([J_x, \sigma \cdot \hat{r}]\) We find:

\[ [J_x, \sigma \cdot \hat{r}] = \sigma_x [L_x, \frac{x}{r}] + \sigma_y [L_x, \frac{y}{r}] + \sigma_z [L_x, \frac{z}{r}] \]
\[ + \frac{1}{2} \frac{x}{r} [\sigma_z, \sigma_x] + \frac{1}{2} \frac{y}{r} [\sigma_x, \sigma_y] + \frac{1}{2} \frac{z}{r} [\sigma_x, \sigma_z] \]
\[ = 0 + i \sigma_y \frac{z}{r} - i \sigma_z \frac{y}{r} \]
\[ + 0 + i \frac{y}{r} \sigma_z - i \frac{z}{r} \sigma_y \]
\[ = 0. \]

By the structure of the above relations, it follows that \([J_k, \sigma \cdot \hat{r}] = 0\) for each component \(J_k\) of \(J\); in particular for \(J_z\). To demonstrate the commutation
A.3. ANSWERS TO PROBLEMS

1. Write a procedure to evaluate radial Coulomb wave functions.

   hyp := proc(a,b,x)
     local f,k,top,bot;
     top := 1;
     bot := 1;
     f := 1;
     if a > 0 then 0
     elif a = 0 then 1
     else
       for k from 1 to -a do
         top := top*(a+k-1);
         bot := bot*(b+k-1);
         f := f + (top*x**k)/(bot*k!);
       od;
     fi;
     end;
   end;

   P := proc(Z,n,l,r)
     if n > l then
       sqrt(Z*(n+l)!/(n-l-1)!)/(n*(2*l+1)!)
         * (2*Z*r/n)**(l+1) * exp(-Z*r/n) * hyp(-n+1,2*l+2,2*Z*r/n);
     else
       0
     fi;
   end;

4.

\[ \frac{L}{\sqrt{J(J+1)}} Y_{JM} \]

\[ = \left( -\frac{1}{\sqrt{2}} (L_x - iL_y) \xi_{+1} + L_0 \xi_0 + \frac{1}{\sqrt{2}} (L_x + iL_y) \xi_{-1} \right) \frac{Y_{JM}}{\sqrt{J(J+1)}} \]

\[ = \left( -\sqrt{\frac{(J-M+1)(J+M)}{2J(J+1)}} \xi_{+1} Y_{JM-1} + \frac{M}{\sqrt{J(J+1)}} \xi_0 Y_{JM} \right. \]

\[ + \sqrt{\frac{(J+M+1)(J-M)}{2J(J+1)}} \xi_{-1} Y_{JM+1} \]

\[ = C(J1J,M-1,1,M)\xi_{+1} Y_{JM-1} + C(J1J,M,0,M)\xi_0 Y_{JM} \]

\[ + C(J1J,M+1,-11,M)\xi_{-1} Y_{JM+1} \]

\[ = Y_{JJM} \]

Answers to Problem Set 3

1. Write a procedure to evaluate radial Coulomb wave functions.

relation for \( J^2 \), we use the identity:

\[ [J^2, \sigma \cdot \hat{r}] = J \cdot [J, \sigma \cdot \hat{r}] + [J, \sigma \cdot \hat{r}] \cdot J = 0 + 0 = 0 \]
2. Evaluate norm and scalar product.

```plaintext
assume(Z>0);
p[3,1] := P(Z,3,1,r);
p[2,1] := P(Z,2,1,r);
norm := int(p[3,1]*p[3,1],r=0..infinity);
scpr := int(p[3,1]*p[2,1],r=0..infinity);
```

3. Plot all $n=5$ wave functions.

```plaintext
plot([P(1,5,0,r),P(1,5,1,r),P(1,5,2,r),P(1,5,3,r),
P(1,5,4,r)],r=0..90);
```

**Answers to Problem Set 4**

1. Input file: (alk.in)

```
19
4 0 -0.15952
5 0 -0.06371
6 0 -0.03444
4 1 -0.10009
5 1 -0.04688
3 2 -0.06140
4 2 -0.03469
```

Output from mod_pot:

- $b = 0.484590, \chi^2 = 3.6 \times 10^{-5}$
- $E_{1s} = -146.188, E_{exp} = -132.56$

(NIST database gives $E_K = 3.607E-03$ MeV = 132.56 (a.u.) for K-shell threshold for Potassium.)

2. For K, $Z = 19, N = 18$, we find $R = 2.9962$
Answers to Problem Set 5

1. The radial $n = 2$ wave functions for $\kappa = \pm 1$ are:

\[
P_{2\kappa}(r) = \sqrt{1 + N/2} \mathcal{N}_{2\kappa} x^{\gamma_1} e^{-x/2} [(N - \kappa)(1 - x/b) - 1]
\]
\[
Q_{2\kappa}(r) = \sqrt{1 - N/2} \mathcal{N}_{2\kappa} x^{\gamma_1} e^{-x/2} [(N - \kappa)(1 - x/b) + 1]
\]

with $x = 2Zr/N$, $\mathcal{N}_{2\kappa} = \sqrt{Z b/[2 \Gamma(b)(N - \kappa)]}$, $b = 2\gamma_1 + 1$, $N = \sqrt{2 + 2\gamma_1}$, $\gamma_1 = \sqrt{1 - \alpha^2 Z^2}$.

The wave functions for $\kappa = -2$ are

\[
P_{2,-2}(r) = \sqrt{1 + \gamma_2/2} \mathcal{N}_{2,-2} y^{\gamma_2} e^{-y/2}
\]
\[
Q_{2,-2}(r) = \sqrt{1 - \gamma_2/2} \mathcal{N}_{2,-2} y^{\gamma_2} e^{-y/2},
\]

with $y = Zr$, $\mathcal{N}_{2,-2} = \sqrt{Z/[2 \Gamma(2\gamma_2 + 1)]}$, $\gamma_2 = \sqrt{4 - \alpha^2 Z^2}$.

2. The normalization condition may be verified by carrying out integrals of the densities in the next problem numerically.

3. Plots of the radial densities are shown below:
4. 
\[ \gamma_1 = \sqrt{1 - \alpha^2 Z^2} \quad \gamma_2 = \sqrt{4 - \alpha^2 Z^2} \quad N = \sqrt{2 + 2 \gamma_1} \]

\[ \langle \frac{1}{r} \rangle_{2s} = \frac{Z}{2N \gamma_1} \quad \langle \frac{1}{r} \rangle_{2p_{1/2}} = \frac{Z}{2N \gamma_1} \quad \langle \frac{1}{r} \rangle_{2p_{3/2}} = \frac{Z}{2 \gamma_2} \]

\[ \langle r \rangle_{2s} = \frac{(6 \gamma_1 + 5) N + 2}{4Z} \quad \langle r \rangle_{2p_{1/2}} = \frac{(6 \gamma_1 + 5) N - 2}{4Z} \quad \langle r \rangle_{2p_{3/2}} = \frac{2 \gamma_2 + 1}{Z} \]

5. 
\[ \Delta E_{nn} = \frac{3Z}{\gamma(2\gamma + 1)(2\gamma + 3)} \frac{N^2}{n_k} \left( \frac{2ZR}{N} \right)^{2\gamma} \times \]
\[ \left\{ (N - k)^2 + (n - k)^2 - 2^2 + n - k \right\} N (N - k) (n - k) \]

<table>
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<th>H (cm(^{-1}))</th>
<th>U (eV)</th>
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<td>272.657</td>
</tr>
<tr>
<td>2s</td>
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<td>51.995</td>
</tr>
<tr>
<td>2p_{1/2}</td>
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</tr>
<tr>
<td>2p_{3/2}</td>
<td>0.0</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Answers to Problem Set 6

1.

2. \( LS - jj \) transformation matrices:

\[
\begin{pmatrix} (s_{1/2p_{1/2}})_{1} \\ (s_{1/2p_{3/2}})_{1} \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \end{pmatrix} \begin{pmatrix} l \end{pmatrix} \]

(A.1)
A.3. ANSWERS TO PROBLEMS

\[
\begin{pmatrix}
(p_{1/2}d_{1/2})_1 \\
(p_{3/2}d_{3/2})_1 \\
(p_{3/2}d_{3/2})_1
\end{pmatrix} = \begin{pmatrix}
\frac{\sqrt{1}}{3} & \frac{\sqrt{1}}{6} & \frac{\sqrt{1}}{2} \\
\frac{1}{15} & \frac{8}{15} & -\frac{2}{5} \\
\frac{3}{5} & -\frac{3}{10} & -\frac{1}{10}
\end{pmatrix} \begin{pmatrix}
^1P_1 \\
^3P_1 \\
^3D_1
\end{pmatrix}
\]

(A.2)

Answers to Problem Set 7

1. Number of substates:

(a) (nsn'ℓ) in LS coupling:

In this case, \( L = \ell \) and there are only two possibilities \(^1L\) and \(^3L\). The first has \(2L + 1\) substates and the second has \((2S + 1)(2L + 1) = 3(2L + 1)\) substates. The total is \(N = 4(2L + 1) = 8L + 4\) substates.

(b) (nsn'ℓ) in jj coupling:

There are two possibilities \((ns_{1/2}n'l_{l-1/2})\) with \(2 \times (2(l - 1/2) + 1) = 4l\) substates and \((ns_{1/2}n'l_{l+1/2})\) with \(2 \times (2(l + 1/2) + 1) = 4l + 4\) substates. The total is again \(N = 8L + 4\) substates.

(c) \((nd)^2\) in LS coupling:

Since \(L + S\) is even we have \(^1S\), \(^3P\), \(^1D\), \(^3F\), and \(^1G\). The number of states is \(N = 1 + 3 \times 3 + 5 + 3 \times 7 + 9 = 45\).

(d) \((nd)^2\) in jj coupling:

We have the jj configurations \((nd_{3/2})^2\), \((nd_{5/2})^2\), and \((nd_{3/2}nd_{5/2})\). For \((nd_{3/2})^2\) only \(J = 0\) and \(2\) are possible with \(1 + 5 = 6\) substates; for \((nd_{5/2})^2\) only \(J = 0, 2, \) and \(4\) are possible with \(1 + 5 + 9 = 15\) substates; for \((nd_{3/2}nd_{5/2})\), \(J = 1, 2, 3, \) and \(4\) are possible with \(3 + 5 + 7 + 9 = 24\) substates. The total number of substates is thus \(N = 6 + 15 + 24 = 45\).

2. Cases (a-d) are normally ordered and have core expectation values 0. Cases (e) and (f) are not normally ordered. The core expectation values for case (e):

\[
\langle a_c a_d a_a a_b \rangle = \delta_{bc} \delta_{ad} - \delta_{bd} \delta_{ac},
\]

and for case (f):

\[
\langle a_c a_b a_d a_a \rangle = \delta_{bc} \delta_{dc}.
\]
3. We have $|I\rangle = a_a|0_c\rangle$ and $|F\rangle = a_m^\dagger a_b a_c|0_c\rangle$. It follows that

$$
\langle F|V_I|I\rangle = \frac{1}{2} \sum_{ijkl} g_{ijkl} \langle 0_c|a_k^\dagger a_m^\dagger a_l a_i : a_j^\dagger a_k : a_a: |0_c\rangle
$$

which, using Wick’s theorem, reduces to

$$
\frac{1}{2} \sum_{ijkl} g_{ijkl} (\delta_{ia}\delta_{jm} - \delta_{im}\delta_{ja})(\delta_{kb}\delta_{lc} - \delta_{lc}\delta_{kb})
$$

$$
= g_{ambc} - g_{amcb} = \tilde{g}_{ambc}
$$

4. The first-order energy is

$$
E^{(1)}(j_v, j_w, J) = \sum_{m'} \sum \frac{J}{J_m} \frac{J}{J_{m'}} - \sum \frac{J}{J_{m'}} \langle 0_c|a_b^\dagger a_w V_I a_l^\dagger a_u |0_c\rangle,
$$

where $w \neq v$ and $a \neq b$ differ only in the values of the magnetic quantum numbers. With the aid of Wick’s theorem, we find

$$
\langle 0_c|a_b^\dagger a_w V_I a_l^\dagger a_u |0_c\rangle = g_{wabv} - g_{wabv} + \Delta_{aw} \delta_{ba} - \Delta_{bw} \delta_{av}
$$

The two-particle part of the first-order energy is

$$
\sum_{m'\cdot s} \sum_{m'\cdot a} \frac{J}{J_m} \frac{J}{J_{m'}} \sum_k \left[ - \frac{J}{J_{m'}} \frac{J}{J_{m'}} \frac{J}{J_k} \frac{J}{J_{m}} \right] X_k(wabv) + \Delta_{aw} \delta_{ba} - \Delta_{bw} \delta_{av}
$$

After summing over $m$ values, this reduces to

$$
\frac{(-1)^{J+j_v-j_a}}{[J]} X_J(wabv) + [J] \sum_k \left\{ \frac{j_v}{j_b} \frac{j_a}{j_w} \frac{J}{k} \right\} X_k(wabv).
$$

This leads to the desired answer on setting $w = v$ and $b = a$.

Answers to Problem Set 8
1. For later use, keep in mind the expansion of the gradient operator in a spherical basis $\nabla = \sum_\mu (-1)^\mu \nabla_\mu \xi_\mu$. Write the wave function for the state $a$ as

$$\psi_a = \frac{P_a(r)}{r} Y_{l_a,m_a}(\hat{r})$$.

One finds:

$$\nabla \psi_a = \frac{d}{dr} \left( \frac{P_a(r)}{r} \right) \hat{r} Y_{l_a,m_a} + \frac{P_a(r)}{r} \nabla Y_{l_a,m_a}$$

$$= \frac{1}{r} \left[ \left( \frac{dP_a}{dr} - \frac{1}{r} P_a(r) \right) Y_{l_a,m_a}^{(-1)} + \sqrt{\frac{l_a}{2l_a+1}} P_a(r) Y_{l_a,m_a}^{(1)} \right]$$

$$= \frac{1}{r} \left[ \left( \frac{dP_a}{dr} - \frac{1}{r} P_a(r) \right) \left( \sqrt{\frac{l_a}{2l_a+1}} Y_{l_a,l_a-1,m_a} - \sqrt{\frac{l_a+1}{2l_a+1}} Y_{l_a,l_a+1,m_a} \right) \right]$$

$$+ \frac{\sqrt{l_a} (l_a+1)}{r} P_a(r) \left( \frac{l_a+1}{2l_a+1} Y_{l_a,l_a-1,m_a} + \frac{l_a}{2l_a+1} Y_{l_a,l_a+1,m_a} \right)$$

$$= \frac{1}{r} \left[ \sqrt{\frac{l_a}{2l_a+1}} \left( \frac{dP_a}{dr} + \frac{l_a}{r} P_a(r) \right) Y_{l_a,l_a-1,m_a} \right. $$

$$- \sqrt{\frac{l_a+1}{2l_a+1}} \left( \frac{dP_a}{dr} - \frac{l_a+1}{r} P_a(r) \right) Y_{l_a,l_a+1,m_a} \right]$$.

Extracting the coefficient of $\xi_\mu$ from the expressions for the vector spherical harmonics in the last lines of the above equation, it follows that

$$(-1)^\mu \nabla_\mu |a\rangle =$$

$$\frac{1}{r} \left[ \sqrt{\frac{l_a}{2l_a+1}} \left( \frac{dP_a}{dr} + \frac{l_a}{r} P_a(r) \right) C(l_a - 1, 1, l_a; m_a - \mu, \mu, m_a) Y_{l_a-1,m_a-\mu}(\hat{r}) \right. $$

$$- \sqrt{\frac{l_a+1}{2l_a+1}} \left( \frac{dP_a}{dr} - \frac{l_a+1}{r} P_a(r) \right) C(l_a + 1, 1, l_a; m_a - \mu, \mu, m_a) Y_{l_a+1,m_a-\mu}(\hat{r}) \right\} \frac{C(l_b, 1, l_a, m_b, \mu, m_a)}{\sqrt{2l_a+1}} \right]$$.

From this, we find

$$\langle b | \nabla_\mu | a\rangle = (-1)^\mu \left\{ \sqrt{l_a} \int_0^\infty P_b(r) \left( \frac{dP_a}{dr} + \frac{l_a}{r} P_a(r) \right) dr \delta_{l_b,l_a-1} \right. $$

$$- \sqrt{l_a+1} \int_0^\infty P_b(r) \left( \frac{dP_a}{dr} - \frac{l_a+1}{r} P_a(r) \right) dr \delta_{l_b,l_a+1} \right\} \frac{C(l_b, 1, l_a, m_b, \mu, m_a)}{\sqrt{2l_a+1}} \right.$$.

One can easily verify that for $l_b = l_a \pm 1$,

$$\frac{C(l_b, 1, l_a, m_b, \mu, m_a)}{\sqrt{2l_a+1}} = (-1)^{1-\mu} \left\{ \begin{array}{c} \frac{l_b m_b}{l_a m_a} \\ 1-\mu \end{array} \right\}$$.
Therefore,

\[ \langle b | \nabla | a \rangle = \left\{ -\sqrt{l_a} \int_0^\infty P_b(r) \left( \frac{dP_a}{dr} + \frac{l_a}{r} P_a(r) \right) dr \delta_{l_b, l_a-1} \\
+ \sqrt{l_a + 1} \int_0^\infty P_b(r) \left( \frac{dP_a}{dr} - \frac{l_a + 1}{r} P_a(r) \right) dr \delta_{l_b, l_a+1} \right\} \]

Now,

\[ \langle l_b | C_1 | l_a \rangle = \begin{cases} 
-\sqrt{l_a} & \text{for } l_b = l_a - 1 \\
\sqrt{l_a + 1} & \text{for } l_b = l_a + 1 
\end{cases} \]

Therefore, finally,

\[ \langle b | \nabla | a \rangle = \langle l_b | C_1 | l_a \rangle \left\{ \int_0^\infty P_b(r) \left( \frac{dP_a}{dr} + \frac{l_a}{r} P_a(r) \right) dr \delta_{l_b, l_a-1} \\
+ \int_0^\infty P_b(r) \left( \frac{dP_a}{dr} - \frac{l_a + 1}{r} P_a(r) \right) dr \delta_{l_b, l_a+1} \right\} \]

2. Let us first consider

\[ \tilde{f}_{k l-1} = \sum_{n \, m_n} \frac{2\omega_{n k}}{3} \langle k l m_k | r| n l - 1 m_n \rangle \cdot \langle n l - 1 m_n | r| k l m_k \rangle \]

\[ = -\frac{2}{3} i \sum_{n \, m_n} \langle k l m_k | r| n l - 1 m_n \rangle \cdot \langle n l - 1 m_n | p| k l m_k \rangle \]

\[ = -\frac{2}{3} i \sum_{n \, m_n} (-1)^\nu \langle k l m_k | r \nu | n l - 1 m_n \rangle \langle n l - 1 m_n | p \nu | k l m_k \rangle \]

\[ = -\frac{2}{3(2l + 1)} \sum_n (-1)^l \langle k l || n l - 1 \rangle \langle n l - 1 || \nabla || k l \rangle \]

\[ = -\frac{2}{3(2l + 1)} |(l||C_1||l - 1)|^2 \sum_n \int_0^\infty dr P_{kl}(r) r P_{nl-1}(r) \times \int_0^\infty dr' P_{nl-1}(r') \left( \frac{dP_{kl}(r')}{dr'} + \frac{l}{r'} P_{kl}(r') \right) \]

Now, we use completeness of the radial wave functions:

\[ \sum_n P_{nl-1}(r) P_{nl-1}(r') = \delta(r - r') \]

to write the sum over \( n \) of the double integral on the last lines of the previous equation as

\[ I = \int_0^\infty dr P_{kl}(r) r \left( \frac{dP_{kl}(r)}{dr} + \frac{l}{r} P_{kl}(r) \right). \]
Since $|\langle l|C_1|l-1\rangle|^2 = l$, we obtain

$$f_{kl}\rightarrow l-1 = -\frac{2l}{3(2l+1)} \int_0^\infty dr P_{kl}(r) r \left( \frac{dP_{kl}(r)}{dr} + \frac{l}{r} P_{kl}(r) \right)$$

$$= -\frac{2l}{3(2l+1)} \int_0^\infty dr \left( \frac{1}{2} \frac{d(r P_{kl}^2)}{dr} + \frac{2l-1}{2} P_{kl}^2 \right)$$

$$= -\frac{2l}{3(2l+1)} \frac{2l-1}{2} = -\frac{l(2l-1)}{3(2l+1)}$$

Using $|\langle l|C_1|l+1\rangle|^2 = l+1$ and following the same argument for the case of intermediate $|n,l+1\rangle$ states, we find

$$f_{kl}\rightarrow l+1 = -\frac{2(l+1)}{3(2l+1)} \int_0^\infty dr P_{kl}(r) r \left( \frac{dP_{kl}(r)}{dr} - \frac{l+1}{r} P_{kl}(r) \right)$$

$$= -\frac{2(l+1)}{3(2l+1)} \int_0^\infty dr \left( \frac{1}{2} \frac{d(r P_{kl}^2)}{dr} - \frac{2l+3}{2} P_{kl}^2 \right)$$

$$= \frac{2(l+1)}{3(2l+1)} \frac{2l+3}{2} = \frac{(l+1)(2l+3)}{3(2l+1)}$$

Note: $f_{kl}\rightarrow l-1 + f_{kl}\rightarrow l+1 = 1$.

Note further: if $l = 0$, only $f_{ks}(l=0)\rightarrow 1$ is possible and from the general result for $f_{kl}\rightarrow l+1$ with $l = 0$,

$$f_{ks} = 1.$$

3. The Al ground state is a $3p$ doublet, the $3p_{3/2}$ state being above the $3p_{1/2}$ state by $\delta E = 112.061$ cm$^{-1}$. The $3p_{3/2} \rightarrow 3p_{1/2}$ transition wavelength is $\lambda = 10^7/\delta E = 892,371$ Å. The transition rate from $a = 3p_{3/2}$ to $b = 3p_{1/2}$ is

$$A_{a\rightarrow b} = \frac{2.69735 \times 10^{13} S_{M1}}{\lambda^3} g_a \text{ s}^{-1},$$

where $S_{M1} = |\langle b|L + 2S|a\rangle|^2$ and $g_a = 2j_a + 1$. Now let us find the reduced matrix element:

$$\langle j_a l_b M_b |L_L + 2S_{1/2} | j_a l_a M_a \rangle = -\frac{j_a M_b}{1/2 \mu_b} \frac{j_a M_a}{1/2 \mu_a} \left[ -\frac{1}{1/2 \mu_a} \langle l_b|L|l_a\rangle \delta_{\mu_a \mu_b} + \frac{1}{1/2 \mu_b} \langle 1/2 \sigma|1/2 \rangle \delta_{l_b l_a} \delta_{m_b m_a} \right]$$
Carrying out the sums over magnetic quantum numbers, this reduces to

\[
\langle j_b l_b M_b | L_\nu + 2S_\nu | j_a l_a M_a \rangle = -\frac{1}{1\nu} \times \\
\sqrt{|j_b| |j_a|} \left[ (-1)^{j_a + l_b + 3/2} \left\{ \begin{array}{ccc} j_b & j_a & 1 \\ l_b & l_a & 1/2 \end{array} \right\} \langle b||L||a \rangle \\
+ (-1)^{j_b + l_b + 3/2} \left\{ \begin{array}{ccc} j_b & j_a & 1/2 \\ 1/2 & 1/2 & l \end{array} \right\} (1/2||\sigma||1/2) \delta_{l_b l_a} \right].
\]

From this, we can read off the reduced matrix element. Furthermore,

\[
\langle b||L||a \rangle = \sqrt{l_a(l_a+1)(2l_a+1)} \delta_{l_b l_a} \text{ and } \langle 1/2||\sigma||1/2 \rangle = \sqrt{6}.
\]

Therefore, for the case \(j_a = l + 1/2\), \(j_b = l - 1/2\), and \(l_a = l_b = l\),

\[
\langle b||M||a \rangle = \sqrt{(2l)(2l + 2)} \left[ \sqrt{\Gamma(\nu)(2l + 1)} \left\{ \begin{array}{ccc} l - 1/2 & l + 1/2 & 1 \\ 1/2 & 1/2 & 1 \end{array} \right\} \\
- \sqrt{6} \left\{ \begin{array}{ccc} l - 1/2 & l + 1/2 & 1 \\ 1/2 & 1/2 & 1 \end{array} \right\} \right]
\]

\[
= 2\sqrt{l(l + 1)} \left[ \frac{1}{\sqrt{2(l + 1)}} - \frac{2}{\sqrt{2(2l + 1)}} \right]
\]

\[
= \sqrt{\frac{2(2l + 1)}{2l + 1}}.
\]

It follows that for \(p\) states, where \(l = 1\), the line strength is \(S_{M1} = 4/3\) and \(g_a = 2j_a + 1 = 4\). For the \(3p\) doublet in Al, the transition rate is

\[
A_{3p_{3/2}-3p_{1/2}} = 2.69735 \times 10^{13} \times \frac{(4/3)}{(10^8/112.061)^3 \times 4} = 1.26526 \times 10^{-5} \text{ s}^{-1}
\]

\[
\tau(\text{3p}_{3/2}) = \frac{1}{A} = 79035.18 \text{ s} = 21 \text{ h} 57 \text{ m} 15 \text{ s}
\]

**Relativistic Calculation:** In a relativistic calculation, the reduced magnetic-dipole matrix element is given by

\[
\langle b||M||a \rangle = 2c \langle b||\sigma^{(0)}||a \rangle = 2c \langle b||\frac{3}{k} j_1^{(0)}||a \rangle
\]

\[
= 2c \frac{\kappa_b + \kappa_a}{2} \langle -\kappa_b || C_1 || \kappa_a \rangle \int_0^\infty dr \frac{3}{k} j_1(kr) (P_b Q_a + P_a Q_b)
\]

We make two approximations: Firstly, \(kr \approx 2\pi a_0/\lambda \approx 4 \times 10^{-6} \ll 1\). This approximation permits us ignore higher-order terms in the expansion of the spherical Bessel function and approximate \(3j_1(kr)/k\) by \(r\). Secondly, we use the Pauli approximation for the atomic wave functions of the \(3p\) states in Aluminum. This approximation, which is valid provided \((\alpha Z)^2 \approx
10^{-5} \ll 1$, permits us to approximate the small-component wave function by
\[
\int_0^\infty dr \left( P_b Q_a + P_a Q_b \right) \approx -\frac{1}{2c} \int_0^\infty dr \left( \frac{dP_b}{dr} \frac{\kappa_a}{r} P_a + P_a \left( \frac{dP_b}{dr} + \frac{\kappa_b}{r} P_b \right) \right) = -\frac{1}{2c} \int_0^\infty dr \frac{d(rP_b P_a)}{dr} + (\kappa_a + \kappa_b - 1) P_b P_a
\]
where we have used the fact that, in the Pauli approximation, $P_b = P_a = P_{3p}$, where $P_{3p}(r)$ is the nonrelativistic $3p$ radial wave function. Therefore, in the Pauli approximation, the magnetic-dipole matrix element for transitions from states with $j_a = l + 1/2$, $\kappa_a = -l - 1$ to states with $j_b = l - 1/2$, $\kappa_b = l$ becomes:
\[
\langle b || M || a \rangle = -2c \frac{\kappa_b + \kappa_a}{2 c} \frac{\kappa_a + \kappa_b - 1}{2 c} \langle -\kappa_b || C_1 || \kappa_a \rangle
\]
\[
= -\frac{1}{2} (l - l - 1)(-l - 1 + l - 1) \langle -\kappa_b || C_1 || \kappa_a \rangle
\]
\[
= -\langle j_b = l - 1/2 || C_1 || j_a = l + 1/2 \rangle
\]
\[
= \frac{\sqrt{2l(l+1)}}{2l+1}.
\]
Therefore, the relativistic matrix element, in the Pauli approximation, agrees precisely with the nonrelativistic matrix element.

### A.4 Answers to Exams

#### Answers to Exam I

1. The state $|JM\rangle$ is an eigenstate of $J^2$, $J_1^2$, and $J_2^2$. Since $J^2 = J_1^2 + J_2^2 + 2(J_1 \cdot J_2)$, we have
\[
\langle J_1 \cdot J_2 || JM \rangle = \lambda |JM\rangle,
\]
with
\[
\lambda = \frac{1}{2} [J(J+1) - J_1(J_1+1) - J_2(J_2+1)]
\]

2. The energy shift is
\[
\Delta E_{njm} = -\mu_0 B (-1)^{j-m} \begin{pmatrix} j & 1 & j \ 
- m & 0 & m \end{pmatrix} \langle j || \sigma || j \rangle
\]
\[
= -\mu_0 B \frac{m}{\sqrt{j(j+1)(2j+1)}} \langle j || \sigma || j \rangle
\]
\[
= \frac{m}{j} \Delta E_{njj}
\]
3. Hartree-Fock Equations:

(a) Nonrelativistic:

\[ h_0 P_{1s} + V_{\text{dir}} P_{1s} - \left[ v_0(1s, r) P_{1s} + v_0(2s, 1s, r) P_{2s} + \frac{1}{3} v_1(2p, 1s, r) P_{2p} \right] = \epsilon_{1s} P_{1s} \]
\[ h_0 P_{2s} + V_{\text{dir}} P_{2s} - \left[ v_0(1s, 2s, r) P_{1s} + v_0(2s, r) P_{2s} + \frac{1}{3} v_1(2p, 2s, r) P_{2p} \right] = \epsilon_{2s} P_{2s} \]
\[ h_0 P_{2p} + V_{\text{dir}} P_{2p} - \left[ \frac{1}{3} v_1(1s, 2p, r) P_{1s} + \frac{1}{3} v_1(2s, 2p, r) P_{2s} + v_0(2p, r) P_{2p} \right] 
+ \frac{2}{5} v_2(2p, r) P_{2p} = \epsilon_{2p} P_{2p} \]

Here,
\[ h_0 P_{nl} = \left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1) - Z}{r} \right) P_{nl} \]

and
\[ V_{\text{dir}} = 2v_0(1s, r) + 2v_0(2s, r) + 6v_0(2p, r) \]

(b) Relativistic: \( R_{nn} = (P_{\kappa\kappa}, Q_{\kappa\kappa}) \)

\[ h_0 R_{1s} + V_{\text{dir}} R_{1s} - \left[ v_0(1s, r) R_{1s} + v_0(2s, 1s, r) R_{2s} + \frac{1}{3} v_1(2p_{1/2}, 1s, r) R_{2p_{1/2}} \right] = \epsilon_{1s} R_{1s} \]
\[ + \frac{2}{3} v_1(2p_{3/2}, 1s, r) R_{2p_{3/2}} \]
\[ h_0 R_{2s} + V_{\text{dir}} R_{2s} - \left[ v_0(1s, 2s, r) R_{1s} + v_0(2s, r) R_{2s} + \frac{1}{3} v_1(2p_{1/2}, 2s, r) R_{2p_{1/2}} \right] = \epsilon_{2s} R_{2s} \]
\[ + \frac{2}{3} v_1(2p_{3/2}, 2s, r) R_{2p_{3/2}} \]
\[ h_0 R_{2p_{1/2}} + V_{\text{dir}} R_{2p_{1/2}} - \left[ \frac{1}{3} v_1(1s, 2p_{1/2}, r) R_{1s} + \frac{1}{3} v_1(2s, 2p_{1/2}, r) R_{2s} \right] = \epsilon_{2p_{1/2}} R_{2p_{1/2}} \]
\[ + v_0(2p_{1/2}, r) R_{2p_{1/2}} + \frac{4}{5} v_2(2p_{1/2}, 2p_{3/2}, r) R_{2p_{3/2}} \]
\[ h_0 R_{2p_{3/2}} + V_{\text{dir}} R_{2p_{3/2}} - \left[ \frac{1}{3} v_1(1s, 2p_{3/2}, r) R_{1s} + \frac{1}{3} v_1(2s, 2p_{3/2}, r) R_{2s} \right] = \epsilon_{2p_{3/2}} R_{2p_{3/2}} \]
\[ + v_0(2p_{3/2}, r) R_{2p_{3/2}} + \frac{4}{5} v_2(2p_{3/2}, 2p_{1/2}, r) R_{2p_{1/2}} \]

Here,
\[ h_0 R_{nn} = \begin{pmatrix}
-\frac{Z}{r} + c^2 & c \left( \frac{\alpha}{r^2} - \frac{\alpha}{r} \right) \\
-c \left( \frac{\alpha}{r^2} + \frac{\alpha}{r} \right) & -\frac{Z}{r} - c^2
\end{pmatrix} R_{nn} \]

and
\[ V_{\text{dir}} = 2v_0(1s, r) + 2v_0(2s, r) + 2v_0(2p_{1/2}, r) + 4v_0(2p_{3/2}, r) \]
A.4. ANSWERS TO EXAMS

4. Hartree-Fock Energies

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<thead>
<tr>
<th>Shell</th>
<th>Energy</th>
<th>Expt.</th>
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<td>Lithium</td>
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<td>2s</td>
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<tr>
<td>3s</td>
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<td>-0.122513</td>
</tr>
</tbody>
</table>

Answers to Final Exam

1. Consider a transition from the \((1s^3d^3)^3D\) state to the \((1s^2p^3)^3P\) state in a helium-like ion:

(a) Show that, in the independent-particle approximation,

\[
\langle (1s^2p^3)^3P | r \parallel (1s^3d^3)^3D \rangle = \langle 2p | r | 3d \rangle
\]

We write

\[
\langle (1s^3d^3)^3D | r \parallel (1s^3d^3)^3D \rangle
\]

\[
= \sum_{m_k} \delta_{m_x m_x} \delta_{x F x I} \delta_{s_x s_x} \delta_{s_x s_x} \langle n l F m^l I | r \parallel m^l I m^l I \rangle
\]

\[
= \sum_{m_k} \delta_{m_x m_x} \delta_{x F x I} \delta_{s_x s_x} \delta_{s_x s_x} \langle n l F m^l I | r \parallel m^l I m^l I \rangle \delta_{s_F s_I}
\]

\[
= (-1)^{l + L_F + 1} \sqrt{|L_I| |L_F|} \left\{ \begin{array}{ccc} L_I & L_F & 1 \\ l_F & l_I & 0 \end{array} \right\} \langle n l F | r \parallel m^l I \rangle \delta_{s_F s_I}
\]

\[
= \langle n l F | r | m^l I \rangle \delta_{s_F s_I}
\]
From this, it follows that
\[
\langle (1snl_F) ^{2S_F+1}L_F || r || (1sml_I) ^{2S_I+1}L_I \rangle = \langle nl_F || ml_I \rangle \delta_{S_FS_I}.
\]
Therefore,
\[
\langle (1s2p) ^{3P} || r || (1s3d) ^{3D} \rangle = \langle 2p || 3d \rangle.
\]

(b) Suppose that one can resolve the fine-structure of the initial and final states. Express the matrix elements \(\langle (1s2p) ^{3P} || r || (1s3d) ^{3D} \rangle\) in terms of \(\langle (1s2p) ^{3P} || r || (1s3d) ^{3D} \rangle\) or \(\langle 2p || 3d \rangle\).

We write
\[
\langle 2S_F+1L_F || r \rangle ^{2S_F+1L_I} J_I \rangle = \sum_{M_k \mu_k} \left[ \left( J_I L_I M_I \right) - \left( L_F M_F \right) \left[ \langle 2S_F+1L_F || r \rangle ^{2S_F+1L_I} \rangle \delta_{\mu_I\mu_F} \right] \right]
\]
\[
\langle 2S_F+1L_F || r \rangle ^{2S_F+1L_I} \rangle = (-1)^{J_I+L_F+S+1} \sqrt{[J_I][J_F]} \left\{ \begin{array}{ccc} J_I & J_F & 1 \\ L_F & L_I & S \end{array} \right\} \times \langle 2S_F+1L_F || r \rangle ^{2S_F+1L_I} \rangle - \frac{1}{J_I}
\]

From this, it follows
\[
\langle 2S_F+1L_F || r \rangle ^{2S_F+1L_I} J_I \rangle = \]
\[
= (-1)^{J_I+L_F+S+1} \sqrt{[J_I][J_F]} \left\{ \begin{array}{ccc} J_I & J_F & 1 \\ L_F & L_I & S \end{array} \right\} \langle 2S_F+1L_F || r \rangle ^{2S_F+1L_I} \rangle.
\]

Therefore,
\[
\langle (1s2p) ^{3P} || r || (1s3d) ^{3D} \rangle = (-1)^{J_I+1} \sqrt{[J_I][J_F]} \left\{ \begin{array}{ccc} J_I & J_F & 1 \\ 1 & 2 & 1 \end{array} \right\} \langle 2p || 3d \rangle.
\]

(c) The intensity of the lines from \(|(1s3d) ^{3D} \rangle\) to \(|(1s2p) ^{3P} \rangle\) is
\[
A_{I-F} \propto \frac{S_{FI}}{[J_I]} = \frac{\langle (1s2p) ^{3P} || r || (1s3d) ^{3D} \rangle^2}{[J_I]}.
\]

By explicitly evaluating the relevant 6j symbols (using MAPLE, for example), show that the ratios of intensities for transitions \(J_I \rightarrow J_F\):
\[
1 \rightarrow 0 : 1 : 1 : 2 \rightarrow 1 : 1 : 2 : 2 \rightarrow 2 : 3 \rightarrow 2
\]
are
\[20 : 15 : 27 : 1 : 9 : 36.\]

From the result of part (b) above, it follows
\[S_{FI} / [J_I] = [J_F] \left\{ J_I \quad J_F \quad 1 \quad 1 \right\} ^2 | \langle 2p\parallel r\parallel 3d \rangle | ^2.\]

Setting \(T(J_F, J_I) = S_{FI} / ([J_I] | \langle 2p\parallel r\parallel 3d \rangle | ^2)\), we find
\[
\begin{align*}
T(0, 1) &= 1/9 = 20/180 \\
T(1, 1) &= 1/12 = 15/180 \\
T(1, 2) &= 3/20 = 27/180 \\
T(2, 1) &= 1/180 = 1/180 \\
T(2, 2) &= 1/20 = 9/180 \\
T(2, 3) &= 1/5 = 36/180
\end{align*}
\]

Multiplying the entries in this table by 180 leads to the desired result.

2. Suppose we choose to describe an atom in lowest order using a potential \(U(r)\) other than the HF potential.

(a) Show that the correction to the first-order energy from the single-particle part of the potential \((V_1)\) for a one electron atom in a state \(v\) is
\[E_v^{(1)} = \Delta_{vv},\]
where \(\Delta = V_{HF} - U\).

We use the fact that the contribution to the first-order energy from \(V_1\) is
\[
E^{(1)} = \langle \Psi_0 | V_1 | \Psi_0 \rangle = \sum_{ij} \Delta_{ij} \langle 0_c | a_i : a_j^\dagger : a_v : a_v^\dagger | 0_c \rangle = \sum_{ij} \Delta_{ij} \delta_{iv} \delta_{jv} = \Delta_{vv}.
\]

(b) Show that the corresponding second-order correction is
\[
E_v^{(2)} = \sum_{na} \frac{\Delta_{na} \Delta_{av} + \Delta_{nv} \Delta_{an}}{\epsilon_n - \epsilon_a} - \sum_{i \neq v} \frac{\Delta_{ii} \Delta_{iv}}{\epsilon_i - \epsilon_v}.
\]

Here, \(i\) runs over \(a\) and \(n\).
First, we note that if we add $V_1$ to the potential, then the expression for the correlation function becomes

$$
\chi^{(1)} = \sum_{ma} \chi^{(1)}_{ma} a_m^\dagger a_a + \sum_m \chi^{(1)}_{mv} a_m^\dagger a_v
$$

$$
+ \sum_{mnab} \chi^{(1)}_{mnab} a_m^\dagger a_n^\dagger a_b a_a + \sum_{mnb} \chi^{(1)}_{mnb} a_m^\dagger a_n^\dagger a_b a_v,
$$

where,

$$
\chi^{(1)}_{ma} = -\frac{\Delta_{ma}}{\epsilon_m - \epsilon_a}
$$

$$
\chi^{(1)}_{va} = -\frac{\Delta_{mv}}{\epsilon_m - \epsilon_v}
$$

$$
\chi^{(1)}_{mnab} = -\frac{1}{2} \frac{g_{mnab}}{\epsilon_m + \epsilon_n - \epsilon_a - \epsilon_b}
$$

$$
\chi^{(1)}_{mnb} = -\frac{1}{2} \frac{\tilde{g}_{mnb}}{\epsilon_m + \epsilon_n - \epsilon_v - \epsilon_b}
$$

The extra terms in the second-order energy from $V_1$ are

$$
E^{(2)} = \langle 0_c | a_v V_1 \left( \sum_{abmn} \chi^{(1)}_{mnab} a_m^\dagger a_n^\dagger a_b a_a + \sum_{mnb} \chi^{(1)}_{mnb} a_m^\dagger a_n^\dagger a_b a_v \right) a_v^\dagger a_v | 0_c \rangle
$$

$$
+ \langle 0_c | a_v V_2 \left( \sum_{am} \chi^{(1)}_{ma} a_m^\dagger a_a + \sum_m \chi^{(1)}_{mv} a_m^\dagger a_v \right) a_v^\dagger a_v | 0_c \rangle
$$

$$
+ \langle 0_c | a_v V_2 \left( \sum_{am} \chi^{(1)}_{ma} a_m^\dagger a_a + \sum_m \chi^{(1)}_{mv} a_m^\dagger a_v \right) a_v^\dagger a_v | 0_c \rangle
$$

$$
= \sum_{ij} \Delta_{ij} \sum_{mnab} \chi^{(1)}_{mnab} \langle 0_c | a_v : a_i^\dagger a_j : a_m^\dagger a_n^\dagger a_b a_a | 0_c \rangle
$$

$$
+ \sum_{ij} \Delta_{ij} \sum_{mnb} \chi^{(1)}_{mnb} \langle 0_c | a_v : a_i^\dagger a_j : a_m^\dagger a_n^\dagger a_b a_v | 0_c \rangle
$$

$$
+ \sum_{ij} \Delta_{ij} \sum_{ma} \chi^{(1)}_{ma} \langle 0_c | a_v : a_i^\dagger a_j : a_m^\dagger a_a a_v | 0_c \rangle
$$

$$
+ \sum_{ij} \Delta_{ij} \sum_{mv} \chi^{(1)}_{mv} \langle 0_c | a_v : a_i^\dagger a_j : a_m^\dagger a_v | 0_c \rangle
$$

$$
+ \frac{1}{2} \sum_{ijkl} g_{ijkl} \sum_{ma} \chi^{(1)}_{ma} \langle 0_c | a_v : a_i^\dagger a_j : a_m^\dagger a_k a_v | 0_c \rangle
$$

$$
+ \frac{1}{2} \sum_{ijkl} g_{ijkl} \sum_{mv} \chi^{(1)}_{mv} \langle 0_c | a_v : a_i^\dagger a_j : a_m^\dagger a_k | 0_c \rangle.
$$

The first and sixth terms above cannot contribute. The remaining
terms give, in order,

\[ E^{(2)} = \sum_{bn} \Delta_{nb} \tilde{\chi}_{vn_{eb}}^{(1)} + \sum_{ma} \Delta_{am} \chi_{ma}^{(1)} - \sum_{a} \Delta_{av} \chi_{va}^{(1)} + \sum_{m} \Delta_{vm} \chi_{mv}^{(1)} + \sum_{ma} \tilde{g}_{va_{vm}} \chi_{ma}^{(1)}. \]

Substituting the values of the correlation coefficients, we find

\[ E^{(2)} = -\sum_{bn} \frac{\Delta_{nb} \tilde{g}_{vn_{eb}}}{\epsilon_n - \epsilon_b} - \sum_{ma} \frac{\Delta_{am} \Delta_{ma}}{\epsilon_m - \epsilon_a} + \sum_{a} \frac{\Delta_{av} \Delta_{va}}{\epsilon_v - \epsilon_a} - \sum_{m} \frac{\Delta_{vm} \Delta_{mv}}{\epsilon_m - \epsilon_v} - \sum_{ma} \frac{\tilde{g}_{va_{vm}} \Delta_{ma}}{\epsilon_m - \epsilon_a}. \]

The second term, which is independent of \( v \), is the contribution of \( \Delta \) to the core energy. The remaining terms are contributions to the valence energy. We therefore find

\[ E^{(2)}_v = -\sum_{bn} \frac{\Delta_{nb} \tilde{g}_{vn_{eb}} + \tilde{g}_{vb_{vn}} \Delta_{ab}}{\epsilon_n - \epsilon_b} - \sum_{i \neq v} \frac{\Delta_{vi} \Delta_{iv}}{\epsilon_i - \epsilon_v}. \]

The first term has an unfortunate sign difference with the result given in the problem. The sign here is correct.
Bibliography


