Many-Electron Atoms

The "degree of difficulty" is given in parentheses after each problem. Your total score on each problem will be the total number of points you earn on the problem (out of twenty) times the degree of difficulty.

I. Zeeman Splitting (1.0)

When an atom is put in a magnetic field, one observes a splitting of the spectral lines. To understand why, we need to recall that both the spin of the electron and its orbital angular momentum serve to give the atom a magnetic moment.

For an atom in an eigenstate of the Hamiltonian, $\hat{L}^2, \hat{S}^2, \hat{J}^2$, and $\hat{J}_z$, Ψ^{L,S,J,M_J}, the magnetic moment from the orbital angular momentum and the spin multiplicity can be taken from Eqs. (3.47) and (3.48) of the third set of notes. That is,

$$\boldsymbol{\mu}_L \equiv -\frac{\beta_e}{\hbar}\,\hat{\boldsymbol{L}}\Psi^{L,S,J,M_J} \tag{I.1}$$

and

$$\begin{aligned}\boldsymbol{\mu}_S &= -g\frac{\beta_e}{\hbar}\,\hat{\boldsymbol{S}}\Psi^{L,S,J,M_J}\\ &\approx -2\frac{\beta_e}{\hbar}\,\hat{\boldsymbol{S}}\Psi^{L,S,J,M_J}\end{aligned}. \tag{I.2}$$

where $\beta_e = \frac{e\hbar}{me}$ is the Bohr magneton and g denotes the anomalous (or Landé) spin factor.

What is the total magnetic moment? We can surmise, from analogy to Eqs. (I.1) and (I.2) that the total magnetic moment will be proportional to $\hat{\boldsymbol{J}}\Psi^{L,S,J,M_J} = \hat{\boldsymbol{L}}\Psi^{L,S,J,M_J} + \hat{\boldsymbol{S}}\Psi^{L,S,J,M_J}$,

$$\begin{aligned}\boldsymbol{\mu}_J &\propto \frac{\beta_e}{\hbar}\,\hat{\boldsymbol{J}}\Psi^{L,S,J,M_J}\\ &= -g_J(L,S)\frac{\beta_e}{\hbar}\,\hat{\boldsymbol{J}}\Psi^{L,S,J,M_J}\end{aligned} \tag{I.3}$$

but the anomalous spin factor forces the constant of proportionality, $g_J(L,S)$ to depend on S and L. (To see this, consider that $g_J = g \approx 2$ when $L = 0$, and $g_J = 1$ when $S = 0$. Presumably when $S > 0$ and $L > 0$, then $1 \le g_J(L,S) \lesssim 2$. $g_J(L,S)$ is called the generalized Landé g-factor, and the standard notation (wherein the same symbol, without the J subscript) is used for both the anomalous spin-factor of the electron and the description of atomic spectra in a magnetic field is unfortunate. Be careful.

We need to find the magnitude of $\boldsymbol{\mu}_J$, because then we can describe the effect of a magnetic field. Because

$$\hat{J}^2\Psi^{L,S,J,M_J} \equiv \hat{\boldsymbol{J}}\cdot\hat{\boldsymbol{J}}\Psi^{L,S,J,M_J} = \hbar^2\left(J(J+1)\right)\Psi^{L,S,J,M_J} \tag{I.4}$$

we know the magnitude of the total angular momentum of the atom is

$$\left|\left\langle \Psi^{L,S,J,M_J}\left|\hat{\boldsymbol{J}}\right|\Psi^{L,S,J,M_J}\right\rangle\right| = \hbar\sqrt{J(J+1)} \tag{I.5}$$

with similar results for the total spin and orbital angular momenta,

$$\left|\left\langle \Psi^{L,S,J,M_J}\left|\hat{\boldsymbol{L}}\right|\Psi^{L,S,J,M_J}\right\rangle\right| = \hbar\sqrt{L(L+1)}$$

$$\left|\left\langle \Psi^{L,S,J,M_J}\left|\hat{\boldsymbol{S}}\right|\Psi^{L,S,J,M_J}\right\rangle\right| = \hbar\sqrt{S(S+1)} \tag{I.6}$$

The magnitude of $\boldsymbol{\mu}_J$ clearly depends on the extent to which the spin and orbital angular momenta are aligned with one another and hence the total magnetic moment of the molecule. To find this, we start with the knowledge that the total magnetic moment is the sum of its orbital and spin contributions,

$$\boldsymbol{\mu}_J = \boldsymbol{\mu}_S + \boldsymbol{\mu}_L$$

$$g_J(L,S)\hat{\boldsymbol{J}}\Psi^{L,S,J,M_J} \approx 2\hat{\boldsymbol{S}}\Psi^{L,S,J,M_J} + \hat{\boldsymbol{L}}\Psi^{L,S,J,M_J}$$

$$\approx \left(2\hat{\boldsymbol{S}} + \hat{\boldsymbol{L}}\right)\Psi^{L,S,J,M_J} \tag{I.7}$$

$$\approx \left(\hat{\boldsymbol{J}} + \hat{\boldsymbol{S}}\right)\Psi^{L,S,J,M_J}$$

If we operate on both sides of this expression with $\hat{\boldsymbol{J}}$ and use Eq. (III.8), we obtain

$$g_J(L,S) \approx 1 + \frac{J(J+1)-L(L+1)+S(S+1)}{2J(J+1)} \tag{I.8}$$

A. Derive Eq. (I.8).

Since the interaction between a magnetic moment and a magnetic field is given by

$$\mathbf{E} = -\boldsymbol{\mu} \cdot \boldsymbol{B} \tag{I.9}$$

we see, from Eq. (I.3) that the effect of placing an atom in a magnetic field is to add a term,

$$\hat{H}_{\boldsymbol{B}} = g_J(L,S)\frac{\beta_e}{\hbar}\hat{\boldsymbol{J}} \cdot \hat{\boldsymbol{B}}, \tag{I.10}$$

to the Hamiltonian. If the magnetic field is uniform and directed along the z-direction, then

$$\hat{H}_{\boldsymbol{B}} = g_J(L,S)\frac{\beta_e}{\hbar}\hat{\boldsymbol{J}} \cdot B_z\hat{z}$$

$$= g_J(L,S)\frac{\beta_e B_z}{\hbar}\hat{\boldsymbol{J}}_z \tag{I.11}$$

B. Using Eq. (I.11), explain why the energy of the atomic state with quantum numbers *L*, *S*, *J*, and M_J is shifted by

$$\Delta E_B = g_J(L,S)\beta_e B_z M_J \tag{I.12}$$

in the presence of a uniform magnetic field with strength B_z.

The ground state term for Oxygen is ^3P.

C. Write out the values of *J* for the Oxygen atom.

D. For each term associated with the ^3P symbol (that is, all the values of *J* from part B), sketch the spectrum in the presence of a magnetic field. Use Hund's third rule to order states with different *J* correctly.

E. The first excited-state term for the Oxygen atom is ^1D. As in part D, sketch the spectrum.

F. In class I stated that, in a magnetic field, the "natural eigenstates" are not the conventional "Cartesian" p-orbitals, $2p_{x,y,z}$, but those depending on the spherical harmonics, $2p_0; 2p_{\pm 1}$. Using the ideas from part E, justify the preceding assertion.

The sort of term diagram you sketched in part D is called the anomalous Zeeman effect, which is the term used to describe the splitting of a non-singlet state in a magnetic field. By contrast, the splitting of the ^1D term is the "normal" Zeeman splitting. The anomalous splitting is called that for precisely the same reason as the "anomalous" g-factor for the electron was so named: there was a long gap between the laying of the foundations of quantum mechanics (ca. 1913 by Bohr) and the explanation of the unexpected

complexity of atomic spectra in magnetic fields (ca. 1928 by Dirac). Imagine being a spectroscopist in the early days, expecting that there would only be 5 states TOTAL in the spectrum of a $2p^2$ atom. Anomalous indeed.

II.   Term Symbols and Electron Coupling (1.0)

A.   Show that if the operators $\hat{A}$ and $\hat{B}$ commute with one another, then the eigenfunctions of $\hat{A}$ can be chosen so that they are also eigenfunctions of $\hat{B}$.

Now, we prove the converse of the result.

B.   Similarly, show that if every eigenfunction of $\hat{B}$ is also an eigenfunction of $\hat{A}$, then $\hat{A}$ and $\hat{B}$ commute.

Because "A" and "B" are true, it follows that the following to statements are *equivalent*: "$\hat{A}$ and $\hat{B}$ have common eigenfunctions" and "$\hat{A}$ and $\hat{B}$ commute."

In class we showed that for an atom, $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ commute with the electronic Hamiltonian,

$$\hat{H}_{el} \equiv \sum_{i=1}^{N} \left(-\tfrac{\nabla_i^2}{2} + v\left(\boldsymbol{r}_i\right) + \sum_{j=i+1}^{N} \frac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|} \right) \tag{II.1}$$

Since the components of the angular momentum do not commute with one another, the atomic wave function can only be an eigenfunction of one of these operators and, by convention, we chose to consider eigenfunctions of the Hamiltonian which are also eigenfunctions of $\hat{L}_z$. In addition, because the Hamiltonian does not depend on spin,

$$\left[\hat{H}_{el}, \hat{S}_x\right] = \left[\hat{H}_{el}, \hat{S}_y\right] = \left[\hat{H}_{el}, \hat{S}_z\right] = \left[\hat{H}_{el}, \hat{S}^2\right] = 0, \tag{II.2}$$

and so we can choose the eigenfunctions of the Hamiltonian to be eigenstates of $\hat{S}^2$ and $\hat{S}_z$ also.

A very useful result about commutators is that

$$\begin{aligned}
\left[\hat{A}, \hat{B}\hat{C}\right] &\equiv \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} \\
&= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} \\
&= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A} \\
&= \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right]
\end{aligned} \tag{II.3}$$

C.   Show that

$$\left[\hat{A}\hat{B}, \hat{C}\right] = \left[\hat{A}, \hat{C}\right]\hat{B} + \hat{A}\left[\hat{B}, \hat{C}\right] \tag{II.4}$$

D.   Show that $\hat{H}_{el}$ and $\hat{L}^2$ commute.

(Hint, use Eq. (II.3) and/or Eq. (II.4))

Because $\hat{H}_{el}$ and $\hat{L}^2$ commute, we can choose the eigenfunctions of an atom to be eigenfunctions of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$. This is the basis of term symbols. Referring to a text (or to the notes on this material),

E. **What are the term symbols for a two p-electrons in an unfilled shell, but all other shells filled?**

F. **What are the term symbols for a $p^2 f^1$ configuration?**

One of the complicating factors of the preceding analysis is that many Slater determinants are not eigenfunctions of $\hat{L}^2$ and $\hat{S}^2$ (though most are eigenfunctions of $\hat{L}_z$ and $\hat{S}_z$.

G. **Show that**

$$\Phi\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{2p_1}\left(\boldsymbol{r}_1\right)\alpha\left(1\right) & \psi_{2p_1}\left(\boldsymbol{r}_2\right)\alpha\left(2\right) \\ \psi_{2p_{-1}}\left(\boldsymbol{r}_1\right)\beta\left(1\right) & \psi_{2p_{-1}}\left(\boldsymbol{r}_2\right)\beta\left(2\right) \end{vmatrix} \tag{II.5}$$

is not an eigenfunction of $\hat{L}^2$ or $\hat{S}^2$ but is an eigenfunction of $\hat{L}_z$ and $\hat{S}_z$.

H. **For which specific values of M_L and M_S does the p^2 configuration have a Slater determinantal wave function?**

III. Spin-Orbit Coupling (1.0)

Because of the electron's spin, it has a magnetic moment. Similarly, referring to Eq. (3.44) in the third set of notes, we observe that the orbital angular momentum of the electron imparts a magnetic moment to the atom. These two magnetic moments interact and can either be aligned with each other to each other or opposed to one another, which causes terms with the same value of L and S but different values of J (reflecting different degrees of "alignment" between the vectors) to split. Typically the state of lowest energy is the one with the smallest value of J when an orbital subshell is less than half-filled, and the state with the highest value of J when the orbital subshell is more than half-filled.[1]

The form of the spin-orbital interaction is

$$\begin{aligned} \hat{H}_{S.O.} &= \sum_{i=1}^{N} \frac{Z}{4\pi\varepsilon_0 r_i^3}\left(\frac{-e}{2mc}\hat{\boldsymbol{L}}\left(\boldsymbol{r}_i\right)\cdot -g\frac{e}{2mc}\hat{\boldsymbol{S}}\left(i\right)\right) \\ &\approx \sum_{i=1}^{N} \frac{Ze^2}{8\pi\varepsilon_0 m^2 c^2 r_i^3}\left(\hat{\boldsymbol{L}}\left(\boldsymbol{r}_i\right)\cdot\hat{\boldsymbol{S}}\left(i\right)\right) \end{aligned} \tag{III.1}$$

Recalling the first problem on the second homework set, you will be unsurprised that, in general,

$$\left\langle \frac{Z}{r^n} \right\rangle \propto Z^{n+1} \tag{III.2}$$

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[1]   The reason for this is related to the term symbols for the atom. Recall that the terms for a subshell with p electrons is the same as that for the subshell occupied with h electron holes (or electron vacancies)—or the lack of particles. This is why, for instance, the term symbols for p^1 and p^5, p^2 and p^4, d^1 and d^9, d^2 and d^8, etc. are the same. The hole is exactly a "negative electron", since the sum of an electron and a hole must be zero. Thus the electron hole will have the same Landé g factor as the electron but opposite charge. Thus, while the magnetic moment of the electron is $\boldsymbol{\mu}_S^e \equiv -g\cdot\frac{e}{mc}\hat{\boldsymbol{S}}$, the magnetic moment of the hole is $\boldsymbol{\mu}_S^h \equiv -g\cdot\frac{-e}{mc}\hat{\boldsymbol{S}} = g\cdot\frac{e}{mc}\hat{\boldsymbol{S}} = -\boldsymbol{\mu}_S^e$. It follows that what is a favorable effect for a shell that is less than half-filled (which is to have the orbital and spin magnetic moments opposite one another, so that J is small) is an unfavorable effect for a shell that is more than half-filled, where having the orbital and spin-magnetic moments of the electron holes opposed to one another requires that the orbital and spin magnetic moments of the electrons be aligned.

which leads us to conclude that the size of the spin-orbit interaction grows with atomic number, Z, as Z^4. Thus, while spin-orbit effects are not very important for first row atoms, they rapidly increase in importance as we move down the periodic table, until they become much more important than the electrostatic effects that drove light atoms to form states with easily identified values of $\hat{L}_z$ and $\hat{S}_z$.

The total atomic Hamiltonian, including spin-orbit effects, is

$$\hat{H}_{atom} = \hat{H}_{el} + \hat{H}_{S.O.}$$

$$= \sum_{i=1}^{N} \left(-\frac{\nabla_i^2}{2} + v(\boldsymbol{r}_i) + \frac{Z}{2c^2 r_i^3}\left(\hat{\boldsymbol{L}}(\boldsymbol{r}_i)\cdot\hat{\boldsymbol{S}}(i)\right) + \sum_{j=i+1}^{N}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}\right) \tag{III.3}$$

In Eq. (III.3) we introduced atomic units into the spin-orbit term.

A. **Show that** $\left[\hat{L}_z, \hat{H}_{S.O.}\right] = \left(\frac{Z}{2c^2 r_i^3}\right)\left\{\hat{S}_x\left(i\hat{L}_y\right) - \hat{S}_y\left(i\hat{L}_x\right)\right\} \neq 0$.

Similar to the result in part **I**, we have that

$$\left[\hat{S}_z, \hat{H}_{S.O.}\right] = \left(\frac{Z}{2c^2 r_i^3}\right)\left\{\hat{L}_x\left(i\hat{S}_y\right) - \hat{L}_y\left(i\hat{S}_x\right)\right\} \neq 0 \tag{III.4}$$

It follows from Eq. (III.4) and its analogue for $\hat{L}_z$ that for small atoms (where the size of the spin-orbit term in the Hamiltonian is small)

$$\left\langle \Psi \left\| \left[\hat{H}_{atom}, \hat{L}_z\right] \right\| \Psi \right\rangle \approx 0$$

$$\left\langle \Psi \left\| \left[\hat{H}_{atom}, \hat{S}_z\right] \right\| \Psi \right\rangle \approx 0. \tag{III.5}$$

and so the eigenstates of the atomic Hamiltonian, Eq. (III.3), are approximate eigenfunctions of $\hat{L}_z$ and $\hat{S}_z$ for small atoms.

Using perturbation theory, we can approximate the energy splitting induced by spin-orbit coupling. Let $\Psi^{L,S,J}$ be an eigenstate of the electronic Hamiltonian, Eq. (II.1), and an eigenstate of $\hat{L}^2$, $\hat{S}^2$, and $\hat{J}^2$. From first-order perturbation theory, we find that the spin-orbit interaction gives different energies to states with the same value of S and L but different values of J. In particular we predict that the energy of the $^{2S+1}A(L)_J$ term will be given by

$$E_{^{2S+1}A(L)_J} \equiv A(L,S)\cdot\left(J(J+1) - L(L+1) - S(S+1)\right) \tag{III.6}$$

where $A(L,S) \equiv \frac{\hbar^2}{2}\cdot\left\langle \Psi^{L,S,J}\left\|\left(\frac{Z}{2c^2 r_i^3}\right)\right\|\Psi^{L,S,J}\right\rangle$. Because $\left(\frac{Z}{2c^2 r_i^3}\right) > 0$, $A(L,S)$ is usually greater than zero

for shells that are less than half-filled. Referring to the first footnote, we note that for shells that are more than half-filled it is more appropriate to use the spin-magnetic of the hole than that of the electron in the first line of Eq. (III.1), which changes the sign of the perturbation, and thus the sign of $A(L,S)$. Summarizing

$$A(L,S) \gtrsim 0 \quad \text{(less than half-filled shells)}$$

$$A(L,S) \lesssim 0 \quad \text{(more than half-filled shells)} \tag{III.7}$$

where the odd-looking inequality is used to stress the fact that Hund's third rule is not infrequently violated, especially for excited states.

B.   Derive Eq. (III.6). You will find it helpful to use the result

$$\hat{J}^2 = \left(\hat{\boldsymbol{J}}\cdot\hat{\boldsymbol{J}}\right) = \left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right)\cdot\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right)$$
$$= \hat{L}^2 + \hat{S}^2 + 2\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\right)$$

(III.8)

C.   Using Eq. (III.7), derive Hund's third rule (that small values of J are energetically favorable when subshells that are less than half-filled, but large values of J for shells that are more than half-filled).

As established in part I, because $\hat{L}_z$ and $\hat{S}_z$ do not commute with the atomic Hamiltonian, Eq. (III.3), when the spin-orbit interaction is included, we should not use M_L and M_S to label states atoms with large atomic number. However, we can still use $\hat{L}^2$, $\hat{S}^2$, $\hat{J}^2$, and $\hat{J}_z$ to describe these states.

D.   Show that $\left[\hat{L}^2,\hat{H}_{S.O.}\right]=\left[\hat{J}^2,\hat{H}_{S.O.}\right]=\left[\hat{J}_z,\hat{H}_{S.O.}\right]=0$. You may find it helpful to use your result from part A and Eq. (III.4).

From part L, we realize that L, S, J, M_J are "good quantum numbers" for the atomic Hamiltonian with or without spin-orbit interaction.

For heavy atoms, one typically uses j-j coupling. We will carry out the procedure for the p^2 configuration.

Step 1.   Write down the value largest possible value of j, $j_{\max} = l + s$, for each electron in question.

Step 2.   Write down the possible values for j for this electron.

Step 3.   Combine these values of j to form a "term symbol" for j-j coupling. Sometimes a fourth step is added, wherein the total value of J is computed. This is easily done for inequivalent electrons, but figuring out the restrictions for equivalent electrons is more difficult and, as we are about to see, often unnecessary.   For two electrons $\left|j_1 - j_2\right| \leq J \leq \left|j_1 + j_2\right|$ (but some specific terms may be missing) and for three (or more) electrons the result is similar, insofar as the total J must be between $\left|\sum_{i=1}^{m}(\pm)j_i\right| \leq J \leq \left|\sum_{i=1}^{m}j_i\right|$ where the $(\pm)$ signs are chosen to make the minimum value of J as small as possible (usually $\frac{1}{2}$).

E.   Show that the j-j coupling terms for the p^2 configuration are

$$\left(\tfrac{1}{2},\tfrac{1}{2}\right);\left(\tfrac{1}{2},\tfrac{3}{2}\right);\left(\tfrac{3}{2},\tfrac{3}{2}\right)$$

(III.9)

Because the p^2 electron configuration is less than half-filled small values of j_1 and j_2 are favored, so the terms in Eq. (III.9) are listed in order of increasing energy.

A more detailed treatment allows us to recognize that only a few specific values of J are allowed, and so the only terms are

$$\left(\tfrac{1}{2},\tfrac{1}{2}\right)_0 ;\left(\tfrac{1}{2},\tfrac{3}{2}\right)_1 ;\left(\tfrac{1}{2},\tfrac{3}{2}\right)_2 ;\left(\tfrac{3}{2},\tfrac{3}{2}\right)_0 ;\left(\tfrac{3}{2},\tfrac{3}{2}\right)_2$$

(III.10)

In the limit of infinite atomic number, spin-orbit interactions are so strong that every term with the same (j,j) symbol (regardless of the value of J) has the same energy.

It is rare that you see j-j coupling performed. The main reason has to do with the fact that L, S, J — the quantum numbers conveyed in the Russell-Saunder's term symbol, are still "good quantum numbers" when spin-orbit effects are included. In addition, there is often a sort of "non-crossing" rule that is

operational, whereby the terms in light atoms map smoothly over to the heavy-atom terms. To see this, we can plot the energy of the follow terms vs. atomic number. (The zero of energy is set to the lowest-energy term).

Atom	Energy (in wave numbers = cm^{-1})				
	$^3P_0$	$^3P_1$	$^3P_2$	$^3D_2$	$^3S_0$
He ($2p^2$ state)	0	0	0	1,659	18,240
C	0	16.4	43.5	10,194	21,648
Si	0	77	223	6,299	15,394
Ge	0	557	1,410	7,125	16,367
Sn	0	1,692	3,427	8,613	17,162
Pb	0	7,819	10,650	21,457	29,467

F. Referring to the table of microstates you used to find the Russell-Saunder's term symbol, explain why there is no $\left(\frac{3}{2}, \frac{3}{2}\right)_3$ term.
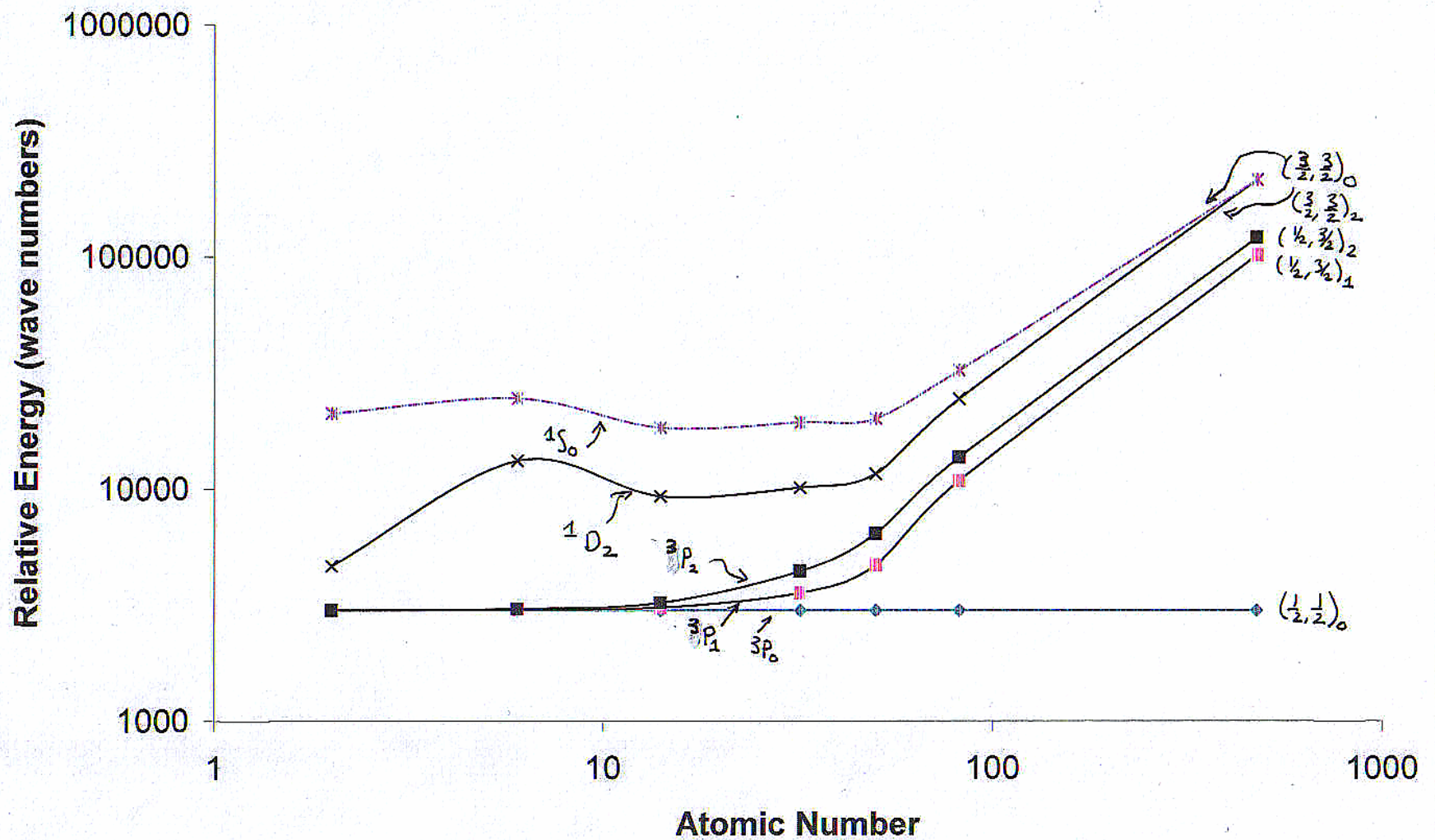
G. Referring to the table of microstates you used to find the Russell-Saunder's term symbol, why is the ^1D state associated with $\left(\frac{3}{2}, \frac{3}{2}\right)_2$.

The take-home message is well summarized by the figure on the next page. In general, it is OK to use Russell-Saunders coupling and the associated term symbols, and this is true even for large values of Z. Hund's rules tend to order states correctly for heavy atoms also. (Remember Hund's rules aren't totally reliable even for light atoms, so sometimes Hund's rules fail for a heavy atoms for non-relativistic reasons.)

However, for heavy atoms, the states are best understood not as "J splittings of the Russell-Saunders terms" but as splittings away from the simple j-j coupling results. That is, since the degeneracies in the limit of zero atomic number (no J splitting) and infinite atomic number (no J-splitting; the equivalent j-j coupling terms have the same energy) group different states, qualitative prediction of an atom's spectrum should be motivated based on its place in the progression between the "light atom" and "heavy atom" limit. In practice, I find that up until the second row transition metals, the Russell-Saunders scheme is qualitatively useful. After that point, it helps to sketch both schemes (as below) and "connect the dots." There are a number of excellent references on atomic energy levels, so finding the scheme most appropriate to your system is not difficult.

Note one key thing about the figure: even at lead (Z=82), the splittings relative to the j-j limit are quite large. This is a general trend, and persists through the few "usable" elements after lead.

Types of Coupling

Relative Energy (wave numbers) vs Atomic Number

Curves labeled: $^1S_0$, $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $(\frac{3}{2},\frac{3}{2})_0$, $(\frac{3}{2},\frac{3}{2})_2$, $(\frac{1}{2},\frac{3}{2})_2$, $(\frac{1}{2},\frac{3}{2})_1$, $(\frac{1}{2},\frac{1}{2})_0$

IV. The Orbital Model for the Atom (1.4)

To better understand the nature of screening, let us compare the relative energies of the $1s2s$ and $1s2p$ triplet states in 2-electron atoms. To do this we will introduce the Hartree Equations.

Hartree asked what the best wave function of the form

$$\Psi_{Hartree}\left(\boldsymbol{r}_1, \sigma_1\left(1\right); \boldsymbol{r}_2, \sigma_2\left(2\right); \ldots; \boldsymbol{r}_N, \sigma_N\left(N\right)\right) = \prod_{i=1}^{N} \phi_i\left(\boldsymbol{r}_i\right)\sigma_i\left(i\right) \tag{IV.1}$$

would be, where the orbitals are constrained to be orthonormal

$$\left\langle \phi_i\sigma_i \middle| \phi_j\sigma_j \right\rangle = \delta_{ij}. \tag{IV.2}$$

Here $\sigma_i\left(i\right)$ denotes the spin ($\alpha\left(i\right)$ or $\beta\left(i\right)$ for the ith electron; equation (IV.2) indicates that non-orthogonal orbitals must have different spint.

Equation (IV.1) is called a Hartree-product wave function, and it is not antisymmetric. This can be easily remedied by taking the orbitals that result from the Hartree method and placing them in a Slater determinant, however. (Of course, it is better (but more complicated!) to use seek the best *antisymmetric* product of orbitals—the best Slater determinantal wave function. That method is called the Hartree-Fock method, after Vladimer Fock, who extended Hartree's work in this manner.)

We now derive the so-called Hartree equations, which are the equations for the best possible orbitals in a Hartree-product wave function.

A. Show that the total energy of the Hartree-product wave function can be written as

$$
\begin{aligned}
E_{Hartree}\left[\left\{\phi_i, \sigma_i\right\}_{i=1}^{N}\right] &= \left\langle \prod_{m=1}^{N} \phi_m\left(\boldsymbol{r}_m\right)\sigma_m\left(m\right) \middle| \sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i}\right) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{|r_i - r_j|} \middle| \prod_{n=1}^{N} \phi_n\left(\boldsymbol{r}_n\right)\sigma_n\left(n\right) \right\rangle \\
&= \sum_{i=1}^{N}\left\langle \phi_i\left(\boldsymbol{r}\right) \middle| \left(-\frac{\nabla^2}{2} - \frac{Z}{r}\right) \middle| \phi_i\left(\boldsymbol{r}\right) \right\rangle + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\left\langle \phi_i\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right) \middle| \frac{1}{|r - r'|} \middle| \phi_i\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right) \right\rangle
\end{aligned} \tag{IV.3}
$$

Noting that the first term contains the Hamiltonian of the one-electron atom, we find it convenient to introduce a shorthand notation, namely,

$$h\left(\boldsymbol{r}\right) \equiv -\frac{\nabla^2}{2} - \frac{Z}{r}. \tag{IV.4}$$

B. What is the interpretation of the second term in Eq. (IV.3)?

We can use the techniques introduced in the previous problem to find the best orbitals for the Hartree product. In particular, we wish to minimize the energy, Eq. (IV.3), subject to the orthonormality constraint, Eq. (IV.2). There is a sophisticated way to do this (using Lagrange multipliers to force the constraint), and if you do not remember this technique, then you should revisit your calculus book. The Hartree method is special, and a more primitive approach will suffice here.

Using the development from the previous problem, require that changes in the orbital, $\phi_\alpha\left(\boldsymbol{r}\right)$, when all the other orbitals are fixed, do not lead to a change in the energy. This ensures that $\phi_\alpha\left(\boldsymbol{r}\right)$ is the "best possible" orbital.

$$\left(\frac{\delta E\left[\left\{\phi_i\right\}_{i=1}^{\infty}\right]}{\delta\phi_\alpha\left(\boldsymbol{r}\right)}\right)_{\phi_{i\neq\alpha}} = 0. \tag{IV.5}$$

To evaluate this relationship, it is helpful to introduce a more efficient procedure than that used in problem 4. First of all,

C. Show that the functional derivative of a sum is the sum of the functional derivatives. That is,

$$\frac{\delta F[\phi(\boldsymbol{r})] + G[\phi(\boldsymbol{r})]}{\delta \phi(\boldsymbol{r})} = \frac{\delta F[\phi(\boldsymbol{r})]}{\delta \phi(\boldsymbol{r})} + \frac{\delta G[\phi(\boldsymbol{r})]}{\delta \phi(\boldsymbol{r})}$$ (IV.6)

Another useful relation is the "product rule".

D. Show that the functional derivative of the product of two functionals is given by

$$\frac{\delta\left(F[\phi(\boldsymbol{r})]G[\phi(\boldsymbol{r})]\right)}{\delta \phi(\boldsymbol{r})} = G[\phi(\boldsymbol{r})]\frac{\delta F[\phi(\boldsymbol{r})]}{\delta \phi(\boldsymbol{r})} + F[\phi(\boldsymbol{r})]\frac{\delta G[\phi(\boldsymbol{r})]}{\delta \phi(\boldsymbol{r})}$$ (IV.7)

There are several chain rules also. Notably

- If f is a function of the functional, $F[\phi]$, then

$$\frac{\delta f\left(F[\phi]\right)}{\delta \phi(\boldsymbol{r})} = \frac{df}{dF} \cdot \frac{\delta F[\phi]}{\delta \phi(\boldsymbol{r})}$$ (IV.8)

- If F is a functional of $\phi(\boldsymbol{r})$, and $\phi(\boldsymbol{r})$ is a functional of $f(\boldsymbol{r})$, then

$$\frac{\delta F[\phi[f;\boldsymbol{r}]]}{\delta f(\boldsymbol{r})} = \int \frac{\delta F[\phi]}{\delta \phi(\boldsymbol{r}')} \cdot \frac{\delta \phi(\boldsymbol{r}')}{\delta f(\boldsymbol{r})} d\boldsymbol{r}'$$ (IV.9)

- If F is a functional of $\phi(\boldsymbol{r})$, which is a function of ζ, then

$$\frac{dF[\phi(\zeta,\boldsymbol{r})]}{d\zeta} = \int \frac{\delta F[\phi]}{\delta \phi(\boldsymbol{r}')} \cdot \frac{d\phi(\boldsymbol{r}')}{d\zeta} d\boldsymbol{r}'$$ (IV.10)

Equation (IV.9) is useful for describing the way the energy depends on the basis set used to expand the orbitals (the orbitals are functionals of the basis set, and the energy is a functional of the orbitals). Equation (IV.10) is used, for instance, to describe how the energy depends on the effective nuclear charge for each orbital.

Finally, there is the Gelfand-Fomin formula, which says that if you are given an integral whose integrand is a function of the function in question,

$$F[\phi(\boldsymbol{r})] \equiv \int f\left(\phi(\boldsymbol{r}), \nabla\phi(\boldsymbol{r}), \nabla^2\phi(\boldsymbol{r}), \dots\right) d\boldsymbol{r},$$ (IV.11)

then

$$\frac{\delta F[\phi]}{\delta \phi(\boldsymbol{x})} = \frac{\partial f}{\partial \phi(\boldsymbol{x})} - \nabla \cdot \frac{\partial f}{\partial\left(\nabla\phi(\boldsymbol{x})\right)} + \nabla^2 \frac{\partial f}{\partial\left(\nabla^2\phi(\boldsymbol{x})\right)} - \nabla \cdot \nabla^2 \frac{\partial f}{\partial\left(\nabla^3\phi(\boldsymbol{x})\right)} + \dots$$ (IV.12)

Equation (IV.12) is very useful, but the "derivative parts" should be used with great caution, since this simple form is only obtained when certain surface integrals vanish. Nonetheless, I'm sure you'll agree its preferable to the way you worked problem IV.

Now we can evaluate Eq. (IV.5). Even though $\phi_\alpha(\boldsymbol{r})$ is normalized, $\phi_\alpha(\boldsymbol{r}) + \delta\phi_\alpha(\boldsymbol{r})$ might not be, so we need to generalize Eq. (IV.3) to non-normalized integrals. Going through the derivation in part **A**, it becomes apparent that

$$E_{Hartree}\left[\{\phi_i,\sigma_i\}_{i=1}^N\right] = \sum_{i=1}^N \frac{\left\langle\phi_i(\boldsymbol{r})\left|\hat{h}(\boldsymbol{r})\right|\phi_i(\boldsymbol{r})\right\rangle}{\left\langle\phi_i(\boldsymbol{r})\middle|\phi_i(\boldsymbol{r})\right\rangle} + \sum_{i=1}^N \sum_{j=i+1}^N \frac{\left\langle\phi_i(\boldsymbol{r})\phi_j(\boldsymbol{r}')\left|\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\right|\phi_i(\boldsymbol{r})\phi_j(\boldsymbol{r}')\right\rangle}{\left\langle\phi_i(\boldsymbol{r})\middle|\phi_i(\boldsymbol{r})\right\rangle\left\langle\phi_j(\boldsymbol{r})\middle|\phi_j(\boldsymbol{r})\right\rangle}$$ (IV.13)

So

$$0 = \frac{\delta E_{Hartree}}{\delta \phi_\alpha(\boldsymbol{x})}$$

$$= \frac{\delta}{\delta \phi_\alpha(\boldsymbol{x})} \left[\sum_{i=1}^{N} \frac{\left\langle \phi_i(\boldsymbol{r}) \middle| \hat{h}(\boldsymbol{r}) \middle| \phi_i(\boldsymbol{r}) \right\rangle}{\left\langle \phi_i(\boldsymbol{r}) \middle| \phi_i(\boldsymbol{r}) \right\rangle} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{\left\langle \phi_i(\boldsymbol{r}) \phi_j(\boldsymbol{r}') \middle| \frac{1}{|r-r'|} \middle| \phi_i(\boldsymbol{r}) \phi_j(\boldsymbol{r}') \right\rangle}{\left\langle \phi_i(\boldsymbol{r}) \middle| \phi_i(\boldsymbol{r}) \right\rangle \left\langle \phi_j(\boldsymbol{r}) \middle| \phi_j(\boldsymbol{r}) \right\rangle} \right]$$

$$\overset{\text{Eq. (V.6)}}{=} \frac{\delta}{\delta \phi_\alpha(\boldsymbol{x})} \left[\sum_{i=1}^{N} \frac{\left\langle \phi_i(\boldsymbol{r}) \middle| \hat{h}(\boldsymbol{r}) \middle| \phi_i(\boldsymbol{r}) \right\rangle}{\left\langle \phi_i(\boldsymbol{r}) \middle| \phi_i(\boldsymbol{r}) \right\rangle} \right]$$

$$+ \frac{\delta}{\delta \phi_\alpha(\boldsymbol{x})} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{\left\langle \phi_i(\boldsymbol{r}) \phi_j(\boldsymbol{r}') \middle| \frac{1}{|r-r'|} \middle| \phi_i(\boldsymbol{r}) \phi_j(\boldsymbol{r}') \right\rangle}{\left\langle \phi_i(\boldsymbol{r}) \middle| \phi_i(\boldsymbol{r}) \right\rangle \left\langle \phi_j(\boldsymbol{r}) \middle| \phi_j(\boldsymbol{r}) \right\rangle}$$

(IV.14)

Since all the orbitals except $\phi_\alpha(\boldsymbol{r})$ are unaffected by this derivative, we can simplify this result to

$$0 = \frac{\delta}{\delta \phi_\alpha(\boldsymbol{x})} \left[\frac{\left\langle \phi_\alpha(\boldsymbol{r}) \middle| \hat{h}(\boldsymbol{r}) \middle| \phi_\alpha(\boldsymbol{r}) \right\rangle}{\left\langle \phi_\alpha(\boldsymbol{r}) \middle| \phi_\alpha(\boldsymbol{r}) \right\rangle} \right] + \frac{\delta}{\delta \phi_\alpha(\boldsymbol{x})} \sum_{j=\alpha+1}^{N} \frac{\left\langle \phi_\alpha(\boldsymbol{r}) \phi_j(\boldsymbol{r}') \middle| \frac{1}{|r-r'|} \middle| \phi_\alpha(\boldsymbol{r}) \phi_j(\boldsymbol{r}') \right\rangle}{\left\langle \phi_\alpha(\boldsymbol{r}) \middle| \phi_\alpha(\boldsymbol{r}) \right\rangle \left\langle \phi_j(\boldsymbol{r}) \middle| \phi_j(\boldsymbol{r}) \right\rangle}$$

$$+ \frac{\delta}{\delta \phi_\alpha(\boldsymbol{x})} \sum_{i=1}^{\alpha-1} \frac{\left\langle \phi_i(\boldsymbol{r}) \phi_\alpha(\boldsymbol{r}') \middle| \frac{1}{|r-r'|} \middle| \phi_i(\boldsymbol{r}) \phi_\alpha(\boldsymbol{r}') \right\rangle}{\left\langle \phi_i(\boldsymbol{r}) \middle| \phi_i(\boldsymbol{r}) \right\rangle \left\langle \phi_\alpha(\boldsymbol{r}) \middle| \phi_\alpha(\boldsymbol{r}) \right\rangle}$$

(IV.15)

The first term is just the variational principle for the one-electron atom (compare problem IV.C). So

$$\frac{\delta}{\delta \phi_\alpha(\boldsymbol{x})} \left[\frac{\left\langle \phi_\alpha(\boldsymbol{r}) \middle| \hat{h}(\boldsymbol{r}) \middle| \phi_\alpha(\boldsymbol{r}) \right\rangle}{\left\langle \phi_\alpha(\boldsymbol{r}) \middle| \phi_\alpha(\boldsymbol{r}) \right\rangle} \right] = 2\hat{h}\phi_\alpha(\boldsymbol{x}) - 2\left\langle \phi_\alpha(\boldsymbol{r}) \middle| \hat{h}(\boldsymbol{r}) \middle| \phi_\alpha(\boldsymbol{r}) \right\rangle \phi_\alpha(\boldsymbol{x})$$

(IV.16)

(you may assume the orbital is real).

Next, use the chain-rule (Eq. (IV.8)), the product rule (Eq. (IV.7)), and the Gelfand-Fomin formula (Eq. (IV.12)) to show that

$$\frac{\delta}{\delta\phi_\alpha(x)}\frac{\left\langle\phi_\alpha(r)\phi_j(r')\left|\frac{1}{|r-r'|}\right|\phi_\alpha(r)\phi_j(r')\right\rangle}{\langle\phi_\alpha(r)|\phi_\alpha(r)\rangle\langle\phi_j(r)|\phi_j(r)\rangle}$$

$$=\frac{1}{\langle\phi_\alpha(r)|\phi_\alpha(r)\rangle\langle\phi_j(r)|\phi_j(r)\rangle}\left(\frac{\delta}{\delta\phi_\alpha(x)}\left\langle\phi_\alpha(r)\phi_j(r')\left|\frac{1}{|r-r'|}\right|\phi_\alpha(r)\phi_j(r')\right\rangle\right)$$

$$+\left\langle\phi_\alpha(r)\phi_j(r')\left|\frac{1}{|r-r'|}\right|\phi_\alpha(r)\phi_j(r')\right\rangle\frac{\delta}{\delta\phi_\alpha(x)}\frac{1}{\langle\phi_\alpha(r)|\phi_\alpha(r)\rangle\langle\phi_j(r)|\phi_j(r)\rangle}$$

$$=\frac{1}{1\cdot1}\left(\frac{\delta}{\delta\phi_\alpha(x)}\iint\phi_\alpha^2(r)\frac{\phi_j^2(r')}{|r'-r|}dr'dr\right)$$

$$+\iint\phi_\alpha^2(r)\frac{\phi_j^2(r')}{|r'-r|}dr'dr\frac{\delta}{\delta\phi_\alpha(x)}\frac{1}{\langle\phi_\alpha(r)|\phi_\alpha(r)\rangle\cdot1}$$

$$=\left(\int(2\phi_\alpha(x))\frac{\phi_j^2(r')}{|r'-x|}dr'\right)$$

$$+\iint\phi_\alpha^2(r)\frac{\phi_j^2(r')}{|r'-r|}dr'dr\left(\frac{-1}{\left(\langle\phi_\alpha(r)|\phi_\alpha(r)\rangle\right)^2}\frac{\delta}{\delta\phi_\alpha(x)}\langle\phi_\alpha(r)|\phi_\alpha(r)\rangle\right)$$

$$=\left(2\int\frac{\phi_j^2(r')}{|r'-x|}dr'\right)\phi_\alpha(x)+\iint\phi_\alpha^2(r)\frac{\phi_j^2(r')}{|r'-r|}dr'dr\left(\frac{-1}{(1)^2}\frac{\delta}{\delta\phi_\alpha(x)}\int(\phi_\alpha(r))^2dr\right) \tag{IV.17}$$

$$=2\left(\int\frac{\phi_j^2(r')}{|r'-x|}dr'\right)\phi_\alpha(x)-2\left\langle\phi_\alpha(r)\phi_j(r')\left|\frac{1}{|r-r'|}\right|\phi_\alpha(r)\phi_j(r')\right\rangle\phi_\alpha(x)$$

Using these results, you can:

E. **Show that the orbital, $\phi_\alpha(r)$ satisfies a one-electron Schrödinger equation, namely**

$$\left(\hat{h}(r)+\sum_{\substack{i=1;\\i\neq\alpha}}^N\int\frac{|\phi_i(r')|^2}{|r-r'|}dr'\right)\phi_\alpha(r)=\varepsilon_\alpha\phi_\alpha(r) \tag{IV.18}$$

where

$$\varepsilon_\alpha\equiv\left\langle\psi_\alpha(r)\left|\hat{h}(r)+\sum_{i\neq\alpha}^N\int\frac{|\psi_i(r')|^2}{|r-r'|}dr'\right|\psi_\alpha(r)\right\rangle$$

$$=\left\langle\psi_\alpha(r)|\hat{h}(r)|\psi_\alpha(r)\right\rangle+\sum_{\substack{i=1;\\i\neq\alpha}}^N\left\langle\phi_\alpha(r)\phi_i(r')\left|\frac{1}{|r-r'|}\right|\phi_\alpha(r)\phi_i(r')\right\rangle \tag{IV.19}$$

There is an equation like (IV.18) for each value of α, $\alpha=1,2,\ldots,N,N+1,N+2,\ldots$. When $\alpha>N$, we say $\phi_\alpha(r)$ is an unoccupied or "virtual orbital." (The "virtual orbital" terminology is associated with the role of this orbital in the theory of electron correlation. The important point, at present, is that the orbital is not occupied.)

Solving Eq. (IV.18) without a computer is very difficult. To see why, note that the potential in the Hartree equations depends on the orbitals used. This is not a normal eigenvalue problem, then, and must be solved to "self consistency. That is, solve Eq. (IV.18) for $\psi_\alpha(\boldsymbol{r})$. Call this $\psi_\alpha^{(0)}(\boldsymbol{r})$. This changes the value of the Hartree potential,

$$v_\beta^{Hartree}(\boldsymbol{r}) \equiv \sum_{i\neq\beta}^{N} \int \frac{\left|\psi_i(\boldsymbol{r}')\right|^2}{\left|\boldsymbol{r}-\boldsymbol{r}'\right|} d\boldsymbol{r}' \tag{IV.20}$$

for all the other orbitals, $\phi_{\beta\neq\alpha}(\boldsymbol{r})$. Solving the Hartree equation for the other orbitals, one obtains $\psi_\beta^{(0)}(\boldsymbol{r})$. Substituting the revised orbitals, $\left\{\psi_\beta^{(0)}(\boldsymbol{r})\right\}_{\beta\neq\alpha}^{N}$, into the expression for $v_\alpha^{Hartree}(\boldsymbol{r})$ gives one a new equation for the αth orbital, yielding $\psi_\alpha^{(1)}(\boldsymbol{r})$. The other orbitals in the system are then refined again. One continues in this manner until the process converges, that is, until the orbitals (and also the ε_α's) are not changing very much.

F. Describe, in words, the physical interpretation of Eq. (IV.18)? Why do we leave out the $i=\alpha$ term?

We wish to clarify the interpretation of the quantities ε_α. Because Eq. (IV.19) looks like an energy expression, we call ε_α the "orbital energy" of the αth orbital. It is important to note that the total energy is **not** the sum of the orbital energies.

G. Show that the total energy can be written as

$$E_{Hartree}\left[\left\{\phi_i\right\}_{i=1}^{N}\right] = \sum_{i=1}^{N}\varepsilon_i - \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\left\langle\psi_i(\boldsymbol{r})\psi_j(\boldsymbol{r}')\left|\frac{1}{\left\|\boldsymbol{r}-\boldsymbol{r}'\right\|}\right|\psi_i(\boldsymbol{r})\psi_j(\boldsymbol{r}')\right\rangle \tag{IV.21}$$

The second term in Eq. (IV.21) is a correction for the "double counting" of the electron-electron repulsion energy.

Consider solving Eq. (IV.18) for an unoccupied orbital, $\phi_\beta(\boldsymbol{r})$ with $\beta > N$. ($\phi_\beta(\boldsymbol{r})$ is sometimes called a "virtual" orbital because it doesn't represent a real "single electron" state of an electron, but just a state that the electron could be "promoted" to.) In this case, Equation (IV.18) becomes

$$\left[\hat{h}(\boldsymbol{r}) + \sum_{i=1}^{N}\int\frac{\left|\psi_i(\boldsymbol{r}')\right|^2}{\left|\boldsymbol{r}-\boldsymbol{r}'\right|}d\boldsymbol{r}'\right]\phi_\beta(\boldsymbol{r}) = \varepsilon_\beta\phi_\beta(\boldsymbol{r}) \tag{IV.22}$$

Now, consider what happens if we excite an electron from an occupied orbital, $\varepsilon_{\alpha\leq N}$, to the unoccupied orbital, ε_β. The new wave function is

$$\Psi_{\substack{\uparrow\\\alpha}}^{\beta}\left(\boldsymbol{r}_1,\sigma(1);\boldsymbol{r}_2,\sigma(2);\ldots;\boldsymbol{r}_N,\sigma(N)\right) = \left[\prod_{i\neq\alpha}^{N}\phi_i(\boldsymbol{r}_i)\sigma_i(i)\right]\phi_\beta(\boldsymbol{r}_\alpha)\sigma_\beta(\alpha). \tag{IV.23}$$

The energy of this wave function is, then, from Eq. (IV.3),

$$E_{\;\;\alpha}^{\beta}{\uparrow}\left[\{\phi_i,\sigma_i\}_{i=1}^{N}\right]$$

$$=\left\langle\left[\prod_{\substack{i\neq\alpha}}^{N}\phi_i\left(\boldsymbol{r}_i\right)\sigma_i\left(i\right)\right]\phi_\beta\left(\boldsymbol{r}_\alpha\right)\sigma_\beta\left(\alpha\right)\middle|\sum_{i=1}^{N}\hat{h}\left(\boldsymbol{r}_i\right)+\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{|r_i-r_j|}\middle|\left[\prod_{\substack{i\neq\alpha}}^{N}\phi_i\left(\boldsymbol{r}_i\right)\sigma_i\left(i\right)\right]\phi_\beta\left(\boldsymbol{r}_\alpha\right)\sigma_\beta\left(\alpha\right)\right\rangle$$

$$=\sum_{\substack{i=1\\i\neq\alpha}}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\middle|\hat{h}\left(\boldsymbol{r}\right)\middle|\phi_i\left(\boldsymbol{r}\right)\right\rangle+\left\langle\phi_\beta\left(\boldsymbol{r}\right)\middle|\hat{h}\left(\boldsymbol{r}\right)\middle|\phi_\beta\left(\boldsymbol{r}\right)\right\rangle$$

$$+\sum_{\substack{i=1\\i\neq\alpha}}^{N}\sum_{\substack{j=i+1\\j\neq\alpha}}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_i\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right)\right\rangle+\sum_{\substack{i=1\\i\neq\alpha}}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_i\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\right\rangle$$

$$=\sum_{i=1}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\middle|\hat{h}\left(\boldsymbol{r}\right)\middle|\phi_i\left(\boldsymbol{r}\right)\right\rangle+\left\langle\phi_\beta\left(\boldsymbol{r}\right)\middle|\hat{h}\left(\boldsymbol{r}\right)\middle|\phi_\beta\left(\boldsymbol{r}\right)\right\rangle-\left\langle\phi_\alpha\left(\boldsymbol{r}\right)\middle|\hat{h}\left(\boldsymbol{r}\right)\middle|\phi_\alpha\left(\boldsymbol{r}\right)\right\rangle$$

$$+\sum_{i=1}^{N}\sum_{j=i+1}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_i\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right)\right\rangle-\sum_{i=1}^{\alpha-1}\left\langle\phi_i\left(\boldsymbol{r}\right)\phi_\alpha\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_i\left(\boldsymbol{r}\right)\phi_\alpha\left(\boldsymbol{r}'\right)\right\rangle$$

$$-\sum_{j=\alpha+1}^{N}\left\langle\phi_\alpha\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_\alpha\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right)\right\rangle$$

$$+\sum_{i=1}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_i\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\right\rangle-\left\langle\phi_\alpha\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_\alpha\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\right\rangle$$

$$=\sum_{i=1}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\middle|\hat{h}\left(\boldsymbol{r}\right)\middle|\phi_i\left(\boldsymbol{r}\right)\right\rangle+\sum_{i=1}^{N}\sum_{j=i+1}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_i\left(\boldsymbol{r}\right)\phi_j\left(\boldsymbol{r}'\right)\right\rangle$$

$$+\left\langle\phi_\beta\left(\boldsymbol{r}\right)\middle|\hat{h}\left(\boldsymbol{r}\right)\middle|\phi_\beta\left(\boldsymbol{r}\right)\right\rangle+\sum_{i=1}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_i\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\right\rangle$$

$$-\left\langle\phi_\alpha\left(\boldsymbol{r}\right)\middle|\hat{h}\left(\boldsymbol{r}\right)\middle|\phi_\alpha\left(\boldsymbol{r}\right)\right\rangle-\sum_{i\neq\alpha}^{N}\left\langle\phi_i\left(\boldsymbol{r}\right)\phi_\alpha\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_i\left(\boldsymbol{r}\right)\phi_\alpha\left(\boldsymbol{r}'\right)\right\rangle \qquad\text{(IV.24)}$$

$$-\left\langle\phi_\alpha\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_\alpha\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\right\rangle$$

$$=E_{Hartree}+\varepsilon_\beta-\varepsilon_\alpha-\left\langle\phi_\alpha\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_\alpha\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\right\rangle$$

It follows that the excitation energy is

$$E_{\;\;\alpha}^{\beta}{\uparrow}-E_{Hartree}\approx\varepsilon_\beta-\varepsilon_\alpha-\left\langle\phi_\alpha\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\middle|\tfrac{1}{|r-r'|}\middle|\phi_\alpha\left(\boldsymbol{r}\right)\phi_\beta\left(\boldsymbol{r}'\right)\right\rangle \qquad\text{(IV.25)}$$

The "correction term" to the orbital energy difference is often described as the "attraction of the excited electron", $\phi_\beta\left(\boldsymbol{r}\right)$, for the "hole" it left behind, $\phi_\alpha\left(\boldsymbol{r}\right)$. The idea is that when we excite an electron from $\phi_\alpha\left(\boldsymbol{r}\right)$, the electron density decreases from $\rho\left(\boldsymbol{r}\right)$ to $\rho\left(\boldsymbol{r}\right)-\left|\phi_\alpha\left(\boldsymbol{r}\right)\right|^2$. This means that an electron in an excited state orbital will be "attracted" to this "hole" in the electron density with a potential like

$$\int\frac{-\left|\phi_\alpha\left(\boldsymbol{r}\right)\right|^2}{|\boldsymbol{r}-\boldsymbol{x}|}d\boldsymbol{r} \qquad\text{(IV.26)}$$

The energetic "cost" of keeping the electron in an excited state, then, is not just the cost of putting an electron into a higher-energy orbital, $\varepsilon_\beta-\varepsilon_\alpha$, because there is an "energetic benefit" because of the attraction between the electron and the "hole" it left behind which, from Eq. (IV.26), we estimate to be

$$E_{e^-,h^+}=\iint\frac{-\left|\phi_\alpha^2\left(\boldsymbol{r}\right)\right|\left|\phi_\beta^2\left(\boldsymbol{x}\right)\right|}{|\boldsymbol{r}-\boldsymbol{x}|}d\boldsymbol{r}d\boldsymbol{x}<0 \qquad\text{(IV.27)}$$

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This energetic benefit would not be expected, for instance, if we form an anion by adding an electron to $\phi_\beta(\boldsymbol{r})$ without first removing the electron from $\phi_\alpha(\boldsymbol{r})$. Approximating the energy of the anion with

$$\Psi^{\beta}_{\underset{free}{\uparrow}}\left(\boldsymbol{r}_1,\sigma(1);\boldsymbol{r}_2,\sigma(2);\ldots;\boldsymbol{r}_N,\sigma(N)\right) = \left[\prod_{i=1}^{N}\phi_i(\boldsymbol{r}_i)\sigma_i(i)\right]\phi_\beta(\boldsymbol{r}_\alpha)\sigma_\beta(\alpha) \tag{IV.28}$$

H.   **Show that the electron affinity is simply**

$$EA_\beta \equiv E_{neutral} - E^{\beta}_{\underset{free}{\uparrow}} = -\varepsilon_\beta \tag{IV.29}$$

By the same sort of derivation, we find that the energy required to remove an electron from the αth orbital to form the cation wavefunction,

$$\Psi^{free}_{\underset{\alpha}{\uparrow}}\left(\boldsymbol{r}_1,\sigma(1);\boldsymbol{r}_2,\sigma(2);\ldots;\boldsymbol{r}_N,\sigma(N)\right) = \prod_{i\neq\alpha}^{N}\phi_i(\boldsymbol{r}_i)\sigma_i(i). \tag{IV.30}$$

is

$$IP_\alpha \approx E^{free}_{\underset{\alpha}{\uparrow}} - E_{neutral} = -\varepsilon_\alpha. \tag{IV.31}$$

In general, orbital energies are associated with the ionization potentials and electron affinities of a system.

I.   **Explain why Eqs. (IV.23), (IV.28), and (IV.30) are not exact wave functions for the system in the Hartree approximation. (That is, the orbitals in these wave functions are not solutions to the Hartree equations.)**

J.   **Is the excitation energy from Eq. (IV.25) greater than or less than the exact excitation energy that would be computed with the Hartree approximation? What about the electron affinity, Eq. (IV.29) and the ionization potential, Eq. (IV.31).**
     We can solve the Hartree equations "by hand" for the three-electron atom to deduce whether the 2s or 2p orbital fills first. It is, however, quite tedious. Let us simply approximate the orbital energy of the 2s and 2p orbitals, assuming that these orbitals have the *exact same form* as they do in the 1-electron atom with nuclear charge Z. We obtain

$$\varepsilon_{2s} \approx -\frac{Z^2}{8} + \frac{23}{54}Z$$
$$\varepsilon_{2p} \approx -\frac{Z^2}{8} + \frac{118}{243}Z \tag{IV.32}$$

K.   **Based on these formula, what is the smallest value of *Z* that can stabilize a third electron? What does this imply about the form of the orbitals in a many-electron atom?**
     (The actual answer is that the third electron is stabilized as long as $Z > 2$.

L. **What can you say about the relative spacing of the 2s and 2p orbitals as the atomic number increases?**

V. Approximating the Energy of the Helium Atom (2.0)

In this problem we will consider the how to approximate the energy of the Helium atom. In the lecture we considered the 1s-orbital in Helium to have the following form,

$$\psi_{1s}\left(\boldsymbol{r};\zeta\right) = \sqrt{\frac{\zeta^3}{\pi}}e^{-\zeta r} \tag{V.1}$$

and approximate the energy using the variational principle. That is, we approximated the Helium atom wave function with

$$\Psi_\zeta\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right) = \psi_{1s}\left(\zeta,\boldsymbol{r}_1\right)\psi_{1s}\left(\zeta,\boldsymbol{r}_2\right) \tag{V.2}$$

and then chose the effective nuclear charge, ζ, so that the energy of the Helium atom,

$$E\left(\zeta\right) = \frac{\left\langle\Psi_\zeta\left|\hat{H}\right|\Psi_\zeta\right\rangle}{\left\langle\Psi_\zeta\left|\Psi_\zeta\right.\right\rangle}. \tag{V.3}$$

We find the optimum value of ζ from

$$\frac{\partial E\left(\zeta\right)}{\partial\zeta} = 0\,, \tag{V.4}$$

which gives

$$\zeta = 1.6875 = \tfrac{27}{16}$$
$$E = -2.848. \tag{V.5}$$

One way to improve the wave function further is to "split" the 1s-orbital into two components,

$$\psi_{1s}^{(a)}\left(\boldsymbol{r};\zeta\right) = \sqrt{\frac{\zeta_a^3}{\pi}}e^{-\zeta_a r} \tag{V.6}$$

$$\psi_{1s}^{(b)}\left(\boldsymbol{r};\zeta\right) = \sqrt{\frac{\zeta_b^3}{\pi}}e^{-\zeta_b r}. \tag{V.7}$$

This is called a "double-zeta" or "split-zeta" basis set. Eckhart used this formalism to create a function of the form

$$\Psi_{\zeta_a,\zeta_b}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right) \propto \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right)\right) \tag{V.8}$$

They he evaluated

$$E\left(\zeta_a,\zeta_b\right) = \frac{\left\langle\Psi_{\zeta_a,\zeta_b}\left|\hat{H}\right|\Psi_{\zeta_a,\zeta_b}\right\rangle}{\left\langle\Psi_{\zeta_a,\zeta_b}\left|\Psi_{\zeta_a,\zeta_b}\right.\right\rangle} \tag{V.9}$$

and found, by minimizing the energy with respect to ζ_a and ζ_b, that

$$\zeta_a = 1.19$$
$$\zeta_b = 2.18 \tag{V.10}$$
$$E = -2.876$$

Let us add the spin function back to Eq. (V.8), which gives us

$$\Psi_{\zeta_a,\zeta_b}\left(\boldsymbol{r}_1,s_1;\boldsymbol{r}_2,s_2\right) \propto \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right)\right)\left(\alpha\left(1\right)\beta\left(2\right) - \alpha\left(2\right)\beta\left(1\right)\right). \tag{V.11}$$

One might expect that the Eckhart function can be expressed as a Slater determinate. It can not. It can be written as a sum of two Slater determinates, however,

$$
\Psi_{\zeta_a,\zeta_b}\left(\boldsymbol{r}_1,s_1;\boldsymbol{r}_2,s_2\right) \propto
\begin{vmatrix}
\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right)\alpha\left(1\right) & \psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right)\alpha\left(2\right) \\
\psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\beta\left(1\right) & \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\beta\left(2\right)
\end{vmatrix}
+
\begin{vmatrix}
\psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\alpha\left(1\right) & \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\alpha\left(2\right) \\
\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right)\beta\left(1\right) & \psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right)\beta\left(2\right)
\end{vmatrix}
$$

$$
= \psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right)\alpha\left(1\right)\psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\beta\left(2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\alpha\left(1\right)\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right)\beta\left(2\right) \tag{V.12}
$$

$$
-\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right)\alpha\left(2\right)\psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\beta\left(1\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\alpha\left(2\right)\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right)\beta\left(1\right)
$$

$$
= \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right)\right)\left(\alpha\left(1\right)\beta\left(2\right) - \alpha\left(2\right)\beta\left(1\right)\right)
$$

While Eq. (V.12) is a Slater determinate, it is not really an orbital product wave function because the $\psi_{1s}^{(a)}\left(\boldsymbol{r}\right)$ and $\psi_{1s}^{(b)}\left(\boldsymbol{r}\right)$ are not orthogonal. However, $\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}\right)\right)$ and $\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}\right)\right)$ are orthogonal since

$$
\int \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}\right)\right)^* \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}\right)\right)d\boldsymbol{r}
$$

$$
= \int \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}\right)\right)^* \psi_{1s}^{(a)}\left(\boldsymbol{r}\right)d\boldsymbol{r} + \int \left(\psi_{1s}^{(b)}\left(\boldsymbol{r}\right)\right)^* \psi_{1s}^{(a)}\left(\boldsymbol{r}\right)d\boldsymbol{r} \tag{V.13}
$$

$$
- \int \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}\right)\right)^* \psi_{1s}^{(b)}\left(\boldsymbol{r}\right)d\boldsymbol{r} - \int \left(\psi_{1s}^{(b)}\left(\boldsymbol{r}\right)\right)^* \psi_{1s}^{(b)}\left(\boldsymbol{r}\right)d\boldsymbol{r}
$$

$$
= 0
$$

and we can

A.   Show that

$$
\Psi_{\zeta_a,\zeta_b}\left(\boldsymbol{r}_1,s_1;\boldsymbol{r}_2,s_2\right) \propto \frac{1}{2}
\begin{vmatrix}
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\alpha\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\alpha\left(2\right) \\
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\beta\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\beta\left(2\right)
\end{vmatrix}
$$

$$
- \frac{1}{2}
\begin{vmatrix}
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\alpha\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\alpha\left(2\right) \\
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\beta\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\beta\left(2\right)
\end{vmatrix}. \tag{V.14}
$$

The best one can do with the split-ζ basis set is to choose a wave function of the form

$$
\Psi_{k_{1s^2},2s^2,1s2s}\left(\boldsymbol{r}_1,s_1;\boldsymbol{r}_2,s_2\right) \propto k_{1s^2}
\begin{vmatrix}
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\alpha\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\alpha\left(2\right) \\
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\beta\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\beta\left(2\right)
\end{vmatrix}
$$

$$
+ k_{2s^2}
\begin{vmatrix}
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\alpha\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\alpha\left(2\right) \\
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\beta\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\beta\left(2\right)
\end{vmatrix} \tag{V.15}
$$

$$
+ k_{1s2s}\left(
\begin{vmatrix}
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\alpha\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\alpha\left(2\right) \\
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\beta\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\beta\left(2\right)
\end{vmatrix}
\right.
$$

$$
\left. +
\begin{vmatrix}
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\alpha\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\alpha\left(2\right) \\
\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\right)\beta\left(1\right) & \left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right) - \psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right)\right)\beta\left(2\right)
\end{vmatrix}
\right)
$$

where k_{1s^2}, k_{2s^2}, and k_{1s2s} are determined from the variational principle. This was done in a famous paper by Shull and Löwdin, and the energy is -2.877 --a mere $\frac{1}{1000}$th of a Hartree is gained relative to the Eckhart function. One may conclude that single excitations are not very important. This is a result of Brillouin's

theorem, which says (roughly) that given the best Slater determinant, including effects from single-electron excitations (the $1s2s$ term in Eq. (V.15)) has no direct effect. The only reason $k_{1s2s} \neq 0$ is because there is a slight correction to the $2s^2$ states energy from the $1s2s$ state, and a shift in the energy of the $2s^2$ state causes a correspondingly slight shift in the $1s2s$ state.

There is another way to improve the energy of the model using the double-zeta basis set. Choose the orbital

$$\psi_{1s}^{(a,b)}(\boldsymbol{r}) = \psi_{1s}^{(a)}(\boldsymbol{r}) + c_b \psi_{1s}^{(b)}(\boldsymbol{r});$$

(V.16)

that is, mix the two different basis functions together. Then, form the wave function

$$\Psi_{c_b}(\boldsymbol{r}_1, \boldsymbol{r}_2) \propto \psi_{1s}^{(a,b)}(\boldsymbol{r}_1)\psi_{1s}^{(a,b)}(\boldsymbol{r}_2)$$

(V.17)

calculate

$$E(c_b) = \frac{\left\langle \Psi_{c_b} \middle| \hat{H} \middle| \Psi_{c_b} \right\rangle}{\left\langle \Psi_{c_b} \middle| \Psi_{c_b} \right\rangle}$$

(V.18)

and calculate c_b from

$$\frac{\partial E}{\partial c_b} = 0$$

(V.19)

B. Use Eq. (V.19) to determine c_b. Evaluate $E(c_b)$.

The orbital from Eq. (V.16) is an approximation to the $1s$ orbital in this system. The $2s$ orbital can be constructed as

$$\psi_{2s}^{(a,b)}(\boldsymbol{r}) = \psi_{1s}^{(a)}(\boldsymbol{r}) + d_b \psi_{1s}^{(b)}(\boldsymbol{r})$$

(V.20)

where d_b is determined by the requirement that the 1s and 2s orbitals be orthogonal,

$$\left\langle \psi_{1s}^{(a)}(\boldsymbol{r}) + c_b \psi_{1s}^{(b)}(\boldsymbol{r}) \middle| \psi_{1s}^{(a)}(\boldsymbol{r}) + d_b \psi_{1s}^{(b)}(\boldsymbol{r}) \right\rangle = 0$$

(V.21)

This gives (if I did my math right)

$$d_b = \frac{c_b \left\langle \psi_{1s}^{(a)}(\boldsymbol{r}) \middle| \psi_{1s}^{(b)}(\boldsymbol{r}) \right\rangle - 1}{c_b + \left\langle \psi_{1s}^{(a)}(\boldsymbol{r}) \middle| \psi_{1s}^{(b)}(\boldsymbol{r}) \right\rangle}$$

(V.22)

C. Solve for d_b. Plot $\psi_{1s}^{(a,b)}(\boldsymbol{r})$ and $\psi_{2s}^{(a,b)}(\boldsymbol{r})$.

When you evaluate $E(c_b)$, you will find that the energy of this wave function is greater than the Eckhart wave function. To see why, note that the electronic wavefunction from Eq. (V.17) gives a probability distribution function,

$$\left| \Psi_{c_b}(\boldsymbol{r}_1, \boldsymbol{r}_2) \right|^2 \propto \left| \psi_{1s}^{(a,b)}(\boldsymbol{r}_1) \right|^2 \left| \psi_{1s}^{(a,b)}(\boldsymbol{r}_2) \right|^2 = \begin{vmatrix} \psi_{1s}^{(a,b)}(\boldsymbol{r}_1)\alpha(1) & \psi_{1s}^{(a,b)}(\boldsymbol{r}_2)\alpha(2) \\ \psi_{1s}^{(a,b)}(\boldsymbol{r}_1)\beta(1) & \psi_{1s}^{(a,b)}(\boldsymbol{r}_2)\beta(2) \end{vmatrix}$$

(V.23)

which is a product of two one-electron distribution functions. If the probability of two events, say, an electron being at $\boldsymbol{r}_1$ and an electron being at $\boldsymbol{r}_2$, is the product of the probabilities of the two events occurring separately (cf. Eq. (V.23)), then those two events are "independent"—they are uncorrelated. We say that Eq. (V.17) (and also Eq. (V.2)) neglect electron correlation. Moreover, by definition, no Slater determinant includes electron correlation (although, for more than two electrons, Eqs. like (V.23) no longer hold). The Eckhart function however crudely, accounts for electron correlation. In particular, Eq. (V.11) describes radial (or "in-out") correlation, because a function like $\psi_{1s}^{(a)}(\boldsymbol{r}_1)\psi_{1s}^{(b)}(\boldsymbol{r}_2)$ with $\zeta_a < \zeta_b$ allows the first electron to be "far from the nucleus when the second electron is close to it, while the second term in Eq. (V.11),

$\psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right)$, allows the second electron to be far from the nucleus when the first electron is close to it. That is, a wave function like Eckhart's gives a very primitive model for how electrons "avoid each other".

One might expect that one could systematically refine the Helium atom in this way: add more and more different values of ζ, increasing the "flexibility" of our $1s$ function and, simultaneously, allowing one to include Slater determinants corresponding to the $3s^2$ and $4s^2$ configurations (among others) in the expansion of Eq. (V.15).

D. **Write a linear combination of the Slater determinants (cf. Eq. (V.15)) corresponding to the $1s^2$, $2s^2$, $3s^2$, and $4s^2$. How would one determine k_{1s^2}, k_{2s^2}, k_{3s^2}, and k_{4s^2}. (You don't actually need to determine them.)**

If one proceeded to carry out the preceding exercise, one would find that the energy gained from adding all possible s-functions (including the single excitations) is very modest, leveling out at about $E = -2.879$. This is to be contrasted with the exact energy

$$E_{exact}^{He} = -2.9037 \text{ Hartree} \tag{V.24}$$

In fact, most of the "additional gain" above the Eckhart function arises because additional ζ values allow us to better approximate the true shapes of the $1s$ and $2s$ orbitals, and not the importance of Slater determinants from electron configurations like $3s^2$ or $4s^2$. For example, if you had used 15 different values of ζ in constructing the 1s orbital,

$$\psi_{1s}^{(15)}\left(\boldsymbol{r}\right) = \sum_{i=1}^{15} c_i \sqrt{\frac{\zeta_i^3}{\pi}} e^{-\zeta_i r} \tag{V.25}$$

you would get an energy of $E = -2.8617$ Hartree, which is slightly lower than your result in part B, indicating that more than 2 ζ-values are needed to model the 1s orbital.

In order to better approximate the energy, we return to our discussion of electron correlation. The Eckhart function models the tendency of electrons to "correlate" so that when one electron is close to the nucleus, the other is far away. This is called "radial" or "in-out" correlation and it accounts for about 40% of the total "correlation energy." The other type of correlation is called angular correlation: if there is an electron on one side of the nucleus, the other electron tends to stay on the "other side" of the nucleus. This accounts for about 60% of the electron correlation in He. Why is angular correlation more important? In radial correlation electrons "avoid one another" but in angular correlation not only do the electrons avoid one another, they keep the nucleus between them. The effect is obvious from the following figure: when electrons keep the nucleus between them their potential energy decreases.
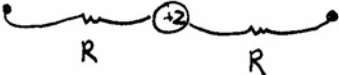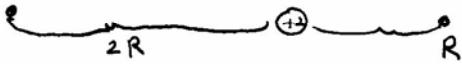
angular correlation

radial correlation

$$V = -\frac{Z}{R} - \frac{Z}{R} + \frac{1}{2R}$$
$$= -\frac{4Z+1}{R}$$

$$V = -\frac{Z}{R} - \frac{Z}{2R} + \frac{1}{R}$$
$$= -\frac{3Z+2}{2R}$$

$$V = -\frac{Z}{R} - \frac{Z}{2R} + \frac{1}{3R}$$
$$= -\frac{3Z + 2/3}{2R}$$

Angular correlations are modeled by mixing in configurations like $1s2p$, $2p^2$, $1s3d$, $3d^2$, etc..

The simplest configuration that models angular correlation is probably that of Taylor and Parr, namely

$$
\Psi_{c_{1s},c_{2p}}(\boldsymbol{r}_1,\boldsymbol{r}_2) = c_{1s}
\begin{vmatrix}
\psi_{1s}^{TP}(\boldsymbol{r}_1)\alpha(1) & \psi_{1s}^{TP}(\boldsymbol{r}_2)\alpha(2) \\
\psi_{1s}^{TP}(\boldsymbol{r}_1)\beta(1) & \psi_{1s}^{TP}(\boldsymbol{r}_2)\beta(2)
\end{vmatrix}
+ c_{2p}
\left(
\begin{vmatrix}
\psi_{2p_x}^{TP}(\boldsymbol{r}_1)\alpha(1) & \psi_{2p_x}^{TP}(\boldsymbol{r}_2)\alpha(2) \\
\psi_{2p_x}^{TP}(\boldsymbol{r}_1)\beta(1) & \psi_{2p_x}^{TP}(\boldsymbol{r}_2)\beta(2)
\end{vmatrix}
+
\begin{vmatrix}
\psi_{2p_y}^{TP}(\boldsymbol{r}_1)\alpha(1) & \psi_{2p_y}^{TP}(\boldsymbol{r}_2)\alpha(2) \\
\psi_{2p_y}^{TP}(\boldsymbol{r}_1)\beta(1) & \psi_{2p_y}^{TP}(\boldsymbol{r}_2)\beta(2)
\end{vmatrix}
+
\begin{vmatrix}
\psi_{2p_z}^{TP}(\boldsymbol{r}_1)\alpha(1) & \psi_{2p_z}^{TP}(\boldsymbol{r}_2)\alpha(2) \\
\psi_{2p_z}^{TP}(\boldsymbol{r}_1)\beta(1) & \psi_{2p_z}^{TP}(\boldsymbol{r}_2)\beta(2)
\end{vmatrix}
\right)
\quad \text{(V.26)}
$$

$$
= \left[c_{1s}\psi_{1s}^{TP}(\boldsymbol{r}_1)\psi_{1s}^{TP}(\boldsymbol{r}_2) + c_{2p}
\begin{pmatrix}
\psi_{2p_x}^{TP}(\boldsymbol{r}_1)\psi_{2p_x}^{TP}(\boldsymbol{r}_2) \\
+\psi_{2p_y}^{TP}(\boldsymbol{r}_1)\psi_{2p_y}^{TP}(\boldsymbol{r}_2) \\
+\psi_{2p_z}^{TP}(\boldsymbol{r}_1)\psi_{2p_z}^{TP}(\boldsymbol{r}_2)
\end{pmatrix}
\right] (\alpha(1)\beta(2) - \alpha(2)\beta(1))
$$

where

$$\psi_{1s}^{TP}(\boldsymbol{r}) = \sqrt{\frac{(1.69)^3}{\pi}}\, e^{-1.69r}$$

$$\psi_{2p_{\{x,y,z\}}}(\boldsymbol{r}) = \sqrt{\frac{5^3}{32\pi}} \cdot \left(5\cdot\{x,y,z\}\right) e^{-5r/2}. \qquad \text{(V.27)}$$

Before we proceed further, we simplify the form of Eq. (V.26). We do this by substituting Eqs. (V.27) into Eq. (V.26), using the relationship between spherical and Cartesian coordinates

20

$$x = r\sin(\theta)\cos(\phi)$$
$$y = r\sin(\theta)\sin(\phi) \tag{V.28}$$
$$z = r\cos(\theta)$$

and simplifying.

E.   Show that Equation (V.26) can be written as

$$\Psi_{c_{1s},c_{2p}}(\boldsymbol{r}_1,\boldsymbol{r}_2) = c_{1s}\left(\frac{4.83}{\pi}e^{-1.69(r_1+r_2)}\right)$$

$$+c_{2p}\left(\frac{3125}{32\pi}r_1r_2e^{-\left(5(r_1+r_2)\big/2\right)}\begin{pmatrix}\cos(\theta_1)\cos(\theta_2)\\+\sin(\theta_1)\sin(\theta_2)\cos(\phi_1-\phi_2)\end{pmatrix}\right) \tag{V.29}$$

(We ignore the spin factor here; it does not affect the energy since the Hamiltonian is spin-independent.

Next we evaluate

$$E(c_{1s},c_{2p}) = \frac{\left\langle\Psi_{c_{1s},c_{2p}}\left|\hat{H}\right|\Psi_{c_{1s},c_{2p}}\right\rangle}{\left\langle\Psi_{c_{1s},c_{2p}}\left|\Psi_{c_{1s},c_{2p}}\right.\right\rangle}\Psi_{c_{1s},c_{2p}}(\boldsymbol{r}_1,\boldsymbol{r}_2) \tag{V.30}$$

and obtain the minimum energy values for c_{1s} and c_{2p} by solving the simultaneous equations

$$\frac{\partial E(c_{1s},c_{2p})}{\partial c_{1s}} = 0$$
$$\frac{\partial E(c_{1s},c_{2p})}{\partial c_{2s}} = 0 \tag{V.31}$$

For convenience, we define

$$\Psi_{1s}^{TP}(\boldsymbol{r}_1,\boldsymbol{r}_2) \equiv \left(\frac{4.83}{\pi}e^{-1.69(r_1+r_2)}\right)$$

$$\Psi_{2p}^{TP}(\boldsymbol{r}_1,\boldsymbol{r}_2) \equiv \left(\frac{3125}{32\pi}r_1r_2e^{-\left(5(r_1+r_2)\big/2\right)}\left(\cos(\theta_1)\cos(\theta_2)+\sin(\theta_1)\sin(\theta_2)\cos(\phi_1-\phi_2)\right)\right)$$

$$\varepsilon_{1s} \equiv \left\langle\Psi_{1s}^{TP}(\boldsymbol{r}_1,\boldsymbol{r}_2)\left|\hat{H}\right|\Psi_{1s}^{TP}(\boldsymbol{r}_1,\boldsymbol{r}_2)\right\rangle \tag{V.32}$$

$$\varepsilon_{2p} \equiv \left\langle\Psi_{2p}^{TP}(\boldsymbol{r}_1,\boldsymbol{r}_2)\left|\hat{H}\right|\Psi_{2p}^{TP}(\boldsymbol{r}_1,\boldsymbol{r}_2)\right\rangle$$

$$\beta_{1s,2p} = \beta_{2p,1s} \equiv \left\langle\Psi_{1s}^{TP}(\boldsymbol{r}_1,\boldsymbol{r}_2)\left|\hat{H}\right|\Psi_{2p}^{TP}(\boldsymbol{r}_1,\boldsymbol{r}_2)\right\rangle$$

Note that ε_{1s} and ε_{2p} can be interpreted as the energies of the Slater determinants associated with the $1s^2$ and $2p^2$ configurations, respectively.

F.   Show that

$$E(c_{1s},c_{2p}) = \frac{c_{1s}^2\varepsilon_{1s} + c_{2p}^2\varepsilon_{2p} + 2c_{1s}c_{2p}\beta_{1s,2p}}{c_{1s}^2 + c_{2p}^2} \tag{V.33}$$

You can assume that the coefficients of the wave functions are real.

From Eqs. (V.31) and (V.33), we have

$$\frac{\partial E\left(c_{1s}, c_{2p}\right)}{\partial c_{2p}} = \frac{2c_{1s}\varepsilon_{1s} + 2c_{2p}\beta_{1s,2p}}{\left(c_{1s}^2 + c_{2p}^2\right)} - \frac{2c_{1s}\left(c_{1s}^2\varepsilon_{1s} + c_{2p}^2\varepsilon_{2p} + 2c_{1s}c_{2p}\beta_{1s,2p}\right)}{\left(c_{1s}^2 + c_{2p}^2\right)^2}$$

$$0 = \frac{2c_{1s}\varepsilon_{1s} + 2c_{2p}\beta_{1s,2p}}{\left(c_{1s}^2 + c_{2p}^2\right)} - \frac{2c_{1s}E\left(c_{1s}, c_{2p}\right)}{\left(c_{1s}^2 + c_{2p}^2\right)} \tag{V.34}$$

$$0 = \left(\varepsilon_{1s} - E\left(c_{1s}, c_{2p}\right)\right)c_{1s} + c_{2p}\beta_{1s,2p}$$

$$c_{1s} = \left(\frac{\beta_{1s,2p}}{E\left(c_{1s}, c_{2p}\right) - \varepsilon_{1s}}\right)c_{2p}$$

and similarly

$$c_{2p} = \left(\frac{\beta_{1s,2p}}{E\left(c_{1s}, c_{2p}\right) - \varepsilon_{2p}}\right)c_{1s}. \tag{V.35}$$

Note that if $\beta = 0$ then there is no correction to the wave function.

Substituting Eq. (V.35) into Eq. (V.34) gives

$$c_{1s} = \left(\frac{\beta_{1s,2p}}{E\left(c_{1s}, c_{2p}\right) - \varepsilon_{1s}}\right)\left(\frac{\beta_{1s,2p}}{E\left(c_{1s}, c_{2p}\right) - \varepsilon_{2p}}\right)c_{1s}$$

$$1 = \frac{\beta_{1s,2p}^2}{\left(E\left(c_{1s}, c_{2p}\right) - \varepsilon_{1s}\right)\left(E\left(c_{1s}, c_{2p}\right) - \varepsilon_{2p}\right)} \tag{V.36}$$

G.   Solve Eq. (V.36) for E, obtaining

$$E = \frac{\left(\varepsilon_{1s} + \varepsilon_{2p}\right)}{2} \pm \frac{\left(\varepsilon_{1s} - \varepsilon_{2p}\right)}{2}\sqrt{1 + \left(\frac{2\beta_{1s,2p}}{\left(\varepsilon_{1s} - \varepsilon_{2p}\right)}\right)^2} \tag{V.37}$$

If we assume that $2\beta \ll \left|\alpha_{\alpha} - \alpha_b\right|$, then we can use the geometric series

$$(1 + x)^k = 1 + k \cdot x + \frac{k(k-1)}{2}x^2 + \frac{k(k-1)(k-3)}{3!}x^3 + \ldots \tag{V.38}$$

to obtain

$$E \approx \varepsilon_{1s} - \frac{\beta^2}{\varepsilon_{2p} - \varepsilon_{1s}} \tag{V.39}$$

as an approximation to the ground state energy.

H.   Derive Eq. (V.39).

If we do all the integrals, we obtain the Taylor-Parr energy of -2.869 Hartree.

We can include both radial and angular correlation by combining the approaches in Eqs. (V.11) and (V.26). This gives a wave function of the form

$$\Psi_{c_{1s}, c_{2p}}\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) = \begin{vmatrix} c_{1s}\left(\psi_{1s}^{(a)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(b)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(b)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(a)}\left(\boldsymbol{r}_2\right)\right) \\ +c_{2p}\begin{pmatrix} \psi_{2p_x}^{TP}\left(\boldsymbol{r}_1\right)\psi_{2p_x}^{TP}\left(\boldsymbol{r}_2\right) + \psi_{2p_y}^{TP}\left(\boldsymbol{r}_1\right)\psi_{2p_y}^{TP}\left(\boldsymbol{r}_2\right) \\ +\psi_{2p_z}^{TP}\left(\boldsymbol{r}_1\right)\psi_{2p_z}^{TP}\left(\boldsymbol{r}_2\right) \end{pmatrix}\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right) \end{vmatrix} \tag{V.40}$$

Choosing the coefficients in Eq. (V.40) so as to minimize the energy, we obtain $E \approx -2.895$ Hartree. The error is still over $5\ \frac{kcal}{mol}$.

I. Referring to Eq. (V.35), explain why states with energies that are very different from the true ground state energy are less important than those whose energies are close by. For example, suppose that $\beta_{1s,2p} = \beta_{1s,3p} = \beta_{1s,4p}$, etc.. Which of the associated configurations, $2p^2$, $3p^2$, or $4p^2$ will make the most important contribution to the ground state?

J. Based on Eq. (V.39), why do you expect the relative importance of electron correlation to decrease as the atomic number increases.

In fact, the correlation energy of the 2-electron atom approaches a constant ($\varepsilon_{1s} - E \approx .0464$) as the atomic number goes to infinity, and the relative size of the correlation energy ($\frac{\varepsilon_{1s} - E}{E}$) approaches zero.

VI. The Spin-Orbit Interaction (.7)

In this problem we'll describe what the spin-orbit interaction is. Imagine that you are an electron, orbiting the nucleus. Then, from your perspective, the nucleus is a moving charge.[2] Moving charges (= currents) produce magnetic fields. The magnetic field due to the moving nucleus interacts with the magnetic moment of the electron, and this is the spin-orbit interaction.

Now we will add some mathematics to this qualitative picture. You may have seen (or you may not have seen) the formula for electric and magnetic fields in a moving frame. That is, suppose that in the "rest frame" of the nucleus, there is only an electric field, which is equal to

$$\boldsymbol{E}(\boldsymbol{r}) = -\nabla\Phi(\boldsymbol{r}) \tag{VI.1}$$

where $\Phi(\boldsymbol{r})$ is the electrostatic potential. An electron at $\boldsymbol{r}$ in an *N*-electron atom feels an electrostatic potential due to the nucleus and *N-1* other electrons moves in an electrostatic potential of

$$\Phi(\boldsymbol{r}) = \frac{Z}{r} + \sum_{i=1}^{N-1} \frac{-1}{|\boldsymbol{r} - \boldsymbol{r}_i|} \tag{VI.2}$$

due to the nuclei and the electrons. For any molecule containing a "heavy" atom, clearly the sum will be dominated by the nucleus. Consequently, we will neglect the second term in Eq. (VI.2). (That is, we are neglecting the so-called "orbit-orbit" interaction, which couples the orbital angular momenta of the electrons together.) This gives

$$\Phi(\boldsymbol{r}) = \frac{Z}{r}$$
$$\boldsymbol{E}(\boldsymbol{r}) = -\frac{Z}{r^2}\hat{r} \tag{VI.3}$$

where $\hat{r}$ is the unit vector in the radial direction.

Now, let us transform to a coordinate system that moves with the electrons. In this coordinate system the electric field and magnetic field are given by

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[2] This, of course, is the reason why Galileo had problems with the pope; from the standpoint of earth it is essentially impossible to determine whether the sun is orbiting the earth (Platonic picture) or the earth is orbiting the sun (Copernican picture). From the standpoint of pre-Renaissance humans, it sure looked like the sun was orbiting the earth. Ditto, from the perspective of an electron, it looks like the nucleus is orbiting you.

$$E'(r) = \frac{1}{\sqrt{1 - \frac{|v(r)|^2}{c^2}}}\left[\left(E(r) - \frac{v(r) \times B(r)}{c}\right) - \frac{1}{1 + \sqrt{1 - \frac{|v(r)|^2}{c^2}}}\left(\frac{v(r)}{c}\right)\left(\frac{v \cdot E(r)}{c}\right)\right]$$

$$B'(r) = \frac{1}{\sqrt{1 - \frac{|v(r)|^2}{c^2}}}\left[\left(B(r) - \frac{v(r) \times E(r)}{c}\right) - \frac{1}{1 + \sqrt{1 - \frac{|v(r)|^2}{c^2}}}\left(\frac{v(r)}{c}\right)\left(\frac{v \cdot B(r)}{c}\right)\right]$$

(VI.4)

Here E' and B' are the electric and magnetic fields for a particle with velocity $v(r)$ and c is the speed of light. Now, there is no magnetic field due to the nucleus, so $B = 0$.[3] So

$$E'(r) = \frac{1}{\sqrt{1 - \frac{|v(r)|^2}{c^2}}}\left[E(r) - \frac{1}{1 + \sqrt{1 - \frac{|v(r)|^2}{c^2}}}\left(\frac{v(r)}{c}\right)\left(\frac{v \cdot E(r)}{c}\right)\right]$$

$$B'(r) = \frac{-1}{\sqrt{1 - \frac{|v(r)|^2}{c^2}}}\frac{v(r) \times E(r)}{c}$$

(VI.5)

A. Using Eq. (VI.5), argue that

$$E'(r) = E(r) + \mathcal{O}\left(\frac{v^2}{c^2}\right)$$

$$B'(r) = -\frac{v(r) \times E(r)}{c} + \mathcal{O}\left(\frac{v^3}{c^3}\right)$$

(VI.6)

Here $v = |v|$ is the speed and $\mathcal{O}\left(\frac{v^k}{c^k}\right)$ denotes that we are neglecting terms of order $\frac{v^k}{c^k}$ (and smaller).

Recall that the interaction strength between a magnetic field and the spin magnetic moment is given by

$$E_{\mathrm{magnetic}} \equiv -\boldsymbol{\mu}_S \cdot B.$$

(VI.7)

Also, recall that the angular momentum operator is given by

$$L = r \times p$$

(VI.8)

B. Show that

$$E_{magnetic} = -\boldsymbol{\mu}_S \cdot \left(\frac{Z}{cr^3} L\right)$$

$$= \frac{gZ}{2c^2 r^3} S \cdot L$$

$$\approx \frac{Z}{c^2 r^3} S \cdot L.$$

(VI.9)

This result is off by a factor of two. The reason is because we have assumed that the spin of the electron is the same in the "moving frame" and the "rest frame"; we have not considered the proper relativistic way to take the spin from one frame to the other. To understand why this is important, consider that the electron is moving in a non-uniform magnetic field due to the nucleus. Just like the Stern-Gerlach apparatus (wherein an electron beam was passed through a nonuniform magnetic field) this "measures" the spin of the electrons, causing them to precess about the direction of the field. Thus, the motion of the

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[3] This, of course, is not strictly true. The nuclear spin is produces a magnetic moment, and this enters into Eq. (VI.4). The effect is usually small, but the coupling between the electron spin and the nuclear spin is important in NMR spectroscopy, for example. In addition, the spins of the other electrons in the system produce a magnetic field (which leads to the so-called spin-spin interaction) and the orbitals of the other electrons in the system produce a magnetic field (which leads to the spin-other-orbit interaction). These effects and the orbit-orbit interaction, however, are smaller than the spin-orbit interaction for heavy atoms (because the magnitude of the spin-orbit interaction grows more quickly with Z). For He, however, all the effects are rather important.

electrons causes the spin to change. Thus, in the "moving nucleus" frame (in which the electron is at rest), the electron's spin cannot perfectly align with the magnetic field due to the "moving nucleus;" instead it precesses about the optimal alignment. This reduces the strength of the spin-orbit interaction by a factor of two, giving the correct result of

$$E_{magnetic}^{correct} \approx \frac{Z}{2c^2 r^3} \boldsymbol{S} \cdot \boldsymbol{L}. \tag{VI.10}$$

C. Using Eq. (VI.10), argue that the Hamiltonian for an *N*-electron atom *including* spin-orbit effects can be written as

$$\hat{H} = \sum_{i=1}^{N} \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + \frac{Z}{4c^2} \frac{\hat{J}^2\left(\boldsymbol{r}_i\right) - \hat{L}^2\left(\boldsymbol{r}_i\right) - \hat{S}^2\left(\boldsymbol{r}_i\right)}{r_i^3} \right) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|} \tag{VI.11}$$

VII. The Form of the Wave Function Close to the Nucleus of an Atom (.8)

Suppose we are given an *N*-electron *P*-atom molecule. The electronic Hamiltonian is

$$\hat{H} = \sum_{i=1}^{N} \left(\frac{-\nabla_i^2}{2} - \sum_{\alpha=1}^{P} \frac{Z}{\left|\boldsymbol{r}_i - \boldsymbol{R}_\alpha\right|} \right) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|} \tag{VII.1}$$

Now, suppose that

$$\left|\boldsymbol{r}_1 - \boldsymbol{R}_1\right| \ll \left|\boldsymbol{r}_k - \boldsymbol{R}_\alpha\right| \qquad k \text{ and } \alpha \text{ are not both equal to 1.}$$

$$\left|\boldsymbol{r}_1 - \boldsymbol{R}_1\right| \ll \left|\boldsymbol{r}_i - \boldsymbol{r}_j\right| \qquad 1 \leq i, j \leq N \tag{VII.2}$$

That is, electron one and nucleus one are closer to coalescence than any other pairing of electrons and nuclei or electrons and electrons. Then we have that

$$\frac{1}{\left|\boldsymbol{r}_1 - \boldsymbol{R}_1\right|} \gg \frac{1}{\left|\boldsymbol{r}_k - \boldsymbol{R}_\alpha\right|} \qquad k, \alpha \neq 1$$

$$\frac{1}{\left|\boldsymbol{r}_1 - \boldsymbol{R}_1\right|} \gg \frac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|} \qquad 1 \leq i, j \leq N \tag{VII.3}$$

Choose the origin of the coordinate system to be at $\boldsymbol{R}_1$. That is, choose $\boldsymbol{R}_1 = \boldsymbol{0}$.

A. Show that the electronic Schrödinger equation can be written as

$$\left(\begin{array}{l} -\dfrac{\nabla_1^2}{2} - \dfrac{Z_1}{r_1} - \displaystyle\sum_{\alpha=2}^{P} \dfrac{Z_\alpha}{\left|\boldsymbol{r}_1 - \boldsymbol{R}_\alpha\right|} + \displaystyle\sum_{j=2}^{\infty} \dfrac{1}{\left|\boldsymbol{r}_j - \boldsymbol{r}_1\right|} \\ + \displaystyle\sum_{i=2}^{N} \left(-\dfrac{\nabla_i^2}{2} - \displaystyle\sum_{\alpha=1}^{P} \dfrac{Z}{\left|\boldsymbol{r}_i - \boldsymbol{R}_\alpha\right|} \right) + \displaystyle\sum_{i=2}^{N} \displaystyle\sum_{j=i+1}^{N} \dfrac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|} \end{array} \right) \Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right) = E\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right) \tag{VII.4}$$

B. Derive the next two equations:

$$\left(\begin{array}{l} -\dfrac{\nabla_1^2}{2} - \dfrac{Z_1}{r_1} - \displaystyle\sum_{\alpha=2}^{P} \dfrac{Z_\alpha}{R_\alpha} + \displaystyle\sum_{j=2}^{N} \dfrac{1}{r_j} + \displaystyle\sum_{\alpha=2}^{P} \mathcal{O}\left(\dfrac{r_1}{R_\alpha}\right) + \displaystyle\sum_{j=2}^{N} \mathcal{O}\left(\dfrac{r_1}{r_j}\right) \\ + \displaystyle\sum_{i=2}^{N} \left(-\dfrac{\nabla_i^2}{2} - \displaystyle\sum_{\alpha=1}^{P} \dfrac{Z_\alpha}{\left|\boldsymbol{r}_i - \boldsymbol{R}_\alpha\right|} \right) + \displaystyle\sum_{i=2}^{N} \displaystyle\sum_{j=i+1}^{N} \dfrac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|} \end{array} \right) \Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right) = E\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right) \tag{VII.5}$$

$$\left(-\frac{\nabla_1^2}{2} - \frac{Z_1}{r_1} - \mathcal{O}\left(r_1^0\right) + \mathcal{O}\left(r_1\right) \right) \Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right) = 0$$

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When r_1 is small, the higher order terms in Eq. (VII.5) are very small compared to the terms we are including. Expanding $\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right)$ in a power series about $\boldsymbol{r}_1 = 0$ we have

$$\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right) = \sum_{n=0}^{\infty} \frac{r^n}{n!} \left.\frac{\partial^n \Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right)}{\partial^n r_1}\right|_{r_1=0} \tag{VII.6}$$

C. Show that Eq. (VII.5) is solved (up to constant terms) by

$$\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right) = \Psi\left(0, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right)\left(1 - Z_1 r_1 + \mathcal{O}\left(r_1^2\right)\right). \tag{VII.7}$$

D. Show that Eq. (VII.7) can be rewritten as

$$\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right) = \Psi\left(0, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right)\left(e^{-Z_1 r_1} + \mathcal{O}\left(r_1^2\right)\right). \tag{VII.8}$$

Equation (VII.8) indicates that, very near an atomic nucleus, electrons behave very much like electrons in the hydrogen atom. This, of course, is because when the dominant force on the electron is from a single nucleus, it *feels* a force very much like the force it feels in the hydrogen atom. Note that the form of the solution is *forced* by the fact that in order for Eq. (VII.5) to hold, the kinetic energy term must "cancel out" the potential term. (That is the secret to making this derivation more rigorous.)[4]

E. Show that

$$Z_1 = -\left.\frac{d \ln \Psi\left(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N\right)}{d r_1}\right|_{r_1=0} \tag{VII.9}$$

F. Explain why Eq. (VII.9) is often called the coalescence cusp condition.

VIII. The N/Z Expansion of the Atomic Energy (1.0)

Consider that the ground state wave function for the one-electron atom has the form

$$\Psi\left(\boldsymbol{r}\right) \propto \sqrt{\tfrac{Z^3}{\pi}} e^{-Zr} \tag{VIII.1}$$

Thus, if we were to change variables to

$$\boldsymbol{x} = Z\boldsymbol{r} \tag{VIII.2}$$

that every one-electron atom would have the *same* wave function. Way back in 1930, Hylleraas recognized that if one applied the same coordinate transformation to the many-electron atom, one could write the Schrödinger equation in a semi-universal form;

$$\left(\sum_{i=1}^{N}\left(-\frac{\nabla_{x_i}^2}{2} - \frac{1}{x_i}\right) + \frac{1}{Z}\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|\boldsymbol{x}_i - \boldsymbol{x}_j\right|}\right)\Psi\left(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N\right) = \frac{E(Z)}{Z^2}\Psi\left(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N\right) \tag{VIII.3}$$

A. Derive Eq. (VIII.3)

Equation (VIII.3) is most commonly employed for the 2-electron atom. In this case, one has

$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{x_1} - \frac{1}{x_2} + \frac{1}{Z\left|\boldsymbol{x}_1 - \boldsymbol{x}_2\right|}\right)\Psi\left(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N\right) = \frac{E(Z)}{Z^2}\Psi\left(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N\right) \tag{VIII.4}$$

One can use perturbation theory to find the energy. Specifically, one has

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[4] There is a much more rigorous way, due to Kato, to derive these results. However, here I want to stress how "reasonable" the result is, rather than the high-powered mathematics required to prove it properly.

$$E(Z) = Z^2 \sum_{n=0}^{\infty} \varepsilon_n \left(\frac{1}{Z}\right)^n$$

<div style="text-align:right">(VIII.5)</div>

$$= \sum_{n=0}^{\infty} \varepsilon_n \left(\frac{1}{Z}\right)^{n-2}$$

Clearly, the ground state energy of the Hamiltonian in Eq. (VIII.4) is given by

$$\mathcal{E}_0 = \sum_{n=0}^{\infty} \varepsilon_n \left(\frac{1}{Z}\right)^n = \frac{E(Z)}{Z^2}$$

<div style="text-align:right">(VIII.6)</div>

B. Show that $\varepsilon_0 = -1$ and $\varepsilon_1 = \frac{5}{8}$.

Equation (VIII.5) is called the $\frac{1}{Z}$-expansion for the energy of a 2-electron atom.

Inspecting Eq. (VIII.5), one expects that the expansion will be extraordinarily good for large atoms, as in that case terms with $n \geq 2$ will be of negligible importance. On the other hand, it is not surprising that Eq. (VIII.5) fails to converge when

$$\frac{1}{Z} < \frac{1}{Z_{critical}} = 1.09766$$

<div style="text-align:right">(VIII.7)</div>

This implies that

$$Z_{critical} = .911029.$$

<div style="text-align:right">(VIII.8)</div>

One can—albeit with *great* difficulty—compute the energy of an atom with atomic charge $Z_{critical}$. It is *exactly* equal to

$$E_{critical} = -\frac{Z_{critical}^2}{2}.$$

<div style="text-align:right">(VIII.9)</div>

It is commonly true that perturbation series cease converging at a point where the solution changes *qualitatively*.

C. Can you explain what the qualitative difference is between systems with $Z < Z_{critical}$ and systems with $Z > Z_{critical}$?

There is a theorem, due to Darboux, that says that if a function has a branch point at $x = \lambda$ with characteristic exponent κ; that is, if

$$f(x) \propto (\lambda - x)^{\kappa},$$

<div style="text-align:right">(VIII.10)</div>

then the Taylor series,

$$f(x) = \sum_{n=0}^{\infty} f_n x^n$$

<div style="text-align:right">(VIII.11)</div>

will converge for $-\lambda \leq x \leq \lambda$. In addition,

$$\frac{f_{n+1}}{f_n} \sim \frac{1}{\lambda}\left(1 - \frac{(1+\kappa)}{n}\right)$$

<div style="text-align:right">(VIII.12)</div>

will be valid for large *n*. (There are addition terms of order $\frac{1}{n^2}$ and higher that we have neglected.)

D. Confirm Eq. (VIII.12) when $f(x)$ is given by Eq. (VIII.10).

Equation (VIII.10) plays a key role in this theory. Back in 1966 Stillinger fit the values of ε_n for $n = 0, 1, \ldots, 21$ using Eq. (VIII.12) and found that

$$E \propto f(Z)\left(\frac{1}{.8941} - \frac{1}{Z}\right)^{6/5}$$

<div style="text-align:right">(VIII.13)</div>

where $f(Z)$ is a well-behaved function for all $|Z| > .8941$. This arguably provided the first good estimate for $Z_{critical}$. Unfortunately, Stillinger's analysis was not quite right, and subsequent work showed that the actual

expansion as a term proportional to $\dfrac{1}{\sqrt{n}}$, which was neglected in Stillinger's work. This led to the improved estimate for $Z_{critical}$ in Eq. (VIII.8).

For atoms with more than two electrons, one commonly uses the expansion from March and White, namely

$$E\left(Z,N\right) = Z^2 \left(\sum_{m=0}^{\infty} \left(\sum_{n=0}^{\infty} a_{nm} N^{m+\frac{1}{3}-\frac{n}{3}} \right) \left(\frac{1}{Z} \right)^m \right) \tag{VIII.14}$$

E. Show that Eq. (VIII.14) can be rewritten as

$$E\left(Z,N\right) = Z^{7/3} \left(\sum_{m=0}^{\infty} \left(\sum_{n=0}^{\infty} a_{nm} N^{-\frac{n}{3}} \right) \left(\frac{N}{Z} \right)^{m+\frac{1}{3}} \right) \tag{VIII.15}$$

F. Show that Eq. (VIII.15) can be rewritten as

$$E\left(Z,N\right) = Z^{7/3} \left(\sum_{m=0}^{\infty} a_{0m} \left(\frac{N}{Z} \right)^{m+\frac{1}{3}} \right) + Z^2 \left(\sum_{m=0}^{\infty} a_{1m} \left(\frac{N}{Z} \right)^{m} \right) + Z^{5/3} \left(\sum_{m=0}^{\infty} a_{2m} \left(\frac{N}{Z} \right)^{m-\frac{1}{3}} \right) + \ldots$$

$$= \sum_{n=0}^{\infty} \left[\left(\sum_{m=0}^{\infty} a_{nm} \left(\frac{N}{Z} \right)^{m-n/3} \right) Z^{(7-n)/3} \right] \tag{VIII.16}$$

$$= \sum_{n=0}^{\infty} \phi_n \left(\tfrac{N}{Z} \right) Z^{(7-n)/3}$$

Clearly, Eq. (VIII.16) converges rapidly for large atomic numbers, Z. This is useful because we know that in the limit of large atomic numbers, the Mulliken-Itzkowski-Margrave electronegativity

$$\chi\left(N,Z\right) \equiv -\left(\frac{\partial E}{\partial N} \right)_Z \approx \frac{I+A}{2}. \tag{VIII.17}$$

where IP and EA denote the ionization potential and electron affinity respectively.

G. Show that

$$\chi\left(N,Z\right) \equiv -\sum_{n=0}^{\infty} \left(\frac{\partial \phi_n \left(\frac{N}{Z} \right)}{\partial \left(\frac{N}{Z} \right)} \right)_{\frac{N}{Z}=1} Z^{(4-n)/3} \tag{VIII.18}$$

This result is especially powerful because, in the limit of large Z, the *exact* electronegativity of neutral atoms is zero.

H. Use this fact and Eq. (VIII.18) to argue that for neutral atoms in the limit of large atomic number, the electronegativity should be (very roughly) proportional to $Z^{-\frac{1}{3}}$.

Along any given column of the periodic table, one does indeed find that the electronegativity reduces (roughly) as $Z^{-\frac{1}{3}}$. Clearly higher order effects ($Z^{-\frac{2}{3}}$ is never very small in the periodic table) are still important in describing, among other things, the fact the electronegativity of the halogens and Nobel gases surpasses that of the alkali metals and alkaline earths.

IX. Slater Determinants as Descriptions of Atomic Terms (.8)

Let's suppose the p orbitals we are considering have the following properties:

$$\psi_0 \left(r,\theta,\phi\right) = r \cdot f\left(r\right) Y_1^0 \left(\theta,\phi\right)$$

$$\psi_{\pm 1} \left(r,\theta,\phi\right) = r \cdot \frac{f\left(r\right)}{\sqrt{2}} Y_1^{\pm 1} \left(\theta,\phi\right). \tag{IX.1}$$

A. Show that

$$\psi_0\left(r\right) = \psi_z\left(r\right) = zf\left(r\right) \tag{IX.2}$$

$$\frac{\psi_1\left(\boldsymbol{r}\right) + \psi_{-1}\left(\boldsymbol{r}\right)}{\sqrt{2}} = \psi_x\left(\boldsymbol{r}\right) = xf\left(r\right) \tag{IX.3}$$

$$\frac{\psi_1\left(\boldsymbol{r}\right) - \psi_{-1}\left(\boldsymbol{r}\right)}{i\sqrt{2}} = \psi_y\left(\boldsymbol{r}\right) = yf\left(r\right) \tag{IX.4}$$

B. Write out the term diagram for this electron configuration. Which Slater determinants are associated with each spectroscopic term?

C. Show that

$$\Phi\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{-1}\left(\boldsymbol{r}_1\right)\alpha\left(1\right) & \psi_1\left(\boldsymbol{r}_1\right)\beta\left(1\right) \\ \psi_{-1}\left(\boldsymbol{r}_2\right)\alpha\left(2\right) & \psi_1\left(\boldsymbol{r}_2\right)\beta\left(2\right) \end{vmatrix} \tag{IX.5}$$

is not an eigenfunction of $\hat{S}^2$ but is an eigenfunction of $\hat{S}_z$.

D. The Slater determinant in Eq. (IX.5) is not an eigenfunction of $\hat{L}^2$ either, though it is an eigenfunction of $\hat{L}_z$. Can you explain why this is in words? (No equations!)

We consider that the p electrons move in an effective potential due to the nucleus and the other electrons,

$$V\left(r\right) = -\frac{Z}{r} + \int \frac{\rho_{core}\left(x\right)}{\left|\boldsymbol{r} - \boldsymbol{x}\right|} d\boldsymbol{x} \tag{IX.6}$$

where $\rho_{core}\left(\boldsymbol{x}\right)$ is the electron density associated with the closed subshells. Assume that

$$\left[-\frac{\nabla^2}{2} - \frac{Z}{r} + \int \frac{\rho\left(x\right)}{\left|\boldsymbol{r} - \boldsymbol{x}\right|} d\boldsymbol{r}\right]\psi_m\left(\boldsymbol{r}\right) = \varepsilon\psi_m\left(\boldsymbol{r}\right) \tag{IX.7}$$

That is the orbitals given in Eqs. (IX.1)-(IX.4) are eigenfunctions of the one-electron "effective" Hamiltonian,

$$\hat{h}\left(\boldsymbol{r}\right) = -\frac{\nabla^2}{2} + V\left(\boldsymbol{r}\right), \tag{IX.8}$$

where $V\left(r\right)$ is given by Eq. (IX.6). The Schrödinger equation for the p-electrons in the effective potential due to the other electrons and the atomic nucleus is then

$$\left(\hat{h}\left(\boldsymbol{r}_1\right) + \hat{h}\left(\boldsymbol{r}_2\right) + \frac{1}{\left|\boldsymbol{r}_1 - \boldsymbol{r}_2\right|}\right)\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) = E\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right). \tag{IX.9}$$

We have a very simple relationship between the energy of the terms in this case.

$$\frac{E\left(^1S\right) - E\left(^1D\right)}{E\left(^1D\right) - E\left(^3P\right)} = \frac{3}{2} \tag{IX.10}$$

We will first introduce some notation for the key integrals; we have that

$$J_{ij} = \iint \frac{\left|\psi_i\left(\boldsymbol{r}_1\right)\right|^2 \left|\psi_j\left(\boldsymbol{r}_2\right)\right|^2}{\left|\boldsymbol{r}_1 - \boldsymbol{r}_2\right|} d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$\tag{IX.11}$$

$$K_{ij} = \iint \frac{\left(\psi_i\left(\boldsymbol{r}_1\right)\psi_j^*\left(\boldsymbol{r}_1\right)\right)\left(\psi_i\left(\boldsymbol{r}_2\right)\psi_j^*\left(\boldsymbol{r}_2\right)\right)^*}{\left|\boldsymbol{r}_1 - \boldsymbol{r}_2\right|} d\boldsymbol{r}_1 d\boldsymbol{r}_2.$$

E. **Write the energy of the state with** $M_L = 1, M_S = 1$ **in terms of** ε **(from Eq. (IX.7)),** J_{ij}**, and** K_{ij}**.**

F. **Write the energy of the state with** $M_L = 2, M_S = 0$ **in terms of** ε **(from Eq. (IX.7)),** J_{ij}**, and** K_{ij}**.**

Going any further than this requires us to evaluate a lot of integrals (and if you wish to do them, I'll give you an appropriate number of points), but you could, by evaluating the integrals in Eqs. (IX.11), derive Eq. (IX.10)