

The Many-Electron Atom

I. Introduction

Most systems of chemical interest have more than one electron and, indeed, more than one atom. However, many essential chemical principles follow from atomic structure, and so we will start by considering many-electron atoms. The starting point is, of course, the Schrödinger equation in the Born-Oppenheimer approximation, which for an N -electron atom with atomic number Z is (cf. Eq. (1.20))

$$\sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (3.1)$$

Here, the first term is the kinetic energy of electron i , the second term is its electron-nuclear attraction potential (we assume the nucleus is at the origin, $\mathbf{R} = 0$), and the third term is the electron-electron repulsion potential between electron i and the other electrons in the system). If $N > 1$, no exact solutions to this equation are known and, indeed, it is believed that the wave functions of many-electron atoms are infinitely complex (in the sense that there is no way to “write down” what they are). The essential problem is, as we shall see, the conflict between the electron-electron repulsion term, which couples electrons together in an intricate dance of mutual avoidance, and the electron-nuclear attraction, which induces electrons into frequenting the regions of space nearest the nucleus. An electron “wants” to be close to the nucleus and far away from the other electrons at the same time, and it goes to great lengths to do so, introducing extraordinary complexity into the electronic wave function. Describing, however approximately, the intricate dance of the electrons is called the problem of electron correlation, but we won’t have much to say about that right now.

II. The Helium Atom

A. The Introduction of Orbitals

The key elements of the many-electron atom can already be understood by considering the two-electron, Helium-like, atom. The Schrödinger equation simplifies to

$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) = E \Psi(\mathbf{r}_1, \mathbf{r}_2) \quad (3.2)$$

Again, the problem is the electron-electron repulsion term. Let us start by ignoring the electron-electron repulsion term. Then the 2-electron Hamiltonian becomes the sum of two electronic Hamiltonians and the Schrödinger equation becomes:

$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) = E \Psi(\mathbf{r}_1, \mathbf{r}_2) \quad (3.3)$$

We can solve this equation with separation of variables: take $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1) \psi(\mathbf{r}_2)$, substitute into Eq. (3.3), and simplify:

$$\begin{aligned} \left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} \right) \phi(\mathbf{r}_1) \psi(\mathbf{r}_2) &= E \phi(\mathbf{r}_1) \psi(\mathbf{r}_2) \\ \psi(\mathbf{r}_2) \left(-\frac{\nabla_1^2}{2} - \frac{Z}{r_1} \right) \phi(\mathbf{r}_1) + \phi(\mathbf{r}_1) \left(-\frac{\nabla_2^2}{2} - \frac{Z}{r_2} \right) \psi(\mathbf{r}_2) &= E \phi(\mathbf{r}_1) \psi(\mathbf{r}_2) \end{aligned} \quad (3.4)$$

If we assume that $\phi_{n_1, l_1, m_1}(\mathbf{r}_1)$ and $\psi_{n_2, l_2, m_2}(\mathbf{r}_2)$ are wave-functions for the one-electron atom with atomic number Z , then

$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} \right) \phi_{n_1, l_1, m_1}(\mathbf{r}_1) \psi_{n_2, l_2, m_2}(\mathbf{r}_2) = E_{n_1, l_1, m_1} + E_{n_2, l_2, m_2} \phi_{n_1, l_1, m_1}(\mathbf{r}_1) \psi_{n_2, l_2, m_2}(\mathbf{r}_2) \quad (3.5)$$

$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} \right) \phi_{n_1, l_1, m_1}(\mathbf{r}_1) \psi_{n_2, l_2, m_2}(\mathbf{r}_2) = \left(-\frac{Z}{2n_1^2} - \frac{Z}{2n_2^2} \right) \phi_{n_1, l_1, m_1}(\mathbf{r}_1) \psi_{n_2, l_2, m_2}(\mathbf{r}_2) .$$

This is a very poor model for the 2-electron atom, since we neglected the electron-electron repulsion potential, a term that has about the same size as the electron-nuclear attraction. (The electron-nuclear attraction energy is about twice the size of the electron-electron repulsion energy. Contrast this with the Born-Oppenheimer approximation, where the terms neglected in Eq. (1.26) are about 2000 times smaller than the terms retained.) As a consequence the ground state energy in the “repulsionless” Helium atom is -4 Hartree, as compared to the exact (within the non-relativistic and Born-Oppenheimer approximations) energy of -2.9037 Hartree. This error is about 700 kcal/mol (2900 kJ/mol), which is horrible by any standard. Clearly, we must do better.

But before we do better, we should discuss what we have learned: in the absence of electron-electron repulsion, the wave function is a product of hydrogenic orbitals and the total energy is a sum of hydrogenic energies. This provides a basis for chemistry, in which we discuss the s, p, and d-orbitals on many-electron atoms (and even atoms in molecules) by presuming that they look like—and have energies similar to—one-electron atoms’ orbitals. This is an assumption of course, but there is a large body of experimental, theoretical, and, most importantly, practical experience that suggests that even though “hydrogenic orbital paradigm” may not be mathematically valid, it is conceptually useful.

B. Perturbation Theoretic Corrections to the Orbital Model

We can compute corrections to the simple orbital-based approach of Eq. (3.5) using perturbation theory. To do this, write the Hamiltonian as

$$H^\lambda \equiv \left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{\lambda}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \quad (3.6)$$

$$H^\lambda \Psi^\lambda(\mathbf{r}_1, \mathbf{r}_2) = E^\lambda \Psi^\lambda(\mathbf{r}_1, \mathbf{r}_2)$$

and use the fact that the known “hydrogenic solutions”, Eq. (3.5), are the exact solutions to the Schrödinger equation with $\lambda = 0$. We can correct the energy by writing the Taylor series in λ , namely

$$E = E|_{\lambda=0} + \lambda \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda=0} + \frac{\lambda^2}{2!} \left. \frac{\partial^2 E}{\partial \lambda^2} \right|_{\lambda=0} + \dots \quad (3.7)$$

We are most interested in the case $\lambda = 1$,

$$E_{2 \text{ el. atom}} = E|_{\lambda=0} + \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda=0} + \frac{1}{2!} \left. \frac{\partial^2 E}{\partial \lambda^2} \right|_{\lambda=0} + \dots \quad (3.8)$$

We can evaluate $\frac{\partial E}{\partial \lambda}$ using first-order perturbation theory or, what amounts to the same thing, the Hellmann-Feynman theorem. So

$$\begin{aligned}
\frac{\partial E}{\partial \lambda} &= \left\langle \phi_{1,0,0} \mathbf{r}_1 \psi_{1,0,0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_{1,0,0} \mathbf{r}_1 \psi_{1,0,0} \mathbf{r}_2 \right\rangle \\
&= \iint \phi_{1,0,0}^2(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{1,0,0}^2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \iint \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr_1} \right)^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr_2} \right)^2 d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \iint \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr_1} \right)^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr_2} \right)^2 d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \frac{Z^6}{\pi^2} \iint e^{-2Zr_1} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-2Zr_2} d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \frac{Z^6}{\pi^2} \iint \frac{e^{-2Z(\mathbf{r}_1 + \mathbf{r}_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2
\end{aligned} \tag{3.9}$$

The integral in Eq. (3.9) is a bit tricky; the key idea is that

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{\max(r, r')} \left(1 + A \cdot \left(\frac{\min(r, r')}{\max(r, r')} \right) + \frac{3A^2 - 1}{2} \left(\frac{\min(r, r')}{\max(r, r')} \right)^2 + \dots \right). \tag{3.10}$$

The “angular” terms, $A \theta, \phi; \theta', \phi'$, do not contribute when the wave functions are spherically symmetric (that is, if the wave functions are s -orbitals), so in this case

$$\begin{aligned}
\frac{\partial E}{\partial \lambda} &= \frac{Z^6}{\pi^2} \iint \frac{e^{-2Z(\mathbf{r}_1 + \mathbf{r}_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \frac{Z^6}{\pi^2} \int_0^\infty \int_0^\pi \int_0^\pi \int_0^\infty \int_0^\pi \int_0^\pi \int_0^\infty \frac{e^{-2Z(\mathbf{r}_1 + \mathbf{r}_2)}}{r_1} r_1^2 r_2^2 \sin \theta_1 \sin \theta_2 dr_2 d\theta_2 d\phi_2 dr_1 d\theta_1 d\phi_1 \Bigg\}_{r_2 < r_1} \\
&\quad + \frac{Z^6}{\pi^2} \int_0^\infty \int_0^\pi \int_0^\pi \int_0^\infty \int_0^\pi \int_0^\pi \int_{r_1}^\infty \frac{e^{-2Z(\mathbf{r}_1 + \mathbf{r}_2)}}{r_2} r_1^2 r_2^2 \sin \theta_1 \sin \theta_2 dr_2 d\theta_2 d\phi_2 dr_1 d\theta_1 d\phi_1 \Bigg\}_{r_2 > r_1} \\
&= 4\pi^2 \frac{Z^6}{\pi^2} \left[\int_0^\infty \int_0^{r_1} e^{-2Z(\mathbf{r}_1 + \mathbf{r}_2)} r_1^2 r_2^2 dr_2 dr_1 + \int_0^\infty \int_{r_1}^\infty e^{-2Z(\mathbf{r}_1 + \mathbf{r}_2)} r_1^2 r_2^2 dr_2 dr_1 \right] \\
&= 16Z^6 \int_0^\infty e^{-2Zr_1} \left(r_1 \int_0^{r_1} r_2^2 e^{-2Zr_2} dr_2 + r_1^2 \int_{r_1}^\infty r_2 e^{-2Zr_2} dr_2 \right) dr_1
\end{aligned} \tag{3.11}$$

The key integral is obtained by integration by parts, namely,

$$\int x^n e^{-ax} dx = e^{-ax} \left(-\frac{x^n}{a} - \sum_{k=1}^n \frac{n(n-1)(n-2)\cdots(n-k+1)}{a^{k+1}} x^{n-k} \right). \tag{3.12}$$

So

$$\begin{aligned}
\frac{\partial E}{\partial \lambda} &= 16Z^6 \int_0^\infty e^{-2Zr_1} \left(r_1 \int_0^{r_1} r_2^2 e^{-2Zr_2} dr_2 + r_1^2 \int_{r_1}^\infty r_2 e^{-2Zr_2} dr_2 \right) dr_1 \\
&= 16Z^6 \int_0^\infty e^{-2Zr_1} \left[r_1 \cdot \left[e^{-2Zr_1} - \frac{r_1^2}{2Z} - \frac{1}{2Z^2} r_1 - \frac{1}{4Z^3} \right] - \left[\frac{1}{4Z^2} r_1^2 - \frac{1}{4Z^3} r_1 \right] \right] dr_1 \\
&= 16Z^6 \int_0^\infty e^{-2Zr_1} \left[\frac{r_1}{4Z^3} + e^{-2Zr_1} \left(\frac{1}{4Z^2} r_1^2 - \frac{1}{4Z^3} r_1 \right) \right] dr_1 \\
&= 4Z^3 \int_0^\infty e^{-2Zr_1} \left[r_1 - e^{-2Zr_1} \left(\frac{1}{4Z^2} r_1^2 + r_1 \right) \right] dr_1
\end{aligned} \tag{3.13}$$

We evaluate this last integral to obtain

$$\begin{aligned}
\frac{\partial E}{\partial \lambda} &= 4Z^3 \int_0^\infty e^{-2Zr_1} \left[r_1 - e^{-2Zr_1} \left(\frac{1}{4Z^2} r_1^2 + r_1 \right) \right] dr_1 \\
&= 4Z^3 \left[\frac{1}{2Z^2} - Z \left(\frac{2}{4Z^3} \right) - \left(\frac{1}{4Z^2} \right) \right] \\
&= Z \left[1 - \frac{1}{8} - \frac{1}{4} \right] \\
&= \frac{5Z}{8}
\end{aligned} \tag{3.14}$$

If we neglect the higher order terms in Eq. (3.8), then we obtain the energy

$$E_{2, \text{el. atom}}^{\text{theory}} = -Z^2 + \frac{5Z}{8} \text{ Hartree} \tag{3.15}$$

which, for the Helium atom, gives

$$\begin{aligned}
E_{\text{He}}^{\text{theory}} &= -\frac{11}{4} \text{ Hartree} \\
&= -2.75 \text{ Hartree}
\end{aligned} \tag{3.16}$$

One can refine this result by going to higher orders of perturbation theory. However, this is not entirely straightforward. If one does the perturbation theory in a clever way, one can get accurate results not only for the Helium atom, but also for the other two-electron atoms of chemical relevance, specifically the hydride ion, lithium cation, and beryllium dication.

C. The Effective Nuclear Charge and Hartree-Fock Theory

To make further progress, it is helpful to consider the perturbation theory treatment more carefully. Note that perturbation theory amounts to evaluating the energy of the approximate wave function

$$\Psi_{2\text{-el. atom}}^{\text{approx.}}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2) \tag{3.17}$$

That is, the perturbation theory energy is obtained by evaluating

$$\begin{aligned}
E &= \langle \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2) | \hat{H} | \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2) \rangle \\
&= 2E_Z^{1.\text{el.}} + \langle \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2) | V_{ee} | \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2) \rangle
\end{aligned} \tag{3.18}$$

where we have approximated the wave function as a simple product of the 1s-orbitals of the one-electron atom with atomic number Z . Here, $E_Z^{1.\text{el.}}$ is the energy of the one-electron atom and $\langle V_{ee} \rangle$ is the electron-electron repulsion energy for this approximate wave function. Comparing to Eq. (3.7),

we recognize that $\frac{\partial E}{\partial \lambda}$ is just the electron-electron repulsion energy. No convincing argument has been made for choosing the product of the hydrogenic wave functions to approximate the wave function of the two-electron atom.

To improve our choice of orbitals, we need to thoroughly understand the implications of our preceding analysis. To this end, reexpress the result from Eq. (3.13) as

$$\langle V_{ee} \rangle = \int_0^\infty \left(\frac{Z^3}{\pi} \right) e^{-2Zr_1} \frac{1}{r_1} [1 - e^{-2Zr_1} Zr_1 + 1] 4\pi r_1^2 dr_1 \quad (3.19)$$

and note the similarity of this form to the nuclear-electron attraction energy

$$\begin{aligned} \langle V_{ne} \rangle &= \int_0^\infty \sqrt{\frac{Z^3}{\pi}} e^{-Zr_1} \frac{-Z}{r_1} \sqrt{\frac{Z^3}{\pi}} e^{-Zr_1} 4\pi r_1^2 dr_1 \\ &= \int_0^\infty \frac{Z^3}{\pi} e^{-2Zr_1} \frac{-1}{r_1} Z 4\pi r_1^2 dr_1 \end{aligned} \quad (3.20)$$

Comparing Eqs. (3.19) and (3.20), we see that the effect of the electron-electron repulsion is to reduce the nuclear charge an electron feels at a given distance, r from the nucleus from Z to

$$Z_{\text{eff}}(r) \equiv Z - 1 + e^{-2Zr} Zr + 1. \quad (3.21)$$

Observing Eq. (3.21), we see that the effective nuclear charge at the nucleus is just the “bare” nuclear charge (Z) and far from the nucleus the effective nuclear charge is $Z - 1$,¹ because an electron far from the nucleus feels an attractive force from the nucleus but a repulsive force due to the other electron. For intermediate r , the effective nuclear charge is between Z and $Z - 1$, and is depicted in figure 3.1. Because each electron essentially “shields” or “covers” the nuclear charge, reducing its potency to the second electron, we speak of this effect as “nuclear shielding”. Sometimes the effective nuclear charge is called the “dressed” nuclear charge. (The picture is that the electron cloud acts as a sort of veil, concealing the “naked” nuclear charge from the electrons in an atom.)

This suggests that the “best” orbital is not the 1s orbital, but an orbital with an effective nuclear charge which depends on r , that is,

$$\psi_{1s}^{He}(r) \propto e^{-\zeta(r)r}, \quad (3.22)$$

where $\zeta(r)$ is an effective nuclear charge which, consistent with Eq. (3.21), generally varies with r . Equation (3.22) is, in fact, an exact form for the 1s-orbital in 2-electron atoms. Unfortunately, it is quite difficult to find the correct form of $\zeta(r)$ and if one, for example, tries to use Eq. (3.21) and sets $\zeta(r) = Z_{\text{eff}}(r)$, one encounters extremely unpleasant integrals (integrals containing exponentials of exponentials are the worst of them).

¹ For an N -electron atom, the effective nuclear charge at the nucleus is still Z , but the effective nuclear charge at long range is $Z - N + 1 = Q + 1$. Here Q is the total charge of the molecule (-1 for an anion, zero for a neutral molecule, $+1$ for a cation, $+2$ for a dication, etc.).

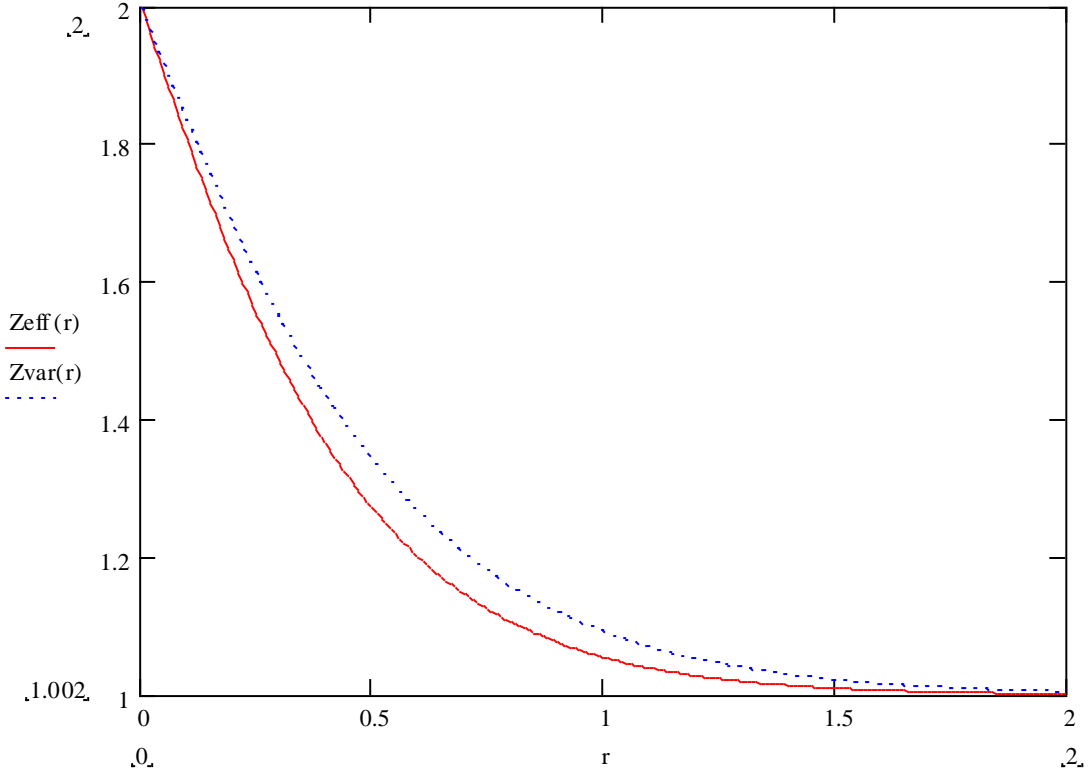


Figure 3.1. Effective nuclear charge in the Helium atom (in the 1s-orbital approximation). $Z_{\text{eff}}(r)$ is from Eq. (3.21). $Z_{\text{var}}(r) = Z - 1 + e^{-2\zeta r} \zeta r + 1$ is computed from the “shielded” wave function considered in Eq. (3.23).

It is not too painful, however, to perform the analysis if we choose $\zeta(r) = \zeta$, where ζ is just a constant throughout space. Then, we have an approximate wave function of

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{\zeta^3}{\pi} e^{-\zeta(r_1 + r_2)} \quad (3.23)$$

and we choose ζ using the variational principle. That is, we minimize the energy,

$$\begin{aligned} E(\zeta) &= \left\langle \frac{\zeta^3}{\pi} e^{-\zeta(r_1 + r_2)} \left| \left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \right| \frac{\zeta^3}{\pi} e^{-\zeta(r_1 + r_2)} \right\rangle \\ &= \left\langle \frac{\zeta^3}{\pi} e^{-\zeta(r_1 + r_2)} \left| \left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{\zeta}{r_1} - \frac{\zeta}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \right| \frac{\zeta^3}{\pi} e^{-\zeta(r_1 + r_2)} \right\rangle, \\ &\quad + \left\langle \frac{\zeta^3}{\pi} e^{-\zeta(r_1 + r_2)} \left| \left(\frac{\zeta - Z}{r_1} + \frac{\zeta - Z}{r_2} \right) \right| \frac{\zeta^3}{\pi} e^{-\zeta(r_1 + r_2)} \right\rangle \end{aligned} \quad (3.24)$$

with respect to ζ . The second term in Eq. (3.24) can be evaluated as

$$\begin{aligned}
& \left\langle \frac{\zeta^3}{\pi} e^{-\zeta r_1 + r_2} \left| \left(\frac{\zeta - Z}{r_1} + \frac{\zeta - Z}{r_2} \right) \right| \frac{\zeta^3}{\pi} e^{-\zeta r_1 + r_2} \right\rangle \\
&= 2 \left\langle \frac{\zeta^3}{\pi} e^{-\zeta r_1 + r_2} \left| \left(\frac{\zeta - Z}{r_1} \right) \right| \frac{\zeta^3}{\pi} e^{-\zeta r_1 + r_2} \right\rangle \\
&= 2 \int_0^\infty \frac{\zeta^3}{\pi} e^{-2\zeta r_1} \left(\frac{\zeta - Z}{r_1} \right) 4\pi r_1^2 dr_1 \int_0^\infty \frac{\zeta^3}{\pi} e^{-2\zeta r_2} 4\pi r_2^2 dr_2 \\
&= 8\zeta^3 (\zeta - Z) \int_0^\infty e^{-2\zeta r_1} r_1 dr_1 \\
&= 8\zeta^3 (\zeta - Z) \left(\frac{1}{2\zeta^2} \right) \\
&= 2\zeta (\zeta - Z)
\end{aligned} \tag{3.25}$$

The first term in Eq. (3.24) is identical to the energy of the 2-electron atom with atomic number ζ in the perturbation theory (or unscreened orbital) approximation (cf. Section IIB), so

$$E(\zeta) = -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - Z) \tag{3.26}$$

To find the minimum with respect to ζ , we solve

$$\begin{aligned}
\frac{\partial E}{\partial \zeta} &= 0 = -2\zeta + \frac{5}{8} + 4\zeta - 2Z \\
&\downarrow \\
\zeta &= Z - \frac{5}{16}
\end{aligned} \tag{3.27}$$

and so

$$\begin{aligned}
E(\zeta) &= -\left(Z - \frac{5}{16}\right)^2 + \frac{5}{8}\left(Z - \frac{5}{16}\right) - 2\left(Z - \frac{5}{16}\right)\left(Z - \frac{5}{16}\right) \\
&= -\left(Z - \frac{5}{16}\right)^2
\end{aligned} \tag{3.28}$$

For Helium this gives

$$\begin{aligned}
\zeta &\approx 1.6875 \\
E &\approx -2.848 \text{ Hartree}
\end{aligned} \tag{3.29}$$

It is instructive to consider what happens if we bite the bullet and allow the effective nuclear charge in Eq. (3.22) to vary with r . If we do this, and choose $\zeta(r)$ to minimize the energy, we find that the energy is

$$E_{HF} = -2.862 \text{ Hartree}. \tag{3.30}$$

This is sometimes called the Hartree-Fock energy. Allowing the effective nuclear charge to depend on r and choose the effective nuclear charge that minimizes the energy,

$$E_{HF} = \min_{\zeta(r)} \frac{\left\langle e^{-\zeta r_1} e^{-\zeta r_2} \left| \hat{H} \right| e^{-\zeta r_1} e^{-\zeta r_2} \right\rangle}{\left\langle e^{-\zeta r_1} e^{-\zeta r_2} \left| e^{-\zeta r_1} e^{-\zeta r_2} \right\rangle} \tag{3.31}$$

is equivalent to searching over every possible functional form for the $1s$ orbital since any nodeless orbital can be expressed using a form with effective nuclear charges.² The usual statement of the Hartree-Fock method is that one searches over all possible orbitals for those that minimize the energy,

$$E_{HF} = \min_{\phi, r} \frac{\langle \phi \ r_1 \ \phi \ r_2 \ | \hat{H} \ | \phi \ r_1 \ \phi \ r_2 \rangle}{\langle \phi \ r_1 \ \phi \ r_2 \ | \phi \ r_1 \ \phi \ r_2 \rangle} \quad (3.32)$$

The reason this works well, however, is because the Hartree-Fock method makes direct contact with the concept of an effective nuclear charge. Thus, in the Hartree-Fock method each electron moves in the average potential due to the nucleus and the other electron; this is why the Hartree-Fock method is often called the “mean [electric] field” approximation.

D. Electron Correlation

The Hartree-Fock energy is still not very good. Compared to the exact energy, $(-2.9037 \text{ Hartree})$, Eq. (3.30) is in error by $26 \frac{\text{kcal}}{\text{mol}}$ ($110 \frac{\text{kJ}}{\text{mol}}$). These errors are similar to the strength of a chemical bond, and so further refinements are necessary.

But if we have chosen the best possible choice of the $1s$ orbitals, why is our energy so poor. The reason is that we have assumed that the electrons are uncorrelated: note that the wave function in Eq. (3.17) gives

$$|\Psi \ r_1, r_2|^2 = |\psi_{1s} \ r_1|^2 |\psi_{1s} \ r_2|^2. \quad (3.33)$$

That is, the probability of observing one electron at r_1 and one electron r_2 simultaneously is just the product of the probabilities of observing an electron at r_1 and an electron at r_2 independently. This does not agree with our intuition: because of the electron-electron repulsion term in the Hamiltonian for the two-electron atom (Eq. (3.2)), we expect that if the electron is at r_1 , the probability of observing another electron near r_1 is small. That is, we expect that the motions of the electrons are “correlated” so that they are rarely close together. Equation (3.33) is inconsistent with this observation.

One of the consequences of electron correlation is that the exact wave function depends on the distance between the electrons. To see this, write the Schrödinger equation for the many-electron atom in the form

$$\sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \right) \Psi \ r_1, r_2, \dots, r_N = \left(E - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|r_i - r_j|} \right) \Psi \ r_1, r_2, \dots, r_N \quad (3.34)$$

Note that the operators on the left-hand side of the equation do not “couple” the electrons. However, the electron-electron repulsion potential on the right-hand-side of the equation couples the electrons. The exact wave functions *must* incorporate a dependence on the interelectron distances $|r_i - r_j|$. (The right-hand side of Eq. (3.34) has a dependence on the interelectron distances, so Eq. (3.34) cannot be satisfied unless the left-hand side of Eq. (3.34) depends on the distance between electrons. However, the left-hand side of Eq. (3.34) will not have any terms depending on the interelectronic distances unless the wave function depends on the distance between the electrons. Consequently, it must be true that the exact wave function (which satisfies the Schrödinger equation, and thus also its trivial rearrangement Eq. (3.34)) contains a dependence on the interelectron distances, $|r_i - r_j|$.)

Hylleraas realized this and introduced wave functions for the Helium atom that depend explicitly on the interelectronic coordinate. His original functions looked like

² Just take $\zeta(r) = \ln\left((\phi(r))^{1/r}\right)$. Then $\exp(-r\zeta(r)) = \exp\left(-r \ln\left(\sqrt[r]{\phi(r)}\right)\right) = \phi(r)$.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \propto e^{-\zeta r_1} e^{-\zeta r_2} [1 + b|\mathbf{r}_1 - \mathbf{r}_2| + c|\mathbf{r}_1 - \mathbf{r}_2|^2] \quad (3.35)$$

but nowadays people tend to favor forms more similar to

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \propto e^{-\zeta(r_1 + r_2 + \kappa|\mathbf{r}_1 - \mathbf{r}_2|)}, \quad (3.36)$$

that is, putting the correlation term in the exponential. Truthfully, very few calculations of this type have been carried out for systems with more than a few electrons because the integrals required quickly become intractable. (The statistical techniques underlying so-called “variational Monte-Carlo” calculations are an exception.)

Choosing ζ , b , and c , in Eq. (3.35) to minimize the energy, we obtain a reasonable answer ($E = -2.9024$ Hartree, which is an error slightly less than a $\frac{\text{kcal}}{\text{mol}}$).

Our results for the Helium atom are summarized in Table 3.1.

Table 3.1. Energies of the Helium atom in various approximate treatments.

Wave Function/Computational Method	Energy (Hartree)
neglect of V_{ee} , Eq. (3.3)	-4.000
First order perturbation theory with V_{ee} , Eq. (3.6)	-2.75
Constant Effective Nuclear Charge, ζ . Eq. (3.23)	-2.848
Hartree Fock, position-dependent effective nuclear charge. Eq. (3.22)	-2.862
Hylleraas (includes electron correlation). Eq. (3.35)	-2.9024
Exact	-2.9037

III. Spin

A. Spin Angular Momentum

In constructing eigenfunctions for atoms with more than two electrons we encounter a dilemma that we ignored when considering the Helium atom. Electrons have spin. That is, it is not enough to specify where an electron is in a molecule, we must also specify its spin.

It should be emphasized that electrons do not really spin. Rather, electron spin is a relativistic effect, and follows naturally from Dirac’s relativistic extension of the Schrödinger equation. Just because spin arises naturally in relativistic treatments of the electron does not mean that slow electrons do not have spin: every electron has spin; electron spin is an intrinsic property of the electron. Electron spin is measurable: the electron spin is measured in electron-spin resonance spectroscopies (ESR, EPR, ...). In fact, the spin of an electron is the same type of phenomenon as the spin of a proton (or other nucleus) that is measured in nuclear-magnetic-resonance experiments.

If an electron is not really spinning, then why do we speak of an “electron spin”. The reason is historical, a spinning charged particle has a magnetic moment, and it was observed in the early days of quantum mechanics that if one assumed that the electrons had spin you could explain certain effects, notably the “anomalous” Zeeman splitting of spectral lines in magnetic fields. The most explicit experimental measurement, however, is from the Stern-Gerlach experiment, wherein a stream of electrons (as from the beta decay of a proton-deficient radioactive nucleus) is placed in a magnetic field. One sees that the electron beam splits into two parts. See Figure 3.2.

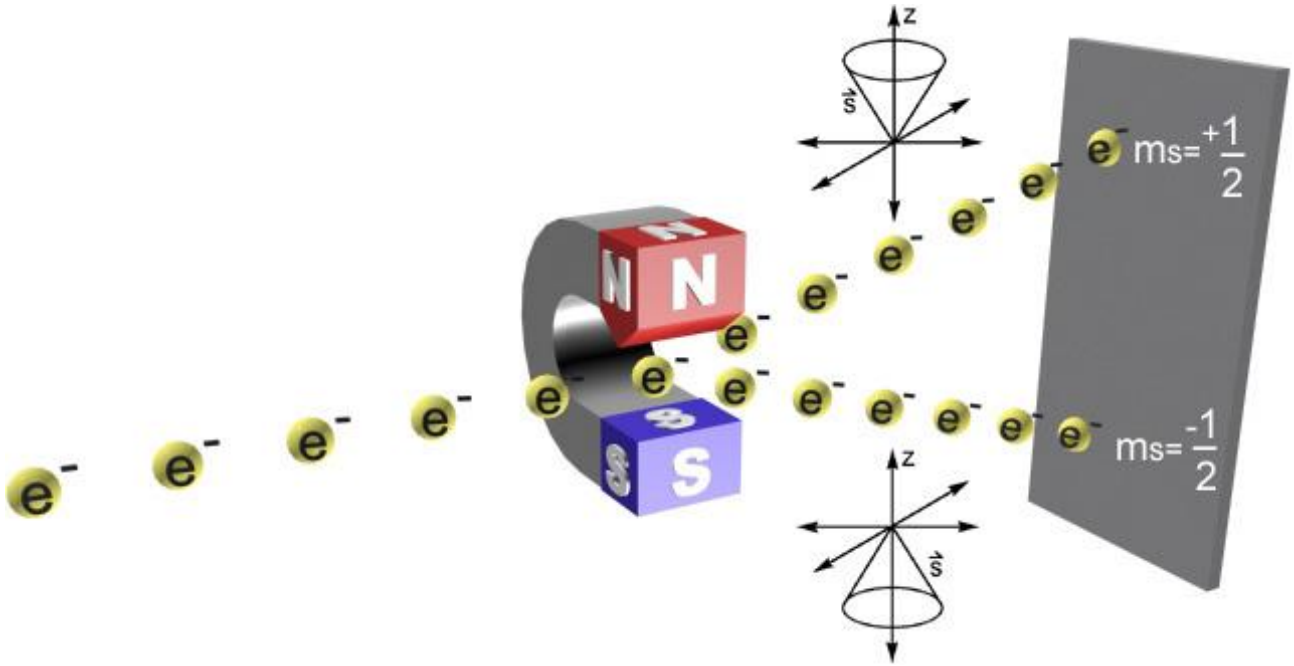


Figure 3.2. The Stern-Gerlach experiment. When a beam of electrons is passed through an inhomogeneous magnetic field, the beam is separated according to whether the spin-angular momenta of the electrons is pointed into or away from the magnetic field.

This is a weird result. Recall the earlier treatment of angular momentum in the rigid rotor. We have

$$\hat{L}^2 Y_l^m(\theta, \phi) = l(l+1) \hbar^2 Y_l^m(\theta, \phi) \quad (3.37)$$

and

$$\hat{L}_z Y_l^m(\theta, \phi) = m \hbar Y_l^m(\theta, \phi) \quad (3.38)$$

with

$$m = -l, -l+1, \dots, l-1, l \quad (3.39)$$

Also recall that

$$[\hat{L}_x, \hat{L}^2] = [\hat{L}_y, \hat{L}^2] = [\hat{L}_z, \hat{L}^2] = 0 \quad (3.40)$$

but

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y \end{aligned} \quad (3.41)$$

That is, we can measure the total magnitude of the orbital angular momentum and any ONE of its components component ($\langle L_x \rangle$, $\langle L_y \rangle$ or $\langle L_z \rangle$). The orbital angular momentum about the x , y , or z axis (whichever we choose) will take one of the values, $m = -l, -l+1, \dots, l-1, l$. The *picture* is the orbital angular momentum is a vector with magnitude $\hbar \sqrt{l(l+1)}$, but in measuring the projection of this angular momentum along one axis we force the angular momentum to assume some discrete value, $m = -l, -l+1, \dots, l-1, l$, consequently “scrambling” its components in other directions. It is spooky quantum mechanical stuff.

Now, we said that when we measured the spin-angular momentum of the electron we observed two spots. Referring to the rule, Eq. (3.39), since there are only two spots if $l = \frac{1}{2}$. To avoid

confusion, however, for the spin we refer to this as the total spin, and say that the electron has “half-integral” spin, $S = \frac{1}{2} \hbar$. We specify the orbital angular momentum about the z -axis with m_l and the spin-angular momentum about the same axis with m_s . Now, if we assumed that the spin-angular momentum acts like a true angular momentum we should have, corresponding to Eqs. (3.37) to (3.39)

$$\hat{S}^2 Y_S^{m_s} = \hbar^2 S(S+1) Y_S^{m_s} \quad (3.42)$$

$$\hat{S}_z Y_S^{m_s} = \hbar m_s Y_S^{m_s} \quad (3.43)$$

$$m_s = -S, -S+1, \dots, S-1, S \quad (3.44)$$

For a one-electron system, $S = \frac{1}{2}$ and $m_s = \pm \frac{1}{2}$. Corresponding to the commutation relations for the orbital angular momentum, we have

$$[\hat{S}_x, \hat{S}^2] = [\hat{S}_y, \hat{S}^2] = [\hat{S}_z, \hat{S}^2] = 0 \quad (3.45)$$

and

$$\begin{aligned} [\hat{S}_x, \hat{S}_y] &= i\hbar \hat{S}_z \\ [\hat{S}_y, \hat{S}_z] &= i\hbar \hat{S}_x \\ [\hat{S}_z, \hat{S}_x] &= i\hbar \hat{S}_y \end{aligned} \quad (3.46)$$

We have elected to use the above notation because it is reminiscent of the spherical harmonics, but it must be emphasized that the spin of an electron does not depend on its position in space. Thus, $Y_S^{m_s}$ is just a fancy notation for saying “the eigenfunction of \hat{S}^2 and \hat{S}_z with quantum numbers m_s and S , respectively. It means nothing more.

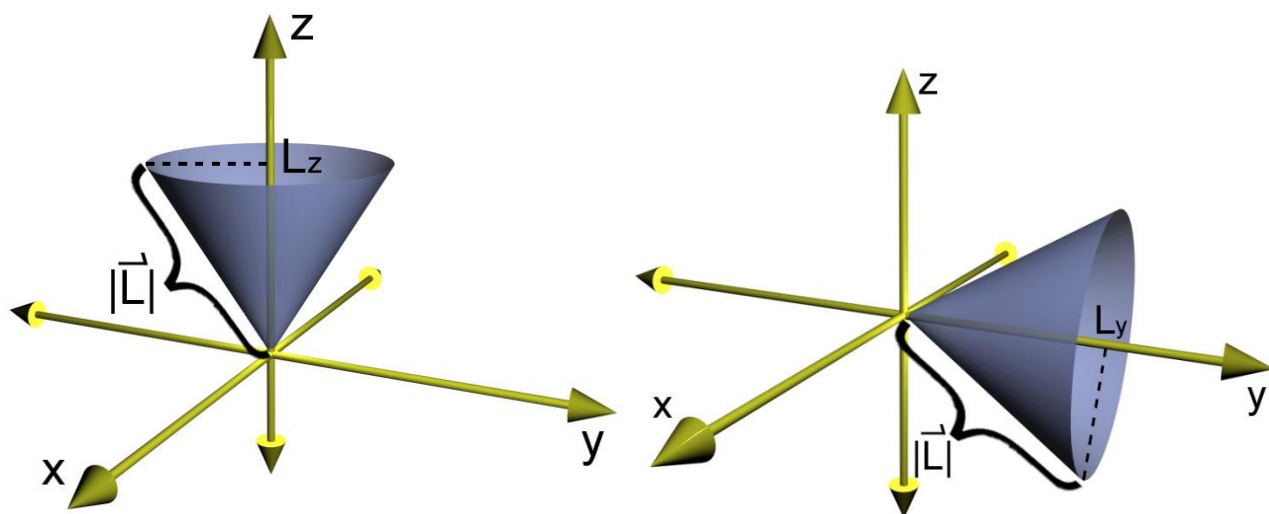


Figure 3.3. A pictorial representation of why $[\hat{L}_z, \hat{L}_y] \neq 0$, and thus one cannot simultaneously measure orbital angular momenta in the z and y directions. When one measures an atom's orbital angular momentum about the z axis, direction, $\hat{L}_z \Psi_{\tau} = m_{l_z} \hbar \Psi_{\tau}$, one finds that the atom's angular momentum vector is precessing (rotating) about the z -axis. The atom's angular momentum vector, \mathbf{L} , is not perfectly aligned with the z -axis: because $\hat{L}^2 \Psi_{\tau} = \hbar^2 l(l+1) \Psi_{\tau}$, the magnitude of the orbital angular momentum is always greater than its projection along any axis. (Mathematically, $|\mathbf{L}| = \sqrt{\mathbf{L} \cdot \mathbf{L}} = \hbar l \sqrt{\frac{l+1}{l}} > m_{l_z}$.) Thus, knowing \hat{L}^2 and \hat{L}_z only restricts the orbital angular momentum to the "cone" of values shown here, and the projection of the angular momentum along the y axis is undefined. Thus, if one *measures* the angular momentum along the y axis, one will observe all possible values, one of which is shown here. After measuring the angular momentum about the y axis, the orbital angular momentum vector is precessing about the y -axis, and is confined to a cone about this axis. Thus, measuring m_{l_y} caused the value of m_{l_z} to become undefined. Since we can't measure both the y and the z components of the orbital angular momentum at the same time, \hat{L}_y and \hat{L}_z do not commute.

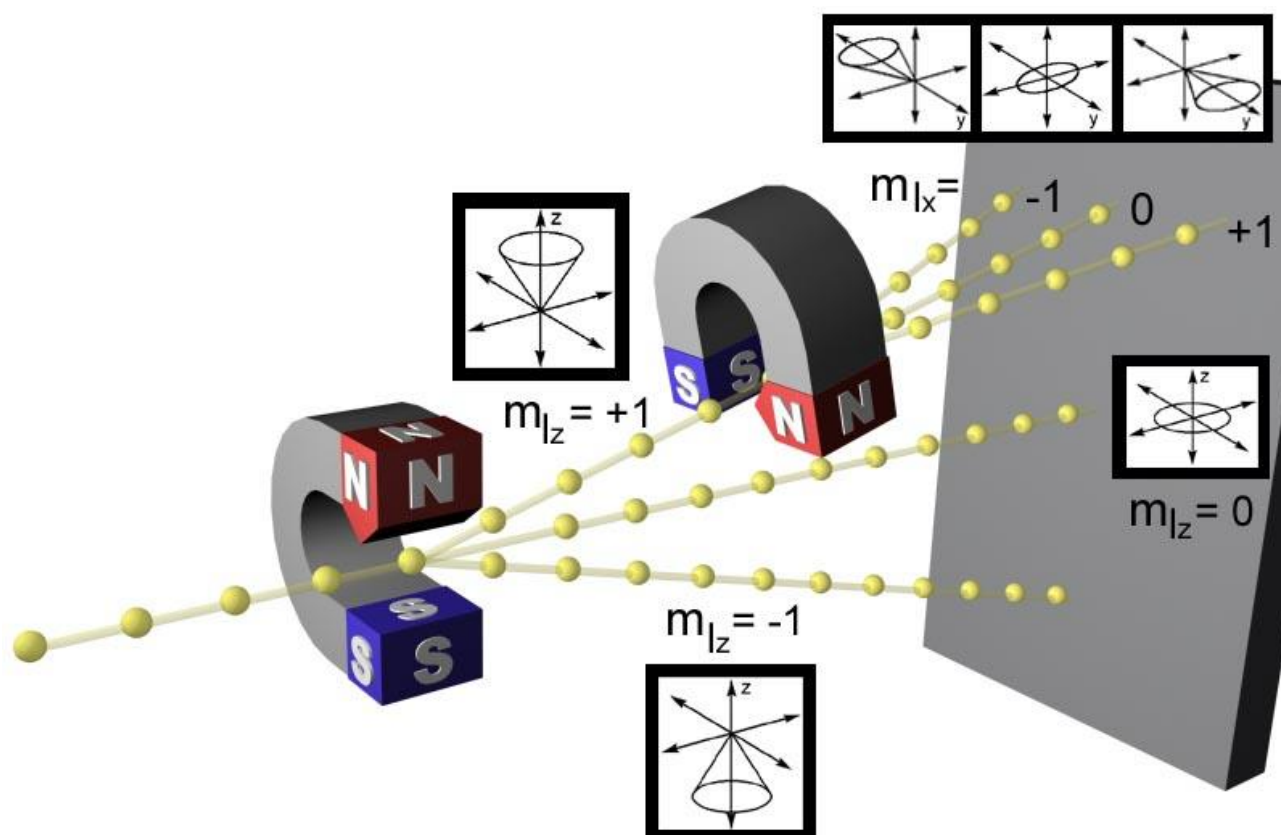


Figure 3.4. A “double” Stern-Gerlach experiment. When a beam of atoms is passed through an inhomogeneous magnetic field, the atoms are separated according to the component of their orbital angular momentum, m_l , in the direction of the field. Here, the first magnet measures the angular momentum in the z direction, and forces each atom to “declare” itself as one of the eigenstates of \hat{L}_z . But the second magnetic field measures the orbital angular momentum in the y direction, forcing the atom to declare itself as an eigenstate of \hat{L}_y .

The interpretation of the commutation relations is similar to that for the angular momenta. In figure 2.5 we pass an electron beam through a Stern-Gerlach apparatus whose field is oriented in the z -direction and, by so doing, measure $\langle \hat{S}_z \rangle$. Now, let’s try to be clever, and measure $\langle \hat{S}_x \rangle$ for the electrons with $m_s = \frac{1}{2}$. To do this, we can just put another Stern-Gerlach apparatus with the field in the y -direction. We get two beams. But now, let’s suppose we want to measure $\langle \hat{S}_z \rangle$ again. We observe two spots—even though all the electrons had $m_s = \frac{1}{2}$ before we fed them into the second Stern-Gerlach apparatus. That is, in measuring $\langle \hat{S}_y \rangle$ we “scrambled up” the eigenstates of $\langle \hat{S}_z \rangle$.³ Spooky quantum mechanics. (But not that spooky. If we had oriented the second Stern-Gerlach apparatus so that the field is in the z -direction (the same direction as the first experiment), no further splitting would occur.⁴)

³ This is a consequence of the fact \hat{S}_y and \hat{S}_z do not commute.

⁴ This result follows from the fact that any operator—in this case, \hat{S}_z —commutes with itself.

This “spooky” behavior is directly analogous to the behavior we observe for orbital angular momenta of atoms, which is why we choose to think in terms of a “spin-angular momentum” even though we know the electron is not really spinning. That is, since the electron spin acts like an angular momentum, we pretend it is an angular momentum.

The magnetic moment due to an orbiting electron is simply⁵

$$\boldsymbol{\mu}_L = \frac{-e}{2m_e c} \hat{\mathbf{L}}. \quad (3.47)$$

The relationship for the spin, by contrast, is

$$\boldsymbol{\mu}_S = g \cdot \frac{-e}{2m_e c} \hat{\mathbf{S}} \quad (3.48)$$

where g , the anomalous spin-factor (nowadays more frequently referred to as the Landé g factor), is

$$g = 2.00115965219 \quad (3.49)$$

which is, for our purposes, simply 2. Dirac’s equation not only predicted the existence of the spin, but predicted that $g = 2$. Unfortunately, Dirac’s theory also predicted that $g = 2$ for a proton (any NMR guru knows that $g_{\text{proton}} \approx 5.6$) and $g = 0$ for neutron (but $g_{\text{neutron}} \approx -3.8$). The electron’s g factor is slightly greater than 2 for precisely the same reason the proton’s is much greater than 2 and the neutron’s is substantially less than zero; the corrections arise from quantum field theory and won’t be treated any further in this course.

Based on the form of Eqs. (3.47) and (3.48), one often introduces the so-called Bohr magneton, $\beta_e = \frac{e\hbar}{2m_e c}$, in terms of which

$$\boldsymbol{\mu}_L = -\frac{\beta_e}{\hbar} \hat{\mathbf{L}} \quad (3.50)$$

$$\boldsymbol{\mu}_S \approx -2 \frac{\beta_e}{\hbar} \hat{\mathbf{S}} \quad (3.51)$$

⁵ Some authors choose a different sign convention. The key is the interaction with a magnetic field, which gives a contribution to the Hamiltonian of $-\boldsymbol{\mu} \cdot \mathbf{B}$ in the present convention but would give $\boldsymbol{\mu} \cdot \mathbf{B}$ with the alternative choice.

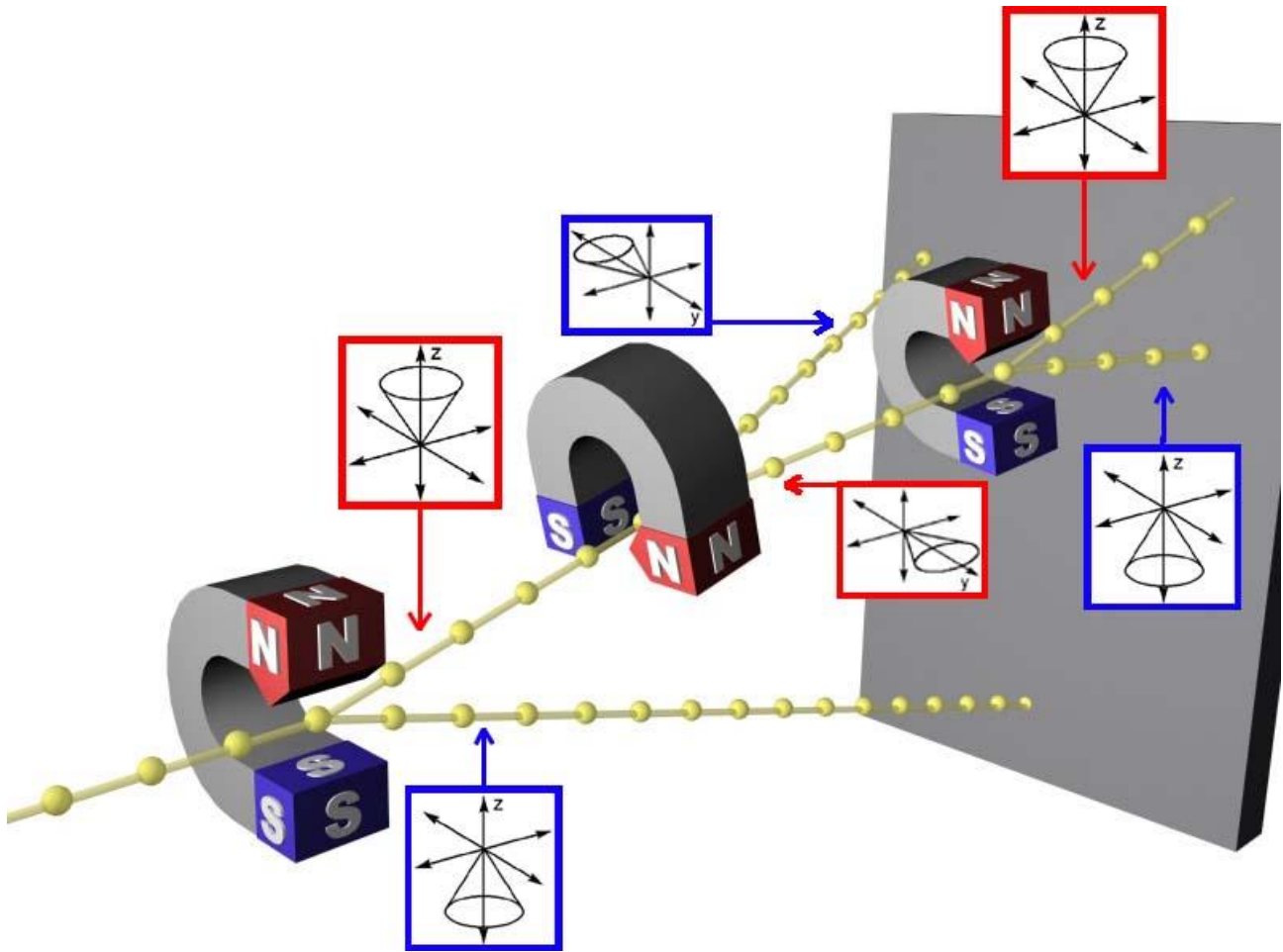


Figure 3.5. A “triple” Stern-Gerlach experiment. When a beam of electrons is passed through an inhomogeneous magnetic field, the electrons are separated according to the component of their spin angular momentum in the direction of the field. Here, the first magnet measures the angular momentum in the z direction, and forces each atom to “declare” itself as one of the eigenstates of \hat{S}_z . But the second magnetic field measures the orbital angular momentum in the y direction, forcing the atom to declare itself as an eigenstate of \hat{S}_y . This “scrambles” the angular momentum about the z -axis, and so when we pass the electron beam through another Stern-Gerlach magnet aligned with the z -axis, we observe both eigenstates of \hat{S}_z .

B. The Pauli-Exclusion Principle

No feature of the electron spin is more important to chemistry than the Pauli-exclusion principle. To introduce the Pauli exclusion principle, let us consider the many-electron Hamiltonian for an arbitrary system,

$$\sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - v(\mathbf{r}_i) + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (3.52)$$

Here $v(\mathbf{r})$, called the “external potential” is just the potential felt by electrons due to “non-electrons”—e.g., nuclei. (Referring back to Eq. (3.1) we see that, for an atom, $v(\mathbf{r}) = -\frac{Z}{r}$.) Now, let’s use what we learned in the previous section and specify the spin of the electrons. Since the spin of the electrons does not depend on their position, we typically write the spin of electron i as σ_i ,

which serves to emphasis the fact that the spin of the electron does not depend on \mathbf{r}_i . Then, we can rewrite Eq. (3.52) as

$$\sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - v(\mathbf{r}_i) + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N) = E \Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N). \quad (3.53)$$

Often it is convenient to denote the spatial and spin coordinates of an electron together, e.g., $\mathbf{x}_i \equiv \mathbf{r}_i, \sigma_i$. Sometimes I do this, but for right now we should write the dependence of the wave function on the electron spin explicitly.

Let's suppose $\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N)$ is an eigenfunction of the Hamiltonian in Eq. (3.52); that is, $\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N)$ solves the Schrödinger equation. We want to construct another solution of the Schrödinger equation, so we write

$$\Phi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N) = \kappa \cdot \Psi(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1; \mathbf{r}_3, \sigma_3; \mathbf{r}_4, \sigma_4; \dots; \mathbf{r}_N, \sigma_N) \quad (3.54)$$

That is, since electrons are indistinguishable particles, we expect that relabeling the electrons in this fashion doesn't change the wave function in any meaningful way, for all we have done is to "count" the electrons in a different order. In particular, since electrons are indistinguishable particles, relabeling the electrons cannot change any property of the system. For example, the probability of observing an electron with a given spin at a given point in space, $|\Psi|^2 = \Psi^* \Psi$ cannot change. Ergo⁶

$$\begin{aligned} |\Phi|^2 &= |\Psi|^2 \\ \Phi^* \Phi &= |\Psi|^2 \\ \kappa \cdot \Psi^* \kappa \cdot \Psi &= |\Psi|^2 \\ \kappa \cdot \kappa^* |\Psi|^2 &= |\Psi|^2 \\ |\kappa|^2 &= 1 \\ \kappa &= \pm 1 \end{aligned} \quad (3.55)$$

If we substitute this result into Eq. (3.53), we obtain

$$\begin{aligned} \sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - v(\mathbf{r}_i) + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Phi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N) \\ = \sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - v(\mathbf{r}_i) + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \kappa \cdot \Psi(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1; \mathbf{r}_3, \sigma_3; \dots; \mathbf{r}_N, \sigma_N) \\ = \kappa E \cdot \Psi(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1; \mathbf{r}_3, \sigma_3; \dots; \mathbf{r}_N, \sigma_N) \end{aligned} \quad (3.56)$$

That is, $\kappa \cdot \Psi(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1; \mathbf{r}_3, \sigma_3; \mathbf{r}_4, \sigma_4; \dots; \mathbf{r}_N, \sigma_N)$ is an eigenfunction of the Hamiltonian with the same energy as the original wave function (before we exchanged the positions and spins and electrons one and two). This is true because the Hamiltonian is symmetric with respect to exchange of electronic position (and, if we had chosen a spin-dependent Hamiltonian, it would also be symmetric with respect to spin). More explicitly, $\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \hat{H}(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N)$ and so

⁶ The analysis in Eq. (3.55) is also consistent with choosing $\kappa = \pm i$, where $i = \sqrt{-1}$. However, this solution does not seem to possess any physical importance.

$$\begin{aligned}
\hat{H} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) &= \hat{H} \Psi(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1; \mathbf{r}_3, \sigma_3; \dots; \mathbf{r}_N, \sigma_N) \\
&= \hat{H} \Psi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N) \\
&= E \Psi(\mathbf{q}_1, \sigma_2; \mathbf{q}_2, \sigma_1; \mathbf{q}_3, \sigma_3; \dots; \mathbf{q}_N, \sigma_N)
\end{aligned} \tag{3.57}$$

In the third line, we perform a change of coordinates (with $\mathbf{q}_1 = \mathbf{r}_2$ and $\mathbf{q}_2 = \mathbf{r}_1$) to regain the original form of the Schrödinger equation. Note that if κ was not a constant but instead depended on the positions and spins of the electrons, Eq. (3.56) would not hold.

What have we learned? Given an eigenfunction of a Hamiltonian, when we exchange the spatial and spin-coordinates of two electrons, we still have an eigenfunction. Similarly, if we exchange the spatial and spin coordinates of two electrons and multiply the eigenfunction by -1, we also have an eigenfunction. So which is it?

The answer to this question can be regarded as a mystery of modern physics (though one can “derive” the result, trying to explain it in elementary and intuitive language seems impossible). The gist of the matter is that if a particle has half-integral spin (e.g., an electron), then $\kappa = -1$: when we exchange the positions and spins of two electrons, we change the sign of the wave function. Thus, for electrons,

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N) = -1 \cdot \Psi(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1; \mathbf{r}_3, \sigma_3; \dots; \mathbf{r}_N, \sigma_N). \tag{3.58}$$

This has far-reaching consequences for chemistry. For example, suppose that electrons one and two are at the same position and have the same spin, that is, $\sigma_2 = \sigma_1$. Then, from Eq. (3.58)

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) = -1 \cdot \Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_1, \sigma_1; \mathbf{r}_3, \sigma_3; \dots; \mathbf{r}_N, \sigma_N). \tag{3.59}$$

However if $\Psi = -\Psi$, then

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) = 0. \tag{3.60}$$

Taking the complex square of Eq. (3.60), we have

$$|\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N)|^2 = 0 \tag{3.61}$$

The probability of observing two electrons with the same spin at the same place is zero. More colloquially, two electrons with the same spin can never be at the same place at the same time.

What does the Pauli exclusion principle have to say about the probability of observing two electrons with *different* spin at the same place at the same time? Nothing at all. However, the presence of the electron-electron repulsion operator in the electronic Hamiltonian means that it is unfavorable for electrons to be close together. However, even though the $\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ operator becomes infinite as $|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow 0$, there is some (albeit small) probability of observing two electrons with different spins at the same point in space. This counter-intuitive effect is due, essentially, to the uncertainty principle: just as one can never say exactly where an electron is, one can never say exactly where an electron is not. Recall the form of the 1s-orbital in Hydrogen. The probability of observing an electron at the nucleus is not infinite (though it is large): just because it is “infinitely favorable” for the electron to be at the nucleus ($-\frac{Z}{r} \rightarrow -\infty$ as $r \rightarrow 0$) does not mean there is an infinite probability of the electron being at the nucleus. The non-infinite electron density at the nucleus and the non-zero electron density when two same-spin electrons are at the same place are manifestations of the same effect. (This is an essential consequence of the form of the kinetic energy operator and the fact $\frac{\hbar^2}{2m} \neq 0$.)

Particles with half-integral spin have antisymmetric wave functions ($\kappa = -1$) and are called fermions. Particles with integer spin have symmetric wave functions ($\kappa = 1$) and are called bosons.

Protons, electrons, and neutrons are fermions. Photons are bosons. Though two fermions with the same spin can never be at the same place, bosons with the same spin have an enhanced probability of being at the same place at the same time. That is, while no two fermions can be in the same state, bosons have an enhanced probability of being in the same state. This, for instance, is behind the phenomenon of stimulated emission: a laser beam is nothing more than a lot of photons in the same state. Many interesting physical phenomena happen when a “composite” particle has integer spin. For instance, the ${}^4_2\text{He}$ atom has integer spin, and so liquid Helium becomes superfluid at low temperatures, giving rise to a number of weird effects (e.g., one can stir a superfluid without encountering any resistance.) Superconductivity is a similar effect, in which two electrons “pair”, forming a “Cooper pair”, a composite particle with integer spin. The Cooper pair acts like a boson, allowing many Cooper pairs to be in the exact same state and allowing electricity to be conducted without resistance.

Since an electron can have $m_s = \pm \frac{1}{2}$, we typically denote the spin-quantum number of an electron with $\sigma \ i \equiv \alpha \ i$ when $m_s = \frac{1}{2}$ and $\sigma \ i = \beta \ i$ when $m_s = -\frac{1}{2}$.⁷

⁷ Different authors choose different conventions here. This choice is most standard, but it doesn’t matter how one chooses to define $\alpha(i)$ and $\beta(i)$ as long as one is consistent.

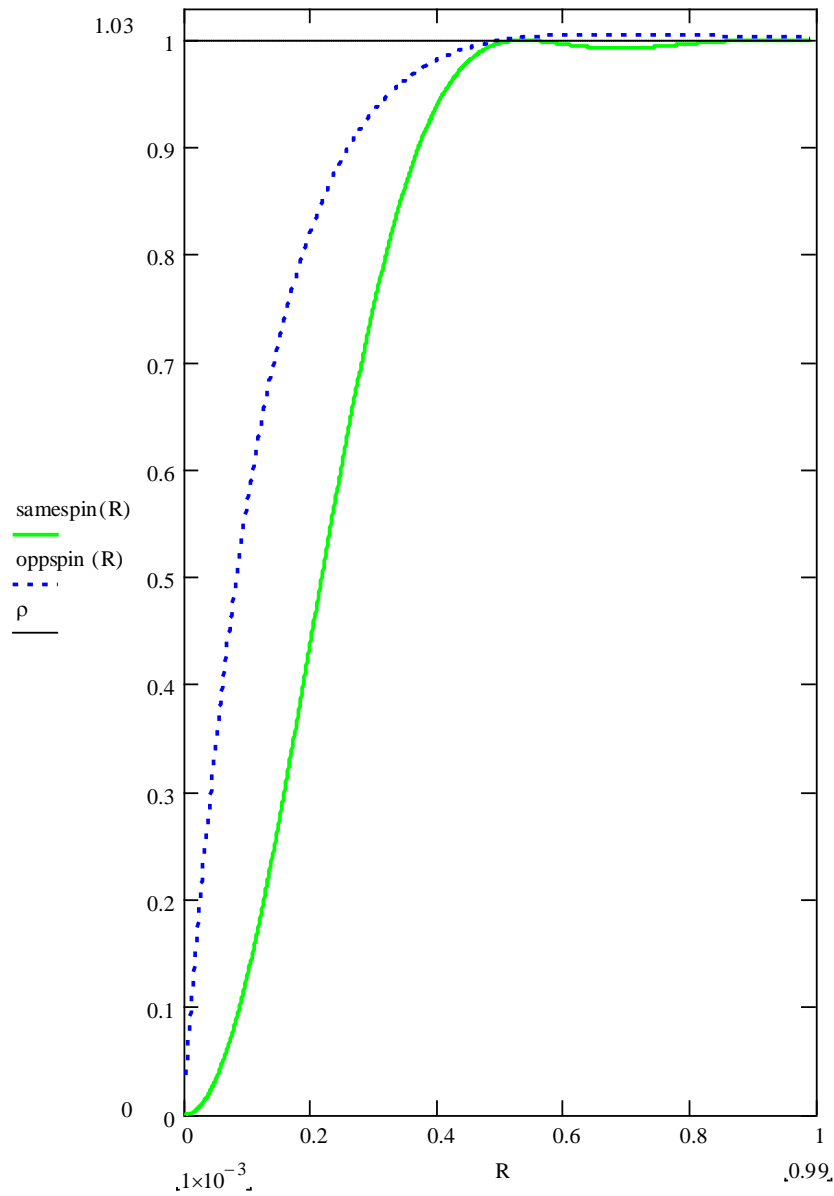


Figure 3.6. The relative probability of observing same spin (solid line) and opposite spin (dashed line) electrons a distance R apart from each other in the free electron gas with unit density. The free electron gas consists of electrons moving in the absence of any nuclei (or any potential at all, and is a primitive model for the electronic structure of metals.

C. The Lithium Atom and the Slater Determinant

For many-electron atoms, the ideas are similar to those for Helium. At first one ignores the electron-electron repulsion; this gives a separable Hamiltonian whose eigenfunctions are simple products of the hydrogenic functions. Then, one modifies these orbitals to account for electron-electron repulsion (nuclear shielding, electron correlation, etc.) using increasingly sophisticated tools. One obtains orbitals that vaguely resemble the Hydrogenic functions (insofar as their symmetry and nodal structure is concerned). Then, one forms a wave function from these orbitals that satisfies the Pauli exclusion principle that is, one forms a wave function that is properly antisymmetric.

As a concrete example, consider the Lithium atom. We might write the approximate ground state wave function

$$\Psi_{Li} \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 = \psi_{1s} \mathbf{r}_1 \alpha 1 \psi_{1s} \mathbf{r}_2 \beta 2 \psi_{2s} \mathbf{r}_3 \alpha 3 \quad (3.62)$$

but this function is not antisymmetric. We can make this function antisymmetric by writing

$$\Psi_{Li} \mathbf{r}_1, \sigma 1 ; \mathbf{r}_2, \sigma 2 ; \mathbf{r}_3, \sigma 3 = \frac{1}{\sqrt{6}} \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \alpha 1 \psi_{1s} \mathbf{r}_2 \beta 2 \psi_{2s} \mathbf{r}_3 \alpha 3 \\ -\psi_{1s} \mathbf{r}_2 \alpha 2 \psi_{1s} \mathbf{r}_1 \beta 1 \psi_{2s} \mathbf{r}_3 \alpha 3 \\ -\psi_{1s} \mathbf{r}_3 \alpha 3 \psi_{1s} \mathbf{r}_2 \beta 2 \psi_{2s} \mathbf{r}_1 \alpha 1 \\ -\psi_{1s} \mathbf{r}_1 \alpha 1 \psi_{1s} \mathbf{r}_3 \beta 3 \psi_{2s} \mathbf{r}_2 \alpha 2 \\ +\psi_{1s} \mathbf{r}_2 \alpha 2 \psi_{1s} \mathbf{r}_3 \beta 3 \psi_{2s} \mathbf{r}_1 \alpha 1 \\ +\psi_{1s} \mathbf{r}_3 \alpha 3 \psi_{1s} \mathbf{r}_1 \beta 1 \psi_{2s} \mathbf{r}_2 \alpha 2 \end{pmatrix} \quad (3.63)$$

Equation (3.63) just includes all the possible ways of arranging the electrons in the orbitals from Eq. (3.62), with each term multiplied by the factor of -1 or $1 = -1^2$ implied by the Pauli principle. Note what happens if we allow the third electron to go into a 1s-orbital (as opposed to a 2s-orbital). Then

$$\Psi_{Li} \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 = 0 \quad (3.64)$$

That is, the Pauli exclusion principle requires that no more than two electrons can ever occupy any given orbital. Stated differently, no two electrons can have the same values for all four quantum numbers, n, l, m_l, m_s .

Writing antisymmetric wave functions like Eq. (3.63) is already quite tedious, and it gets exceedingly tedious as the number of electrons increases. (For Neon, there are actually $10! = 3,628,800$ terms in the wave function.) Needless to say, writing out such wave functions becomes impossible. As a shorthand, we write wave functions as a *Slater determinant*,

$$\Phi \mathbf{r}_1, \sigma 1 ; \dots ; \mathbf{r}_N, \sigma N \equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1 \mathbf{r}_1 \sigma_1 1 & \psi_1 \mathbf{r}_2 \sigma_1 2 & \cdots & \psi_1 \mathbf{r}_N \sigma_1 N \\ \psi_2 \mathbf{r}_1 \sigma_2 1 & \psi_2 \mathbf{r}_2 \sigma_2 2 & \cdots & \psi_2 \mathbf{r}_N \sigma_2 N \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N \mathbf{r}_1 \sigma_N 1 & \psi_N \mathbf{r}_2 \sigma_N 2 & \cdots & \psi_N \mathbf{r}_N \sigma_N N \end{vmatrix} \quad (3.65)$$

where $\psi_i \mathbf{r}$ denote the spatial orbitals and the $\sigma_i j$ denote the spin-states of the electrons.

The interpretation of a Slater determinant is that the spatial orbital $\psi_1 \mathbf{r}$, which holds an electron with spin σ_1 , could contain electron one, or electron two, or electron three, ... or electron N .

Similarly, the spatial orbital $\psi_2 \mathbf{r}$, which contains an electron with spin σ_2 , could contain electron one, or electron two, or electron three, ... or electron N . And so on. On the other hand, if we read the columns of Eq. (3.65), we see that electron one could have spin σ_1 and be in the orbital $\psi_1 \mathbf{r}$, or it could have spin σ_2 and be in the orbital $\psi_2 \mathbf{r}$, or it could have spin σ_3 and be in the orbital $\psi_3 \mathbf{r}$, ..., or it could have spin σ_N and be in the orbital $\psi_N \mathbf{r}$. Similarly, electron two could have spin σ_1 and be in the orbital $\psi_1 \mathbf{r}$, or it could have spin σ_2 and be in the orbital $\psi_2 \mathbf{r}$, or it could have spin σ_3 and be in the orbital $\psi_3 \mathbf{r}$, ..., or it could have spin σ_N and be in the orbital $\psi_N \mathbf{r}$. And so on.

As an explicit example, we can rewrite the wave function for the Lithium atom in Eq. (3.63) using a Slater determinant. We have:

$$\Phi_{\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \mathbf{r}_3, \sigma_3} \equiv \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_{1s} \mathbf{r}_1 \alpha 1 & \psi_{1s} \mathbf{r}_2 \alpha 2 & \psi_{1s} \mathbf{r}_3 \alpha 3 \\ \psi_{1s} \mathbf{r}_1 \beta 1 & \psi_{1s} \mathbf{r}_2 \beta 2 & \psi_{1s} \mathbf{r}_3 \beta 3 \\ \psi_{2s} \mathbf{r}_1 \alpha 1 & \psi_{2s} \mathbf{r}_2 \alpha 2 & \psi_{2s} \mathbf{r}_3 \alpha 3 \end{vmatrix} \quad (3.66)$$

When the orbitals in an $N \times N$ Slater determinant are orthogonal and normalized, the normalization constant is $\frac{1}{\sqrt{N!}}$. Otherwise the Slater determinant must be explicitly normalized.

There are several key results about Slater determinants. First of all, the determinant of the transpose of a matrix equals the determinant of a matrix,

$$|D| = |D^T|. \quad (3.67)$$

Indeed, the notation for Slater determinants listed in Eq. (3.65) is not the conventional notation; it is more conventional to use the transposed form,

$$\Phi_{\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N} \equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1 \mathbf{r}_1 \sigma_1 1 & \psi_2 \mathbf{r}_1 \sigma_2 1 & \dots & \psi_N \mathbf{r}_1 \sigma_N 1 \\ \psi_1 \mathbf{r}_2 \sigma_1 2 & \psi_2 \mathbf{r}_2 \sigma_2 2 & \dots & \psi_N \mathbf{r}_2 \sigma_N 2 \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1 \mathbf{r}_N \sigma_1 N & \psi_2 \mathbf{r}_N \sigma_2 N & \dots & \psi_N \mathbf{r}_N \sigma_N N \end{vmatrix} \quad (3.68)$$

Because of Eq. (3.67), both forms are acceptable.

Second, if two columns (or rows) in a matrix are equal, then the determinant of that matrix is 0. For example, in Eq. (3.65), if $\psi_1 \mathbf{r} = \psi_2 \mathbf{r}$ and $\sigma_1 1 = \sigma_2 1$, the first and second rows of the matrix are equal and so the determinant is zero. This is consistent with the Pauli-exclusion principle: we cannot put two electrons with the same spin in the same orbital. Similarly, if the first and second columns in Eq. (3.68) are equal, this implies that the spatial and spin coordinates for electrons 1 and 2 are the same. Again, the determinant must be zero, which is consistent with the Pauli-exclusion principle.

Finally, if we exchange two rows or two columns in a matrix, its determinant is multiplied by -1 . This is consistent with the requirement that the wave function be antisymmetric with respect to the exchange of the coordinates of the electrons (exchanging to columns in Eq. (3.65)). In addition, from Eq. (3.65) we see that changing the way electrons are assigned to orbitals (as by swapping two rows of the matrix) also changes the sign of the wave function.

Partly because Slater determinants take up a lot of space on the page but mostly because quantum chemists are lazy, we often use the following shorthand for Slater determinants

$$\Phi \equiv \begin{vmatrix} \psi_1 \sigma_1 & \psi_2 \sigma_2 & \dots & \psi_N \sigma_N \end{vmatrix}. \quad (3.69)$$

For instance, the Slater determinant for the Lithium atom (Eq. (3.66)) could be written as

$$\Phi \equiv \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha \end{vmatrix}, \quad (3.70)$$

which conveys all the essential information required to fill in Slater determinant.

IV. Labeling Atomic States

A. Good Quantum Numbers

You should recall from the first semester of this course that whenever two operators commute:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} = 0, \quad (3.71)$$

the operators can be chosen to have simultaneous eigenfunctions. That is, the eigenfunctions of \hat{A} can be chosen in such a way that they are also eigenfunctions of \hat{B} .

Applying this theorem to the atomic Hamiltonian, Eq. (3.1), we have that

$$[\hat{H}, \hat{L}_x] = [\hat{H}, \hat{L}_y] = [\hat{H}, \hat{L}_z] = [\hat{H}, \hat{L}^2] = [\hat{H}, \hat{S}_x] = [\hat{H}, \hat{S}_y] = [\hat{H}, \hat{S}_z] = [\hat{H}, \hat{S}^2] = 0. \quad (3.72)$$

We defined all these operators for a single electron in IIIA, and for a many-electron system we need merely sum over the one-electron operators:

$$\hat{S}_z \quad 1, 2, \dots, N = \sum_{i=1}^N \hat{S}_z \quad i \quad (3.73)$$

$$\begin{aligned} \hat{S}^2 \quad 1, 2, \dots, N &\equiv \sum_{i=1}^N \hat{\mathbf{S}} \quad i \cdot \sum_{j=1}^N \hat{\mathbf{S}} \quad j \\ &= \sum_{i=1}^N \hat{S}_x^2 \quad i + \hat{S}_y^2 \quad i + \hat{S}_z^2 \quad i \end{aligned} \quad (3.74)$$

$$+ \sum_{i=1}^N \sum_{j \neq i}^N \hat{S}_x \quad i \hat{S}_x \quad j + \hat{S}_y \quad i \hat{S}_y \quad j + \hat{S}_z \quad i \hat{S}_z \quad j$$

$$\hat{L}_z \quad \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N = \sum_{i=1}^N \hat{L}_z \quad \mathbf{r}_i \quad (3.75)$$

$$\begin{aligned} \hat{L}^2 \quad \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N &\equiv \sum_{i=1}^N \hat{\mathbf{L}} \quad \mathbf{r}_i \cdot \sum_{j=1}^N \hat{\mathbf{L}} \quad \mathbf{r}_j \\ &= \sum_{i=1}^N \hat{L}_x^2 \quad \mathbf{r}_i + \hat{L}_y^2 \quad \mathbf{r}_i + \hat{L}_z^2 \quad \mathbf{r}_i \\ &+ \sum_{i=1}^N \sum_{j \neq i}^N \hat{L}_x \quad \mathbf{r}_i \hat{L}_x \quad \mathbf{r}_j + \hat{L}_y \quad \mathbf{r}_i \hat{L}_y \quad \mathbf{r}_j + \hat{L}_z \quad \mathbf{r}_i \hat{L}_z \quad \mathbf{r}_j \end{aligned} \quad (3.76)$$

Equations (3.74) and (3.76) are not convenient formulae for the \hat{S}^2 and \hat{L}^2 operators, respectively. It is far more convenient to use the various forms that are derived from the ladder operators,

$$\begin{aligned} \hat{M}_+ &= \hat{M}_x + i\hat{M}_y \\ \hat{M}_- &= \hat{M}_x - i\hat{M}_y \end{aligned} \quad (3.77)$$

Here we have adopted the general notation, $\hat{M} = \hat{L}, \hat{S}$, to emphasize that the following treatment is valid for both orbital angular momentum and spin-angular momentum. One has

$$\hat{M}_+ Y_l^m = \hbar \sqrt{l(l+1) - m(m+1)} Y_l^{m+1} \quad (3.78)$$

and

$$\hat{M}_- Y_l^m = \hbar \sqrt{l(l+1) - m(m-1)} Y_l^{m-1} \quad (3.79)$$

and so

$$\begin{aligned} \hat{M}_x Y_l^m &= \frac{1}{2} \hat{M}_+ + \hat{M}_- Y_l^m \\ &= \frac{\hbar}{2} \sqrt{l(l+1) - m(m+1)} Y_l^{m+1} + \sqrt{l(l+1) - m(m-1)} Y_l^{m-1} \end{aligned} \quad (3.80)$$

and

$$\begin{aligned} \hat{M}_y Y_l^m &= \frac{i}{2} \hat{M}_+ - \hat{M}_- Y_l^m \\ &= \frac{i\hbar}{2} \sqrt{l(l+1) - m(m+1)} Y_l^{m+1} - \sqrt{l(l+1) - m(m-1)} Y_l^{m-1} \end{aligned} \quad (3.81)$$

Equations (3.80) and (3.81) allow one to compute expectation values for \hat{S}^2 and \hat{L}^2 using Eqs. (3.74) and (3.76), respectively. Yet another method follows directly from the definition of the Ladder operators, namely,

$$\hat{M}_+ \hat{M}_- = \hat{M}^2 - \hat{M}_z^2 + \hbar \hat{M}_z \quad (3.82)$$

$$\hat{M}_- \hat{M}_+ = \hat{M}^2 - \hat{M}_z^2 - \hbar \hat{M}_z \quad (3.83)$$

and so

$$\hat{M}^2 = \frac{1}{2} \hat{M}_+ \hat{M}_- + \hat{M}_- \hat{M}_+ + \hat{M}_z^2 \quad (3.84)$$

Using any of equations (3.82)-(3.84), along with the operative definition of the ladder operators (Eqs. (3.78) and (3.79)) will allow one to operate with \hat{S}^2 and \hat{L}^2 efficiently. It is important to note that, for many electrons, Eqs. (3.82) still holds, with

$$\hat{M}_+ 1, 2, \dots, N \equiv \sum_{i=1}^N \hat{M}_+ i \quad (3.85)$$

$$\hat{M}_- 1, 2, \dots, N \equiv \sum_{i=1}^N \hat{M}_- i \quad (3.86)$$

and

$$\hat{M}_z^2 1, 2, \dots, N \equiv \sum_{i=1}^N \hat{M}_z i \sum_{j=1}^N \hat{M}_z j. \quad (3.87)$$

It remains for us to demonstrate that \hat{L}^2 , \hat{S}^2 , \hat{L}_z and \hat{S}_z actually do commute with the atomic Hamiltonian. For the spin operators, \hat{S}^2 and \hat{S}_z , this is easy: since the atomic Hamiltonian, Eq. (3.1), does not depend on spin, operating on the Hamiltonian with the spin operators has no effect, and so the Hamiltonian and the spin operators commute,

$$[\hat{H}, \hat{S}^2] = [\hat{H}, \hat{S}_x] = [\hat{H}, \hat{S}_y] = [\hat{H}, \hat{S}_z] = 0 \quad (3.88)$$

Equation (3.88) is true not only for atoms, but also for molecules and, more generally, any system for which the Hamiltonian does not depend on spin. When one deals with relativistic effects, the spin-orbit coupling term introduces spin dependence into the Hamiltonian and Eq. (3.88) is no longer valid.

To demonstrate that \hat{L}_z and \hat{L}^2 commute with the atomic Hamiltonian, we rewrite the Hamiltonian in Eq. (3.1) as a sum of its one-electron and two-electron parts,

$$\begin{aligned} \sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) &= \sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \right) + \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &= \hat{H}_{1\text{el.}} + \hat{V}_{ee} \end{aligned} \quad (3.89)$$

Because

$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \quad (3.90)$$

if we can show that $[\hat{L}^2, \hat{H}_{1,el}] = [\hat{L}^2, V_{ee}] = [\hat{L}_z, H_{1,el}] = [\hat{L}_z, V_{ee}] = 0$, then we will have demonstrated that \hat{L}_z and \hat{L}^2 commute with the atomic Hamiltonian. To this end, we rewrite the one-electron portion of the Hamiltonian as

$$\begin{aligned} \hat{H}_{1,el} &\equiv \sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \right) \\ &= \sum_{i=1}^N \frac{-1}{2r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} + \frac{\hat{L}_i^2}{2r_i^2} - \frac{Z}{r_i} \\ &= \sum_{i=1}^N \frac{-1}{2r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{Z}{r_i} + \frac{\hat{L}_i^2}{2r_i^2} \end{aligned} \quad (3.91)$$

Now, the angular momentum about any given axis of a spherically symmetric orbit (that is, any orbit that depends only on r) is necessarily zero—such functions have no angular momentum at all. This follows directly from the form of the angular momentum operators in spherical coordinates, namely,

$$\hat{L}_x \equiv i\hbar \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \quad (3.92)$$

$$\hat{L}_y \equiv -i\hbar \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \quad (3.93)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}. \quad (3.94)$$

That is, since none of the components of the angular momentum operator depend on r , each component of the angular momentum operator commutes with any function that depends only on r . For this reason, we can write

$$\begin{aligned} \hat{L}_x \mathbf{r}_n \left(\sum_{i=1}^N \frac{-1}{2r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{Z}{r_i} + \frac{\hat{L}_i^2}{2r_i^2} \right) &= \left(\sum_{i=1}^N \hat{L}_x \mathbf{r}_n \frac{-1}{2r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{Z}{r_i} + \frac{\hat{L}_i^2}{2r_i^2} \right) \\ &= \sum_{i \neq n} \frac{-1}{2r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{Z}{r_i} + \frac{\hat{L}_i^2}{2r_i^2} \hat{L}_x \mathbf{r}_n + \hat{L}_x \mathbf{r}_n \frac{-1}{2r_n^2} \frac{\partial}{\partial r_n} r_n^2 \frac{\partial}{\partial r_n} - \frac{Z}{r_n} + \frac{\hat{L}_n^2}{2r_n^2} \\ &= \sum_{i \neq n} \left(\frac{-1}{2r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{Z}{r_i} + \frac{\hat{L}_i^2}{2r_i^2} \right) \hat{L}_x \mathbf{r}_n + \hat{L}_x \mathbf{r}_n \left(\frac{-1}{2r_n^2} \frac{\partial}{\partial r_n} r_n^2 \frac{\partial}{\partial r_n} - \frac{Z}{r_n} + \frac{\hat{L}_n^2}{2r_n^2} \right) \hat{L}_x \mathbf{r}_n \\ &= \sum_{i \neq n} \left(\frac{-1}{2r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{Z}{r_i} + \frac{\hat{L}_i^2}{2r_i^2} \right) \hat{L}_x \mathbf{r}_n + \hat{L}_x \mathbf{r}_n \left(\frac{-1}{2r_n^2} \frac{\partial}{\partial r_n} r_n^2 \frac{\partial}{\partial r_n} - \frac{Z}{r_n} + \frac{\hat{L}_n^2}{2r_n^2} \right) \hat{L}_x \mathbf{r}_n \\ &= \sum_{i \neq n} \left(\frac{-1}{2r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{Z}{r_i} + \frac{\hat{L}_i^2}{2r_i^2} \right) \hat{L}_x \mathbf{r}_n + \hat{L}_x \mathbf{r}_n \left(\frac{-1}{2r_n^2} \frac{\partial}{\partial r_n} r_n^2 \frac{\partial}{\partial r_n} - \frac{Z}{r_n} + \frac{\hat{L}_n^2}{2r_n^2} \right) \hat{L}_x \mathbf{r}_n \\ &= \left(\sum_{i=1}^N \left(\frac{-1}{2r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{Z}{r_i} + \frac{\hat{L}_i^2}{2r_i^2} \right) \right) \hat{L}_x \mathbf{r}_n \end{aligned} \quad (3.95)$$

In the first line we use the fact that $\hat{L}_x \mathbf{r}_n$ only operates on the coordinates of electron n . Then we use the fact that $\hat{L}_x \mathbf{r}_n$ and any spherically symmetric operator commute (A spherically symmetric operator is a function of r_n alone; it has no dependence on θ_n and/or ϕ_n .) Finally we use the fact that $[\hat{L}_x, \hat{L}^2] = 0$. The derivation in (3.95) is easily extended to the other components of the orbital angular momentum, and it then follows from the identity in Eq. (3.90) that

$$\left[\hat{H}_{1 \text{ el.}}, \hat{L}_x \right] \equiv \left[\hat{H}_{1 \text{ el.}}, \sum_{i=1}^N \hat{L}_x \mathbf{r}_i \right] = \sum_{i=1}^N \left[\hat{H}_{1 \text{ el.}}, \hat{L}_x \mathbf{r}_i \right] = \sum_{i=1}^N 0 = 0. \quad (3.96)$$

Using the identity

$$\left[\hat{A}, \hat{B}\hat{C} \right] = \left[\hat{A}, \hat{B} \right] \hat{C} + \hat{B} \left[\hat{A}, \hat{C} \right] \quad (3.97)$$

we have that

$$\left[\hat{H}_{1 \text{ el.}}, \hat{L}_x^2 \right] = \left[\hat{H}_{1 \text{ el.}}, \hat{L}_x \hat{L}_x \right] = \left[\hat{H}_{1 \text{ el.}}, \hat{L}_x \right] \hat{L}_x + \hat{L}_x \left[\hat{H}_{1 \text{ el.}}, \hat{L}_x \right] = 0 \cdot \hat{L}_x + \hat{L}_x \cdot 0 = 0. \quad (3.98)$$

Similarly,

$$\left[\hat{H}_{1 \text{ el.}}, \hat{L}_y^2 \right] = \left[\hat{H}_{1 \text{ el.}}, \hat{L}_z^2 \right] = 0 \quad (3.99)$$

and so, using identity (3.90) again, we have

$$\left[\hat{H}_{1 \text{ el.}}, \hat{L}^2 \right] = \left[\hat{H}_{1 \text{ el.}}, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \right] = \left[\hat{H}_{1 \text{ el.}}, \hat{L}_x^2 \right] + \left[\hat{H}_{1 \text{ el.}}, \hat{L}_y^2 \right] + \left[\hat{H}_{1 \text{ el.}}, \hat{L}_z^2 \right] = 0 \quad (3.100)$$

We now turn our attention to the electron-electron repulsion term. For convenience, we single out a single term and examine

$$\hat{L}_x \mathbf{r}_i \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \psi \mathbf{r}_i, \mathbf{r}_j, \quad (3.101)$$

where $\psi \mathbf{r}_i, \mathbf{r}_j$ is an arbitrary function. To evaluate this, it is most useful to use the real form of the angular momentum operator,

$$\hat{\mathbf{L}} \equiv \mathbf{r} \times \mathbf{p} = -i\hbar \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}, \quad z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}, \quad x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right] \quad (3.102)$$

and so

$$\begin{aligned} \hat{L}_x \mathbf{r}_i \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \psi \mathbf{r}_i, \mathbf{r}_j &= -i\hbar \left(y_i \frac{\partial}{\partial z_i} - z_i \frac{\partial}{\partial y_i} \right) \left(\frac{1}{\sqrt{x_i - x_j^2 + y_i - y_j^2 + z_i - z_j^2}} \right) \psi \mathbf{r}_i, \mathbf{r}_j \\ &= \left(\frac{1}{\sqrt{x_i - x_j^2 + y_i - y_j^2 + z_i - z_j^2}} \right) \left(-i\hbar \left(y_i \frac{\partial}{\partial z_i} - z_i \frac{\partial}{\partial y_i} \right) \right) \psi \mathbf{r}_i, \mathbf{r}_j \\ &\quad + \psi \mathbf{r}_i, \mathbf{r}_j \left(i\hbar \left(y_i \frac{z_i - z_j}{\sqrt{x_i - x_j^2 + y_i - y_j^2 + z_i - z_j^2}} - z_i \frac{y_i - y_j}{\sqrt{x_i - x_j^2 + y_i - y_j^2 + z_i - z_j^2}} \right) \right) \end{aligned} \quad (3.103)$$

$$\left[\hat{L}_x, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] = i\hbar \frac{(y_i z_i - y_i z_j)}{\left(\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} \right)^3} \psi \mathbf{r}_i, \mathbf{r}_j$$

Now, exchanging variables, we obtain, by the same argument,

$$\begin{aligned} \left[\hat{L}_x \mathbf{r}_j, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] &= i\hbar \frac{(y_j z_j - y_j z_i)}{\left(\sqrt{x_i - x_j^2 + y_i - y_j^2 + z_i - z_j^2} \right)^3} \psi \mathbf{r}_i, \mathbf{r}_j \\ &= - \left[\hat{L}_x \mathbf{r}_i, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \end{aligned} \quad (3.104)$$

Adding Eqs. (3.103) and (3.104), we see that

$$\begin{aligned} \hat{L}_x \mathbf{r}_i \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \psi(\mathbf{r}_i, \mathbf{r}_j) + \hat{L}_x \mathbf{r}_j \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \psi(\mathbf{r}_i, \mathbf{r}_j) &= \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \hat{L}_x \mathbf{r}_i \psi(\mathbf{r}_i, \mathbf{r}_j) + \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \hat{L}_x \mathbf{r}_j \psi(\mathbf{r}_i, \mathbf{r}_j) \\ \left[\hat{L}_x \mathbf{r}_i + \hat{L}_x \mathbf{r}_j, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \psi(\mathbf{r}_i, \mathbf{r}_j) &= 0 \end{aligned} \quad (3.105)$$

Again, using Eq. (3.90), we have

$$\left[\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \hat{L}_x \right] = \left[\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \sum_{n=1}^N \hat{L}_x \mathbf{r}_n \right] = \left[\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \sum_{n \neq i, j} \hat{L}_x \mathbf{r}_n \right] + \left[\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \hat{L}_x \mathbf{r}_i + \hat{L}_x \mathbf{r}_j \right] = 0. \quad (3.106)$$

If n is not equal to i or j , $\left[\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \hat{L}_x \mathbf{r}_n \right] = 0$ because $\hat{L}_x \mathbf{r}_n$ does not operate on electrons i or j . With one more application of (3.90) and this result, along with Eq. (3.105) we find that

$$\left[\hat{L}_x, V_{ee} \right] = 0. \quad (3.107)$$

An alternative derivation of this result is given at the end of this chapter.

The equations

$$\left[\hat{L}_y, V_{ee} \right] = 0 \quad (3.108)$$

and

$$\left[\hat{L}_z, V_{ee} \right] = 0 \quad (3.109)$$

are derived in much the same manner; the derivation of

$$\left[\hat{L}^2, V_{ee} \right] = 0 \quad (3.110)$$

mirrors Eq. (3.100). Because

$$\left[\hat{L}_x, \hat{H} \right] = \left[\hat{L}_x, \hat{H}_{1 \text{ el.}} + V_{ee} \right] = \left[\hat{L}_x, \hat{H}_{1 \text{ el.}} \right] + \left[\hat{L}_x, V_{ee} \right] = 0 \quad (3.111)$$

(and similar arguments for \hat{L}_y , \hat{L}_z , and \hat{L}^2), the validity of Eqs. (3.72) is established.

Before proceeding to a discussion of the implications of these commutation relations, we should discuss the importance of Eq. (3.104). Equation (3.104) implies that

$$\left[\hat{L}_x \mathbf{r}_j, \hat{V}_{ee} \right] \neq 0 \quad (3.112)$$

and, thus

$$\left[\hat{L}_x \mathbf{r}_j, \hat{H} \right] \neq 0 \quad (3.113)$$

and

$$\left[\hat{L}^2 \mathbf{r}_j, \hat{H} \right] \neq 0. \quad (3.114)$$

While the total orbital angular momentum commutes with the Hamiltonian, the orbital angular momentum of a single electron, j , does not commute with the Hamiltonian. Moreover, since

$$\left[\hat{L}_x, \hat{H}_{1 \text{ el.}} \right] = \left[\hat{L}^2, \hat{H}_{1 \text{ el.}} \right] = 0, \quad (3.115)$$

this result is a consequence of the electron-electron repulsion operator. It is important to note, then, that the orbital angular momentum, l , and the magnetic quantum number, m , of a single electron are no longer defined in a many-electron atom. This is true even in the ground-state Helium atom, where a Slater determinantal wave function for the ground state would predict that $l_1 = l_2 = m_{l_1} = m_{l_2} = 0$.

This serves to emphasize the importance of electron correlation, for it is the electron-electron repulsion term that “torques” the electrons in their orbit, making it impossible to measure the orbital angular momentum of a single electron in a many-electron atom. In addition, this demonstrates that not only do Slater determinants give quantitatively poor accuracy for many molecular properties, they

also give a *qualitatively* unreasonable description of the system, with the assignment of electrons to orbitals with well-defined orbital angular momenta being among the worst of the approximations.

Any set of mutually commuting operators can be chosen to have common eigenfunctions. We have shown that \hat{L}^2 , \hat{S}^2 , and each component of $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ commute with the atomic Hamiltonian. However, because different components of the orbital angular momentum operator, $\hat{\mathbf{L}}$, and the spin-angular momentum operator, $\hat{\mathbf{S}}$, do not commute with one another (cf. Eqs. (3.41) and (3.46), respectively), we cannot choose the atomic wave functions to commute with all three components of the orbital angular momentum and spin-angular momentum, but only one. By convention, we choose the z -components, \hat{L}_z and \hat{S}_z . It follows that

$$\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z, \hat{H} \quad (3.116)$$

are a mutually commuting set of observables and so we can choose the eigenfunctions of the Hamiltonian in so that they are also eigenfunctions of $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$. We thus say that the eigenvalues of $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$ are “good quantum numbers” and use them to label atomic states. The mutual eigenfunctions of these operators can be denoted Ψ_i^{L,S,M_L,M_s} , with the eigenvalues

$$\hat{H}\Psi_i^{L,S,M_L,M_s} = E_i\Psi_i^{L,S,M_L,M_s} \quad (3.117)$$

$$\hat{L}^2\Psi_i^{L,S,M_L,M_s} = \hbar^2 L(L+1) \Psi_i^{L,S,M_L,M_s} \quad (3.118)$$

(compare Eq. (3.37)),

$$\hat{L}_z\Psi_i^{L,S,M_L,M_s} = \hbar M_L \cdot \Psi_i^{L,S,M_L,M_s} \quad (3.119)$$

(compare Eq. (3.38)),

$$\hat{S}^2\Psi_i^{L,S,M_L,M_s} = \hbar^2 S(S+1) \Psi_i^{L,S,M_L,M_s} \quad (3.120)$$

(compare Eq. (3.42)), and

$$\hat{S}_z\Psi_i^{L,S,M_L,M_s} = \hbar M_S \cdot \Psi_i^{L,S,M_L,M_s} \quad (3.121)$$

(compare Eq. (3.43)). $\hbar\sqrt{L(L+1)}$ is referred to as the total orbital angular momentum of the atom, $\hbar M_L$ is the total orbital angular momentum about the z -axis (magnetic quantum number), $\hbar\sqrt{S(S+1)}$ is the total spin, and $\hbar M_S$ is the projection of the total spin onto the z -axis. From the fact $-l \leq m_l \leq l$, we have that

$$-L \leq M_L \leq L \quad (3.122)$$

and so a state for which the magnitude of the orbital angular momentum is $\hbar\sqrt{L(L+1)}$ has a $2L+1$ -fold degeneracy. Similarly, because $-\frac{1}{2} \leq m_s \leq \frac{1}{2}$ we have that

$$-S \leq M_S \leq S \quad (3.123)$$

and so a state with total spin-angular momentum $\hbar\sqrt{S(S+1)}$ is $2S+1$ -fold degenerate.

B. The Total Angular Momentum, \mathbf{J} .

For the treatment of magnetic effects, it is important to consider the sum of the orbital and spin angular momenta,

$$\hat{\mathbf{J}} \equiv \hat{\mathbf{L}} + \hat{\mathbf{S}}. \quad (3.124)$$

For an atom,

$$[\hat{H}, \hat{J}_x] = [\hat{H}, \hat{L}_x] + [\hat{H}, \hat{S}_x] = 0 \quad (3.125)$$

and

$$\begin{aligned}
[\hat{H}, \hat{J}^2] &= [\hat{H}, \mathbf{J} \cdot \mathbf{J}] \\
&= [\hat{H}, \mathbf{J}] \cdot \mathbf{J} + \mathbf{J} \cdot [\hat{H}, \mathbf{J}] \\
&= [\hat{H}, \hat{L}_x + \hat{S}_x] \hat{L}_x + \hat{S}_x + \hat{L}_x + \hat{S}_x [\hat{H}, \hat{L}_x + \hat{S}_x] \\
&\quad + (y \text{ and } z \text{ components}) \\
&= [\hat{H}, \hat{L}_x] + [\hat{H}, \hat{S}_x] \hat{L}_x + \hat{S}_x + \hat{L}_x + \hat{S}_x [\hat{H}, \hat{L}_x] + [\hat{H}, \hat{S}_x] \\
&\quad + (y \text{ and } z \text{ components}) \\
&= 0
\end{aligned} \tag{3.126}$$

\hat{J}^2 , \hat{L}^2 , \hat{S}^2 , and \hat{J}_z , form a mutually commuting set of operators, and so we can choose atomic states to be eigenfunctions of \hat{J}^2 , \hat{L}^2 , and \hat{S}^2 . One has, from the definition,

$$\begin{aligned}
\hat{J}_z \Psi_i^{L,S,M_L,M_s} &\equiv \hat{L}_z + \hat{S}_z \Psi_i^{L,S,M_L,M_s} \\
&= \hat{L}_z \Psi_i^{L,S,M_L,M_s} + \hat{S}_z \Psi_i^{L,S,M_L,M_s} \\
&= \hbar M_L + M_s \Psi_i^{L,S,M_L,M_s} \\
&\equiv \hbar M_J \Psi_i^{L,S,M_L,M_s}
\end{aligned} \tag{3.127}$$

On the other hand,

$$\begin{aligned}
[\hat{J}^2, \hat{L}_z] &= [\hat{L}^2 + \hat{S}^2 + 2\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}, \hat{L}_z] \\
&= 2\hat{\mathbf{S}} \cdot [\hat{\mathbf{L}}, \hat{L}_z] \\
&= 2\hat{\mathbf{S}} \cdot [L_x, \hat{L}_z] + [L_y, \hat{L}_z] \\
&= 2\hat{\mathbf{S}} \cdot i\hbar \hat{L}_x - \hat{L}_y
\end{aligned} \tag{3.128}$$

and similarly

$$[\hat{J}^2, \hat{S}_z] \neq 0. \tag{3.129}$$

so an eigenstate of \hat{L}_z and \hat{S}_z will not also be an eigenstate of \hat{S}^2 .

The permissible values of the J quantum number can be understood from the expression

$$\begin{aligned}
\hat{J}^2 &= \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} + \hat{\mathbf{S}} \\
&= \hat{L}^2 + \hat{S}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}
\end{aligned} \tag{3.130}$$

It is useful to consider that the classical analogue of this expression is

$$|J|^2 = |L|^2 + |S|^2 + 2|L||S|\cos\theta \tag{3.131}$$

which reveals that the value of J will be determined by the degree to which the electrons' total orbital angular momentum and total spin-angular momentum are aligned. When \mathbf{L} and \mathbf{S} are “aligned”, then $J = L + S$ and when \mathbf{L} and \mathbf{S} are opposed, then $J = |L - S|$. So $\hat{J}^2 \Psi_i^{J,L,S,M_J}$ lies in the range

$$\hbar^2 |L - S| |L - S| + 1 \Psi_i^{J,L,S,M_J} \leq \hat{J}^2 \Psi_i^{J,L,S,M_J} \leq \hbar^2 L + S L + S + 1 \Psi_i^{J,L,S,M_J} \tag{3.132}$$

which restricts the J quantum number to the range

$$|L - S| \leq J \leq L + S. \tag{3.133}$$

Just as for M_L and M_S ,

$$-J \leq M_J \leq J. \quad (3.134)$$

The reason $[\hat{J}^2, \hat{L}_z] \neq 0$ is largely because the orbital angular momentum and spin-angular momentum can be aligned to different degrees without changing the value of M_L or M_S . If we refer to the figure 3.7, we see even though M_L , and L determine the “cone” of permissible orbital angular momentum vectors, this is insufficient to fully specify \mathbf{L} . Thus we do not know where to place the cone of permissible spin angular momentum vectors (which is determined from M_S and S) and this would be, in any event, insufficient information to determine \mathbf{S} . It follows that the length of the vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is not fully determined by M_S, M_L, S , and L . Referring again to the figure, it is clear why this is so: even when M_S, M_L, S , and L are specified, the $|\mathbf{J}| = |\mathbf{L} + \mathbf{S}|$ is not because the points at the top of the cone are different distances from the origin. Thus, one cannot simultaneously specify M_S, M_L, S, L , and J . If one specifies the total size of the orbital and spin angular momentum but not their projection on an axis, one can determine many different values of J ($J = L + S, L + S - 1, \dots, |L - S|$), each associated with many different values of $M_J = J, J - 1, \dots, -J$.

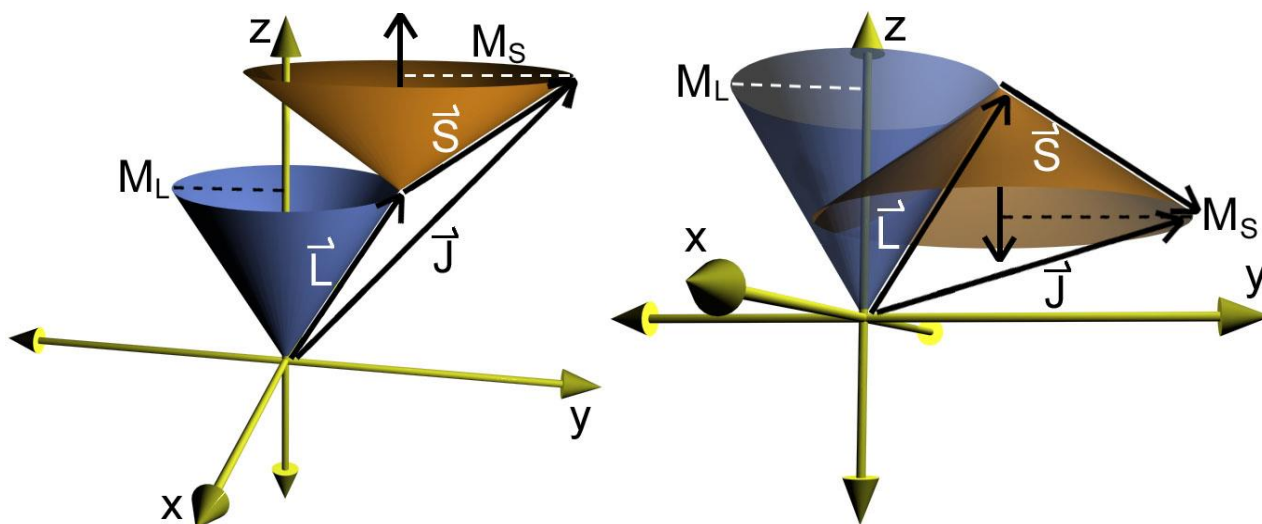


Figure 3.7. Pictorial view of the total angular momentum vector, $\mathbf{J} = \mathbf{L} + \mathbf{S}$. When \mathbf{L} and \mathbf{S} are aligned, $|\mathbf{J}|$ has its maximum value; when the orbital angular momentum and spin-angular momentum vectors are opposed, $|\mathbf{J}|$ has its minimum value. In addition, $[\hat{J}^2, \hat{L}_z] \neq 0$ and $[\hat{J}^2, S_z] \neq 0$. This is because even if M_L and M_S are specified, there are still many different possible values for $|\mathbf{J}|$, which corresponds to the distance between the open end of the cone of possible spin-angular momenta and the origin.

C. Term Symbols for Atomic States; Russell-Saunders Coupling

For light atoms, we can ignore the spin-orbit interaction, which is the interaction between the magnetic moment induced by electrons' orbital angular momenta and magnetic moment due to the electrons' spins. A good rule of thumb is that until one enters the second row transition metals (so

$Z \leq 38$), then L - S , or Russell-Saunders, coupling is fine.⁸ That is, even though \hat{L}^2 and \hat{S}^2 do not commute with the spin-orbit Hamiltonian, the value of the commutator is small and so we can successfully assign atomic spectra by assigning to each state a specific value of L and S . Neglecting spin-orbit effects, then, we can label atomic electronic states in terms of L , S , and J . When we do this we speak of assigning atomic terms, and call the symbol for each state the “term symbol”. The standard notation is

$$^{2S+1}A L_J \quad (3.135)$$

where $2S + 1$ is recognized as the multiplicity of the spin state (recall that there are $2S + 1$ possible values for M_s , namely $-S \leq M_s \leq S$), J is the total angular momentum (orbital + spin), and $A L$ denotes the dependence on the total orbital angular momentum, where

$$\begin{aligned} A 0 &\rightarrow S && \text{"sharp"} \\ A 1 &\rightarrow P && \text{"principle"} \\ A 2 &\rightarrow D && \text{"diffuse"} \\ A 3 &\rightarrow F && \text{"fundamental"} \\ A 4 &\rightarrow G \\ A 5 &\rightarrow H \\ &\vdots \end{aligned} \quad (3.136)$$

Table 3.2 lists terms symbols for some important electron configurations.

Table 3.2. Term Symbols for some important electron configurations. Primed orbitals are understood to have different principle quantum numbers from unprimed orbitals.

Terms for Equivalent Electrons	
Electron Configuration	Terms
$s^2; p^6; d^{10}; f^{14}$ (filled subshells)	1S
s^1	2S
$p^1; p^5$	2P
$p^2; p^4$	$^3P; ^1D; ^1S$
p^3	$^4S; ^2D; ^2P$
$d^1; d^9$	2D
$d^2; d^8$	$^3F; ^3P; ^1G; ^1D; ^1S$
$d^3; d^7$	$^4F; ^4P; ^2H; ^2G; ^2F; 2^2D; ^2P$
$d^4; d^6$	$^5D; ^3H; ^3G; 2^3F; ^3D; 2^3P; ^1I; 2^1G; ^1F; 2^1D; 2^1S$
d^5	$^6S; ^4G; ^4F; ^4D; ^4P; ^2I; ^2H; 2^2G; 2^2F; 3^2D; ^2P; ^2S$

⁸ In practice, Russell-Saunders coupling is often used for atoms that are far heavier, through the Lanthanides and beyond. At this point one must be extra careful, Russell-Saunders coupling is usually qualitatively reliable, but it is not a rigorously valid approach.

Terms for Inequivalent Electrons	
Electron Configuration	Terms
$s^1 s'^1$	$^3S; ^1S$
$s^1 p^1$	$^3P; ^1P$
$s^1 d^1$	$^3D; ^1D$
$p^1 p'^1$	$^3D; ^1D; ^3P; ^1P; ^3S; ^1S$
$p^1 d^1$	$^3F; ^1F; ^3D; ^1D; ^3P; ^1P$
$d^1 d'^1$	$^3G; ^1G; ^3F; ^1F; ^3D; ^1D; ^3P; ^1P; ^3S; ^1S$

You, no doubt, have seen term symbols in other courses and (probably) you know some rather clever ways to derive the term symbols for a system. What follows is a very intuitive (and rigorous) approach. As a (difficult) example, I will show how to derive the term symbols for the $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2 4p^2 5s^1$ excited state of Manganese. If you can do this, you can do any of them.

Step 1. Eliminate the closed subshells. Closed subshells do not contribute to the term; they have $L = S = 0$.

Ex. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2 4p^2 5s^1 \rightarrow 3d^2 4p^2 5s^1$

Step 2. Determine if you have any “inequivalent” electrons: electrons with different values of l or n (principle quantum number). If so, deal with each set of equivalent electrons separately, and then we’ll couple them together at the end.

Ex. The $3d$, $4p$, and $5s$ electrons are inequivalent.

Step 3. For each set of equivalent electrons, determine the term symbols.

- Construct all the nonzero Slater determinants with electrons in the orbitals in question.
- Calculate M_L and M_S for these states, and make a table of microstates.
- Find the largest value of M_S in the table, M_S^{\max} .
- Find the largest value of M_L in the table, M_L^{\max} .
- There is a $^{2M_S^{\max}+1}A$ M_L^{\max} term. Eliminate one Slater determinant (it does not matter which one if there are more than one) for each permissible value of M_L and M_S . That is, eliminate *one* state for all values of M_S and M_L that satisfy the inequality $-M_S^{\max}, -M_L^{\max} \leq M_S, M_L \leq M_S^{\max}, M_L^{\max}$.
- Examining your table of microstates, go back to state c. Do this until no Slater determinants remain.

Example: $5s^1$ configuration.

$$\begin{array}{cc}
 M_S/M_L & 0 \\
 \frac{1}{2} & |\psi_{5s}\alpha| \\
 -\frac{1}{2} & |\psi_{5s}\beta|
 \end{array} \quad (3.137)$$

$M_S^{\max} = 1; M_L^{\max} = 0 \rightarrow ^2S$. The term symbol is 2S

Example: $4p^2$ configuration.

M_S/M_L	2	1	0	-1	-2
1	0	$\left \psi_{4p_1} \alpha \quad \psi_{4p_0} \alpha \right $	$\left \psi_{4p_1} \alpha \quad \psi_{4p_{-1}} \alpha \right $	$\left \psi_{4p_{-1}} \alpha \quad \psi_{4p_0} \alpha \right $	0
0	$\left \psi_{4p_1} \alpha \quad \psi_{4p_1} \beta \right $	$\begin{pmatrix} \left \psi_{4p_1} \alpha \quad \psi_{4p_0} \beta \right \\ \left \psi_{4p_1} \beta \quad \psi_{4p_0} \alpha \right \end{pmatrix}$	$\begin{pmatrix} \left \psi_{4p_0} \alpha \quad \psi_{4p_0} \beta \right \\ \left \psi_{4p_1} \alpha \quad \psi_{4p_{-1}} \beta \right \\ \left \psi_{4p_1} \beta \quad \psi_{4p_{-1}} \alpha \right \end{pmatrix}$	$\begin{pmatrix} \left \psi_{4p_{-1}} \alpha \quad \psi_{4p_0} \beta \right \\ \left \psi_{4p_{-1}} \beta \quad \psi_{4p_0} \alpha \right \end{pmatrix}$	$\left \psi_{4p_{-1}} \alpha \quad \psi_{4p_{-1}} \beta \right $
-1	0	$\left \psi_{4p_1} \beta \quad \psi_{4p_0} \beta \right $	$\left \psi_{4p_1} \beta \quad \psi_{4p_{-1}} \beta \right $	$\left \psi_{4p_{-1}} \beta \quad \psi_{4p_0} \beta \right $	0

Now $M_L^{\max} = M_S^{\max} = 1$. **So we have a 3P state.**

After eliminating the matrix elements for the 3P state, we have

M_S/M_L	2	1	0	-1	-2
1	0	—	—	—	0
0	$\left \psi_{4p_1} \alpha \quad \psi_{4p_1} \beta \right $	$\begin{pmatrix} — \\ \left \psi_{4p_1} \beta \quad \psi_{4p_0} \alpha \right \end{pmatrix}$	$\begin{pmatrix} — \\ \left \psi_{4p_1} \alpha \quad \psi_{4p_{-1}} \beta \right \\ \left \psi_{4p_1} \beta \quad \psi_{4p_{-1}} \alpha \right \end{pmatrix}$	$\begin{pmatrix} — \\ \left \psi_{4p_{-1}} \beta \quad \psi_{4p_0} \alpha \right \end{pmatrix}$	$\left \psi_{4p_{-1}} \alpha \quad \psi_{4p_{-1}} \beta \right $
-1	0	—	—	—	0

The dashes show the elements we removed. Now $M_S^{\max} = 0, M_L^{\max} = 2$. **We have a 1D state.**

Now, eliminating these elements (denoted with a + in Eq. (3.140)) we have

M_S/M_L	2	1	0	-1	-2
1	0	—	—	—	0
0	+	$\begin{pmatrix} — \\ + \end{pmatrix}$	$\begin{pmatrix} — \\ + \\ \left \psi_{4p_1} \beta \quad \psi_{4p_{-1}} \alpha \right \end{pmatrix}$	$\begin{pmatrix} — \\ + \end{pmatrix}$	+
-1	0	—	—	—	0

Now $M_S^{\max} = M_L^{\max} = 0$. **We have a 1S state.**

The term symbols are $^3P, ^1D, ^1S$.

Example: $3d^2$ configuration.

Note that the matrices in the previous example are always symmetric. For this reason, we only explicitly consider the terms with $M_S, M_L \geq 0$, and use symmetry to determine the others.

M_S/M_L	4	3	2	1	0
1	0	$\left \psi_{3d_2} \alpha \quad \psi_{3d_1} \alpha \right $	$\left \psi_{3d_2} \alpha \quad \psi_{3d_0} \alpha \right $	$\begin{pmatrix} \left \psi_{3d_1} \alpha \quad \psi_{3d_0} \alpha \right \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-1}} \alpha \right \end{pmatrix}$	$\begin{pmatrix} \left \psi_{3d_1} \alpha \quad \psi_{3d_{-1}} \alpha \right \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-2}} \alpha \right \end{pmatrix}$
0	$\left \psi_{3d_2} \alpha \quad \psi_{3d_2} \beta \right $	$\begin{pmatrix} \left \psi_{3d_2} \alpha \quad \psi_{3d_1} \beta \right \\ \left \psi_{3d_2} \beta \quad \psi_{3d_1} \alpha \right \end{pmatrix}$	$\begin{pmatrix} \left \psi_{3d_2} \alpha \quad \psi_{3d_0} \beta \right \\ \left \psi_{3d_2} \beta \quad \psi_{3d_0} \alpha \right \\ \left \psi_{3d_1} \beta \quad \psi_{3d_1} \alpha \right \end{pmatrix}$	$\begin{pmatrix} \left \psi_{3d_1} \alpha \quad \psi_{3d_0} \beta \right \\ \left \psi_{3d_1} \beta \quad \psi_{3d_0} \alpha \right \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-1}} \beta \right \\ \left \psi_{3d_2} \beta \quad \psi_{3d_{-1}} \alpha \right \end{pmatrix}$	$\begin{pmatrix} \left \psi_{3d_1} \alpha \quad \psi_{3d_{-1}} \beta \right \\ \left \psi_{3d_1} \beta \quad \psi_{3d_{-1}} \alpha \right \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-2}} \beta \right \\ \left \psi_{3d_2} \beta \quad \psi_{3d_{-2}} \alpha \right \\ \left \psi_{3d_0} \alpha \quad \psi_{3d_0} \beta \right \end{pmatrix}$

(3.141)

Now $M_S^{\max} = 1, M_L^{\max} = 3$, so **we have a 3F term.** Eliminating the appropriate determinants,

M_S/M_L	4	3	2	1	0
1	0	—	—	$\begin{pmatrix} - \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-1}} \alpha \right \end{pmatrix}$	$\begin{pmatrix} - \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-2}} \alpha \right \end{pmatrix}$
0	$\left \psi_{3d_2} \alpha \quad \psi_{3d_2} \beta \right $	$\begin{pmatrix} - \\ \left \psi_{3d_2} \beta \quad \psi_{3d_1} \alpha \right \end{pmatrix}$	$\begin{pmatrix} - \\ \left \psi_{3d_2} \beta \quad \psi_{3d_0} \alpha \right \\ \left \psi_{3d_1} \beta \quad \psi_{3d_1} \alpha \right \end{pmatrix}$	$\begin{pmatrix} - \\ \left \psi_{3d_1} \beta \quad \psi_{3d_0} \alpha \right \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-1}} \beta \right \\ \left \psi_{3d_2} \beta \quad \psi_{3d_{-1}} \alpha \right \end{pmatrix}$	$\begin{pmatrix} - \\ \left \psi_{3d_1} \beta \quad \psi_{3d_{-1}} \alpha \right \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-2}} \beta \right \\ \left \psi_{3d_2} \beta \quad \psi_{3d_{-2}} \alpha \right \\ \left \psi_{3d_0} \alpha \quad \psi_{3d_0} \beta \right \end{pmatrix}$

(3.142)

Now we have $M_S^{\max} = M_L^{\max} = 1$, so **we have a 3P term.** Eliminating the appropriate determinants

M_S/M_L	4	3	2	1	0
1	0	—	—	$\begin{pmatrix} - \\ + \end{pmatrix}$	$\begin{pmatrix} - \\ + \end{pmatrix}$
0	$\left \psi_{3d_2} \alpha \quad \psi_{3d_2} \beta \right $	$\begin{pmatrix} - \\ \left \psi_{3d_2} \beta \quad \psi_{3d_1} \alpha \right \end{pmatrix}$	$\begin{pmatrix} - \\ \left \psi_{3d_2} \beta \quad \psi_{3d_0} \alpha \right \\ \left \psi_{3d_1} \beta \quad \psi_{3d_1} \alpha \right \end{pmatrix}$	$\begin{pmatrix} - \\ + \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-1}} \beta \right \\ \left \psi_{3d_2} \beta \quad \psi_{3d_{-1}} \alpha \right \end{pmatrix}$	$\begin{pmatrix} - \\ + \\ \left \psi_{3d_2} \alpha \quad \psi_{3d_{-2}} \beta \right \\ \left \psi_{3d_2} \beta \quad \psi_{3d_{-2}} \alpha \right \\ \left \psi_{3d_0} \alpha \quad \psi_{3d_0} \beta \right \end{pmatrix}$

(3.143)

Now $M_S^{\max} = 0, M_L^{\max} = 4$. **We have a 1G term.** Eliminating the appropriate determinants,

$$\begin{array}{cccccc}
M_S/M_L & 4 & 3 & 2 & 1 & 0 \\
1 & 0 & - & - & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} \\
0 & \pm \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ + \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ + \\ \pm \end{pmatrix} \\
& & \begin{pmatrix} \psi_{3d_1}\beta & \psi_{3d_1}\alpha \end{pmatrix} & \begin{pmatrix} \psi_{3d_2}\beta & \psi_{3d_{-1}}\alpha \end{pmatrix} & \begin{pmatrix} \psi_{3d_2}\beta & \psi_{3d_{-2}}\alpha \end{pmatrix} & \begin{pmatrix} \psi_{3d_0}\alpha & \psi_{3d_0}\beta \end{pmatrix}
\end{array} \quad (3.144)$$

We now have $M_S^{\max} = 0$, $M_L^{\max} = 2$. **This gives a 1D term.** Eliminating the determinants,

$$\begin{array}{cccccc}
M_S/M_L & 4 & 3 & 2 & 1 & 0 \\
1 & 0 & - & - & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} \\
0 & \pm \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ + \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ + \\ \pm \end{pmatrix} \\
& & \begin{pmatrix} \psi_{3d_0}\alpha & \psi_{3d_0}\beta \end{pmatrix} & \begin{pmatrix} \psi_{3d_0}\alpha & \psi_{3d_0}\beta \end{pmatrix} & \begin{pmatrix} \psi_{3d_0}\alpha & \psi_{3d_0}\beta \end{pmatrix} & \begin{pmatrix} \psi_{3d_0}\alpha & \psi_{3d_0}\beta \end{pmatrix}
\end{array} \quad (3.145)$$

which leaves us with just a single remaining microstate, which is 1S .

The terms for the $3d^2$ configuration are thus $^3F, ^3P, ^1G, ^1D, ^1S$.

You will note that there are a lot of “patterns” in the table of microstates, Eq. (3.141). These patterns are the basis for the “fast” ways to find term symbols. I, for one, find the above method more “chemical.”

Step 4: Couple together the nonequivalent terms. This is done by vector addition. Thus, when an $L = 2$ term to an $L = 1$ term, it is possible to get a $L = 3$ term (from $M_L = 2 + 1$, and $L = 2$ term (from $M_L = 1 + 1 = 2 + 0$), and an $L = 1$ term (from $M_L = 1 + 0 = 0 + 1 = 2 - 1$). One could figure this out using diagrams like the above, but there is no need since we don’t have to worry about the Pauli exclusion principle (since the orbitals are inequivalent). The gist is that one obtains states with

$$\begin{aligned}
L_{coupled} &= L_1 + L_2, L_1 + L_2 - 1, \dots, |L_1 - L_2| \\
S_{coupled} &= S_1 + S_2, S_1 + S_2 - 1, \dots, |S_1 - S_2|
\end{aligned} \quad (3.146)$$

These rules are similar to the rule for the permissible values of J , and the detailed argument for Eq. (3.146) can be derived from an equation similar to Eq. **Error! Reference source not found.**

Example:

Couple the $3d^2$ ($^3F, ^3P, ^1G, ^1D, ^1S$) and $4p^2$ ($^3P, ^1D, ^1S$) terms.

$$^3F \sim ^3P \rightarrow ^5G, ^3G, ^1G; ^5F, ^3F, ^1F, ^5D, ^3D, ^1D$$

$$^3F \sim ^1D \rightarrow ^3H, ^3G, ^3F, ^3D, ^3P$$

$$\begin{aligned}
{}^3F &\sim {}^1S \rightarrow {}^3F \\
{}^3P &\sim {}^3P \rightarrow {}^5D, {}^3D, {}^1D, {}^5P, {}^3P, {}^1P, {}^5S, {}^3S, {}^1S \\
{}^3P &\sim {}^1D \rightarrow {}^3F, {}^3D, {}^3P \\
{}^3P &\sim {}^1S \rightarrow {}^3P \\
{}^1G &\sim {}^3P \rightarrow {}^3H, {}^3G, {}^3F \\
{}^1G &\sim {}^1D \rightarrow {}^1I, {}^1H, {}^1G, {}^1F, {}^1D \\
{}^1G &\sim {}^1S \rightarrow {}^1G \\
{}^1D &\sim {}^3P \rightarrow {}^3F, {}^3D, {}^3P \\
{}^1D &\sim {}^1D \rightarrow {}^1G, {}^1F, {}^1D, {}^1P, {}^1S \\
{}^1D &\sim {}^1S \rightarrow {}^1D \\
{}^1S &\sim {}^3P \rightarrow {}^3P \\
{}^1S &\sim {}^1D \rightarrow {}^1D \\
{}^1S &\sim {}^1S \rightarrow {}^1S
\end{aligned}$$

Example: Couple the terms from the $3d^2 4p^2$ configuration to those from the $5s^1$ configuration.

Using the terms from the first example (the grouping parentheses are merely to make it easier to see from which term in the first example these terms are derived)

$${}^3F \sim {}^3P \sim {}^2S \rightarrow {}^6G, {}^4G, {}^4G, {}^2G, {}^2G; {}^6F, {}^4F, {}^4F, {}^2F, {}^2F, {}^6D, {}^4D, {}^4D, {}^2D, {}^2D$$

$${}^3F \sim {}^1D \sim {}^2S \rightarrow {}^4H, {}^2H, {}^4G, {}^2G, {}^4F, {}^2F, {}^4D, {}^2D, {}^4P, {}^2P$$

$${}^3F \sim {}^1S \sim {}^2S \rightarrow {}^4F, {}^2F$$

$${}^3P \sim {}^3P \sim {}^2S \rightarrow {}^6D, {}^4D, {}^4D, {}^2D, {}^2D, {}^6P, {}^4P, {}^4P, {}^2P, {}^2P, {}^6S, {}^4S, {}^4S, {}^2S, {}^2S$$

$${}^3P \sim {}^1D \sim {}^2S \rightarrow {}^4F, {}^2F, {}^4D, {}^2D, {}^4P, {}^2P$$

$${}^3P \sim {}^1S \sim {}^2S \rightarrow {}^4P, {}^2P$$

$${}^1G \sim {}^3P \sim {}^2S \rightarrow \cancel{({}^4H, {}^2H)} \cancel{({}^4G, {}^2G)} \cancel{({}^4F, {}^2F)}$$

$${}^1G \sim {}^1D \sim {}^2S \rightarrow {}^2I, {}^2H, {}^2G, {}^2F, {}^2D$$

$${}^1G \sim {}^1S \sim {}^2S \rightarrow {}^2G$$

$${}^1D \sim {}^3P \sim {}^2S \rightarrow \cancel{({}^4F, {}^2F)} \cancel{({}^4D, {}^2D)} \cancel{({}^4P, {}^2P)}$$

$${}^1D \sim {}^1D \sim {}^2S \rightarrow {}^2G, {}^2F, {}^2D, {}^2P, {}^2S$$

$${}^1D \sim {}^1S \sim {}^2S \rightarrow {}^2D$$

$${}^1S \sim {}^3P \sim {}^2S \rightarrow \cancel{({}^4P, {}^2P)}$$

$${}^1S \sim {}^1D \sim {}^2S \rightarrow {}^2D$$

$${}^1S \sim {}^1S \sim {}^2S \rightarrow {}^2S$$

Augmenting these terms with the subscripts appropriate to J is easy, and (in obvious shorthand) gives

$$\begin{aligned}
{}^3F \sim {}^3P \sim {}^2S &\rightarrow \left\{ \begin{aligned} &{}^6G_{\frac{13}{2}, \frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}}, {}^4G_{\frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}}, {}^4G_{\frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}}, {}^2G_{\frac{9}{2}, \frac{7}{2}}, {}^2G_{\frac{9}{2}, \frac{7}{2}}; \\ &{}^6F_{\frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^4F_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}}, {}^4F_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}}, {}^2F_{\frac{7}{2}, \frac{5}{2}}, {}^2F_{\frac{7}{2}, \frac{5}{2}}, \\ &{}^6D_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^4D_{\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^4D_{\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2D_{\frac{5}{2}, \frac{3}{2}}, (D_{\frac{5}{2}, \frac{3}{2}}) \end{aligned} \right\} \\
{}^3F \sim {}^1D \sim {}^2S &\rightarrow \left\{ \begin{aligned} &(H_{\frac{13}{2}, \frac{11}{2}, \frac{9}{2}, \frac{7}{2}}, {}^2H_{\frac{11}{2}, \frac{9}{2}})(G_{\frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}}, {}^2G_{\frac{9}{2}, \frac{7}{2}}) \\ &(F_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}}, {}^2F_{\frac{7}{2}, \frac{5}{2}})(D_{\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2D_{\frac{5}{2}, \frac{3}{2}})(P_{\frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2P_{\frac{3}{2}, \frac{1}{2}}) \end{aligned} \right\} \\
{}^3F \sim {}^1S \sim {}^2S &\rightarrow (F_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}}, {}^2F_{\frac{7}{2}, \frac{5}{2}}) \\
{}^3P \sim {}^3P \sim {}^2S &\rightarrow \left\{ \begin{aligned} &(D_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^4D_{\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}})(D_{\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2D_{\frac{5}{2}, \frac{3}{2}})(D_{\frac{5}{2}, \frac{3}{2}}) \\ &(P_{\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^4P_{\frac{5}{2}, \frac{3}{2}, \frac{1}{2}})(P_{\frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2P_{\frac{3}{2}, \frac{1}{2}})(P_{\frac{3}{2}, \frac{1}{2}}) \\ &(S_{\frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^4S_{\frac{3}{2}, \frac{1}{2}})(S_{\frac{3}{2}, \frac{1}{2}}, {}^2S_{\frac{1}{2}})(S_{\frac{1}{2}}) \end{aligned} \right\} \\
{}^3P \sim {}^1D \sim {}^2S &\rightarrow (F_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}}, {}^2F_{\frac{7}{2}, \frac{5}{2}})(D_{\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2D_{\frac{5}{2}, \frac{3}{2}})(P_{\frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2P_{\frac{3}{2}, \frac{1}{2}}) \\
{}^3P \sim {}^1S \sim {}^2S &\rightarrow (P_{\frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2P_{\frac{3}{2}, \frac{1}{2}}) \\
{}^1G \sim {}^3P \sim {}^2S &\rightarrow (H_{\frac{13}{2}, \frac{11}{2}, \frac{9}{2}, \frac{7}{2}}, {}^2H_{\frac{11}{2}, \frac{9}{2}})(G_{\frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}}, {}^2G_{\frac{9}{2}, \frac{7}{2}})(F_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}}, {}^2F_{\frac{7}{2}, \frac{5}{2}}) \\
{}^1G \sim {}^1D \sim {}^2S &\rightarrow {}^2I_{\frac{13}{2}, \frac{11}{2}}, {}^2H_{\frac{11}{2}, \frac{9}{2}}, {}^2G_{\frac{9}{2}, \frac{7}{2}}, {}^2F_{\frac{7}{2}, \frac{5}{2}}, {}^2D_{\frac{5}{2}, \frac{3}{2}} \\
{}^1G \sim {}^1S \sim {}^2S &\rightarrow {}^2G_{\frac{9}{2}, \frac{7}{2}} \\
{}^1D \sim {}^3P \sim {}^2S &\rightarrow (F_{\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}}, {}^2F)(D_{\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2D_{\frac{5}{2}, \frac{3}{2}})(P_{\frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2P_{\frac{3}{2}, \frac{1}{2}}) \\
{}^1D \sim {}^1D \sim {}^2S &\rightarrow {}^2G_{\frac{9}{2}, \frac{7}{2}}, {}^2F_{\frac{7}{2}, \frac{5}{2}}, {}^2D_{\frac{5}{2}, \frac{3}{2}}, {}^2P_{\frac{3}{2}, \frac{1}{2}}, {}^2S_{\frac{1}{2}} \\
{}^1D \sim {}^1S \sim {}^2S &\rightarrow {}^2D_{\frac{5}{2}, \frac{3}{2}} \\
{}^1S \sim {}^3P \sim {}^2S &\rightarrow (P_{\frac{5}{2}, \frac{3}{2}, \frac{1}{2}}, {}^2P_{\frac{3}{2}, \frac{1}{2}}) \\
{}^1S \sim {}^1D \sim {}^2S &\rightarrow {}^2D_{\frac{5}{2}, \frac{3}{2}} \\
{}^1S \sim {}^1S \sim {}^2S &\rightarrow {}^2S_{\frac{1}{2}}
\end{aligned} \tag{3.147}$$

If you can do a problem like the preceding, you can do any term symbols at all, guaranteed.

In the preceding derivation of the term symbols, we used Slater determinants to represent atomic states. When there is only one Slater determinant with a given value of M_L and M_S , it is clear that this Slater determinant must not only be an eigenfunction of M_L and M_S , but be an eigenfunction of \hat{L}^2 and \hat{S}^2 : otherwise the state assigned to this Slater determinant would not belong to the molecular term to which it was assigned. For instance, in Eq. (3.138), we can state without uncertainty that

$$\left| \psi_{4p_1} \alpha \quad \psi_{4p_0} \alpha \right|, \left| \psi_{4p_1} \alpha \quad \psi_{4p_{-1}} \alpha \right|, \left| \psi_{4p_{-1}} \alpha \quad \psi_{4p_0} \alpha \right|, \left| \psi_{4p_1} \beta \quad \psi_{4p_0} \beta \right|, \left| \psi_{4p_1} \beta \quad \psi_{4p_{-1}} \beta \right|, \left| \psi_{4p_{-1}} \beta \quad \psi_{4p_0} \beta \right| \quad \text{are}$$

eigenfunctions of \hat{L}^2 and \hat{S}^2 with eigenvalues $2\hbar^2 = L(L+1)\hbar^2$ and $2\hbar^2 = S(S+1)\hbar^2$ respectively. Similarly, we are certain that $|\psi_{4p_1}\alpha\ \psi_{4p_1}\beta|$ and $|\psi_{4p_{-1}}\alpha\ \psi_{4p_{-1}}\beta|$ are eigenfunctions of \hat{L}^2 and \hat{S}^2 with eigenvalues $6\hbar^2 = L(L+1)\hbar^2$ and $0 = S(S+1)\hbar^2$ respectively.

However, sometimes there were multiple Slater determinants available for a given value of M_L and M_S . When this is the case, there is no unique way to pick a single Slater determinant for the term in question. In this case, none of the listed Slater determinants will be an eigenfunction of \hat{L}^2 and \hat{S}^2 . However, by taking linear combinations of these Slater determinants one will obtain eigenfunctions of \hat{L}^2 and \hat{S}^2 .

Finding the correct linear combinations is a straightforward, if tedious, exercise in matrix diagonalization. Often one can often determine the Slater determinant for the term of interest by applying the raising and lowering operators, Eqs. (3.78) and (3.79), to a Slater determinant that is unambiguously associated with the term of interest. Since the raising and lowering operators only change the value of M_L or M_S , the result is a linear combination of Slater determinants with the appropriate values for M_L, M_S, L, S . For example, applying \hat{L}_- to the Slater determinant corresponding to the $M_L = 2, M_S = 0$ microstate of the 1D term of the p^2 configuration, $|\psi_{4p_1}\alpha\ \psi_{4p_1}\beta|$ (cf. Eq. (3.138)), one obtains a representation for the $M_L = 1, M_S = 0$ microstate of the 1D term, namely,

$$\begin{aligned}\hat{L}_- |\psi_{4p_1}\alpha\ \psi_{4p_1}\beta| &\propto \hat{L}_- 1 + \hat{L}_- 2 |\psi_{4p_1}\alpha\ \psi_{4p_1}\beta| \\ &\propto |\psi_{4p_0}\alpha\ \psi_{4p_1}\beta| + |\psi_{4p_1}\alpha\ \psi_{4p_0}\beta|.\end{aligned}\tag{3.148}$$

Note that this microstate is not associated with a single Slater determinant but, instead, a mixture between two Slater determinants.

By far the most important thing to remember is that, in general, a Slater determinant will not be an eigenfunction of \hat{L}^2 and \hat{S}^2 . That is, Slater determinant wave functions do not necessarily correspond to the term symbols used to label states in atomic spectra.

D. Hund's Rules for the Most Stable States of a Molecule

Given several terms using the same orbitals, it is important to know their energies. (In the absence of electromagnetic fields, the various M_L and M_S states associated with a single term all have the same energy.) For instance, in our example problem, where $^6G_{\frac{3}{2}}$ is predicted to be the lowest excited state. (But see below: I wouldn't trust this prediction.) This is determined using Hund's rules:

- Hund's Rule #1:** *The higher the multiplicity of a state, the lower its energy.*
- Hund's Rule #2:** *Among states of equal multiplicity, the one with the highest value of L has the lowest energy.*
- Hund's Rule #3:** *If spin-orbit effects are considered, then for a given value of S and L , the state with the lowest value of J is the lowest energy state when the unfilled subshell is less than half-filled. If the subshell is more than half-filled, then the highest value of J is most stable.*

It must be emphasized that Hund's rules (especially the third rule) are occasionally violated. In general, they are reliable for ground states and low-lying excited states, because these states are

well-described by a single electron configuration. For states that are poorly described by a single electron configuration, Hund's rules are unreliable. In section VI.A. we will consider more reliable revisions to Hund's rules.

Hund's rules can't really be derived, but they can be rationalized.

1. Rationalization of Hund's rule #1; Maximum Multiplicity

Let us consider $1s^1 2p^1$ configuration of Helium. Making the table of microstates, we have

M_S/M_L	1	0	-1	
1	$\left \psi_{1s} \alpha \quad \psi_{2p_1} \alpha \right $	$\left \psi_{1s} \alpha \quad \psi_{2p_0} \alpha \right $	$\left \psi_{1s} \alpha \quad \psi_{2p_{-1}} \alpha \right $	
0	$\left(\begin{array}{c} \left \psi_{1s} \alpha \quad \psi_{2p_1} \beta \right \\ \left \psi_{1s} \beta \quad \psi_{2p_1} \alpha \right \end{array} \right)$	$\left(\begin{array}{c} \left \psi_{1s} \alpha \quad \psi_{2p_0} \beta \right \\ \left \psi_{1s} \beta \quad \psi_{2p_0} \alpha \right \end{array} \right)$	$\left(\begin{array}{c} \left \psi_{1s} \alpha \quad \psi_{2p_{-1}} \beta \right \\ \left \psi_{1s} \beta \quad \psi_{2p_{-1}} \alpha \right \end{array} \right)$	(3.149)
-1	$\left \psi_{1s} \beta \quad \psi_{2p_1} \beta \right $	$\left \psi_{1s} \beta \quad \psi_{2p_0} \beta \right $	$\left \psi_{1s} \beta \quad \psi_{2p_{-1}} \beta \right $	

and so there are both 3P and 1P states. The eigenstates for the 1P can be deduced from one of the “unambiguous” 3P states using the ladder-operator method referred to earlier. Taking, in particular, the $M_S = 1, M_L = 0$ microstate of the 3P , we can construct a wave function for the $M_L = M_S = 0$ microstate:

$$\begin{aligned}
\hat{S}_- \left| \psi_{1s} \alpha \quad \psi_{2p_0} \alpha \right| &\propto \hat{S}_- 1 + \hat{S}_- 2 \left| \psi_{1s} \alpha \quad \psi_{2p_0} \alpha \right| \\
&\propto \hbar \sqrt{\frac{1}{2} \cdot \frac{1}{2} + 1 - \frac{1}{2} \cdot \frac{1}{2} - 1} \left| \psi_{1s} \beta \quad \psi_{2p_0} \alpha \right| \\
&\quad + \hbar \sqrt{\frac{1}{2} \cdot \frac{1}{2} + 1 - \frac{1}{2} \cdot \frac{1}{2} - 1} \left| \psi_{1s} \alpha \quad \psi_{2p_0} \beta \right|. \\
&\propto \left| \psi_{1s} \beta \quad \psi_{2p_0} \alpha \right| + \left| \psi_{1s} \alpha \quad \psi_{2p_0} \beta \right| \\
&\propto \psi_{1s}(\mathbf{r}_1) \beta(1) \psi_{2p_0}(\mathbf{r}_2) \alpha(2) - \psi_{1s}(\mathbf{r}_2) \beta(2) \psi_{2p_0}(\mathbf{r}_1) \alpha(1) \\
&\quad + \psi_{1s}(\mathbf{r}_1) \alpha(1) \psi_{2p_0}(\mathbf{r}_2) \beta(2) - \psi_{1s}(\mathbf{r}_2) \alpha(2) \psi_{2p_0}(\mathbf{r}_1) \beta(1) \\
&\propto \psi_{1s}(\mathbf{r}_1) \psi_{2p_0}(\mathbf{r}_2) - \psi_{1s}(\mathbf{r}_2) \psi_{2p_0}(\mathbf{r}_1) \quad \alpha(2) \beta(1) + \alpha(1) \beta(2)
\end{aligned} \tag{3.150}$$

The $M_L = M_S = 0$ microstate of the 1P state is easily determined since it must be orthogonal to Eq. (3.150), and so

$$\begin{aligned}
\hat{S}_- \left| \psi_{1s} \alpha \quad \psi_{2p_0} \alpha \right| &\propto \hat{S}_- 1 + \hat{S}_- 2 \left| \psi_{1s} \alpha \quad \psi_{2p_0} \alpha \right| \\
&\propto \hbar \sqrt{\frac{1}{2} \cdot \frac{1}{2} + 1 - \frac{1}{2} \cdot \frac{1}{2} - 1} \left| \psi_{1s} \beta \quad \psi_{2p_0} \alpha \right| \\
&\quad + \hbar \sqrt{\frac{1}{2} \cdot \frac{1}{2} + 1 - \frac{1}{2} \cdot \frac{1}{2} - 1} \left| \psi_{1s} \alpha \quad \psi_{2p_0} \beta \right|. \\
\Psi^{^1P}(\mathbf{r}_1, \mathbf{r}_2) &\propto \left| \psi_{1s} \beta \quad \psi_{2p_0} \alpha \right| - \left| \psi_{1s} \alpha \quad \psi_{2p_0} \beta \right| \\
&\propto \psi_{1s}(\mathbf{r}_1) \psi_{2p_0}(\mathbf{r}_2) + \psi_{1s}(\mathbf{r}_2) \psi_{2p_0}(\mathbf{r}_1) \quad \alpha(2) \beta(1) - \alpha(1) \beta(2)
\end{aligned} \tag{3.151}$$

Combining this result, we see that the wave functions of both states can be conveniently summarized as

$$\begin{aligned}
\Psi_{1P/3P} \mathbf{r}_1, \mathbf{r}_2 &\propto \begin{vmatrix} \psi_{1s}\beta & \psi_{2p_0}\alpha \\ \psi_{1s}\alpha & \psi_{2p_0}\beta \end{vmatrix} \\
&\propto \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \quad \alpha \ 2 \ \beta \ 1 \mp \alpha \ 1 \ \beta \ 2
\end{aligned} \tag{3.152}$$

We can now evaluate the energy of these two states. We have

$$\begin{aligned}
E_{1P/3P} &\propto \left\langle \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \left| \frac{-\nabla_1^2}{2} - \frac{2}{r_1} + \frac{-\nabla_2^2}{2} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \right\rangle \\
&\propto \left\langle \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \left| \frac{-\nabla_1^2}{2} - \frac{2}{r_1} \right| \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \right\rangle \\
&\quad + \left\langle \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \left| \frac{-\nabla_2^2}{2} - \frac{2}{r_2} \right| \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \right\rangle \\
&\quad + \left\langle \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \right\rangle \\
&\propto \left\langle \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \left| \begin{pmatrix} E_{1s}^{He^+} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm E_{2p}^{He^+} \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \right. \right\rangle \\
&\quad + \left\langle \begin{pmatrix} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \left| \begin{pmatrix} E_{2p}^{He^+} \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ \pm E_{1s}^{He^+} \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \end{pmatrix} \right. \right\rangle \\
&\quad + \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \right\rangle \\
&\quad + \left\langle \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle \\
&\quad \pm \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle \\
&\quad \pm \left\langle \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \right\rangle \\
&\propto 2 \left(E_{1s}^{He^+} + E_{2p}^{He^+} \right) + 2 \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \right\rangle \\
&\quad \pm 2 \left\langle \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle
\end{aligned} \tag{3.153}$$

If we normalize the wave function, we find that Eq. (3.153) gives:

$$\begin{aligned}
E_{1P/3P} &\equiv E_{1s}^{He^+} + E_{2p}^{He^+} + \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \right\rangle \\
&\quad \pm \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle \\
&= h_{1s} + h_{2p} + J_{1s,2p} \pm K_{1s,2p}
\end{aligned} \tag{3.154}$$

where h_{1s} and h_{2p} represent the one-electron energies (in this case, the energy of a 1s and 2p electron in the Helium cation). The ‘‘Coulomb integral’’

$$J_{ij} \equiv \left\langle \psi_i \mathbf{r}_1 \psi_j \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_i \mathbf{r}_1 \psi_j \mathbf{r}_2 \right\rangle \quad (3.155)$$

accounts for the Coulomb repulsion between the electrons, and the “exchange integral”

$$K_{ij} \equiv \left\langle \psi_i \mathbf{r}_1 \psi_j \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_j \mathbf{r}_1 \psi_i \mathbf{r}_2 \right\rangle \quad (3.156)$$

accounts for the effects of the Pauli exclusion principle.

The Coulomb integral is easily seen to be positive. We have that

$$\begin{aligned} J_{ij} &\equiv \left\langle \psi_i \mathbf{r}_1 \psi_j \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_i \mathbf{r}_1 \psi_j \mathbf{r}_2 \right\rangle \\ &= \iint \frac{|\psi_i \mathbf{r}_1|^2 |\psi_j \mathbf{r}_2|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\geq 0 \end{aligned} \quad (3.157)$$

because $|\psi_i \mathbf{r}_1|^2$, $|\psi_j \mathbf{r}_2|^2$, and $\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ are all nonnegative, and the integral of a nonnegative function must also be nonnegative.⁹

The exchange integral is always positive (for any pair of orbitals). Rewriting Eq. (3.156) in integral form we have that

$$\begin{aligned} K_{ij} &\equiv \left\langle \psi_i \mathbf{r}_1 \psi_j \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_j \mathbf{r}_1 \psi_i \mathbf{r}_2 \right\rangle \\ &= \iint \frac{\psi_i^* \mathbf{r}_1 \psi_j \mathbf{r}_1^* \psi_i^* \mathbf{r}_2 \psi_j \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\geq 0 \end{aligned} \quad (3.158)$$

which is the Coulomb repulsion between an distribution, $\psi_i \mathbf{r}_1 \psi_j \mathbf{r}_1$ and itself. The “self-repulsion” of a charge distribution is always positive, so the exchange integral is also positive. Pictorially, this result follows from the fact that when $\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ is large, then $|\mathbf{r}_1 - \mathbf{r}_2|$ is small.

Whenever the positions of the first and second electrons are sufficiently close together, $\psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_1$ and $\psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_2$ will have the same sign. Thus, in regions where $\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ is large, the integrand in Eq. (3.158) is positive. (Even though the integrand can be negative when $|\mathbf{r}_1 - \mathbf{r}_2|$ is large enough, in these cases $\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ is smaller, so the contribution to the value of the integral from these regions is smaller.)

Because of the symmetry of the 1s and 2p orbitals, it is especially easy to show that the exchange integral, K_{ij} , is greater than zero in this case. Break the integral in Eq. (3.154) into parts based on the sign of the 2p-orbital. We have

⁹ The fact that the integral of a nonnegative function must not be negative is perhaps unfamiliar. However, if you think of the integral as a Riemann sum it is obvious (since the sum of positive numbers must always be positive). Geometrically, the result here (in six dimensions) is the analogue of the one-dimensional result wherein the area under a positive-valued function must always be positive.

$$\begin{aligned}
K_{1s,2p} &\equiv \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle \\
&= \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle_{\substack{z_1 > 0 \\ z_2 > 0}} \\
&\quad + \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle_{\substack{z_1 > 0 \\ z_2 < 0}} \\
&\quad + \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle_{\substack{z_1 < 0 \\ z_2 < 0}} \\
&\quad + \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle_{\substack{z_1 < 0 \\ z_2 > 0}}
\end{aligned} \tag{3.159}$$

Using the symmetry of the $2p_z$ orbital, $\psi_{2p_0}(x, y, z) = -\psi_{2p_0}(x, y, -z)$, we see that the first and third terms in Eq. (3.159) are the same, as are the second and fourth terms. Thus

$$K_{1s,2p} = 2 \left(\left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle_{\substack{z_1 > 0 \\ z_2 > 0}} + \left\langle \psi_{1s} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \right\rangle_{\substack{z_1 > 0 \\ z_2 < 0}} \right) \tag{3.160}$$

Writing the integrals explicitly for clarity, we have

$$\begin{aligned}
\frac{1}{2} K_{1s,2p} &\equiv \left(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \psi_{1s} \mathbf{r}_1 \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \right) \\
&\quad + \left(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} \psi_{1s} \mathbf{r}_1 \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \right)
\end{aligned} \tag{3.161}$$

Now, we choose the 1s-orbital to be positive and the 2p-orbital to be positive for $z > 0$. Then, the first orbital in Eq. (3.161) $z_1 > 0, z_2 > 0$ is seen to be positive and the second orbital is seen to be negative. Next we use the symmetry of the 2p-orbital and recognize that

$$\psi_{1s}(x, y, z) \psi_{2p_0}(x, y, z) = -\psi_{1s}(x, y, -z) \psi_{2p_0}(x, y, -z). \tag{3.162}$$

We can change coordinates, then, from $z \rightarrow -z$, obtaining

$$\begin{aligned}
\frac{1}{2} K_{1s,2p} &\equiv \left(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \psi_{1s} \mathbf{r}_1 \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \right) \\
&\quad + \left(- \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} \psi_{1s} \mathbf{r}_1 \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \frac{1}{|\mathbf{r}_1 - x_2, y_2, -z_2|} dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \right) \\
&= \left(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \psi_{1s} \mathbf{r}_1 \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - x_2, y_2, -z_2|} \right) dy_1 dz_1 dx_2 dy_2 dz_2 \right)
\end{aligned} \tag{3.163}$$

The because the 1s and $2p_0$ orbitals are positive for $z > 0$,

$$\psi_{1s} \mathbf{r}_1 \psi_{1s} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_2 \psi_{2p_0} \mathbf{r}_1 > 0 \tag{3.164}$$

Because the limits of integration imply that $z_1 > 0$ and $z_2 > 0$,

$$\begin{aligned}
|\mathbf{r}_1 - \mathbf{r}_2| &= \sqrt{x_1 - x_2^2 + y_1 - y_2^2 + z_1 - z_2^2} \\
&< \sqrt{x_1 - x_2^2 + y_1 - y_2^2 + z_1 - (-z_2)^2} = |\mathbf{r}_1 - x_2, y_2, -z_2|
\end{aligned} \tag{3.165}$$

and so

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - x_2, y_2, -z_2|} > 0. \quad (3.166)$$

It follows from Eqs. (3.164), and (3.166) that each term in the integrand in Eq. (3.163) is positive, and so

$$K_{1s,2p} > 0. \quad (3.167)$$

Referring to Eq. (3.154), we see that

$$\begin{aligned} E_{1P} - E_{3P} &\equiv 2K_{1s,2p} > 0 \\ &\sim 2048 \text{ cm}^{-1} \quad \text{experiment} \\ &\sim .009 \text{ Hartree} \quad \text{experiment} \end{aligned} \quad (3.168)$$

That is, the triplet state has lower energy than the singlet state.

The precise explanation for this result is a bit complicated, but it is useful to remember that the Pauli-exclusion principle means that two electrons with the same spin can never be at the same place. Since it is energetically unfavorable for two electrons to be at the same place (because it increases the electron-electron repulsion energy), this tends to lower electron-electron repulsion energy. Indeed, as we observed in the preceding derivation the difference in energy between the singlet and triplet states is precisely due to a decrease in the electron-electron repulsion energy: all the other terms (kinetic and potential) are, in the approximation considered above, identical for the singlet and triplet states.

It should be pointed out, however, that once one considers the effects of electron correlation, such simple intuitive arguments may or may not be valid. It is expected, however, that whenever a single Slater determinant (or a symmetry-induced linear combination like that considered here) is a good approximation to the wave function, the present argument should be valid.

2. Rationalization of Hund's Rule #2; Maximum Orbital Angular Momentum

To interpret the effect of L on the energy we consider, for example, the $2p^2$ state of the Helium atom. From Eq. (3.138) we recognize that there are 3P , 1D , and 1S configurations for this state, and Hund's rules predicts that

$$E_{3P} < E_{1D} < E_{1S}. \quad (3.169)$$

This ordering of states is, in fact, observed not only for Helium—for He

$$\begin{aligned} E_{1D} - E_{3P} &\approx .008 \text{ Hartree} \\ E_{1S} - E_{1D} &\approx .083 \text{ Hartree} \end{aligned} \quad (3.170)$$

—but other atoms where the only unfilled subshell contains p-orbitals (C, Si, and the rest of the Group 14 elements).

If we do the same sort of approach as was used in the first Hund's rules (but matters are much more complicated now), we observe that

$$\begin{aligned} E_{1D} - E_{3P} &\approx \frac{6}{25} G \\ E_{1S} - E_{1D} &\approx \frac{9}{25} G \end{aligned} \quad (3.171)$$

where G is a positive quantity related to the Coulomb repulsion between electrons. Clearly Eq. (3.171), which predicts

$$\frac{E_{1S} - E_{1D}}{E_{1D} - E_{3P}} \approx \frac{3}{2}. \quad (3.172)$$

Equation (3.172) is not accurate for the $2p^2$ configuration of Helium (cf. Eq. (3.170)), which serves to emphasize the unreliability of simple orbital models in this case (and for excited states in general).

Hund's second rule says that, among states with the same multiplicity, larger values of L are more stable. The "picture" behind this is that, in a $2p_+$ orbital, electrons move in a clockwise fashion in an annulus-shaped orbital near the origin, while electrons in a $2p_-$ orbital move in a counterclockwise fashion. Thus, the electron repulsion associated with the $|2p_+\alpha \ 2p_+\beta|$ state is less than that associated with the $|2p_+\alpha \ 2p_-\beta|$ state because the electrons "encounter" each other less frequently.¹⁰ Referring to Eq. (3.138) we see that the energy of the $|2p_+\alpha \ 2p_+\beta|$ microstate has the same energy as the 1D term while the less favorable $|2p_+\alpha \ 2p_-\beta|$, $|2p_-\alpha \ 2p_+\beta|$, and $|2p_0\alpha \ 2p_0\beta|$ states contribute to the 1S state. (The $|2p_0\alpha \ 2p_0\beta|$ state is higher in energy because the $2p_0$ orbital is roughly half the size of the $2p_{\pm 1}$ orbitals. This follows from the fact that BOTH the $2p_x$ and the $2p_y$ orbitals are formed from the spatially identical $2p_+$ and $2p_-$ orbitals.)

3. Rationalization of Hund's Third Rule

Unlike the first and second rules, Hund's third rule pertains to the splitting *within* a single atomic term, rather than the spacing between terms. Hund's third rule states that for shells that are less than half-filled, the smaller values of J are associated with lower energy. For example, the 3P_1 state of Carbon lies 16 cm^{-1} higher in energy than ground state (3P_0). (The 3P_2 state lies 43 cm^{-1} higher.) The splitting increases as one moves down the periodic table: the 3P_1 and 3P_2 states of Silicon are 77 cm^{-1} and 223 cm^{-1} higher in energy than 3P_0 ground state, respectively. However, for shells that are more than half-filled, larger values of J are associated with lower energy. For shells that are half-filled Hund's third rule provides no guidance; for shells that are close to half-filled (especially if they correspond to excited states), Hund's third rule is unreliable.

Hund's third rule reflects spin-orbit interactions. To understand the spin-orbit interaction, imagine that you could "ride along" with an electron as it orbits the nucleus. From your viewpoint, then, the electron would be still and the nucleus would be moving. Recalling that moving charges "generate" magnetic fields, it is clear that an electron feels not only an electric field from the nucleus, but also a magnetic field. (As the speed of the electron gets very large, the apparent magnetic field becomes very large, overwhelming the effect of the electric field.) This magnetic field, due to the orbit of the electron around the nucleus, interacts with the spin magnetic moment of the electron, $\mu_S \cdot \hat{S} = -g \frac{e}{2mc} \hat{S} \cdot \hat{L}$ (cf. Eq. (3.48)), which leads to what we call the spin-orbit interaction. The spin-orbit interaction is usually omitted in the Hamiltonian (we do not consider "magnetic" effects due to the nucleus, but only the "electric" effects), but to include it we need merely add the extra term

¹⁰ As a child, your professor was prone to being harassed by bullies. The preferred mode of escape (I was swift like the wind) was to run from the bully and find a large tree, swing-set, or other object. Then the bully would run around the swing-set (think "nucleus") to try to catch me and I would proceed to run in the same fashion, keeping the bully on the opposite side of the set (until eventually he would collapse from exhaustion). Clearly the interaction "energy" between the bully and me was minimal when we both ran in a clockwise (or counterclockwise) fashion around the swing-set, since I could keep a large distance from the bully in this case. On the other hand, should I have decided to run counterclockwise whilst the bully ran clockwise....

$$\begin{aligned}
\hat{H}_{S.O.} &= \sum_{i=1}^N \frac{Z}{4\pi\epsilon_0 r_i^3} \hat{\mu}_L \cdot \mathbf{r}_i \cdot \hat{\mu}_S \cdot \mathbf{r}_i \\
&= \sum_{i=1}^N \frac{Z}{4\pi\epsilon_0 r_i^3} \left(\frac{-e}{2mc} \hat{\mathbf{L}} \cdot \mathbf{r}_i \cdot -g \frac{e}{2mc} \hat{\mathbf{S}} \cdot \mathbf{r}_i \right) \\
&= \sum_{i=1}^N \frac{Ze^2}{16\pi\epsilon_0 m^2 c^2 r_i^3} g \hat{\mathbf{L}} \cdot \mathbf{r}_i \cdot \hat{\mathbf{S}} \cdot \mathbf{r}_i
\end{aligned} \tag{3.173}$$

Now, when the orbital angular momentum and spin angular momentum of the electrons are directed against each other, $J = |L - S|$ and $\mathbf{L} \cdot \mathbf{S} < 0$. In this case, the spin-orbit term is attractive (the potential is negative since $\hat{\mathbf{L}} \cdot \mathbf{r}_i \cdot \hat{\mathbf{S}} \cdot \mathbf{r}_i$ will have a negative expectation value). Thus, the spin-orbit term in the Hamiltonian is as small as possible when $\mathbf{L} \cdot \mathbf{S}$ is as small as possible, which occurs when $\mathbf{L} \cdot \mathbf{S} = -|\mathbf{L}||\mathbf{S}|$ and

$$\begin{aligned}
|\mathbf{J}|^2 &= (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = |\mathbf{L}|^2 + 2|\mathbf{L}||\mathbf{S}| + |\mathbf{S}|^2 \\
&= |\mathbf{L} - \mathbf{S}|^2.
\end{aligned} \tag{3.174}$$

Recall that the term symbols for less than half-filled shells and more than half-filled shells were the same (cf. Table 3.2). For example, the $3d^2$ and $3d^8$ electron configurations are associated with the same terms. The picture is that in $3d^8$ electron configuration is a $3d^2$ configuration of *electron holes*. An electron hole is just the absence of an electron; it has a positive charge that “cancels out” an electron. That is, a $3d^8$ configuration is the same as a $3d^{10}$ configuration of electrons plus a $3d^2$ configuration of holes, which cancels out the “extra” two electrons in the $3d^{10}$ configuration. When considering shells that are more than half-filled, it is better to consider electron holes than electrons themselves. (This is true for much the same reason it is better to consider electron holes when developing term symbols for these cases.) However, because holes are positively charged, the spin-orbit interaction for holes is opposite to that for electrons. (Specifically, the spin angular momentum of a “spinning positive charge” is the opposite of that of a negative charge,

$$\hat{\mu}_S^{hole} = g \frac{+e}{2mc} \hat{\mathbf{S}} \cdot \mathbf{r}_i = -\hat{\mu}_S^{electron}.^{11})$$

Because the sign of the spin-orbit Hamiltonian, $\hat{H}_{S.O.}$, (cf. Eq. (3.173)) changes when we consider holes instead of electrons, while it was best to keep the spin and orbital angular momenta of electrons opposed, it is best to keep the spin and orbital angular momenta of holes aligned. So for shells that are more than half-filled, we want $\hat{\mathbf{L}} \cdot \mathbf{r}_i \cdot \hat{\mathbf{S}} \cdot \mathbf{r}_i$ to be as positive as possible, which occurs when $J = L + S$. Ergo, for shells that are more than half filled, large values of J are associated with minimum energy.

V. More on the Hartree-Fock method

At this stage we have shown how to determine the term symbols for an atom and how to determine, for each term, one or more Slater determinants (or linear combinations of Slater determinants) with the specified values of L , S , and J . Just as in the case of the Helium atom, we want to determine which orbitals we should use in the Slater determinant. We could use the Hydrogenic orbitals for the atom in question, but we already saw that this gives poor results for the

¹¹ The Landé g-factor for a hole is the same as that for an electron, $g_{hole} = g_{electron}$

Helium atom; there is no reason to expect that many-electron atoms would be any better. For the Helium atom, it was much better to use Hydrogenic wave functions with an effective nuclear charge. Best of all, we could use Hydrogenic wave functions with a local effective nuclear charge: an effective nuclear charge that depended on the distance from the nucleus.

For example, consider the ground state of Lithium. As a Slater determinant for the ground state we can consider

$$\begin{aligned} \Phi_{\mathbf{r}_1, \sigma 1; \mathbf{r}_2, \sigma 2; \mathbf{r}_3, \sigma 3} &= \begin{vmatrix} \psi_1 \alpha & \psi_1 \beta & \psi_2 \alpha \end{vmatrix} \\ &= \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(\mathbf{r}_1, \alpha) & \psi_1(\mathbf{r}_1, \beta) & \psi_2(\mathbf{r}_1, \alpha) \\ \psi_1(\mathbf{r}_2, \alpha) & \psi_1(\mathbf{r}_2, \beta) & \psi_2(\mathbf{r}_2, \alpha) \\ \psi_1(\mathbf{r}_3, \alpha) & \psi_1(\mathbf{r}_3, \beta) & \psi_2(\mathbf{r}_3, \alpha) \end{vmatrix} \end{aligned} \quad (3.175)$$

where

$$\begin{aligned} \psi_1(\mathbf{r}) &= \psi_{1s}(\zeta_{1s} r, \theta, \phi) \propto e^{-\zeta_{1s} r} \\ \psi_2(\mathbf{r}) &= \psi_{2s}(\zeta_{2s} r, \theta, \phi) \propto (2 - \zeta_{2s} r) e^{-\zeta_{2s} r} \end{aligned} \quad (3.176)$$

That is, we have two orbitals, one of which is “1s-like” and the other of which is “2s-like.” These orbitals should be orthogonal and normalized (just like the 1s and 2s orbitals of the hydrogen atom), though if they are not orthogonal this only changes the normalization constant for the Slater determinant (which is $\sqrt{\frac{1}{3!}}$ for non-orthonormal¹² orbitals). Referring to the analysis preceding Eq. (3.32), it is clear that *any* orbitals can be written in the form of Eqs. (3.176), so we can determine the optimal effective nuclear charges by minimizing the energy with respect to the effective nuclear charges

$$E_{HF}^{Li} \equiv \min_{\zeta_1, \zeta_2} \frac{\langle \psi_1 \alpha \ \psi_1 \beta \ \psi_2 \alpha | \hat{H} | \psi_1 \alpha \ \psi_1 \beta \ \psi_2 \alpha \rangle}{\langle \psi_1 \alpha \ \psi_1 \beta \ \psi_2 \alpha | \psi_1 \alpha \ \psi_1 \beta \ \psi_2 \alpha \rangle} \quad (3.177)$$

or, equivalently, minimizing the energy with respect to every possible choice of orthogonal and normalized orbitals,¹³

$$E_{HF}^{Li} \equiv \min_{\langle \psi_i | \psi_j \rangle = \delta_{ij}} \langle \psi_1 \alpha \ \psi_1 \beta \ \psi_2 \alpha | \hat{H} | \psi_1 \alpha \ \psi_1 \beta \ \psi_2 \alpha \rangle. \quad (3.178)$$

Both methods yield the same approximation to the ground state energy and wave function, but Eq. (3.178) is much more common. Equations (3.178) (or (3.177)) define the *restricted* Hartree-Fock approximation.

Why do we refer to Eq. (3.178) as the “restricted” Hartree-Fock approximation? Inspecting Eq. (3.178), we note that there are two alpha-spin electrons but only one beta-spin electron. Recalling figure 3.6, we recognize that the Pauli exclusion principle will force the 1s electron with α -spin to

¹² *Orthonormal* orbitals are *orthogonal* and *normalized*. We often write this constraint as $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ where δ_{ij} is the Kröneckers delta. The Kröneckers delta is just the identity matrix. That is,

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j. \end{cases}$$

¹³ If the orbitals are orthogonal, then the Slater determinant wave function is normalized. Therefore, in Eq. (3.178) we do not have to divide by the normalization factor, like we did in Eq. (3.177).

stay further away from the 2s electron, while the 1s electron with β -spin is allowed to approach the 2s electron more closely. This suggests that we should choose different orbitals for the α -spin 1s electron and the β -spin 1s electron. This leads to the *unrestricted* Hartree-Fock method,

$$E_{HF}^{Li} \equiv \min_{\substack{\langle \psi_1^\alpha | \psi_2^\alpha \rangle = \delta_{ij} \\ \langle \psi_1^\beta | \psi_1^\beta \rangle = 1}} \left\langle \psi_1^\alpha \alpha \quad \psi_1^\beta \beta \quad \psi_2^\alpha \alpha \middle| \hat{H} \middle| \psi_1^\alpha \alpha \quad \psi_1^\beta \beta \quad \psi_2^\alpha \alpha \right\rangle \quad (3.179)$$

One finds that

- The unrestricted Hartree-Fock energy is lower than the restricted Hartree-Fock energy. This is because the unrestricted Hartree-Fock wave function incorporates a small amount of electron correlation.
- Unfortunately, the unrestricted Hartree-Fock wave function is not an eigenfunction of \hat{S}^2 . We say, then, that the unrestricted Hartree-Fock (UHF) wave function is *spin-contaminated*. For Lithium the UHF wave function is a mixture of the doublet ($S = \frac{1}{2}$) and and quadruplet ($S = \frac{3}{2}$) states.

It is useful, perhaps, to include another, more complicated, example. For example, the orbitals for the nitrogen atom (in its 4S quadruplet ground state) can be determined from

$$E_{RHF}^N \equiv \min_{\langle \psi_i | \psi_j \rangle = \delta_{ij}} \left\langle \psi_1 \alpha \quad \psi_1 \beta \quad \psi_2 \alpha \quad \psi_2 \beta \quad \psi_3 \alpha \quad \psi_4 \alpha \quad \psi_5 \alpha \middle| \hat{H} \middle| \psi_1 \alpha \quad \psi_1 \beta \quad \psi_2 \alpha \quad \psi_2 \beta \quad \psi_3 \alpha \quad \psi_4 \alpha \quad \psi_5 \alpha \right\rangle \quad (3.180)$$

Eq. (3.180) uses the restricted Hartree-Fock (RHF) wave function. Note that we do not have to specify that ψ_1 \mathbf{r} is 1s-like, ψ_2 \mathbf{r} is 2s-like, and $\psi_{3,4,5}$ \mathbf{r} are 2p-like; this will follow naturally from the minimization over all the possible choices of orbitals. The unrestricted Hartree-Fock method reads, instead,

$$E_{UHF}^N \equiv \min_{\langle \psi_i^\sigma | \psi_j^\sigma \rangle = \delta_{ij}} \left\langle \begin{array}{c} \psi_1^\alpha \alpha \quad \psi_1^\beta \beta \quad \psi_2^\alpha \alpha \quad \psi_2^\beta \beta \quad \psi_3^\alpha \alpha \quad \psi_4^\alpha \alpha \quad \psi_4^\alpha \alpha \\ \times \quad \hat{H} \quad \psi_1^\alpha \alpha \quad \psi_1^\beta \beta \quad \psi_2^\alpha \alpha \quad \psi_2^\beta \beta \quad \psi_3^\alpha \alpha \quad \psi_4^\alpha \alpha \quad \psi_4^\alpha \alpha \end{array} \right\rangle \quad (3.181)$$

$E_{RHF}^N > E_{UHF}^N$, which marks the energy of the UHF method as superior. However, while the RHF wave function gives

$$\hat{S}^2 \Phi_{RHF} = \hbar^2 \frac{15}{4} \Phi_{RHF} \quad (3.182)$$

(which is consistent with a quadruplet), the UHF wave function is not an eigenfunction of \hat{S}^2 and, in fact,

$$\left\langle \Phi_{UHF} \middle| \hat{S}^2 \middle| \Phi_{UHF} \right\rangle < \hbar^2 \frac{15}{4} . \quad (3.183)$$

That is, the UHF wave function is a mixture between a quadruplet and a doublet state. (The fact that one can mix an approximate wave function for a doublet state—which is higher in energy than the wave function for the quadruplet by Hund's first rule—with a wave function for the quadruplet state and *improve* the energy over the RHF method gives some hint as to how poor the RHF wave function really is.)

Regardless of all the divers failings of the Hartree-Fock method, it is very popular because the results (orbitals and such) are easy to interpret and the calculations are much easier than the more accurate techniques we'll talk about later in the course. For completeness, we write the Hartree-Fock procedure (either UHF or RHF, depending on whether the spatial parts of α -spin and β -spin orbitals are the same (RHF) or different (UHF)) as

$$E_{HF} \equiv \min_{\langle \psi_i | \psi_j \rangle = \delta_{ij}} \left\langle \begin{vmatrix} \psi_1 \sigma_1 & \psi_2 \sigma_2 & \cdots & \psi_N \sigma_N \end{vmatrix} \hat{H} \begin{vmatrix} \psi_1 \sigma_1 & \psi_2 \sigma_2 & \cdots & \psi_N \sigma_N \end{vmatrix} \right\rangle. \quad (3.184)$$

How should we determine the orbitals in Eq. (3.184)? Recalling Eq. (3.177), one to use the idea of a position-dependent effective nuclear charge, cf. Eq. (3.22). For the Nitrogen atom, for example, we would take

$$\begin{aligned} \psi_{1s}(\mathbf{r}) &\propto e^{-\zeta_{1s} r, \theta, \phi} \\ \psi_{2s}(\mathbf{r}) &\propto (2 - \zeta_{2s} r, \theta, \phi) e^{-\zeta_{2s} r, \theta, \phi} \\ \psi_{2p_m}(\mathbf{r}) &\propto \zeta_{2s} r, \theta, \phi \cdot r e^{-\zeta_{2p} r, \theta, \phi} Y_l^m(\theta, \phi) \end{aligned} \quad (3.185)$$

Using orbitals like (3.185) was already very difficult for the Helium atom, and so we dare not try it for larger systems. Another possibility is to expand the orbitals in a complete set of orthonormal functions, e.g.

$$\psi_a(\mathbf{r}) = \sum_{j=0}^{\infty} k_{aj} \phi_j(\mathbf{r}). \quad (3.186)$$

One might, for example, use the wave functions of the 1-electron atom as the $\phi_j(\mathbf{r})$. This can be (and has been) done, but one must be careful: one must use *all* the states of the Hydrogen atom, including the unbound states (continuum states with positive energy). The positive-energy states are quite difficult to include, and this led people to use more general family of orthogonal functions. For example, Shull and Löwdin used the Laguerre polynomials, and then

$$\psi_{n,l,m} = r^l e^{-Zr} Y_l^m(\theta, \phi) \sum_{j=0}^{\infty} c_{n,l,m,j} L_j(2Zr) \quad (3.187)$$

Any one who has ever tried to evaluate integrals for hydrogenic orbitals can appreciate the difficulties that are encountered for the higher values of j in the above series.

Slater noted that by writing out the Laguerre polynomials and combining coefficients of the same power of r , one can rewrite Eq. (3.187) as a polynomial times a “hydrogenic” scale factor.

$$\psi_{n,l,m} = r^l e^{-Zr} Y_l^m(\theta, \phi) \sum_{k=0}^{\infty} d_{n,l,m,j} \cdot r^k. \quad (3.188)$$

Reasoning that it would be even better to replace Z in Eq. (3.188) with an effective nuclear charge appropriate to the orbital, Slater proposed using a basis set with the following form

$$\chi_{p,l,m}(\mathbf{r}) \propto r^{n_{p,l}-1} e^{-\zeta_{p,l} r} \cdot Y_l^m(\theta, \phi) \quad (3.189)$$

Here $n \geq l + 1$ and $-l \leq m \leq l$, consistent with the hydrogen atom. Functions with the form of Eq. (3.189) are called Slater Type Orbitals (STOs).¹⁴ Slater type orbitals are used in most high-accuracy calculations for atomic systems.

To use Slater-type orbitals in a Hartree-Fock calculation for an atom, one expands s -type functions in terms of s -type Slater orbitals ($l = 0$), p -type functions in terms of p -type Slater orbitals ($l = 1$), etc.. The result is that, for Nitrogen, each orbital in Eq. (3.180) will have an expansion,

¹⁴ Note that Slater-type orbitals are not orthogonal to one another.

$$\begin{aligned}
\psi_1 \mathbf{r} &\rightarrow \psi_{1s} \mathbf{r} = \sum_{p=0}^{\infty} c_{p,1s} r^{n_{p,0}-1} e^{-\zeta_{p,0}r} \\
\psi_1 \mathbf{r} &\rightarrow \psi_{2s} \mathbf{r} = \sum_{p=0}^{\infty} c_{p,2s} r^{n_{p,0}-1} e^{-\zeta_{p,0}r} \\
\psi_{3,4,5} \mathbf{r} &\rightarrow \psi_{2p_{0,\pm 1}} \mathbf{r} = \sum_{p=0}^{\infty} c_{p,2p} r^{n_{p,1}-1} e^{-\zeta_{p,1}r} Y_1^{0,\pm 1} \theta, \phi
\end{aligned} \tag{3.190}$$

and, when this is done quite accurately, the RHF energy is -54.400934 Hartree, which is $.18832$ Hartree above the true energy. For an unrestricted Hartree-Fock calculation, one obtains $E_{UHF} \approx -54.405$ Hartree, which is less than the RHF energy but still far from the true energy of the system. Since the UHF determinant is not an eigenfunction of \hat{S}^2 , it is inappropriate for use in discussing term symbols and spectroscopic states. However, for qualitative purposes, either the unrestricted or the restricted Hartree-Fock orbitals will usually suffice.

VI. More on the Energies of Atomic Terms; Revisions to Hund's Rules

A. The Russell-Meggers and Kutzelnigg-Morgan Rules

In the context of the Hartree-Fock model, it can be helpful to reconsider Hund's rules. As stated before, Hund's rules are general accurate for ground states, but for excited states Hund's rules are not especially reliable. For example, suppose we do a Hartree-Fock calculation for systems with a closed subshells nd^2 configuration, where n is the principle quantum number. The terms are $^3F, ^3P, ^1G, ^1D, ^1S$, and this is the energetic order one would predict from Hund's rules. But the *actual* order that is observed is $^3F, ^1D, ^3P, ^1G, ^1S$. The ground state term is predicted successfully, but not the ordering of the excited states. And what of Cerium, with ground state electron configuration closed subshells $4f^1 5d^1$? The predicted terms (in Hund's rule order) are $^3H; ^3G; ^3F; ^3D; ^3P; ^3S; ^1H; ^1G; ^1F; ^1D; ^1P; ^1S$ but the ground state from a Hartree-Fock calculation (which agrees with experiment) is 1G .

The simple fact is that Hund's rules are not perfect, but with the exception of Cerium, they work for the *ground state* of *every* atom that can be considered using the L-S coupling scheme (as opposed to the j-j coupling scheme required when spin-orbit effects dominate). Excited states are definitely suspect, as has been recognized at least since Slater's work in the late 1920's. One way to resolve this difficulty is to actually perform a calculation and find the level of the energy levels. Often, but not always, the *order* of the states from Hartree-Fock calculations is correct, even though the relative spacing is often poor. (For terms that are not associated with the same electron configuration as the ground state, the Hartree-Fock approximation is much less reliable.)

For systems with two electrons outside a closed subshell, one can avoid direct calculation because alternatives to Hund's rules are available. Hund's first rule is replaced by the Russell-Meggers rule¹⁵, while the second is replaced by what I'll call the Kutzelnigg-Morgan rule.¹⁶

Russell-Meggers rule:¹⁷ Calculate $-1^{L+l_1+l_2} = \pm 1$ where L is the total orbital angular momentum, S is the total spin angular momentum, and l_1 and l_2 are the angular momenta of the orbitals in the electron configuration. States with $-1^{L+l_1+l_2} = -1$ are said to have odd parity (ungerade) (because $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(-\mathbf{r}_1, -\mathbf{r}_2)$) and states with $-1^{L+l_1+l_2} = +1$ are said to have even parity (gerade) (because $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(-\mathbf{r}_1, -\mathbf{r}_2)$). The relative ordering of states is

odd parity singlet states < triplet states < even parity singlet states (3.191)

Kutzelnigg-Morgan rule: Given a choice between two triplet states, the odd-parity state is usually lower in energy. Among states with the same parity and multiplicity, the optimum value of L is approximately¹⁸

$$L_{opt} \approx \frac{l_1 + l_2}{\sqrt{2}}. \quad (3.192)$$

These leads us to conclude that the ground state for Cerium is in fact an odd parity singlet state ($-1^{L+l_1+l_2} = -1^{4+2+3} = -1$) and among the odd-parity singlet states ($L = 0, 2, 4$) the optimal L is

$$L_{opt}^{Ce} \approx \frac{2+3}{\sqrt{2}} \approx 3.53, \quad (3.193)$$

which is closer to $L = 4$ than $L = 2$.

For the d^2 configuration, no odd-parity singlet states are possible. However,

$$L_{opt}^{d^2} \approx \frac{2+2}{\sqrt{2}} \approx 2.83 \quad (3.194)$$

¹⁵ Even though Russell and Meggers' work dates to 1927—just two years after Hund's most important contributions, it seems to have never caught on. This is partly due to the quantitative approach of Slater (which appeared just two years later) and partly due to the fact the Russell-Meggers rule is more complicated and less broadly applicable than Hund's rules. There is a way to extend the Russell-Meggers rule to more than two electrons outside closed subshells, but one must "couple" successive electrons to the 2-electron shell and keep track of the types of interactions that occur; as the number of electrons increases, the number of possibilities burgeons and the bookkeeping becomes complicated.

¹⁶ The Kutzelnigg-Morgan rule dates to 1996. As I've said before: "If the result wasn't derived in the 1920's or '30's, you don't want to know [how it was derived]."

¹⁷ The Russell-Meggers rule is often called the alternating rule.

¹⁸ Actually, Kutzelnigg and Morgan derive that $L_{opt} \approx \frac{l_1+l_2+1}{\sqrt{2}} - \frac{1}{2}$. The approximation in Eq. (3.192) seems to work a bit better when l_1 and l_2 are relatively small. For $l_1+l_2 \geq 5$, I'd use the more exact formula ($L_{opt} \approx \frac{l_1+l_2+1}{\sqrt{2}} - \frac{1}{2}$). Moreover, when $l_1 \ll l_2$ and l_2 is large, one should use the alternative rule (also due to Kutzelnigg and Morgan) that

$$L_{opt}^{l_1 \ll l_2} \approx l_1 + \frac{l_2^2 + \frac{1}{2}l_2 - \frac{1}{2}}{2l_1 + 1}.$$

which is closer to $L = 2$ (1D) than $L = 4$ (1G). So $E[^1D] < E[^1G] < E[^1S]$. Similarly, there are two odd-parity singlet states (3F and 3P), and the Kutzelnigg-Morgan rule dictates that $E[^3F] < E[^3P]$. Combining the Russell-Meggers and Kutzelnigg-Morgan rules, we can infer that $E[^3P] < E[^1G] < E[^1S]$, and also that $E[^1D] > E[^3F]$. However, determining whether the 3P or the 1D state lies lower in energy requires determining whether it is more important that the 1D has closer to the optimum value of L or whether it is more important the 3P is an odd-parity triplet state while 1D is an even parity singlet state? In this case, it turns out that $E[^1D] < E[^3P]$.

B. Rationalization of the Russell-Meggers and Kutzelnigg-Morgan Rules.

Where do these rules come from? The Russell-Meggers rule can be understood by examining the 1P state of a $2p^1 3p^1$ system. One has that

$$\Psi_{^1P} \propto \begin{pmatrix} \psi_{2p_0} \mathbf{r}_1 \psi_{3p_1} \mathbf{r}_2 + \psi_{3p_1} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ -\psi_{2p_1} \mathbf{r}_1 \psi_{3p_0} \mathbf{r}_2 - \psi_{3p_0} \mathbf{r}_1 \psi_{2p_1} \mathbf{r}_2 \end{pmatrix} \alpha \ 1 \ \beta \ 2 \ -\alpha \ 2 \ \beta \ 1 \quad (3.195)$$

Using the fact that

$$\begin{aligned} \psi_{2p_0,\pm 1} \mathbf{r}, \theta, \phi &= R_{2p} \mathbf{r} Y_1^{0,\pm 1} \theta, \phi \\ \psi_{3p_0,\pm 1} \mathbf{r}, \theta, \phi &= R_{3p} \mathbf{r} Y_1^{0,\pm 1} \theta, \phi \end{aligned} \quad (3.196)$$

we can write Eq. (3.195) as

$$\Psi_{^1P} \propto \begin{bmatrix} R_{2p} \mathbf{r}_1 R_{3p} \mathbf{r}_2 - R_{3p} \mathbf{r}_1 R_{2p} \mathbf{r}_2 \\ \times Y_1^0 \theta_1, \phi_1 Y_1^1 \theta_2, \phi_2 - Y_1^1 \theta_1, \phi_1 Y_1^0 \theta_2, \phi_2 \end{bmatrix} \alpha \ 1 \ \beta \ 2 \ -\alpha \ 2 \ \beta \ 1 \quad (3.197)$$

$\Psi_{^1P}$ (Eq. (3.197)) is zero if $\theta_1 = \theta_2$ and $\phi_1 = \phi_2$ or if $r_1 = r_2$.)

For comparison, let's consider the analogous wave functions for the 3P , 3D , and 1D states. We have

$$\begin{aligned} \Psi_{^3P} \propto & \begin{pmatrix} \psi_{2p_0} \mathbf{r}_1 \psi_{3p_1} \mathbf{r}_2 - \psi_{3p_1} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ -\psi_{2p_1} \mathbf{r}_1 \psi_{3p_0} \mathbf{r}_2 + \psi_{3p_0} \mathbf{r}_1 \psi_{2p_1} \mathbf{r}_2 \end{pmatrix} \alpha \ 1 \ \beta \ 2 \ +\alpha \ 2 \ \beta \ 1 \\ & \begin{bmatrix} R_{2p} \mathbf{r}_1 R_{3p} \mathbf{r}_2 + R_{3p} \mathbf{r}_1 R_{2p} \mathbf{r}_2 \\ \times Y_1^0 \theta_1, \phi_1 Y_1^1 \theta_2, \phi_2 - Y_1^1 \theta_1, \phi_1 Y_1^0 \theta_2, \phi_2 \end{bmatrix} \alpha \ 1 \ \beta \ 2 \ +\alpha \ 2 \ \beta \ 1 \end{aligned} \quad (3.198)$$

$$\begin{aligned} \Psi_{^3D} \propto & \begin{pmatrix} \psi_{2p_0} \mathbf{r}_1 \psi_{3p_1} \mathbf{r}_2 - \psi_{3p_1} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \\ +\psi_{2p_1} \mathbf{r}_1 \psi_{3p_0} \mathbf{r}_2 - \psi_{3p_0} \mathbf{r}_1 \psi_{2p_1} \mathbf{r}_2 \end{pmatrix} \alpha \ 1 \ \beta \ 2 \ +\alpha \ 2 \ \beta \ 1 \\ & \begin{bmatrix} R_{2p} \mathbf{r}_1 R_{3p} \mathbf{r}_2 - R_{3p} \mathbf{r}_1 R_{2p} \mathbf{r}_2 \\ \times Y_1^0 \theta_1, \phi_1 Y_1^1 \theta_2, \phi_2 + Y_1^1 \theta_1, \phi_1 Y_1^0 \theta_2, \phi_2 \end{bmatrix} \alpha \ 1 \ \beta \ 2 \ +\alpha \ 2 \ \beta \ 1 \end{aligned} \quad (3.199)$$

and

$$\begin{aligned} \Psi_{1_D} &\propto \left(\psi_{2p_0} \mathbf{r}_1 \psi_{3p_1} \mathbf{r}_2 + \psi_{3p_1} \mathbf{r}_1 \psi_{2p_0} \mathbf{r}_2 \right. \\ &\quad \left. + \psi_{2p_1} \mathbf{r}_1 \psi_{3p_0} \mathbf{r}_2 + \psi_{3p_0} \mathbf{r}_1 \psi_{2p_1} \mathbf{r}_2 \right) \alpha \begin{matrix} 1 & \beta & 2 \\ -\alpha & 2 & \beta & 1 \end{matrix} \\ &\propto \left[\begin{matrix} R_{2p} r_1 R_{3p} r_2 + R_{3p} r_1 R_{2p} r_2 \\ \times Y_1^0 \theta_1, \phi_1 Y_1^1 \theta_2, \phi_2 + Y_1^1 \theta_1, \phi_1 Y_1^0 \theta_2, \phi_2 \end{matrix} \right] \alpha \begin{matrix} 1 & \beta & 2 \\ -\alpha & 2 & \beta & 1 \end{matrix} \end{aligned} \quad (3.200)$$

The Ψ_{3_P} is zero if $\theta_1 = \theta_2$ and $\phi_1 = \phi_2$; Ψ_{3_D} is zero if $r_1 = r_2$. In general, $\Psi_{1_D} \neq 0$ even if $r_1 = r_2$, $\theta_1 = \theta_2$, and $\phi_1 = \phi_2$.

The electron-electron repulsion of these states is computed from

$$V_{ee} \equiv \left\langle \Psi \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \Psi \right\rangle = \iint \frac{|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (3.201)$$

In general,¹⁹

$$\begin{aligned} |\Psi_{1_D}(\mathbf{r}_1, \mathbf{r}_1)|^2 &\propto \left\| \begin{matrix} R_{2p} r_1 R_{3p} r_2 + R_{3p} r_1 R_{2p} r_2 \\ \times Y_1^0 \theta_1, \phi_1 Y_1^1 \theta_2, \phi_2 + Y_1^1 \theta_1, \phi_1 Y_1^0 \theta_2, \phi_2 \end{matrix} \right\|^2 \\ &\quad \times \left\langle \begin{matrix} \alpha & 1 & \beta & 2 \\ -\alpha & 2 & \beta & 1 \end{matrix} \middle| \begin{matrix} \alpha & 1 & \beta & 2 \\ -\alpha & 2 & \beta & 1 \end{matrix} \right\rangle \\ &\propto \left\| \begin{matrix} R_{2p} r_1 R_{3p} r_2 + R_{3p} r_1 R_{2p} r_2 \\ \times Y_1^0 \theta_1, \phi_1 Y_1^1 \theta_2, \phi_2 + Y_1^1 \theta_1, \phi_1 Y_1^0 \theta_2, \phi_2 \end{matrix} \right\|^2 \\ &\geq 0 \end{aligned} \quad (3.202)$$

This means that, in the singlet D state, there is a reasonable probability of observing two electrons in the same place at the same time.

When we examine the triplet states, it is clear that the probability of observing two electrons in the same place at the same time is zero. For example, we have that

$$\begin{aligned} |\Psi_{3_P}(\mathbf{r}_1, \mathbf{r}_1)|^2 &\propto \left\| \begin{matrix} R_{2p} r_1 R_{3p} r_1 + R_{3p} r_1 R_{2p} r_1 \\ \times Y_1^0 \theta_1, \phi_1 Y_1^1 \theta_1, \phi_1 - Y_1^1 \theta_1, \phi_1 Y_1^0 \theta_1, \phi_1 \end{matrix} \right\|^2 \\ &\propto |2R_{2p} r_1 R_{3p} r_1 \cdot 0| \\ &= 0 \end{aligned} \quad (3.203)$$

Focusing on the spatial part of the wave function, it is clear from Eq. (3.198) that the spatial portion of the triplet wave functions is antisymmetric; e.g., $\Psi_{3_P}(\mathbf{r}_1, \mathbf{r}_2) = -\Psi_{3_P}(\mathbf{r}_2, \mathbf{r}_1)$. Writing $\mathbf{c} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}$

and $\mathbf{d} = \frac{\mathbf{r}_2 - \mathbf{r}_1}{2}$, we have that

$$\Psi_{3_P}(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{3_P}(\mathbf{c} - \mathbf{d}, \mathbf{c} + \mathbf{d}) = -\Psi_{3_P}(\mathbf{c} + \mathbf{d}, \mathbf{c} - \mathbf{d}) = -\Psi_{3_P}(\mathbf{r}_2, \mathbf{r}_1) \quad (3.204)$$

Thus, when electrons are close together ($|\mathbf{d}|$ is small), we can expand the wave function in a Taylor series in \mathbf{d} ,

¹⁹ Since we want the probability of observing two electrons in the same place, we “integrate” (more precisely, we sum) over the spin components. This gives the second line of Eq. (3.202).

$$\begin{aligned}\Psi_{3P} \mathbf{c} - \mathbf{d}, \mathbf{c} + \mathbf{d} &= \Psi_{3P} \mathbf{c}, \mathbf{c} + \mathbf{d} \cdot \mathbf{n} \mathbf{c} + \mathcal{O} \mathbf{d} \cdot \mathbf{d} \\ &= 0 + \mathbf{d} \cdot \mathbf{n} \mathbf{c} + \mathcal{O} \mathbf{d} \cdot \mathbf{d} .\end{aligned}\quad (3.205)$$

Equation (3.205) has the property that when we replace \mathbf{d} by $-\mathbf{d}$, the sign of the wave function changes. Here, \mathbf{n} is the vector that is aligned with the nodal surface (the surface on which the wave function, $\Psi_{3P} \mathbf{c} + \mathbf{d}, \mathbf{c} - \mathbf{d}$, is zero for a given value of \mathbf{c}). If we use Eq. (3.205) to calculate the probability of observing two electrons close together, we find that

$$\begin{aligned}|\Psi_{3P} \mathbf{c} - \mathbf{d}, \mathbf{c} + \mathbf{d}|^2 &\propto |\mathbf{d}|^2 \\ |\Psi_{3P} \mathbf{r}_1, \mathbf{r}_2|^2 &\propto |\mathbf{r}_1 - \mathbf{r}_2|^2\end{aligned}\quad (3.206)$$

for small interelectron separations, $|\mathbf{r}_1 - \mathbf{r}_2|$. Comparing this to Eq. (3.202), we conclude that, in accord with the Pauli principle, the probability of observing two electrons in the same place in a triplet state is zero. What is more, the probability of observing two electrons *near* each other is small. (You may wish to refer back to Figure 3.6, which plots the relative probability of same-spin (appropriate to the triplet state) and opposite-spin (appropriate to the singlet state) electrons being close to each other.)

For the 1P state a similar treatment applies. The Taylor series expansion of the wave function for small $\mathbf{d} = \frac{\mathbf{r}_2 - \mathbf{r}_1}{2}$ is

$$\Psi_{1P} \mathbf{c} - \mathbf{d}, \mathbf{c} + \mathbf{d} \propto \Psi \mathbf{c}, \mathbf{c} + \mathbf{d} \cdot \mathbf{n} \mathbf{c} + \mathbf{d} \cdot \mathbf{P} \mathbf{c} \cdot \mathbf{d} + \dots \quad (3.207)$$

Since the probability of observing two electrons in the same place (cf. Eq. (3.197)) is zero, $\Psi \mathbf{c}, \mathbf{c} = 0$. Furthermore, the spatial wave function in Eq. (3.197) is symmetric with respect to the exchange of electrons, so $\mathbf{d} \cdot \mathbf{n} \mathbf{c}$ must be zero also. The term that remains is quadratic in \mathbf{d} , so for small interelectron distances,

$$\begin{aligned}\Psi_{1P} \mathbf{c} - \mathbf{d}, \mathbf{c} + \mathbf{d} &\propto \mathbf{d} \cdot \mathbf{d} \\ \Psi_{1P} \mathbf{r}_1, \mathbf{r}_2 &\propto |\mathbf{r}_1 - \mathbf{r}_2|^2\end{aligned}\quad (3.208)$$

Consequently, analogous to Eq. (3.206), we have that

$$|\Psi_{2P} \mathbf{r}_1, \mathbf{r}_2|^2 \propto |\mathbf{r}_1 - \mathbf{r}_2|^4 \quad (3.209)$$

Thus, the probability of observing two electrons close together in the 1P state is *even smaller than it is for a triplet state*.²⁰

Examining Eq. (3.201) for the electron-electron repulsion energy, it is clear that the electron-electron repulsion energy is large when electrons have a high probability of being close to each other (so that $|\Psi \mathbf{r}_1, \mathbf{r}_2|^2$ is large where $\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ has a large value). For the triplet states, $|\Psi \mathbf{r}_1, \mathbf{r}_2|^2$ is small

²⁰ For example, if $|\mathbf{r}_1 - \mathbf{r}_2| \approx .1$, then we expect the probability of observing two electrons .1 units apart in a triplet state to be proportional to .01. By comparison, the probability of observing two electrons .1 units apart in the 1P state is proportional to a measly .0001. This result can be understood based on the expressions (3.197)-(3.200). The wave function for the 1D state is rarely zero. The wave function for the 3P is zero if either the angular coordinates (3P) are the same. The wave function for the 1D state is zero if the radial coordinates are the same. However, the wave function for the 1P state is zero if *either* the radial coordinates *or* the angular coordinates are the same. Thus, in the 3D state electrons are allowed to have the same radial coordinates; in the singlet 3P state electrons are allowed to have the same angular coordinates. *Both* of these arrangements of electrons are unfavorable and *neither* ever occurs in the 1P state. Thus, the 1P state has a lower energy.

where $\frac{1}{|r_1 - r_2|}$ is large; for the 1P state, $|\Psi(r_1, r_2)|^2$ is *even smaller* where $\frac{1}{|r_1 - r_2|}$ is large. Thus, we predict that the electron-electron repulsion energies will come in the order

$$V_{ee}[^1P] < V_{ee}[^3P] \approx V_{ee}[^3D] < V_{ee}[^1D] \quad (3.210)$$

which gives an ordering of states that agrees with the Russell-Meggers and Kutzelnigg-Morgan rules.²¹

C. The Effects of Orbital Relaxation

You will often find objections to the above argument in books. The reason is that when one *actually* performs unrestricted Hartree-Fock calculations for atoms, one often observes that even though the energies of the states are appropriately ordered,

$$E[^1P] < E[^3P] \approx E[^3D] < E[^1D], \quad (3.211)$$

very often the calculated electron-electron repulsion energies are in *inverted* order, e.g.

$$V_{ee}[^1P] > V_{ee}[^3P] \approx V_{ee}[^3D] > V_{ee}[^1D]. \quad (3.212)$$

This is often cited as evidence that the above argument must be in error. We should not be so hasty, though. Our argument is based on using the same orbitals for each multiplet. (That is, $R_{2p}(r)$ and $R_{3p}(r)$ are held constant in Eqs. (3.197)-(3.200).) When we find the optimal orbitals, we observe that the radial wave function for the 1P state is more compact than that from the 1D state and, indeed, because the electrons are packed closer to the nucleus in the 1P state, the electron-electron repulsion energy in the 1P state can be larger, along the lines of the hypothetical ordering given in Eq. (3.212).

To understand this paradox, suppose you do a Hartree-Fock calculation for the 1D state. One finds the radial wave functions $R_{2p}^{1D}(r)$ and $R_{3p}^{1D}(r)$. If we evaluate the electron-electron repulsion energy of the 3P , 3D , and 1P states using these radial wave functions, we'll obtain the ordering of electron-electron repulsion energies given in Eq. (3.210) and the ordering of energies given in Eq. (3.211). Now, let us find the optimal orbitals for the 3D state. When we shift from the 1D state to

²¹ The relative energies of the 3P and 3D states are computed using the Kutzelnigg-Morgan rule. We can see how this rule is derived (in qualitative) terms from the wave functions considered here. In the 3P state there is a tendency for electrons to stay away from each other angularly; note that there is zero probability of observing the electrons in a 3P state with the same angular coordinate. In the 3D state, there is a tendency for electrons to stay away from each other radially, with zero probability of observing the electrons in a 3D state having the same value of the radial coordinate. In general, the “angular” exclusion rule is more beneficial; in the 3D state it is possible for one electron to “get between” the other electron and the nucleus (so that the nucleus and the two electrons are all in a straight line), which effectively shields the outermost electron from the nucleus. This is impossible in the 3P state. In the first instance, the Kutzelnigg-Morgan rule favors states with odd parity (which have angular exclusion) over states with even parity (which have radial exclusion). The second part of the Kutzelnigg-Morgan rule is useful when there are *several* odd parity states in which the angular coordinate is forbidden to be the same, as then the Kutzelnigg-Morgan rule will distinguish between them. When l_1 and l_2 are not too big, Hund’s second (maximum L) rule tends to hold in the following sense: the odd parity state with the largest L is the most favorable. I picture this as being due to the fact that the spherical harmonics with maximum m_l are “less fragmented” and thus, in some sense, more conducive to electrons “avoiding” each other. (This is an imperfect explanation, since it doesn’t explain why in the $6h^2$ configuration, the optimal angular momentum is $L = 7$ (and not $L = 9$). However, the $6h^2$ configuration is not that important in chemistry. If you should ever need to describe such states, just remember that the Kutzelnigg-Morgan rule works here too ($L_{opt}^{h^2} \approx 7.07$).)

the 3D state, the electron-electron repulsion energy goes down. Now, if the electrons move closer to the nucleus, the electron-nuclear attraction energy decreases but the electron-electron repulsion energy increases, since the electrons are now packed into a smaller region of space. Since the electron-electron repulsion energy is less for the 3D state, it is favorable for the orbitals to contract to the nucleus. Thus, *because* the electron-electron repulsion is smaller in the 3D state than it is in the 1D state when the states use the *same* orbitals, when we find use the Hartree-Fock method to find the *optimum* (lowest-energy) orbitals for the 3D state, we observe that the optimum orbitals are closer to the nucleus. This contraction lowers the energy of the 3D state (recall that the Hartree-Fock method amounts to finding the orbitals that minimize the energy), so that the difference in energy between the 1D and 3D states is even larger than what we would predict if we used the same orbitals in Eqs. (3.200) and (3.199).

Similarly, using the Hartree-Fock orbitals for the 3D state, R_{2p}^{3D} and R_{3p}^{3D} , to compute the electron-electron repulsion energy of the 1P state, we observe that $V_{ee}[^1P] < V_{ee}[^3D]$, in accord with Eq. (3.210). If we implement the Hartree-Fock method, and use the Hartree-Fock (= lowest-energy) orbitals for the 1P state, the energy of the 1P state will be even lower. Again, the general tendency is that since the electron-electron repulsion in the 1P state is relatively weak, it is favorable for the electrons to “move in” towards the nucleus, so that the electron-nuclear attraction energy decreases. After the orbitals have relaxed, the energy ordering will still be the same, but the electron-electron repulsion energy might not be, because the orbitals in the 1P state are more compact than those in the 3P and 3D states, which are in turn more compact than those in the 1D state.

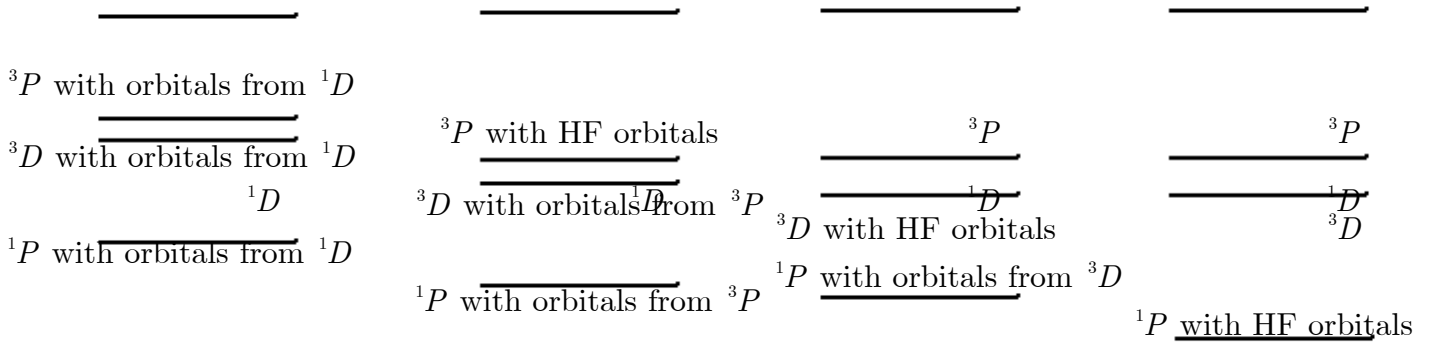


Figure 3.8. In the first figure, all the states are described using the orbitals of the 1D state. Then, the Hartree-Fock orbitals are determined for the 3P state (presuming this is higher in energy than the 3D state) and used to describe the lower-energy states. Next, the Hartree-Fock orbitals are determined for the 3D state. With these “optimum” orbitals, the energy of the 3D state (and usually also the 1P state) goes down. Finally, we determine the lowest-energy orbitals of the 1P state.

VII. Alternative Derivation of $[\hat{H}, \hat{L}_x] = 0$

Insofar as the derivation of $[\hat{H}, \hat{L}_x] = 0$ is one of the harder ones in this course, it seems prudent to present an alternative approach. Both the derivation in section IVA and the derivation here demonstrate important mathematical techniques, so you will be well-advised to master both. As before (cf. Eq. (3.96)), \hat{L}_x commutes with the kinetic energy and electron-nuclear attraction terms in the Hamiltonian, so we need only show that

$$[\hat{L}_x, \hat{V}_{ee}] = 0, \quad (3.213)$$

where

$$\hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (3.214)$$

is the electron-electron repulsion potential. Since the commutator of a sum of operators is the sum of the commutators,

$$\left[\hat{A}, \sum_i \hat{B}_i \right] = \sum_i [\hat{A}, \hat{B}_i] \quad (3.215)$$

we have that

$$\left[\hat{L}_x, \mathbf{r}_1, \dots, \mathbf{r}_N, \hat{V}_{ee} \right] = \left[\hat{L}_x, \mathbf{r}_1, \dots, \mathbf{r}_N, \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] = \sum_{i=1}^N \sum_{j=i+1}^N \left[\hat{L}_x, \mathbf{r}_1, \dots, \mathbf{r}_N, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right]. \quad (3.216)$$

Recalling that (compare Eq. (3.75))

$$\hat{L}_x, \mathbf{r}_1, \dots, \mathbf{r}_N = \sum_{i=1}^N \hat{L}_x, \mathbf{r}_i \quad (3.217)$$

and using the rule for the commutator of a sum again, we have that

$$\begin{aligned} \left[\hat{L}_x, \mathbf{r}_1, \dots, \mathbf{r}_N, \hat{V}_{ee} \right] &= \sum_{i=1}^N \sum_{j=i+1}^N \left[\hat{L}_x, \mathbf{r}_1, \dots, \mathbf{r}_N, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \\ &= \sum_{i=1}^N \sum_{j=i+1}^N \left[\sum_{k=1}^N \hat{L}_x, \mathbf{r}_k, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \\ &= \sum_{i=1}^N \sum_{j=i+1}^N \sum_{k=1}^N \left[\hat{L}_x, \mathbf{r}_k, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \end{aligned} \quad (3.218)$$

Recall that (Eq. (3.102))

$$\hat{L}_x, \mathbf{r}_k = -i\hbar \left(y_k \frac{\partial}{\partial z_k} - z_k \frac{\partial}{\partial y_k} \right) \quad (3.219)$$

Now, it is clear that

$$\begin{aligned}
\hat{L}_x \mathbf{r}_k \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \right) &= -i\hbar \left(y_k \frac{\partial}{\partial z_k} - z_k \frac{\partial}{\partial y_k} \right) \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \right) \\
&= \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \left(-i\hbar \left(y_k \frac{\partial}{\partial z_k} - z_k \frac{\partial}{\partial y_k} \right) \right) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \\
&= \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \hat{L}_x \mathbf{r}_k \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)
\end{aligned} \tag{3.220}$$

unless i or j is equal to k . Thus, unless k equals i or j , we have that²²

$$\left[\hat{L}_x \mathbf{r}_k, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] = 0 \quad k \neq i; k \neq j. \tag{3.221}$$

Using Eq. (3.221), the innermost summation in Eq. (3.218) can be simplified

$$\begin{aligned}
\sum_{k=1}^N \left[\hat{L}_x \mathbf{r}_k, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] &= \left[\hat{L}_x \mathbf{r}_i, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] + \left[\hat{L}_x \mathbf{r}_j, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \\
&= \left[\hat{L}_x \mathbf{r}_i + \hat{L}_x \mathbf{r}_j, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right]
\end{aligned} \tag{3.222}$$

We will show that Eq. (3.222) is zero, which will then imply that Eq. (3.218) for $[\hat{L}_x, \hat{V}_{ee}]$ is also zero.

To evaluate

$$\hat{L}_x \mathbf{r}_i + \hat{L}_x \mathbf{r}_j = -i\hbar \left(y_i \frac{\partial}{\partial z_i} - z_i \frac{\partial}{\partial y_i} + y_j \frac{\partial}{\partial z_j} - z_j \frac{\partial}{\partial y_j} \right), \tag{3.223}$$

it is convenient to use the chain rule, whereby

$$\begin{aligned}
\frac{\partial}{\partial z_i} &= \frac{\partial z_i - z_j}{\partial z_i} \frac{\partial}{\partial z_i - z_j} = \frac{\partial}{\partial z_i - z_j} \\
\frac{\partial}{\partial z_j} &= \frac{\partial z_i - z_j}{\partial z_j} \frac{\partial}{\partial z_i - z_j} = -\frac{\partial}{\partial z_i - z_j}
\end{aligned} \tag{3.224}$$

and, similarly,

$$\begin{aligned}
\frac{\partial}{\partial y_i} &= \frac{\partial}{\partial y_i - y_j} \\
\frac{\partial}{\partial y_j} &= -\frac{\partial}{\partial y_i - y_j}.
\end{aligned} \tag{3.225}$$

Substituting these results into Eq. (3.223), we have that

²² Equation (3.221) can be written in a compact form using the Kronecker delta,

$$\left[\hat{L}_x(\mathbf{r}_k), \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] = (\delta_{ki} + \delta_{kj}) \left[\hat{L}_x(\mathbf{r}_k), \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right].$$

$$\begin{aligned}
\hat{L}_x \mathbf{r}_i + \hat{L}_x \mathbf{r}_j &= -i\hbar \left(y_i \frac{\partial}{\partial z_i - z_j} - z_i \frac{\partial}{\partial y_i - y_j} - y_j \frac{\partial}{\partial z_i - z_j} + z_j \frac{\partial}{\partial y_i - y_j} \right) \\
&= -i\hbar \left(y_i - y_j \frac{\partial}{\partial z_i - z_j} - z_i - z_j \frac{\partial}{\partial y_i - y_j} \right).
\end{aligned} \tag{3.226}$$

Using this result, we have that

$$\begin{aligned}
&\left[\hat{L}_x \mathbf{r}_i + \hat{L}_x \mathbf{r}_j, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \\
&= -i\hbar \left(y_i - y_j \frac{\partial}{\partial z_i - z_j} - z_i - z_j \frac{\partial}{\partial y_i - y_j} \right) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \\
&\quad + \frac{i\hbar}{|\mathbf{r}_i - \mathbf{r}_j|} \left(y_i - y_j \frac{\partial}{\partial z_i - z_j} - z_i - z_j \frac{\partial}{\partial y_i - y_j} \right) \Psi \mathbf{r}_1, \dots, \mathbf{r}_N
\end{aligned} \tag{3.227}$$

The first term in Eq. (3.227) can be simplified using the product rule for derivatives:

$$\begin{aligned}
&-i\hbar \left(y_i - y_j \frac{\partial}{\partial z_i - z_j} - z_i - z_j \frac{\partial}{\partial y_i - y_j} \right) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \\
&= -i\hbar \left[y_i - y_j \frac{\partial}{\partial z_i - z_j} \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \right) - z_i - z_j \frac{\partial}{\partial y_i - y_j} \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \right) \right] \\
&= -i\hbar \left[\Psi \mathbf{r}_1, \dots, \mathbf{r}_N y_i - y_j \frac{\partial}{\partial z_i - z_j} \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) + \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \left(\frac{\partial}{\partial z_i - z_j} \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \right) \right. \\
&\quad \left. - \Psi \mathbf{r}_1, \dots, \mathbf{r}_N z_i - z_j \frac{\partial}{\partial y_i - y_j} \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) - \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \left(\frac{\partial}{\partial y_i - y_j} \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \right) \right]
\end{aligned} \tag{3.228}$$

Combining Eqs. (3.228) and (3.227) all the terms involving differentiation of the wave function cancel out, yielding

$$\begin{aligned}
& \left[\hat{L}_x \mathbf{r}_i + \hat{L}_x \mathbf{r}_j, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \\
&= \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \left(-i\hbar \left(y_i - y_j \frac{\partial}{\partial z_i - z_j} - z_i - z_j \frac{\partial}{\partial y_i - y_j} \right) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \\
&= -i\hbar \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \left(y_i - y_j \frac{\partial}{\partial z_i - z_j} \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) - z_i - z_j \frac{\partial}{\partial y_i - y_j} \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \right) \\
&= -i\hbar \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \left(y_i - y_j \frac{\partial}{\partial z_i - z_j} \left(\frac{1}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}} \right) \right. \\
&\quad \left. - (z_i - z_j) \frac{\partial}{\partial y_i - y_j} \left(\frac{1}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}} \right) \right) \\
&= -i\hbar \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \left(y_i - y_j \frac{\left(-\frac{1}{2} \frac{(y_i - y_j)}{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} \right)}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}} \right. \\
&\quad \left. - (z_i - z_j) \frac{\left(-\frac{1}{2} \frac{(z_i - z_j)}{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} \right)}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}} \right) \\
&= -i\hbar \Psi \mathbf{r}_1, \dots, \mathbf{r}_N \left(\frac{-(y_i - y_j)(z_i - z_j) - (z_i - z_j)(y_i - y_j)}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}} \right) \\
&= 0
\end{aligned} \tag{3.229}$$

The derivation is completed by substituting Eq. (3.229) into the results from Eqs. (3.222) and (3.218) :

$$\begin{aligned}
\left[\hat{L}_x \mathbf{r}_1, \dots, \mathbf{r}_N, \hat{V}_{ee} \right] &= \sum_{i=1}^N \sum_{j=i+1}^N \left[\hat{L}_x \mathbf{r}_1, \dots, \mathbf{r}_N, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \\
&= \sum_{i=1}^N \sum_{j=i+1}^N \left[\sum_{k=1}^N \hat{L}_x \mathbf{r}_k, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \\
&= \sum_{i=1}^N \sum_{j=i+1}^N \sum_{k=1}^N \left[\hat{L}_x \mathbf{r}_k, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \\
&= \sum_{i=1}^N \sum_{j=i+1}^N \left[\hat{L}_x \mathbf{r}_i + \hat{L}_x \mathbf{r}_j, \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \\
&= \sum_{i=1}^N \sum_{j=i+1}^N 0 \\
&= 0
\end{aligned} \tag{3.230}$$