

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. The average degree of difficulty will usually be about 1.0 (and is occasionally a bit more). You must choose *two* problems off this set.

I. Mass Effects in One Electron atoms (.7)

In presenting the molecular Hamiltonian we neglected several effects. Now we want to show that these effects are, in fact, negligible. We will concentrate on the Hydrogen atom in this problem, since we can do all the necessary evaluations analytically.

We neglected the gravitational attraction between the nucleus and the electron in the Hydrogen atom. Specifically, using Newton's law of gravitation, there is a gravitational potential between the electron and the nucleus of

$$V(r) \equiv \frac{-GM_H m_e}{r} \quad (1.1)$$

where $G = 6.672 \cdot 10^{-11} \frac{\text{Nm}^2}{\text{kg}^2}$, m_e is the electron mass, M_H is the mass of the nucleus, and r is the distance between the nucleus and the electron.

- A. Add this term to the Hamiltonian for the hydrogen atom (in the Born-Oppenheimer approximation). How does the energy change?

Hint: You will find this easiest if you convert to atomic units. Remember that a Joule is a Newton-meter ($1 \text{ J} = 1 \text{ Nm}$.)

The Hydrogen atom is a special system because we don't have to neglect the motion of the nucleus. Rather, we can separate the center-of-mass motion from the relative motion of the nucleus and the electrons by defining a center-of-mass coordinate

$$\mathbf{X} \equiv \frac{M\mathbf{R} + m\mathbf{r}}{m + M} \quad (1.2)$$

and a relative position coordinate

$$\mathbf{x} = \mathbf{r} - \mathbf{R}. \quad (1.3)$$

- B. Show that the Hamiltonian for the Hydrogen atom can be written as

$$\hat{H} \equiv \frac{-\hbar^2}{2M_{total}} \nabla_X^2 + \frac{-\hbar^2}{2\mu} \nabla_x^2 - \frac{Ze^2}{4\pi\epsilon_0 |\mathbf{x}|} \quad (1.4)$$

where the total mass is given by $M_{total} = m + M$ and the reduced mass is given by $\mu = \frac{mM}{m+M}$.

- C. Write the Hydrogen atom wave function as a product of two wave functions, $\Psi_{\mathbf{x}, \mathbf{X}} = \psi_{\mathbf{x}} \phi_{\mathbf{X}}$, one for the center-of-mass motion and one for the relative motion. Using the technique of separation of variables, find the lowest-energy state. (Use atomic units; it's easier.)
- D. Compare this energy to the energy of the Hydrogen atom in the Born-Oppenheimer approximation. Which is more important, gravitational attraction (part A) or nuclear motion (part C)?

II. The Hydrogen Atom and the Harmonic Oscillator (.9)

There are a number of different methods for solving the Hydrogen atom problem. One method that you aren't likely to find in any "standard" texts is the following, in which the Hydrogen atom is transformed into a two-dimensional Harmonic Oscillator. In polar coordinates, the radial equation for the isotropic two-dimensional harmonic oscillator is

$$\frac{-1}{2} \left[\frac{d^2 R_{p,q}}{dr^2} + \frac{1}{r} \frac{dR_{p,q}}{dr} \right] + \frac{q^2}{2r^2} R_{p,q} + \frac{1}{2} k r^2 R_{p,q} = \mathcal{E}_{p,q} R_{p,q} . \quad (\text{II.1})$$

The solutions to this equation can be obtained from the results in Cartesian coordinates, where the Schrödinger equation is

$$\frac{-1}{2} \left(\left[\frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right] - k(x^2 + y^2) \right) \Psi_{x,y} = \mathcal{E} \Psi_{x,y} \quad (\text{II.2})$$

and can be solved by separation of variables. One obtains

$$\mathcal{E}_{p,q} = 2p + |q| + 1 \sqrt{k} \quad p = 0, 1, 2, \dots \quad (\text{II.3})$$

$$R_{p,q}(r) \propto e^{-\frac{\sqrt{k}\rho^2}{2}} \rho^q L_p^q(\sqrt{k}\rho^2) . \quad (\text{II.4})$$

(The key identity is the relationship between the Hermite polynomials and the Laguerre polynomials, namely

$$\begin{aligned} H_{2m}(x) &\propto L_m^{1/2}(x^2) \\ H_{2m+1}(x) &\propto L_m^{-1/2}(x^2) . \end{aligned} \quad (\text{II.5})$$

If you are feeling adventurous, I invite you to derive Eqs. (II.3) and (II.4).

To show how this is related to the hydrogenic atom, let's take the radial equation for the hydrogen atom,

$$\frac{-1}{2} \left[\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \right] \psi_{n,l}(r) + \frac{l(l+1)}{2r^2} \psi_{n,l}(r) - \frac{Z}{r} \psi_{n,l}(r) = E_{n,l} \psi_{n,l}(r) \quad (\text{II.6})$$

Define

$$\phi_{n,l}(r) = r \psi_{n,l}(r) . \quad (\text{II.7})$$

A. Show that

$$\left(\frac{-1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) \phi_{n,l}(r) = E_{n,l} \phi_{n,l}(r) \quad (II.8)$$

B. Show that this equation can be rewritten in the form of a 2-D harmonic oscillator, specifically,

$$\frac{-1}{2} \left[\frac{d^2 R_{p,q}}{dx^2} + \frac{1}{x} \frac{dR_{p,q}}{dx} \right] + \frac{2l+1}{2x^2} R_{p,q}(x) + \frac{1}{2} (-8E_{n,l} x^2 R_{p,q}(x) - 4Z R_{p,q}(x)) \quad (II.9)$$

(Hint, use the transformation of variables $x = \sqrt{r}$ and $\phi(x) = xR(x)$)

C. Use Eqs. (II.1) and (II.3) to derive the energy levels of the Hydrogen atom as a function of p and the angular momentum quantum number, l .

D. Use Eqs. (II.1) and (II.4) to derive the radial component of the hydrogen atoms wave function (to within a constant of proportionality).

III. Relativistic corrections for the Hydrogen Atom (1.1)

Before discussing relativistic corrections for the hydrogen atom, we establish a technique for evaluating key integrals. Specifically, we want to have a method for evaluating integrals of the form

$$\langle r^n \rangle \equiv \int_0^\infty \int_0^{2\pi} \int_0^\pi r^n |\Psi_{n,l,m}(r, \theta, \phi)|^2 r^2 \sin \theta d\theta d\phi dr \quad (III.1)$$

where $\Psi_{n,l,m}(r, \theta, \phi) = \psi_{n,l}(r) Y_l^m(\theta, \phi)$ is an eigenfunction for the Hydrogen atom. To do this, start with Eq. (II.8). Multiply both sides of this equation by $r^{\lambda+1} \frac{d\phi_{n,l}}{dr} - \frac{\lambda+1}{2} r^\lambda \phi_{n,l}$ and integrate with respect to r from zero to infinity.

A. Show that one can obtain the recurrence relation

$$\frac{\lambda+1}{n^2} Z^2 \langle r^\lambda \rangle - Z [2\lambda+1] \langle r^{\lambda-1} \rangle + \lambda [l(l+1) - \frac{1}{4} (\lambda+1)(\lambda-1)] \langle r^{\lambda-2} \rangle = 0 \quad (III.2)$$

(Hint: You will need to use integration by parts several times. When integrating by parts, you may assume that $\lambda > 0$. This assumption will be relaxed later.)

B. Show that $\langle r^{-1} \rangle = \frac{Z}{n^2}$.

C. Show that $\langle r \rangle = \frac{1}{2Z} [3n^2 - l(l+1)]$.

(Hint. Because the wave function is normalized, $\langle r^0 \rangle = 1$.)

We need a different method to obtain $\langle r^{-2} \rangle$. We rewrite Eq. (II.8) as

$$\frac{d^2 \phi_{n,l} r}{\phi_{n,l} r^2} = -2E_{n,l} + \frac{l(l+1)}{r^2} - \frac{2Z}{r} \quad (\text{III.3})$$

Suppose $k = n - l$ is constant. Then

$$\frac{d^2 \phi_{n,l} r}{\phi_{n,l} r^2} = \frac{Z^2}{k+l^2} + \frac{l(l+1)}{r^2} - \frac{2Z}{r} \quad (\text{III.4})$$

Differentiating both sides by l we obtain

$$\begin{aligned} \frac{d}{dl} \frac{d^2 \phi_{n,l} r}{\phi_{n,l} r^2} &= \frac{d}{dl} \left(\frac{Z^2}{k+l^2} + \frac{l(l+1)}{r^2} - \frac{2Z}{r} \right) \\ -\frac{d\phi_{n,l} r}{\phi_{n,l} r^2} \frac{d^2 \phi_{n,l} r}{dr^2} + \frac{1}{\phi_{n,l} r} \frac{d}{dl} \frac{d^2 \phi_{n,l} r}{dr^2} &= \frac{-2Z^2}{k+l^3} \frac{d(k+l)}{dl} + \frac{2l+1}{r^2} \\ &= \frac{-2Z^2}{n^3} + \frac{2l+1}{r^2}. \end{aligned} \quad (\text{III.5})$$

D. Show that

$$\int_0^\infty \phi_{n,l} r^2 \left(-\frac{d\phi_{n,l} r}{\phi_{n,l} r^2} \frac{d^2 \phi_{n,l} r}{dr^2} + \frac{1}{\phi_{n,l} r} \frac{d}{dl} \frac{d^2 \phi_{n,l} r}{dr^2} \right) dr = 0 \quad (\text{III.6})$$

(Hint: Use integration by parts. Assume that l is large enough so that the boundary term vanishes.)

E. Use Eqs. (III.5) and (III.6) to show that $\langle r^{-2} \rangle = \frac{2Z^2}{n^3(2l+1)}$.

F. Show that $\langle r^{-3} \rangle = \frac{Z\langle r^{-2} \rangle}{l(l+1)}$.

The spin-orbit correction to the energy for the Hydrogen atom is given by the formula

$$E_{n,l,s,j} = -\frac{Z^2}{2n^2} + \zeta_{n,l} \cdot \begin{cases} \frac{l}{2} & j = l + \frac{1}{2} \\ \frac{l+1}{2} & j = l - \frac{1}{2} \end{cases} \quad (\text{III.7})$$

where $j = l + s$ measures whether the spin- and orbital- angular momenta are aligned. $\zeta_{n,l}$ is defined by

$$\zeta_{n,l} \equiv \int_0^\infty |\phi_{n,l} r|^2 \frac{1}{2c^2} \frac{1}{r} \frac{dV}{dr} dr = \int_0^\infty |\phi_{n,l} r|^2 \frac{1}{2c^2} \frac{1}{r} \frac{d(-\frac{Z}{r})}{dr} dr \quad (\text{III.8})$$

G. Using Eqs. (III.7) and (III.8), what is the first-order change in the energy due to the spin-orbit interaction?

Additional relativistic effects are related to the motion of the electron. Recall that in relativity, we have that the energy of a free electron is given by

$$E^2 = c^2 \mathbf{p} \cdot \mathbf{p} + m_e c^2{}^2. \quad (\text{III.9})$$

(When the momentum, $\mathbf{p} \approx m\mathbf{v}$, is zero, then this reduces to the famous “rest-mass energy” equation of Einstein.) For a bound electron, we will have

$$E = \sqrt{c^2 \mathbf{p} \cdot \mathbf{p} + m_e c^2{}^2} + V(\mathbf{r}) \quad (\text{III.10})$$

where $V(\mathbf{r})$ is the potential interaction term. Insofar as the momentum of the electron is small compared to $m_e c$ (because the electron is assumed to be moving much slower than the speed of light), we can take the expression

$$E = m_e c^2 \sqrt{1 + \frac{\mathbf{p} \cdot \mathbf{p}}{m_e^2 c^2}} + V(\mathbf{r}) \quad (\text{III.11})$$

and expand it using the binomial expansion.

H. Show that this gives

$$E = m_e c^2 + V(\mathbf{r}) + \frac{\mathbf{p} \cdot \mathbf{p}}{2m_e} - \frac{\mathbf{p} \cdot \mathbf{p}{}^2}{8m_e^3 c^2} + \dots \quad (\text{III.12})$$

Substituting the quantum-mechanical momentum operator for the classical momentum, one finds that

$$E = m_e c^2 - \frac{\hbar^2}{2m_e} \nabla^2 + V(\mathbf{r}) - \frac{\left(\frac{-\hbar^2}{2m_e} \nabla^2 \right)^2}{2m_e c^2} + \dots \quad (\text{III.13})$$

The last term shown in this expansion is expected to be a small in size (owing to the factor of c^2 in the denominator) and so we use perturbation theory to evaluate the shift in energy. In particular, the relativistic correction to the energy will be, to first order,

$$\Delta E_{rel}^1 = -\frac{1}{2m_e c^2} \left\langle \Psi_{n,l,m} \left| \left(\frac{-\hbar^2}{2m_e} \nabla^2 \right) \left(\frac{-\hbar^2}{2m_e} \nabla^2 \right) \right| \Psi_{n,l,m} \right\rangle \quad (\text{III.14})$$

I. Show that Eq. (III.14) can be rewritten (in atomic units) as

$$\Delta E_{rel}^1 = -\frac{1}{2c^2} \left\langle \Psi_{n,l,m} \left| \left(-\frac{Z^2}{2n^2} + \frac{Z}{r} \right)^2 \right| \Psi_{n,l,m} \right\rangle. \quad (\text{III.15})$$

(Hint: use the fact that the kinetic energy operator is Hermitian.)

J. Evaluate the integral using the results of parts B and E. Compare the importance of the Spin-Orbit (G) and “scalar relativistic” effects (J).

IV. The Effect of the Size of the Nucleus (.8)

A key result, which we shall have many occasions to use, is the expansion of $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$ in terms of the spherical harmonics. We derive this result here though, admittedly, we will skip a couple key steps. We start with the fact that

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{\sqrt{|\mathbf{r} - \mathbf{r}'|^2}} = \frac{1}{\sqrt{\mathbf{r} - \mathbf{r}' \cdot \mathbf{r} - \mathbf{r}'}} \quad (\text{IV.1})$$

Next, we have that

$$\mathbf{r} - \mathbf{r}' \cdot \mathbf{r} - \mathbf{r}' = \mathbf{r} \cdot \mathbf{r} - 2\mathbf{r} \cdot \mathbf{r}' + \mathbf{r}' \cdot \mathbf{r}' = r^2 - 2rr' \cos \gamma + r'^2 \quad (\text{IV.2})$$

where γ is the angle between the vectors \mathbf{r} and \mathbf{r}' and $r \equiv |\mathbf{r}|$ and $r' \equiv |\mathbf{r}'|$. Equation (IV.2) is just the law of cosines. Substituting Eq. (IV.2) into Eq. (IV.1), we have

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{\sqrt{r^2 - 2rr' \cos \gamma + r'^2}} \quad (\text{IV.3})$$

Define $r_>$ to be the larger of r and r' and $r_<$ to be the smaller of r and r' . Then

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{\sqrt{r_>^2 + r_<^2 - 2r_>r_< \cos \gamma}} = \frac{1}{r_>} \left(\frac{1}{\sqrt{1 + \frac{r_<^2}{r_>^2} - \frac{2r_<}{r_>} \cos \gamma}} \right) \quad (\text{IV.4})$$

A. Use the binomial theorem to obtain

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r_>} \left(1 - \frac{1}{2} \left(\frac{r_<^2}{r_>^2} - \frac{2r_<}{r_>} \cos \gamma \right) + \frac{3}{8} \left(\frac{r_<^2}{r_>^2} - \frac{2r_<}{r_>} \cos \gamma \right)^2 - \frac{5}{16} \left(\frac{r_<^2}{r_>^2} - \frac{2r_<}{r_>} \cos \gamma \right)^3 + \dots \right) \quad (\text{IV.5})$$

At this stage, one can group terms of similar order to obtain the expansion

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r_>} \sum_{l=0}^{\infty} \left(\frac{r_<}{r_>} \right)^l P_l \cos \gamma \quad (\text{IV.6})$$

where the first few Legendre polynomials are given by

$$\begin{aligned} P_0(x) &= 1 \\ P_1(x) &= x \\ P_2(x) &= \frac{1}{2} (3x^2 - 1) \\ P_3(x) &= \frac{1}{2} (5x^3 - 3x) \\ &\vdots \end{aligned} \quad (\text{IV.7})$$

B. Verify the first four terms in the series in Eq. (IV.6).

Unsold's theorem (which is the so-called "sum rule" for spherical harmonics) indicates that

$$P_l \cos \gamma = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_l^m(\theta, \phi) Y_l^m(\theta', \phi') \quad (\text{IV.8})$$

where the points $\mathbf{r} = r, \theta, \phi$ and $\mathbf{r}' = r', \theta', \phi'$ are not expressed in spherical harmonics. Substitution of Eq. (IV.8) in Eq. (IV.6) gives the useful result

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r_>} \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \left(\frac{r_{\leq}}{r_>} \right)^l Y_l^m(\theta, \phi) Y_l^m(\theta', \phi'). \quad (\text{IV.9})$$

We can apply this result to the problem of correcting for the finite size of the nucleus. We have, very roughly, that the radius of the nucleus is

$$R_Z \approx 2.27 \cdot 10^{-5} \text{ Bohr } \sqrt[3]{2Z} \approx 2.86 \cdot 10^{-5} \cdot \sqrt[3]{Z} \quad (\text{IV.10})$$

Suppose the nuclear charge is uniformly distributed in a sphere of this radius. The charge density is then

$$\rho_Z \equiv \frac{\text{charge}}{\text{volume}} \approx \frac{Z}{\frac{4\pi}{3} (2.27 \cdot 10^{-5} \sqrt[3]{2Z})^3} \approx \frac{Z}{2Z \cdot \frac{4\pi}{3} (1.17 \cdot 10^{-14})^3} \approx 1.02 \cdot 10^{13} \frac{e}{\text{Bohr}} \quad (\text{IV.11})$$

inside the sphere and zero outside. The Hamiltonian can then be written as

$$\left(\frac{-\nabla^2}{2} - \int \frac{\rho_{\text{nuclear}}(\mathbf{x})}{|\mathbf{r} - \mathbf{x}|} d\mathbf{x} \right) \Psi(\mathbf{r}) = E \Psi(\mathbf{r}) \quad (\text{IV.12})$$

where

$$\Phi(\mathbf{r}) \equiv - \int \frac{\rho_{\text{nuclear}}(\mathbf{x})}{|\mathbf{r} - \mathbf{x}|} d\mathbf{x} \quad (\text{IV.13})$$

is the Coulomb potential due to the nucleus. Here

$$\rho_{\text{nuclear}}(\mathbf{x}) = \begin{cases} \rho_Z & |\mathbf{x}| = x < R_Z \\ 0 & |\mathbf{x}| = x \geq R_Z \end{cases} \quad (\text{IV.14})$$

To evaluate Eq. (IV.13), we use Eq. (IV.9). Using Eq. (IV.9), we have

$$\begin{aligned} \Phi(\mathbf{r}) &\equiv - \int \frac{\rho_{\text{nuclear}}(\mathbf{x})}{|\mathbf{r} - \mathbf{x}|} d\mathbf{x} \\ &= -\rho_Z \int_0^{R_Z} \int_0^\pi \int_0^{2\pi} \frac{1}{|\mathbf{r} - \mathbf{x}|} x^2 \sin \theta \, dx d\theta d\phi \end{aligned} \quad (\text{IV.15})$$

C. Show that

$$\begin{aligned} \Phi(r < R_Z) &= -2\pi\rho_Z \left(R_Z^2 - \frac{1}{3}r^2 \right) \\ \Phi(r > R_Z) &= -\frac{Z}{r}. \end{aligned} \quad (\text{IV.16})$$

Once we have Eq. (IV.16), we can rewrite the Schrödinger equation (cf. Eq. (IV.12)) as

$$\left(\frac{-\nabla^2}{2} - \frac{Z}{r} + \varepsilon(r) \right) \Psi(\mathbf{r}) = E \Psi(\mathbf{r}) \quad (\text{IV.17})$$

where

$$\varepsilon(r) = \begin{cases} \frac{Z}{r} + \frac{Z}{2R_Z} - \frac{r^2}{R_Z^2} - 3 & r < R_Z \\ 0 & r \geq R_Z \end{cases} \quad (\text{IV.18})$$

is a small perturbation.

D. Use first-order perturbation theory to estimate the energy change in the of a one-electron atom due to the finite size of the nucleus.

Hint: Some of the integrals are quite difficult. However, because R_Z is very small, $\psi(R_Z) \approx \psi(0)$. Ergo, one can replace the wave function by its value at and near zero. The integrals become trivial. In particular, write the radial wave function as

$$R_{n,l}(r) = \sum_{k=0}^{\infty} \frac{r^k}{k!} \left. \frac{dR_{n,l}}{dr} \right|_{r=0} \quad (\text{IV.19})$$

and approximate the integral using only the first non-vanishing term. You will find it helpful to know that

$$L_n^\alpha(0) = \binom{n+\alpha}{\alpha} \equiv \frac{(n+\alpha)!}{\alpha! n!}. \quad (\text{IV.20})$$

and the formula for the wave function in terms of the associated Laguerre polynomials is

$$\Psi_{n,l,m}(r, \theta, \phi) \propto \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \left(\frac{2Zr}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi). \quad (\text{IV.21})$$

E. The approximation used in part D only works for states with $l = 0$. How can you approximate the result when $l > 0$? What do you conclude?

V. Normalization of the Laguerre Polynomials (.8)

The generating function for a sequence of functions, $f_n(x)$, is defined as

$$G(s) = \sum_{n=0}^{\infty} a_n f_n(x) s^n \quad (\text{V.1})$$

A. Explain why

$$\left. \frac{d^n G(s)}{ds^n} \right|_{s=0} \propto f_n(x). \quad (\text{V.2})$$

To show the utility of the generating function, we consider the problem of finding the normalization constant for the Hydrogen atom wave functions. The generating function for the associated Laguerre polynomials is

$$\frac{e^{-\frac{sx}{1-s}}}{1-s} = \sum_{n=0}^{\infty} L_n^p(x) s^n \quad (\text{V.3})$$

Next, construct the integral

$$\int_0^{\infty} x^{p+1} e^{-x} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} L_m^p(x) L_n^p(x) s^m t^n dx. \quad (\text{V.4})$$

The integral in Eq. (V.4) is of the general form

$$E_n(\alpha) = \int_0^{\infty} r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}} \quad (\text{V.5})$$

To evaluate this integral, note that

$$\int_0^{\infty} e^{-\alpha r} dr = -\frac{1}{\alpha} e^{-\alpha r} \Big|_0^{\infty} = \frac{1}{\alpha}. \quad (\text{V.6})$$

Then, one has that

$$\frac{\partial^m E_{n=0}}{\partial \alpha^m} = -1^m \int_0^{\infty} r^m e^{-\alpha r} dr \quad (\text{V.7})$$

so

$$\begin{aligned} \int_0^{\infty} r^m e^{-\alpha r} dr &= -1^m \frac{\partial^m E_{n=0}}{\partial \alpha^m} \\ &= -1^m \frac{\partial^m}{\partial \alpha^m} \alpha^{-1} \\ &= -1^m \left[-1^m \frac{m!}{\alpha^{m+1}} \right] \\ &= \frac{m!}{\alpha^{m+1}}. \end{aligned} \quad (\text{V.8})$$

Equation (V.5) follows.

B. Using Eq. (V.5), show that we can write Eq. (V.4) as

$$\int_0^{\infty} x^{p+1} e^{-x} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} L_m^p(x) L_n^p(x) s^m t^n dx = 1 - s - t + st \sum_{k=0}^{\infty} \frac{p+1+k!}{k!} s^k t^k \quad (\text{V.9})$$

whenever $-1 < st < 1$.

C. Grouping terms of equal powers, show that

$$\int_0^{\infty} x^{p+1} e^{-x} L_m^p(x) L_m^p(x) dx = \frac{(m+p)! (2m+p+1)}{m!} \quad m \geq 1 \quad (\text{V.10})$$

VI. Recursion Relations and Orthogonal Polynomials (.8)

The hydrogen atom wave functions can be written in terms of the associated Laguerre polynomials,

$$\Psi_{n,l,m}^S(r, \theta, \phi) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{n-l-1!}{2n(n+l)!}} \left(\frac{2Zr}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi) \quad (\text{VI.1})$$

A. Use the Rodrigues formula,

$$L_m^k(x) = \frac{1}{m!} \cdot \frac{1}{x^k e^{-x}} \frac{d^m}{dx^m} (x^m x^k e^{-x}) \quad (\text{VI.2})$$

Show that Eq. (VI.1) does, in fact, satisfy the Schrödinger equation for the Hydrogen atom.

(Hint: First substitute in the form of Eq. (VI.1). Then, substitute Eq. (VI.2) into the differential equation for the associated Laguerre polynomial.)

Any orthogonal polynomial satisfies a three-term recursion relation with the general form

$$P_{n+1} x - a_n x + b_n P_n x + c_n P_{n-1} x = 0 \quad (\text{VI.3})$$

where $c_0 = 0$ and $c_n = \frac{a_n}{a_{n-1}}$. A useful result associated with the recursion formula is the Christoffel-Darboux formula,

$$\sum_{n=0}^N P_n x P_n y = \frac{P_N y P_{N+1} x - P_N x P_{N+1} y}{a_N x - y} \quad (\text{VI.4})$$

To derive the Christoffel-Darboux formula, we use induction. First, when $N = 1$

$$\begin{aligned} \sum_{n=0}^1 P_n x P_n y &= \frac{P_0 y P_1 x - P_0 x P_1 y}{a_1 x - y} \\ P_0 x P_0 y &= \frac{P_0 y a_0 x + b_0 P_0 x - P_0 x a_0 y + b_0 P_0 y}{a_0 x - y} \\ &= \frac{a_0 x - y P_0 y P_0 x}{a_0 x - y}. \end{aligned} \quad (\text{VI.5})$$

B. Show that if Eq. (VI.4) holds for $N = M \geq 0$, then it also holds for $N = M + 1$.

When $x = y$, Eq. (VI.4) is an indeterminate form. To simplify, we use L'Hôpital's rule. Specifically, we define the variables

$$\begin{aligned} R &= \frac{x+y}{2} \\ r &= \frac{x-y}{2} \end{aligned} \quad (\text{VI.6})$$

Then

$$\begin{aligned} x &= R + r \\ y &= R - r \end{aligned} \quad (\text{VI.7})$$

So

$$\sum_{n=0}^N P_n x P_n y = \frac{P_N R - r P_{N+1} R + r - P_N R + r P_{N+1} R - r}{2a_N r} \quad (\text{VI.8})$$

Then we can evaluate

$$\lim_{r \rightarrow 0} \frac{P_N R - r P_{N+1} R + r - P_N R + r P_{N+1} R - r}{2a_N r} \quad (\text{VI.9})$$

C. Show that

$$\sum_{n=0}^N P_n R P_n R = \frac{P_N R \frac{dP_{N+1} R}{dR} - P_{N+1} R \frac{dP_N R}{dR}}{a_N} \quad (\text{VI.10})$$

Suppose we are given an M -electron system, where each electron pair occupies an orbital that is related to an orthogonal polynomial. The probability distribution of observing an electron at a point is then the probability of observing an electron in orbital $\psi_0 x$ at a point plus the probability of observing an electron in orbital $\psi_1 x$ at a point plus the probability of observing an electron in orbital $\psi_2 x$ at a point, ..., plus the

probability of observing an electron in $\psi_N(x)$ at a point, where $N = \frac{M}{2}$ is the number of occupied orbitals. We have, then, that

$$\rho(x) = \sum_{n=0}^N 2 \psi_n(x) \psi_n(x) \quad (\text{VI.11})$$

$\rho(x)$ is the electron density.

D. Explain where the factor of 2 in Eq. (VI.11) comes from.

Obviously the Christoffel-Darboux formula (and its extensions) are useful in evaluating this quantity. As an example, consider the harmonic oscillator. (The orbitals for electrons in extended aromatic systems, quantum dots and wells, and many other systems are often approximated in terms of the harmonic oscillator wave functions.) The “orbitals” for harmonically confined electrons in one dimension are

$$\Psi_n(x) = \frac{\sqrt[4]{\omega}}{\sqrt{2^n n! \sqrt{\pi}}} e^{-\frac{\omega x^2}{2}} H_n(x \sqrt{\omega}) \quad (\text{VI.12})$$

where $H_n(x)$ are the Hermite polynomials and ω is the classical frequency of the oscillator. (For the Hermite polynomials, $a_n = 2$, $b_n = 0$, and $c_n = 2n$ in Eq. (VI.3). Using this result, one can approximate the density for harmonically confined electrons. One interesting result is that for large numbers of electrons, the density of a d -dimensional harmonic oscillator is given by

$$\rho(\mathbf{r}) = \lim_{\beta \rightarrow 0} \left(\frac{\omega}{2\pi \sinh \beta \omega} \right)^{\frac{d}{2}} e^{-\tanh\left(\frac{\omega \beta}{2}\right) \omega r^2} \quad (\text{VI.13})$$

E. Argue that when one confines a very large number of electrons, the density approaches uniformity. Can you rationalize this based on the shapes of the harmonic oscillator wave functions?

This is a general tendency: when you concentrate large numbers of electrons in a region of space then one always finds that the electron density tends to approach uniformity. In practice, however, this limit is rarely approached because usually electrons dissociate from the system before a high degree of uniformity is achieved.

VII. Expectation Values in the Hydrogen Atom (.9)

The purpose of this exercise is to gain experience in evaluating operators for atomic wave functions. You will require the form of the 1s, 2s and 2p orbitals:

$$\begin{aligned} \psi_{1s}(r) &= \sqrt{\frac{Z^3}{\pi}} e^{-Zr} \\ \psi_{2s}(r) &= \sqrt{\frac{Z^3}{32\pi}} (2 - Zr) e^{-Zr/2} \\ \psi_{2p_z}(r, \theta) &= \sqrt{\frac{Z^3}{32\pi}} Zr e^{-Zr/2} \cos \theta \end{aligned} \quad (\text{VII.1})$$

You will have to evaluate numerous integrals with of the form

$$E_n \propto \int_0^{\infty} r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}} \quad (\text{VII.2})$$

To evaluate this integral, note that

$$\int_0^{\infty} e^{-\alpha r} dr = -\frac{1}{\alpha} e^{-\alpha r} \Big|_0^{\infty} = \frac{1}{\alpha}. \quad (\text{VII.3})$$

Then, one has that

$$\frac{\partial^m E_{n=0}}{\partial \alpha^m} = -1^m \int_0^{\infty} r^m e^{-\alpha r} dr \quad (\text{VII.4})$$

so

$$\begin{aligned} \int_0^{\infty} r^m e^{-\alpha r} dr &= -1^m \frac{\partial^m E_{n=0}}{\partial \alpha^m} \\ &= -1^m \frac{\partial^m}{\partial \alpha^m} \alpha^{-1} \\ &= -1^m \left[-1^m \frac{m!}{\alpha^{m+1}} \right] \\ &= \frac{m!}{\alpha^{m+1}}. \end{aligned} \quad (\text{VII.5})$$

Equation (V.5) follows.

- A. Compute the expectation value of $\langle r^k \rangle$ for the 1s-orbital, $k \geq -2$.
- B. Compute the expectation value of $\langle r^k \rangle$ for the 2s-orbital, $k \geq -2$.
- C. Compute the expectation value of $\langle r^k \rangle$ for the 2p_z-orbital, $k \geq -2$. Do you expect the same results for other 2p orbitals?
- D. Show that the most probable distance for an electron in a hydrogenic orbital with principle quantum number n and the maximum permissible orbital angular momentum quantum number, $l = n - 1$, is

$$r_{n,l}^{\text{most probable}} = \frac{n^2}{Z} \quad (\text{VII.6})$$

- E. Waller's formula gives the average distance of an electron from the nucleus in any state of a Hydrogenic atom. Show that your results in parts A-C agree with Waller's relation,

$$\langle r \rangle_{n,l,m} \equiv \frac{1}{2Z} [3n^2 - l(l+1)] \quad (\text{VII.7})$$

Often one defines the "radius" of an orbital in a many-electron atom using either Equation (VII.6) or Eq. (VII.7), where Z is replaced with the "effective nuclear charge" for the orbital.

- F. Which definition for the orbital radius predicts larger orbitals? What can you say about the relative size of the two radii when $n \rightarrow \infty$?

Using the effective nuclear charge in the highest occupied orbital as a measure of the “size” of the atom gives an effective approximation to the “covalent” radius. To approximate the van der Waal’s radius of an atom, we solve for the “classical turning point” of an electron. The classical turning point of a particle consists of the place where its total energy and potential energy are equal: at such a point a classical particle has zero kinetic energy and thus it “reverses direction” and begins descending in the potential energy surface. There is very little probability of observing a quantum particle outside the “classically allowed” region defined as those places where the total energy of the electron is greater than the potential energy.

- G. Show that the classical turning point for an electron with energy E in the 1-electron atom is

$$r_{\text{cl. t.p.}} \equiv -\frac{Z}{E} \quad (\text{VII.8})$$

The energy of an electron very far from a many-electron atom is equal to minus the ionization potential of that atom (cf. Eq. (XI.17)).

- H. Using Eq. (XI.27), which relates the ionization potential to the effective nuclear charge, show that the classical turning radius for a many-electron atom is approximately

$$r_{\text{cl. t.p.}} \equiv \sqrt{\frac{2n^2}{IP}} \quad (\text{VII.9})$$

Equation (VII.9) is exact for a one-electron atom.

We can state the Heisenberg Uncertainty principle as

$$\sigma_r \sigma_p \geq \frac{\hbar}{2} \quad (\text{VII.10})$$

where

$$\sigma_r \equiv \sqrt{\langle \mathbf{r} \cdot \mathbf{r} \rangle - \langle \mathbf{r} \rangle \cdot \langle \mathbf{r} \rangle} \quad (\text{VII.11})$$

and

$$\sigma_p \equiv \sqrt{\langle \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} \rangle - \langle \hat{\mathbf{p}} \rangle \cdot \langle \hat{\mathbf{p}} \rangle} \quad (\text{VII.12})$$

are the standard deviations of the position and momentum, respectively.

- I. Show that Eq. (VII.10) is satisfied for the 1s, 2s, and 2p states of the Hydrogenic atom. You should not need any integrals beyond those already computed (but you can compute them if you need to).

VIII. Perturbation Theory for Degenerate States (1.1)

When a set of degenerate orbitals (or wave functions) is placed in an electromagnetic field, the degeneracy is usually partially removed. For this reason, the perturbation theory of degenerate states is a key tool, not only for describing the splitting of spectral lines, but also for describing the removal of the degeneracy of orbitals with different values of the orbital angular momentum quantum number, l , but

the same principle quantum number, n . We will derive the first order perturbation theory results for degenerate states in this problem.

We are given an unperturbed Hamiltonian, \hat{H} , and we label the states using the Schrödinger equation, so

$$\hat{H}\Psi_n \equiv E_n \Psi_n. \quad (\text{VIII.1})$$

We assume that Ψ_n $_{n=0}^{\infty}$ are orthonormal and form a complete set of functions. In addition, we assume that the functions,

$$(\text{VIII.2})$$

form a g -fold degenerate state, so that

$$\begin{aligned} \langle \Psi_n | \hat{H} | \Psi_n \rangle &= E_{k+1} & k+1 \leq n \leq k+g \\ \langle \Psi_n | \hat{H} | \Psi_n \rangle &\neq E_{k+1} & \text{otherwise.} \end{aligned} \quad (\text{VIII.3})$$

Note that for any choice of the coefficients, c_i $_{i=1}^g$,

$$\hat{H} \sum_{i=1}^g c_i \Psi_i = E_{k+1} \sum_{i=1}^g c_i \Psi_i \quad (\text{VIII.4})$$

That is, any linear combination of a set of degenerate eigenvectors is also an eigenvector of the Hamiltonian.

Now, let's consider the “perturbed” Hamiltonian,

$$\hat{H}_{\text{perturbed}} \lambda \equiv \hat{H} + \lambda \hat{V}. \quad (\text{VIII.5})$$

Unless the perturbation has a special symmetry, for $\lambda \neq 0$ the degeneracy is broken. That is,

$$\langle \Psi_{k+1}^\lambda | \hat{H}_{\text{perturbed}} \lambda | \Psi_{k+1}^\lambda \rangle \neq \langle \Psi_{k+2}^\lambda | \hat{H}_{\text{perturbed}} \lambda | \Psi_{k+2}^\lambda \rangle \neq \dots \neq \langle \Psi_{k+g}^\lambda | \hat{H}_{\text{perturbed}} \lambda | \Psi_{k+g}^\lambda \rangle \quad (\text{VIII.6})$$

where

$$\hat{H} + \lambda \hat{V} \Psi^\lambda = E^\lambda \Psi^\lambda \quad (\text{VIII.7})$$

is the Schrödinger equation describing the perturbed system. This means that, even when $0 < |\lambda| \ll 1$ —that is, the perturbation is very, very, small—the wave functions of the perturbed the system might not resemble those of the unperturbed system. In particular, there is almost always some linear combination of the eigenvectors of the previous system (cf. Eq. (VIII.4)) that is not an eigenvector of the perturbed Hamiltonian.

The way around this issue is straightforward, but a bit complicated. You can find standard treatments in most good quantum texts, and what follows is a bit nonstandard, but hopefully easier to follow. The usual procedure is to write the energy and wave function as a Taylor series in λ ,

$$E_n^\lambda = E_n^{\lambda=0} + \lambda \left. \frac{\partial E_n^\lambda}{\partial \lambda} \right|_{\lambda=0} + \frac{1}{2} \lambda^2 \left. \frac{\partial^2 E_n^\lambda}{\partial \lambda^2} \right|_{\lambda=0} + \dots \quad (\text{VIII.8})$$

$$\Psi_n^\lambda = \Psi_n^{\lambda=0} + \lambda \left. \frac{\partial \Psi_n^\lambda}{\partial \lambda} \right|_{\lambda=0} + \frac{1}{2} \lambda^2 \left. \frac{\partial^2 \Psi_n^\lambda}{\partial \lambda^2} \right|_{\lambda=0} + \dots \quad (\text{VIII.9})$$

The problem is that we don't know which of the many possible unperturbed wave functions (cf. Eq. (VIII.4)) to use for the zeroth order approximation to Ψ_n^λ $_{n=k+1}^{k+g}$.

To get around this issue, let's turn the problem on its head. Consider a perturbation of the Hamiltonian which totally removes the degeneracy,

$$\hat{H}^0 = \hat{H} + \mu \hat{V}. \quad (\text{VIII.10})$$

(The perturbation is assumed to be very small, but still large enough to remove the degeneracy.) For this reason,

$$\hat{H}^0 \Psi_n^0 = E_n^0 \Psi_n^0 \quad (\text{VIII.11})$$

and

$$E_0^0 < E_1^0 < \dots < E_{k+1}^0 < E_{k+2}^0 < \dots. \quad (\text{VIII.12})$$

The “perturbed Hamiltonian”,

$$\begin{aligned} \hat{H}^\mu &\equiv \hat{H}^0 - \mu \hat{V} \\ &= \hat{H}^0 + \mu (-\hat{V}), \end{aligned} \quad (\text{VIII.13})$$

is just the original, degenerate, Hamiltonian. The eigenfunctions and eigenvalues of \hat{H}^μ are known since they are just the eigenfunctions of the original system. For clarity, we adopt a naming convention similar to that in Eqs. (VIII.11) and (VIII.12), namely,

$$\hat{H}^\mu \Psi_n^\mu = E_n^\mu \Psi_n^\mu \quad (\text{VIII.14})$$

where, because of the assumed g-fold degeneracy in Eq. (VIII.2),

$$E_0^\mu < E_1^\mu < \dots < E_{k+1}^\mu = E_{k+2}^\mu = \dots = E_{k+g}^\mu < E_{k+g+1}^\mu \dots. \quad (\text{VIII.15})$$

Equations (VIII.11) and (VIII.14) are our working equations. The choice of notation is such that a superscript μ denotes the Hamiltonian, eigenfunctions, and eigenvectors of the original degenerate system, while a superscript 0 denotes the corresponding quantities for the nondegenerate system described with \hat{H}^0 .

Because the eigenfunctions of \hat{H}^μ form a complete set, we can write Ψ_n^0 as

$$\Psi_n^0 = \sum_{i=0}^{\infty} c_{in}^0 \Psi_i^\mu. \quad (\text{VIII.16})$$

As is usual in perturbation theory, we expand quantities in Taylor series. That is,

$$\hat{H}^\mu = \hat{H}^0 + \mu \left. \frac{\partial \hat{H}^\lambda}{\partial \lambda} \right|_{\lambda=\mu} \quad (\text{VIII.17})$$

$$E_n^\mu = E_n^0 + \mu \left. \frac{\partial E_n^\lambda}{\partial \lambda} \right|_{\lambda=\mu} + \frac{\mu^2}{2} \left. \frac{\partial^2 E_n^\lambda}{\partial \lambda^2} \right|_{\lambda=\mu} + \dots \quad (\text{VIII.18})$$

$$c_{in}^\mu = c_{in}^0 + \mu \left. \frac{\partial c_{in}^\lambda}{\partial \lambda} \right|_{\lambda=\mu} + \frac{\mu^2}{2} \left. \frac{\partial^2 c_{in}^\lambda}{\partial \lambda^2} \right|_{\lambda=\mu} + \dots. \quad (\text{VIII.19})$$

We now substitute these expressions into Eq. (VIII.11), so

$$\begin{aligned} \hat{H}^\mu + \mu \hat{V} \sum_{i=0}^{\infty} c_{in}^0 \Psi_i^\mu &= \left(E_n^\mu - \mu \left. \frac{\partial E_n^\lambda}{\partial \lambda} \right|_{\lambda=\mu} - \frac{\mu^2}{2} \left. \frac{\partial^2 E_n^\lambda}{\partial \lambda^2} \right|_{\lambda=\mu} - \dots \right) \sum_{i=0}^{\infty} c_{in}^0 \Psi_i^\mu \\ \hat{H}^\mu + \mu \hat{V} \sum_{i=0}^{\infty} \left(c_{in}^\mu - \mu \left. \frac{\partial c_{in}^\lambda}{\partial \lambda} \right|_{\lambda=\mu} - \frac{\mu^2}{2} \left. \frac{\partial^2 c_{in}^\lambda}{\partial \lambda^2} \right|_{\lambda=\mu} - \dots \right) \Psi_i^\mu & \\ = \left(E_n^\mu - \mu \left. \frac{\partial E_n^\lambda}{\partial \lambda} \right|_{\lambda=\mu} - \frac{\mu^2}{2} \left. \frac{\partial^2 E_n^\lambda}{\partial \lambda^2} \right|_{\lambda=\mu} - \dots \right) \sum_{i=0}^{\infty} \left(c_{in}^\mu - \mu \left. \frac{\partial c_{in}^\lambda}{\partial \lambda} \right|_{\lambda=\mu} - \frac{\mu^2}{2} \left. \frac{\partial^2 c_{in}^\lambda}{\partial \lambda^2} \right|_{\lambda=\mu} - \dots \right) \Psi_i^\mu & \end{aligned} \quad (\text{VIII.20})$$

The standard perturbation theory idea is that the coefficients of $\mu^0 = 1$, μ , μ^2 , etc. must all be equal. This is because in order for

$$f(x) = \sum_{n=0}^{\infty} a_n \mu^n \quad (\text{VIII.21})$$

to be zero everywhere, all the a_n must equal zero. (Otherwise $|f(x)| > 0$ most places.) Thus, in order for two functions to be equal everywhere,

$$f(\mu) \equiv \sum_{n=0}^{\infty} l_n \mu^n = \sum_{n=0}^{\infty} r_n \mu^n \equiv g(\mu) \quad (\text{VIII.22})$$

we must have that $l_\mu = r_\mu$. (Otherwise $f(\mu) - g(\mu) = \sum_{n=0}^{\infty} (l_n - r_n) \mu^n$ would not equal zero.) For this reason, we must have that the coefficients of $\mu^0 = 1$, μ , μ^2 , etc. on the left-hand-side and right-hand-side of Eq. (VIII.20) must be equal.

For $\mu^0 = 1$, this gives the equation

$$\hat{H}^\mu \sum_{i=0}^{\infty} c_{in}^\mu \Psi_i^\mu = E_n^\mu \sum_{i=0}^{\infty} c_{in}^\mu \Psi_i^\mu \quad (\text{VIII.23})$$

Let us first consider the case where E_n^μ is a non-degenerate state. Then we must have that (to within an arbitrary complex phase factor), $c_{in}^\mu = \delta_{in}$. That is, $c_{in}^\mu = 0$ unless $i = n$ when E_n^μ is a non-degenerate state.

When E_n^μ is a degenerate state, any linear combination of the degenerate eigenfunctions will also be an eigenfunction of \hat{H}^μ , cf. Eq. (VIII.4). So if the states $\Psi_{k+1}^\mu, \Psi_{k+2}^\mu, \dots, \Psi_{k+g}^\mu$ are degenerate, then

$$\hat{H}^\mu \sum_{i=k+1}^{k+g} c_{in}^\mu \Psi_i^\mu = E_n^\mu \sum_{i=k+1}^{k+g} c_{in}^\mu \Psi_i^\mu. \quad (\text{VIII.24})$$

That is, $c_{in} = 0$ unless Ψ_i^μ and Ψ_n^μ have the same energy. Recalling that the Kronecker delta, δ_{ij} , is zero unless its arguments are equal ($i = j$), we can summarize the consequences of Eq. (VIII.23) with

$$\hat{H}^\mu \sum_{i=0}^{\infty} \delta_{E_i E_n} c_{in}^\mu \Psi_i^\mu = E_n^\mu \sum_{i=0}^{\infty} \delta_{E_i E_n} c_{in}^\mu \Psi_i^\mu. \quad (\text{VIII.25})$$

This indicates that we can replace c_{in}^μ with $c_{in}^\mu \delta_{E_i E_n}$.

- A. Show that Eq. (VIII.25) actually agrees with the conclusions in the preceding two paragraphs for both non-degenerate and degenerate states.

The “meat” of our treatment is based on the equating the coefficients of $\mu^1 = \mu$ in Eq. (VIII.20).

- B. When you equate the coefficients of μ in Eq. (VIII.20), show that you obtain the equation

$$\sum_{i=0}^{\infty} c_{in}^\mu \hat{V} \Psi_i^\mu = - \sum_{i=0}^{\infty} \left(\left. \frac{\partial E_n^\lambda}{\partial \lambda} \right|_{\lambda=\mu} c_{in}^\mu + E_n^\mu - E_i^\mu \left. \frac{\partial c_{in}^\lambda}{\partial \lambda} \right|_{\lambda=\mu} \right) \Psi_i^\mu. \quad (\text{VIII.26})$$

The easiest way to solve Eq. (VIII.26) is to multiply both sides by Ψ_m^μ and integrate. We obtain

$$\begin{aligned}
\sum_{i=0}^{\infty} c_{in}^{\mu} \langle \Psi_m^{\mu} | \hat{V} | \Psi_i^{\mu} \rangle &= - \sum_{i=0}^{\infty} \left(\frac{\partial E_n^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} c_{in}^{\mu} + E_n^{\mu} - E_i^{\mu} \frac{\partial c_{in}^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} \right) \langle \Psi_m^{\mu} | \Psi_i^{\mu} \rangle. \\
&= - \sum_{i=0}^{\infty} \left(\frac{\partial E_n^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} c_{in}^{\mu} + E_n^{\mu} - E_i^{\mu} \frac{\partial c_{in}^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} \right) \delta_{mi}. \\
&= - \left(\frac{\partial E_n^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} c_{mn}^{\mu} + E_n^{\mu} - E_m^{\mu} \frac{\partial c_{mn}^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} \right)
\end{aligned} \tag{VIII.27}$$

There are two cases in Eq. (VIII.27). In the first case, $E_n^{\mu} = E_m^{\mu}$. The second term on the right-hand-side then vanishes, and we get

$$\sum_{i=0}^{\infty} \langle \Psi_m^{\mu} | \hat{V} | \Psi_i^{\mu} \rangle c_{in}^{\mu} = - \frac{\partial E_n^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} c_{mn}^{\mu} \quad \text{if } E_m^{\mu} = E_n^{\mu} \tag{VIII.28}$$

Because $c_{in}^{\mu} = 0$ unless $E_i^{\mu} = E_n^{\mu}$, this becomes

$$\sum_{i=k+1}^{k+g} \langle \Psi_m^{\mu} | \hat{V} | \Psi_i^{\mu} \rangle c_{in}^{\mu} = - \frac{\partial E_n^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} c_{mn}^{\mu} \quad \text{if } E_m^{\mu} = E_n^{\mu} \tag{VIII.29}$$

This equation is solved by finding the eigenvalues and eigenvectors of the matrix whose elements are $\langle \Psi_m^{\mu} | \hat{V} | \Psi_i^{\mu} \rangle$, with $k+1 \leq i, m \leq k+g$.

C. Show that if $c_n \equiv [c_{k+1,n}^{\mu}, c_{k+2,n}^{\mu}, \dots, c_{k+g,n}^{\mu}]$ is an eigenvector of

$$V \equiv V_{mi} = \langle \Psi_m^{\mu} | \hat{V} | \Psi_i^{\mu} \rangle; \quad k+1 \leq i, m \leq k+g \tag{VIII.30}$$

then Eq. (VIII.29) is satisfied.

The second case in Eq. (VIII.27) arises when $E_m^{\mu} \neq E_n^{\mu}$. In this case, $c_{mn}^{\mu} = 0$, and so Eq. (VIII.27) simplifies to

$$\frac{\sum_{i=0}^{\infty} \langle \Psi_m^{\mu} | \hat{V} | \Psi_i^{\mu} \rangle c_{in}^{\mu}}{E_m^{\mu} - E_n^{\mu}} = \frac{\partial c_{mn}^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} \tag{VIII.31}$$

where $c_{in}^{\mu} = 1$ if $E_i \neq E_n$, but is otherwise determined by Eq. (VIII.29).

We can now substitute our results back into our original expressions. Using Eqs. (VIII.18) and (VIII.19),

$$E_n^0 \approx E_n^{\mu} - \mu \frac{\partial E_n^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} \tag{VIII.32}$$

and

$$\Psi_n^0 = \sum_{i=0}^{\infty} \left(c_{in}^{\mu} - \mu \frac{\partial c_{in}^{\lambda}}{\partial \lambda} \Big|_{\lambda=\mu} \right) \Psi_i^{\mu} \tag{VIII.33}$$

where the coefficients are determined using Eqs. (VIII.25), (VIII.29), and (VIII.31).

D. Suppose \hat{H}^{μ} has no degenerate states. Show that Eqs. (VIII.32) and (VIII.33) reduce to the usual formulae from first-order perturbation theory,

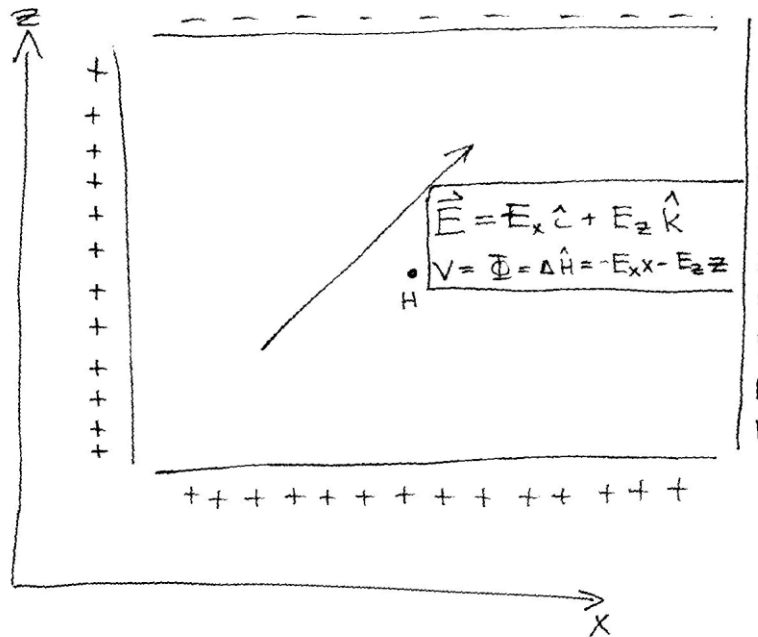
$$E_n^0 = E_n^{\mu} + \langle \Psi_n^{\mu} | \mu \hat{V} | \Psi_n^{\mu} \rangle \tag{VIII.34}$$

$$\Psi_n^0 = \Psi_n^\mu + \sum_{\substack{n=0 \\ n \neq m}}^{\infty} \frac{\langle \Psi_m^\mu | \mu \hat{V} | \Psi_n^\mu \rangle}{E_n^\mu - E_m^\mu} \Psi_m^\mu. \quad (\text{VIII.35})$$

It is important to understand these results; they will be very important in this course!!

IX. Stark Splitting and Orbital Hybridization (.7)

Let us place a Hydrogen atom in an electric field; this can be achieved by placing the atom between capacitors. The geometry of the situation we will consider is below; note that there is no field in the z-direction, and that the fields in the x and y directions need not be the same.



We thus need to consider the effect of the perturbation,

$$\Delta \hat{H} = -E_x x - E_z z \quad (\text{IX.1})$$

on the spectrum of the hydrogen atom. We will calculate the first-order change in energy, which is usually called the first-order Stark effect, after its discoverer. For simplicity, we'll restrict ourselves to the 2s and 2p states,

$$\begin{aligned} \psi_{2s} &= \sqrt{\frac{Z^3}{32\pi}} (2 - Zr) e^{-Zr/2} \\ \psi_{2p_0} &= \sqrt{\frac{Z^3}{32\pi}} Zr e^{-Zr/2} \cos \theta \\ \psi_{2p_{\pm 1}} &= \sqrt{\frac{Z^3}{64\pi}} Zr e^{-Zr/2} \sin \theta e^{\pm i\phi} \end{aligned} \quad (\text{IX.2})$$

Based on the results from problem II, we know that in order to compute the first-order change in energy we only need to construct and diagonalize the perturbation matrix,

$$V_{mn} = \langle \psi_m | -E_x x - E_z z | \psi_n \rangle$$

$$= \langle \psi_m | -E_x r \sin \theta \cos \phi - E_z r \cos \theta | \psi_n \rangle . \quad (\text{IX.3})$$

If I were cruel, I guess I'd let you derive the elements of the perturbation matrix. But you've done enough integrals. The perturbation matrix is (unless I made a math error)

$$V_{2s,2s} = 0 \quad (\text{IX.4})$$

$$V_{2s,2p_0} = -\frac{3}{Z} E_z \quad (\text{IX.5})$$

$$V_{2s,2p_{\pm 1}} = -\frac{3}{\sqrt{2}Z} E_x \quad (\text{IX.6})$$

$$V_{2p_0,2p_{\pm 1}} = 0 \quad (\text{IX.7})$$

$$V_{2p_{+1},2p_{-1}} = 0 \quad (\text{IX.8})$$

$$V_{2p_{\pm 1},2p_{\pm 1}} = 0 \quad (\text{IX.9})$$

$$V_{2p_0,2p_0} = 0 \quad (\text{IX.10})$$

- A. Solve the Eigenvalue problem when $E_x = 0$. What do the eigenvectors of the perturbation matrix remind you of? What are the perturbed energy levels?
- B. Show that the $\psi_{2p_y} r$ is an eigenvector of the perturbation matrix, and that its eigenvalue is zero. That is, this eigenvector is “unperturbed” by an electric field orthogonal to it. It is in this sense that the Cartesian orbitals are the “natural” orbitals for atoms in electric fields.
- C. Show that the first order perturbed energies are

$$E = -\frac{Z^2}{8} \quad (2 \text{ states}) \quad (\text{IX.11})$$

$$E = -\frac{Z^2}{8} \pm \frac{3}{Z} \sqrt{E_x^2 + E_z^2}$$

What is the interpretation of $\sqrt{E_x^2 + E_z^2}$?

X. Wintner's Nodal Theorem (.9)

In class I talked about the fact “interleaving” of nodes for the hydrogen atom. This is a very general property of solutions of the Schrödinger equation (holding, in fact, for any number of electrons). Here we will prove what is sometimes termed “Wintner's nodal theorem”, which is the analogue of the nodal theorem for Sturm-Liouville ordinary differential equations in many dimensions.

Let's start with a wave function, $\Phi_k \tau$. τ can be r , or even something in many more dimensions. Let's suppose that $\Phi_k \tau$ is an eigenfunction for a Hamiltonian,

$$\hat{H} \Phi_k \tau = -\frac{\nabla_\tau^2}{2} + v \tau \quad \Phi_k \tau = E_k \Phi_k \tau , \quad (\text{X.1})$$

where $v(\tau)$ is a potential energy function in the appropriate number of dimensions. Now, let's suppose that we have another wave function, $\Psi_l(\tau)$, that solves the Schrödinger equation

$$\hat{\mathcal{H}}\Psi_l(\tau) = -\frac{\nabla_\tau^2}{2} + \mathcal{V}(\tau) \Psi_l(\tau) = \mathcal{E}_l \Psi_l(\tau). \quad (\text{X.2})$$

Let's suppose $\Phi_k(\tau)$ has n_k nodes, not counting the node at infinite distance from the system (even a 1s orbital has a node at infinite distance!). Let's separate $\Phi_k(\tau)$ into regions where this function does not change sign, Ω_α , $\alpha=1, \dots, n_k+1$, which are separated by nodal surfaces, S_β , $\beta=1, \dots, n_k$, where $S_\beta(\tau)$ is the nodal surface surrounding the region Ω_β .

A. To understand this notation, write the equation for the nodal regions and the nodal surface in the 2s state of the Hydrogen atom.

We use Green's theorem (remember problem 3 in homework set 1) and write

$$\begin{aligned} \iiint_{\Omega_\alpha} \Phi_k(\tau) \nabla_\tau^2 \Psi_l(\tau) - \Psi_l(\tau) \nabla_\tau^2 \Phi_k(\tau) d\tau \\ = \oint_{S_\alpha} \Phi_k(\tau) \nabla_\tau \Psi_l(\tau) \cdot \hat{n}_{S_\alpha} - \Psi_l(\tau) \nabla_\tau \Phi_k(\tau) \cdot \hat{n}_{S_\alpha} dS_\alpha \end{aligned} \quad (\text{X.3})$$

Here, \hat{n}_{S_α} is the inward-looking normal unit vector to the nodal surface, S_α . $-\hat{n}_{S_\alpha}$ is the outward looking unit vector, and this must be used in Green's theorem. The first term on the second line in Eq. (X.3) must be zero because, by definition, $\Phi_k(\tau)$ is zero on its nodal surface.

B. Substituting in the Schrödinger Equations, (X.1) and (X.2), show that

$$\begin{aligned} \iiint_{\Omega_\alpha} \Phi_k(\tau) [2\mathcal{V}(\tau) - 2\mathcal{E}_l] \Psi_l(\tau) - \Psi_l(\tau) [2v(\tau) - 2E_k] \Phi_k(\tau) d\tau \\ = 2 \iiint_{\Omega_\alpha} \Phi_k(\tau) \Psi_l(\tau) [E_k - v(\tau) - \mathcal{E}_l + \mathcal{V}(\tau)] d\tau \\ = \oint_{S_\alpha} \Psi_l(\tau) \nabla_\tau \Phi_k(\tau) \cdot \hat{n}_{S_\alpha} dS_\alpha \end{aligned} \quad (\text{X.4})$$

C. Explain why if $\Phi_k(\tau) < 0$ in the region Ω_α , then $\nabla \Phi_k(\tau) \cdot \hat{n}_{S_\alpha}$ is also less than zero. Similarly, if $\Phi_k(\tau) > 0$ in the region Ω_α , then $\nabla \Phi_k(\tau) \cdot \hat{n}_{S_\alpha}$ is also positive. We write this symbolically as

$$\text{sgn} [\Phi_k(\tau) \in \Omega_\alpha] = \text{sgn} [\nabla \Phi_k(\tau) \cdot \hat{n}_{S_\alpha}] \quad (\text{X.5})$$

Let us assume that $\Psi_l(\tau)$ does not change sign in Ω_α . That is, we assume that $\Psi_l(\tau)$ has no nodes in this region. Then, the sign of the surface integral on the right-hand side of Eq. (X.4) is

$$\text{sgn} \left[\oint_{S_\alpha} \Psi_l(\tau) \nabla_\tau \Phi_k(\tau) \cdot \hat{n}_{S_\alpha} dS_\alpha \right] = \text{sgn} \Psi_l(\tau \in \Omega_\alpha) \text{sgn} \Phi_k(\tau \in \Omega_\alpha) \quad (\text{X.6})$$

and the sign of the volume integral on the left-hand-side of the equation is similarly

$$\begin{aligned} \text{sgn} \left[2 \iiint_{\Omega_\alpha} \Phi_k(\tau) \Psi_l(\tau) [E_k - v(\tau) - \mathcal{E}_l - \mathcal{V}(\tau)] d\tau \right] \\ = \text{sgn} \Psi_l(\tau \in \Omega_\alpha) \text{sgn} \Phi_k(\tau \in \Omega_\alpha) \text{sgn} [E_k - v(\tau) - \mathcal{E}_l - \mathcal{V}(\tau)] \end{aligned} \quad (\text{X.7})$$

where we have assumed that $E_k - v(\tau) - \mathcal{E}_l - \mathcal{V}(\tau)$ does not change sign in the region Ω_α . The key to deriving Eqs. (X.6) and (X.7) is to note that because the integrands do not change sign, the value of the integral must be the same as that of the integrand.

From Eqs. (X.6) and (X.7) we deduce that

$$\begin{aligned} \text{sgn} \Psi_l(\tau \in \Omega_\alpha) \text{sgn} \Phi_k(\tau \in \Omega_\alpha) \\ = \text{sgn} \Psi_l(\tau \in \Omega_\alpha) \text{sgn} \Phi_k(\tau \in \Omega_\alpha) \text{sgn} [E_k - v(\tau) - \mathcal{E}_l - \mathcal{V}(\tau)] \end{aligned} \quad (\text{X.8})$$

whence

$$\begin{aligned} E_k - v(\tau) - \mathcal{E}_l - \mathcal{V}(\tau) &> 0 \\ E_k - v(\tau) &> \mathcal{E}_l - \mathcal{V}(\tau). \end{aligned} \quad (\text{X.9})$$

(Technically we could have that $E_k - v(\tau) = \mathcal{E}_l - \mathcal{V}(\tau)$, but this is just the exceedingly boring case where the eigenvalues and potentials are the same on a given region, so we ignore this case.)

Equation (X.9) is Wintner's nodal theorem. It is an important result, being one of the few tools we have for comparing the nodal structure of eigenfunctions of DIFFERENT Hamiltonians. Choosing $\mathcal{V}(\tau) \rightarrow v(\tau)$ gives especially simple results.

D. Explain why the following is true. Suppose that you are given an eigenstate, Φ_k , of a system with energy E_k . Let $\Phi_{l < k}$ be **any** state with lower energy, $E_l < E_k$. Let Ω_α be **any** “nodal region” of Φ_l . Then Φ_k **must** have a node in Ω_α .

E. Use the result from part D to explain why the “radial” nodes of the “s” orbitals are interleaved (= interlaced).

There are a lot of other interesting consequences of Eq. (X.9) also. For instance, using inequalities like

$$\begin{aligned} -\frac{Z_1^2}{2n_1^2} + \frac{Z_1}{r} &> -\frac{Z_2^2}{2n_2^2} + \frac{Z_2}{r} \\ \frac{Z_2^2}{2n_2^2} - \frac{Z_1^2}{2n_1^2} &> \frac{Z_2 - Z_1}{r} \end{aligned} \quad (\text{X.10})$$

allows us to compare the nodal structures of *different* one-electron atoms.

XI. Rydberg States (1.0)

In many-electron atoms and molecules (even asymmetric molecules!), one observes that the energy-level spacing of highly excited states resemble those of the Hydrogen atom. More precisely, the Energy levels of Rydberg states are written as

$$E_{n,l} = E^+ - \frac{Q + 1}{2} \frac{1}{n - \delta_l}^2 \quad (\text{XI.1})$$

Here, as before, n is the “principle quantum number”. Q is the total charge on the molecule. ($Q = 0$ for a neutral molecule; $Q = +1$ for a cation; etc..) $\delta_l \geq 0$ is called the quantum defect: it measures the extent to which the orbital is “perturbed” by the other electrons in the atom. E^+ is the ground state energy of the $N - 1$ -electron system. It is important to note that the quantum defect tends to be different for each value of the orbital angular momentum quantum number, l . (Typically the quantum defect decreases with increasing l .)

There are several reasons Rydberg states are important in chemistry. First of all, they tend to have high intensities (so they were easy to measure back in the bad old pre-laser days). Second of all, the “selection rules” for allowed and forbidden transitions resemble those of atoms (which, as we’ll learn, are much simpler than those for molecules). Finally, some of the most accurate measurements of the ionization potential of atoms and molecules (especially in the early days of molecular spectroscopy) were made using Rydberg states: back in the 1960’s one could measure the ionization potential of an atom or ion to within a few hundredths of an electron volt by observing various Rydberg series of atoms and molecules.

In this problem, we’ll explain why the Rydberg series exists.

Let’s start by writing the electronic Schrödinger equation for a P-atom N-electron molecule (we’ll use the Born-Oppenheimer approximation),

$$\sum_{n=1}^N \left(-\frac{\nabla_n^2}{2} + \sum_{\alpha=1}^P -\frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \sum_{m=n+1}^N \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \Psi_k^N(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_P) = E_k^N \Psi_k^N(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_P), \quad (\text{XI.2})$$

where E_k^N and Ψ_k^N denoted the energy eigenvalue and eigenfunction of the k^{th} excited state of the N -electron system. Because the nuclear-electron attraction potential depends on the positions of the nuclei, which we consider independently, the nuclear-electron attraction potential is often called the “external” potential (it is, strictly, “external” to the system of electrons, even though the nuclei are embedded in the electron cloud) and denoted

$$v(\mathbf{r}_i) = \sum_{\alpha=1}^P -\frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}. \quad (\text{XI.3})$$

In addition, to a good approximation the nuclei do not relax during the “excitation” of the molecule to an excited state (though, of course, there is relaxation of the molecular geometry subsequent to the electronic excitation), so we consider the nuclei to be fixed in their initial configuration. For this reason, we shall, for notational simplicity, “forget” to denote the dependence on the nuclei in Eq. (XI.2). The Schrödinger equation for the molecule then becomes

$$\sum_{n=1}^N \left(-\frac{\nabla_n^2}{2} + v(\mathbf{r}_n) + \sum_{m=n+1}^N \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \Psi_k^N(\mathbf{r}_1, \dots, \mathbf{r}_N) = E_k^N \Psi_k^N(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (\text{XI.4})$$

Now, suppose electron N is very far from the molecule—so far away that we can effectively “distinguish” it from the other identical electrons in the molecule and so that, to a good approximation, electron N acts “independently” of the other electrons. This allows us to approximate the wave function as

$$\Psi_k^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}, \mathbf{r}_N) = \Psi_0^{N-1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}) f_k(\mathbf{r}_N) \quad (\text{XI.5})$$

where $\Psi_0^{N-1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1})$ is the ground state wave function of the $N-1$ -electron system. That is, we have approximated the wave function as the product of the wave function of the cation and that of a “independent electron” far from the system.

Why is this electron “independent”? Well the probability distribution function of the electrons is:

$$\begin{aligned} \left| \Psi_k^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}, \mathbf{r}_N) \right|^2 &= \left| \Psi_0^{N-1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}) f_k(\mathbf{r}_N) \right|^2 \\ &= \left| \Psi_0^{N-1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}) \right|^2 \left| f_k(\mathbf{r}_N) \right|^2 \end{aligned} \quad (\text{XI.6})$$

Now, just remember that for independent events, the probability of observing A and B is the product of the probabilities, $P(A)P(B)$. (Think—the probability of flipping a coin and it landing “heads” is $\frac{1}{2}$. The probability of flipping a second coin and it landing heads is also $\frac{1}{2}$. The probability of flipping both coins and them both landing heads is thus $\frac{1}{4} = \frac{1}{2} \cdot \frac{1}{2}$. The same is true here: the probability of observing electrons 1, 2, ..., N-1 at some points $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}$ is $\left| \Psi_0^{N-1} \right|^2$. The probability of observing electron N at \mathbf{r}_N is $\left| f_k(\mathbf{r}_N) \right|^2$. The probability of observing both events is given by Eq. (XI.6).

Now, we substitute Eq. (XI.6) into the Schrödinger equation, Eq. (XI.4). We get

$$\begin{aligned} \sum_{n=1}^N \left(-\frac{\nabla_n^2}{2} + \sum_{\alpha=1}^P v(\mathbf{r}_n) + \sum_{m=n+1}^N \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \Psi_{N-1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}) f(\mathbf{r}_N) \\ = E \Psi_{N-1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}) f(\mathbf{r}_N) \end{aligned} \quad (\text{XI.7})$$

A. Show that the N-electron Hamiltonian, \hat{H}_N , can be written as a sum of the $N-1$ -electron Hamiltonian, \hat{H}_{N-1} , and terms involving the N^{th} electron, namely:

$$\hat{H}_N = \hat{H}_{N-1} - \frac{\nabla_N^2}{2} + v(\mathbf{r}_N) + \sum_{m=1}^{N-1} \frac{1}{|\mathbf{r}_m - \mathbf{r}_N|} \quad (\text{XI.8})$$

B. Use (XI.8) to simplify Eq. (XI.7) to the following form:

$$\Psi_0^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) \left(-\frac{\nabla_N^2}{2} + v(\mathbf{r}_N) + \sum_{m=1}^{N-1} \frac{1}{|\mathbf{r}_m - \mathbf{r}_N|} \right) f_k(\mathbf{r}_N) = (E_k^N - E_0^{N-1}) \Psi_0^{N-1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) f_k(\mathbf{r}_N) \quad (\text{XI.9})$$

where E_0^{N-1} is the ground state energy of the cation. Multiply this equation by Ψ_0^{N-1*} and integrate over the first N-1 electronic positions. One obtains

$$\left(-\frac{\nabla_N^2}{2} + v(\mathbf{r}_N) + \left\langle \Psi_0^{N-1} \left| \sum_{m=1}^{N-1} \frac{1}{|\mathbf{r}_m - \mathbf{r}_N|} \right| \Psi_0^{N-1} \right\rangle_{1\dots N-1} \right) f_k(\mathbf{r}_N) = E_k^N - E_0^{N-1} f_k(\mathbf{r}_N), \quad (\text{XI.10})$$

where $\langle | \rangle_{1\dots N-1}$ denotes the fact only the first $N-1$ -electrons are integrated over. Because all the electrons in the cation are identical, we have that

$$\left\langle \Psi_0^{N-1} \left| \sum_{m=1}^{N-1} \frac{1}{|\mathbf{r}_m - \mathbf{r}_N|} \right| \Psi_0^{N-1} \right\rangle_{1\dots N-1} = N-1 \left\langle \Psi_0^{N-1} \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_N|} \right| \Psi_0^{N-1} \right\rangle_{1\dots N-1}. \quad (\text{XI.11})$$

A very useful formula for $\frac{1}{|x-y|}$ exists. Namely,

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{\max r, r'} \left(1 + A \left(\frac{\min r, r'}{\max r, r'} \right) + \frac{3A^2 - 1}{2} \left(\frac{\min r, r'}{\max r, r'} \right)^2 + \dots \right) \quad (\text{XI.12})$$

where

$$\begin{aligned} A &= \cos \alpha \\ &= \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos \phi - \phi' \end{aligned} \quad (\text{XI.13})$$

is the cosine of the angle between the vectors \mathbf{r} and \mathbf{r}' .

Now, since the electron N is very far away from the molecule, the likelihood any electron in the cation is further away than electron N is very, very small. That is, we may assume that almost always,

$$|\mathbf{r}_N| \gg |\mathbf{r}_j|; j = 1, 2, \dots, N-1. \quad (\text{XI.14})$$

(The origin can be set to the “center of charge”, “center of mass”, or any other reasonable point in the “important part” of the molecule.) Using Equation (XI.13) in Eq. (XI.11), one obtains

$$\begin{aligned} N-1 \left\langle \Psi_0^{N-1} \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_N|} \right| \Psi_0^{N-1} \right\rangle_{1\dots N-1} &= N-1 \left\langle \Psi_0^{N-1} \left| \frac{1}{r_N} + A \theta_1, \phi_1, \theta_N, \phi_N \frac{r_1}{r_N^2} \right| \Psi_0^{N-1} \right\rangle_{1\dots N-1} + \dots \\ &= \frac{N-1}{r_N} + \frac{N-1}{r_N^2} \left\langle \Psi_0^{N-1} \left| A \theta_1, \phi_1, \theta_N, \phi_N \cdot r_1 \right| \Psi_0^{N-1} \right\rangle_{1\dots N-1} + \dots \end{aligned} \quad (\text{XI.15})$$

Not only is the N^{th} electron much further from the system than the other electrons, it is also much further from the system than any of the nuclei.

C. Show that

$$v(\mathbf{r}_N) \approx -\frac{\sum_{\alpha=1}^P Z_\alpha}{r_N} - \sum_{\alpha=1}^P A \theta_\alpha, \phi_\alpha, \theta_N, \phi_N \left(\frac{Z_\alpha R_\alpha}{r_N^2} \right) \quad (\text{XI.16})$$

D. Neglect all but the first terms in Eqs. (XI.15) and (XI.16). Show that one obtains

$$-\frac{\nabla_N^2}{2} - \frac{Q+1}{r_N} f_{n,l}(\mathbf{r}_N) = E_k^N - E_0^{N-1} f_{n,l}(\mathbf{r}_N), \quad (\text{XI.17})$$

Where Q is the charge on the molecule. ($Q+1$ is the charge of the cation.)

Equation (XI.17) has the form of a one-electron atom with “effective nuclear charge” $Q + 1 = \sum_{\alpha=1}^P Z_{\alpha} - N - 1$. That is, when an electron is far away from a molecule, it feels only the “total charge” of the cation. Using what we know about the one-electron atom, we can write

$$E_{n,l}^N - E_0^{N-1} = -\frac{(Q+1)^2}{2n^2} \quad (\text{XI.18})$$

This gives, then

$$E_{n,l}^N = E_0^{N-1} - \frac{(Q+1)^2}{2n^2} \quad (\text{XI.19})$$

Equation (XI.19) gives a first approximation to the energy of the Rydberg states. It is accurate for states whose effective configuration is that of the cation (or even an excited state of the cation) plus an electron that is so “excited” that it spends very little time near the nucleus, so that the approximations we made in the derivation are very small.

E. One does not observe Rydberg spectra for anions. Why?

Equation (XI.17) can be used to deduce the long-range decay of a molecule’s wave function. To do this, assume that, for an electron very far from a molecule, the wave function is given by

$$f_{n,l}(\mathbf{r}) = A r^{\frac{Q+1}{2}-1} e^{-\alpha r} [1 + \text{errors of order } \frac{1}{r}, \frac{1}{r^2}, \dots] \quad (\text{XI.20})$$

F. Show that

$$\alpha = \sqrt{2 \cdot IP_{n,l}} \quad (\text{XI.21})$$

where IP is the ionization potential of the state of the N -electron system being studied. Recalling that the wave function of the Hydrogen atom has a characteristic exponential decay that resembles

$$e^{-\sqrt{-2E_{n,l}}r}, \quad (\text{XI.22})$$

we infer that the “energy” of an electron far from the system is just minus one times the ionization potential of the system.

Now we wish to approximate the quantum defect. Using first-order perturbation theory, one can approximate the error in $E_k^N - E_0^{N-1}$ with

$$\Delta_{n,l}^1 \approx \left\langle f_{n,l}(\mathbf{r}_N) \left| \frac{-\sum_{\alpha=1}^P Z_{\alpha} R_{\alpha} A(\theta_{\alpha}, \phi_{\alpha}, \theta_N, \phi_N) + N - 1 \langle \Psi_0^{N-1} | A(\theta_1, \phi_1, \theta_N, \phi_N) \cdot \mathbf{r}_1 | \Psi_0^{N-1} \rangle_{1 \dots N-1}}{r_N^2} \right| f_{n,l}(\mathbf{r}_N) \right\rangle \quad (\text{XI.23})$$

Because the amount of positive charge, $\sum_{\alpha=1}^P Z_{\alpha}$, exceeds the amount of negative charge, $N - 1$, the integrand in Eq. (XI.23) is negative in most regions of space, with

the consequence that $\Delta_{n,l}^1$ is generally negative. This causes the quantum defect to be (in all cases I know of, anyway), positive.

G. Can you explain (just words is OK) why the quantum defect is usually bigger for lower values of the orbital angular momentum quantum number? (In general, $|\Delta_{n,0}^1| > |\Delta_{n,1}^1| > |\Delta_{n,2}^1| > \dots$?)

H. Show that the quantum defect is approximately given by

$$\delta_l \approx -\frac{n^3 \Delta_{n,l}^1}{Q+1} \quad (\text{XI.24})$$

Based on Eq. (XI.1), we can infer that the effective nuclear charge for an orbital with “principle quantum number” n and angular momentum quantum number l . To do this, we rewrite Eq. (XI.1) as

$$E_{n,l}^N - E_0^{N-1} = -\frac{Z_{\text{eff}}^2}{2n^2} \quad (\text{XI.25})$$

to find that we can identify

$$Z_{\text{eff}} \approx Q + 1 - \frac{\delta_l}{n} \quad (\text{XI.26})$$

We may then use Eq. (XI.25) to approximate

$$IP = \frac{Z_{\text{eff}}^2}{2n^2}, \quad (\text{XI.27})$$

where IP is the ionization potential of an atom and n is the row in the periodic table on which the atom resides. The quantum defect can then be approximated from Eq. (XI.26) but because the ground state of an atom is not a Rydberg state, the approximation is usually very poor.

I. Derive Eq. (XI.26).

J. The ionization potential of He is 24.58741 eV , that of Ne is 21.5646 eV , that of Ar is 15.75962 eV , and that of Kr is 13.99961 eV . Similarly, the ionization potential of Be is 9.3227 eV , that of Mg is 7.64624 eV , and that of Ca is 6.11316 eV . Calculate the effective nuclear charge and quantum defect for these atoms.

XII. Solution of the Partial Differential Equation for Hydrogenic Atoms (.7)

A. Solve the radial equation for the one-electron atom,

$$\frac{-1}{2} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} - \frac{Z}{r} R_{n,l}(r) = E_{n,l} R_{n,l}(r) \quad (\text{XII.1})$$

Refer to a good book, and work through their treatment. You need not derive the general form of the recursion relation, but you should derive the form of the 1s, 2s, and 2p radial wave function, establish the formula for

the energy of the hydrogen-like atom, and understand why the angular momentum quantum number is $0 \leq l \leq n-1$.

Lest you think this exercise is pointless, let me mention that when I was in grad. school, one of the spectroscopists in the department was working with a model for his system's spectrum that looked like

$$\left(\frac{-1}{2} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} + \frac{A}{1-r^2} \right) S_{n,l} r = E_{n,l} S_{n,l} r \quad (\text{XII.2})$$

The method for solving this equation is just the same as the H atom, but this is a MUCH, MUCH, MUCH harder equation to solve. (The easiest way to solve the equation is to express the eigenvectors as functions of the hyperbolic cosine of r , if that gives you a hint of the sort of analysis that is involved.) The moral to the story is that you might just run into a "hydrogenic" equation you need to solve one of these days.

XIII. 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,

$$\mu_L \equiv -\frac{\beta_e}{\hbar} \hat{L} \Psi^{L,S,J,M_J} \quad (\text{XIII.1})$$

and

$$\begin{aligned} \mu_S &= -g \frac{\beta_e}{\hbar} \hat{S} \Psi^{L,S,J,M_J} \\ &\approx -2 \frac{\beta_e}{\hbar} \hat{S} \Psi^{L,S,J,M_J} \end{aligned} \quad (\text{XIII.2})$$

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. (XIII.1) and (XIII.2) that the total magnetic moment will be proportional to

$$\begin{aligned} \hat{J} \Psi^{L,S,J,M_J} &= \hat{L} \Psi^{L,S,J,M_J} + \hat{S} \Psi^{L,S,J,M_J}, \\ \mu_J &\propto \frac{\beta_e}{\hbar} \hat{J} \Psi^{L,S,J,M_J} \\ &= -g_J(L,S) \frac{\beta_e}{\hbar} \hat{J} \Psi^{L,S,J,M_J} \end{aligned} \quad (\text{XIII.3})$$

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 $1 \leq g_J(L,S) \lesssim 2$. $g_J(L,S)$ 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 μ_J , because then we can describe the effect of a magnetic field. Because

$$\hat{J}^2 \Psi^{L,S,J,M_J} \equiv \hat{J} \cdot \hat{J} \Psi^{L,S,J,M_J} = \hbar^2 J(J+1) \Psi^{L,S,J,M_J} \quad (\text{XIII.4})$$

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

$$\left| \left\langle \Psi^{L,S,J,M_J} \left| \hat{\mathbf{J}} \right| \Psi^{L,S,J,M_J} \right\rangle \right| = \hbar \sqrt{J(J+1)} \quad (\text{XIII.5})$$

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

$$\begin{aligned} \left| \left\langle \Psi^{L,S,J,M_J} \left| \hat{\mathbf{L}} \right| \Psi^{L,S,J,M_J} \right\rangle \right| &= \hbar \sqrt{L(L+1)} \\ \left| \left\langle \Psi^{L,S,J,M_J} \left| \hat{\mathbf{S}} \right| \Psi^{L,S,J,M_J} \right\rangle \right| &= \hbar \sqrt{S(S+1)} \end{aligned} \quad (\text{XIII.6})$$

The magnitude of μ_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,

$$\begin{aligned} \mu_J &= \mu_S + \mu_L \\ g_J(L,S) \hat{\mathbf{J}} \Psi^{L,S,J,M_J} &\approx 2 \hat{\mathbf{S}} \Psi^{L,S,J,M_J} + \hat{\mathbf{L}} \Psi^{L,S,J,M_J} \\ &\approx 2 \hat{\mathbf{S}} + \hat{\mathbf{L}} \Psi^{L,S,J,M_J} \\ &\approx \hat{\mathbf{J}} + \hat{\mathbf{S}} \Psi^{L,S,J,M_J} \end{aligned} \quad (\text{XIII.7})$$

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

$$g_J(L,S) \approx 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (\text{XIII.8})$$

A. Derive Eq. (XIII.8).

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

$$\mathbf{E} = -\mu \cdot \mathbf{B} \quad (\text{XIII.9})$$

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

$$\hat{H}_B = g_J L, S \frac{\beta_e}{\hbar} \hat{\mathbf{J}} \cdot \hat{\mathbf{B}}, \quad (\text{XIII.10})$$

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

$$\begin{aligned} \hat{H}_B &= g_J L, S \frac{\beta_e}{\hbar} \hat{\mathbf{J}} \cdot B_z \hat{\mathbf{z}} \\ &= g_J L, S \frac{\beta_e B_z}{\hbar} \hat{J}_z \end{aligned} \quad (\text{XIII.11})$$

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

$$\Delta E_B = g_J L, S \beta_e B_z M_J \quad (\text{XIII.12})$$

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.

XIV. Term Symbols and Electron Coupling (.9)

- 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 two 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,

$$\hat{H}_{el} \equiv \sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} + v(\mathbf{r}_i) + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \quad (\text{XIV.1})$$

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,

$$[\hat{H}_{el}, \hat{S}_x] = [\hat{H}_{el}, \hat{S}_y] = [\hat{H}_{el}, \hat{S}_z] = [\hat{H}_{el}, \hat{S}^2] = 0, \quad (\text{XIV.2})$$

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

$$\begin{aligned} [\hat{A}, \hat{B}\hat{C}] &\equiv \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} \\ &= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} \\ &= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A} \\ &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \end{aligned} \quad (\text{XIV.3})$$

C. Show that

$$[\hat{A}\hat{B}, \hat{C}] = [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}] \quad (\text{XIV.4})$$

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

(Hint, use Eq. (XIV.3) and/or Eq. (XIV.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

$$\Phi_{\mathbf{r}_1, \mathbf{r}_2} \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{2p_1}(\mathbf{r}_1) & \alpha & 1 & \psi_{2p_1}(\mathbf{r}_2) & \alpha & 2 \\ \psi_{2p_{-1}}(\mathbf{r}_1) & \beta & 1 & \psi_{2p_{-1}}(\mathbf{r}_2) & \beta & 2 \end{vmatrix} \quad (\text{XIV.5})$$

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?

XV. 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 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

$$\begin{aligned}\hat{H}_{S.O.} &= \sum_{i=1}^N \frac{Z}{4\pi\epsilon_0 r_i^3} \left(\frac{-e}{2mc} \hat{\mathbf{L}} \cdot \mathbf{r}_i - g \frac{e}{2mc} \hat{\mathbf{S}} \cdot \mathbf{r}_i \right) \\ &\approx \sum_{i=1}^N \frac{Ze^2}{8\pi\epsilon_0 m^2 c^2 r_i^3} \hat{\mathbf{L}} \cdot \mathbf{r}_i \cdot \hat{\mathbf{S}}\end{aligned}\quad (\text{XV.1})$$

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

$$\left\langle \frac{Z}{r^n} \right\rangle \propto Z^{n+1} \quad (\text{XV.2})$$

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

$$\begin{aligned}\hat{H}_{atom} &= \hat{H}_{el} + \hat{H}_{S.O.} \\ &= \sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} + v(\mathbf{r}_i) + \frac{Z}{2c^2 r_i^3} \hat{\mathbf{L}} \cdot \mathbf{r}_i \cdot \hat{\mathbf{S}} + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right)\end{aligned}\quad (\text{XV.3})$$

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

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

Similar to the result in part I, we have that

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

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 $\boldsymbol{\mu}_S^e \equiv -g \cdot \frac{e}{mc} \hat{\mathbf{S}}$, the magnetic moment of the hole is $\boldsymbol{\mu}_S^h \equiv -g \cdot \frac{-e}{mc} \hat{\mathbf{S}} = g \cdot \frac{e}{mc} \hat{\mathbf{S}} = -\boldsymbol{\mu}_S^e$. 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.

It follows from Eq. (XV.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)

$$\begin{aligned}\langle \Psi | [\hat{H}_{atom}, \hat{L}_z] | \Psi \rangle &\approx 0 \\ \langle \Psi | [\hat{H}_{atom}, \hat{S}_z] | \Psi \rangle &\approx 0.\end{aligned}\tag{XV.5}$$

and so the eigenstates of the atomic Hamiltonian, Eq. (XV.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. (XIV.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

$$E_{^{2S+1}A L_J} \equiv A L, S \cdot J(J+1) - L(L+1) - S(S+1) \tag{XV.6}$$

where $A L, S \equiv \frac{\hbar^2}{2} \cdot \langle \Psi^{L,S,J} | \frac{Z}{2c^2 r_i^3} | \Psi^{L,S,J} \rangle$. Because $\frac{Z}{2c^2 r_i^3} > 0$, $A L, S$ 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. (XV.1), which changes the sign of the perturbation, and thus the sign of $A L, S$. Summarizing

$$\begin{aligned}A L, S &\gtrsim 0 \quad \text{less than half-filled shells} \\ A L, S &\lesssim 0 \quad \text{more than half-filled shells}\end{aligned}\tag{XV.7}$$

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. (XV.6). You will find it helpful to use the result

$$\begin{aligned}\hat{J}^2 &= \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} + \hat{\mathbf{S}} \\ &= \hat{L}^2 + \hat{S}^2 + 2 \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}\end{aligned}\tag{XV.8}$$

C. Using Eq. (XV.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. (XV.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 $[\hat{L}^2, \hat{H}_{s.o.}] = [\hat{J}^2, \hat{H}_{s.o.}] = [\hat{J}_z, \hat{H}_{s.o.}] = 0$. You may find it helpful to use your result from part A and Eq. (XV.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 $|j_1 - j_2| \leq J \leq |j_1 + j_2|$ (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

$$\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{3}{2}; \frac{3}{2}, \frac{3}{2} \quad (\text{XV.9})$$

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. (XV.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

$$\frac{1}{2}, \frac{1}{2}_0; \frac{1}{2}, \frac{3}{2}_1; \frac{1}{2}, \frac{3}{2}_2; \frac{3}{2}, \frac{3}{2}_0; \frac{3}{2}, \frac{3}{2}_2 \quad (\text{XV.10})$$

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-Saunders 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).

		Energy (in wave numbers = cm^{-1})				
Atom		3P_0	3P_1	3P_2	3D_2	3S_0
He	($2p^2$	0	0	0	1,659	18,240
state)						
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

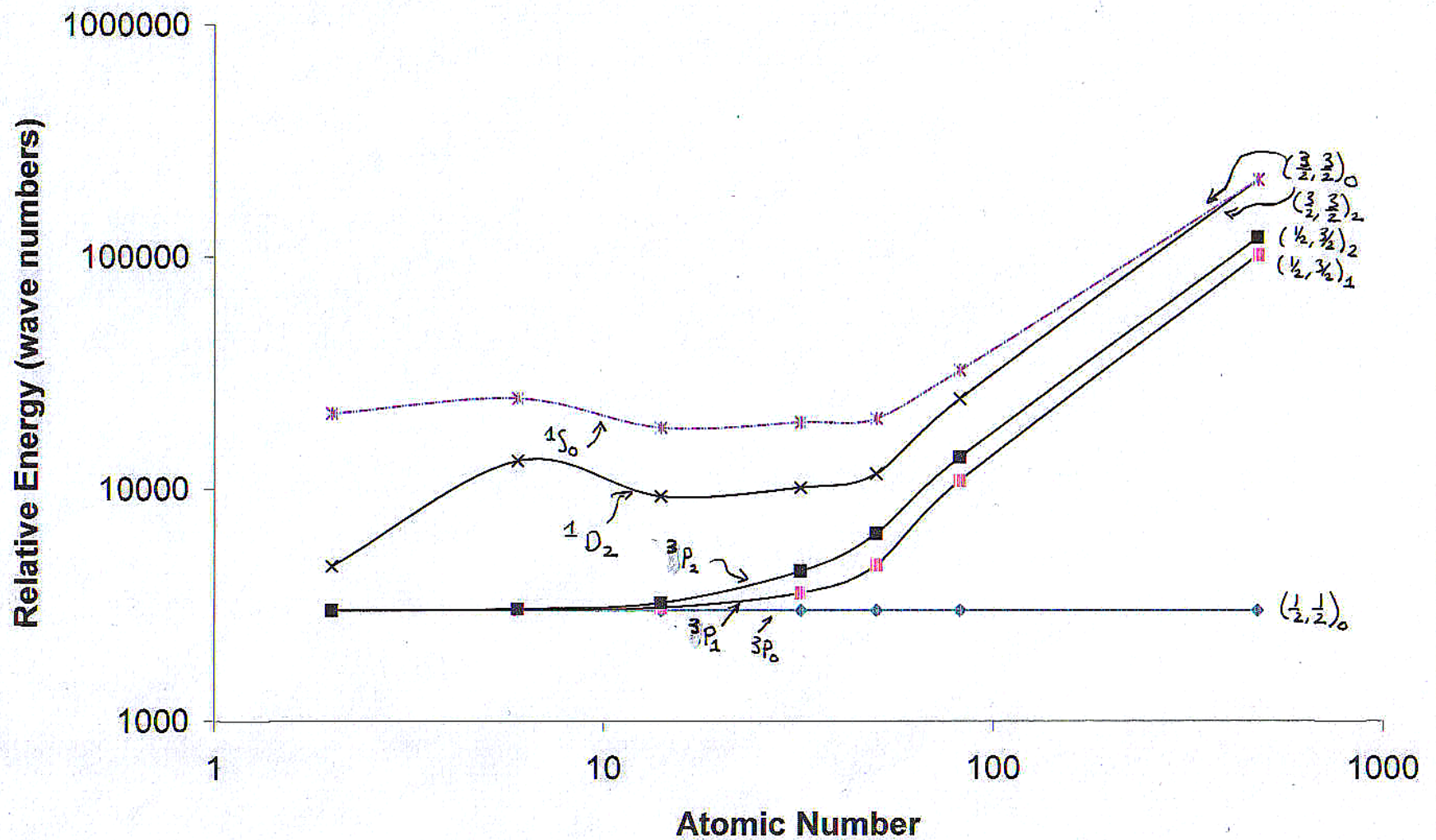
- F. Referring to the table of microstates you used to find the Russell-Saunders's term symbol, explain why there is no $\frac{3}{2}, \frac{3}{2}_3$ term.
- G. Referring to the table of microstates you used to find the Russell-Saunders's term symbol, why is the 1D state associated with $\frac{3}{2},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

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



XVI. The Calculus of Variations and Stationary States (.9)

You were undoubtedly told that the Schrödinger equation (or something like unto it) was the fundamental basis for quantum mechanics. Most modern physicists would disagree with this viewpoint. Rather, variational principles are considered to be much more fundamental. Especially interesting are “stationary” or “stability” principles, and the Schrödinger equation can be derived from such principles. The simplest such principle is the statement that the energy of a “stationary state” is stable with respect to small changes in the wave function. That is, if we take a wave function, Ψ and change it by some small amount, $\delta\Psi$, the energy will only change in a way proportional to the norm (= size) of $|\delta\Psi|^2$. Mathematically, we say that

$$E[\Psi + \delta\Psi] - E[\Psi] \propto \langle \delta\Psi | \delta\Psi \rangle \quad (\text{XVI.1})$$

Equation (XVI.1) is the reason that excited states of molecules are metastable. In fact, were it not for an exotic phenomena called vacuum polarization (which has to do with the ability of empty space to spontaneously generate photons, provided they disappear into the vacuum sufficiently quickly), the excited states of an isolated molecule would have an infinite lifetime.

Equation (XVI.1) is analogous to the condition for a “point of inflection”, maximum, or minimum in a function, namely

$$f(x + dx) - f(x) \propto dx^2 \quad (\text{XVI.2})$$

If you write $f(x)$ as a Taylor series, then Eq. (XVI.2) is seen to imply that the derivative of f with respect to x is zero, which is precisely the familiar condition for stability. Similarly, when Eq. (XVI.1) holds we can say that the functional derivative of E with respect to Ψ is zero.

Recall the definition of the gradient of a function, $\nabla g(\mathbf{r})$ is defined as the vector that maps changes in \mathbf{r} , $d\mathbf{r}$ to changes in $g(\mathbf{r})$, dg , via the formula

$$dg(\mathbf{r}) \equiv g(\mathbf{r} + d\mathbf{r}) - g(\mathbf{r}) = \nabla g(\mathbf{r}) \cdot d\mathbf{r} + \mathcal{O}(d\mathbf{r} \cdot d\mathbf{r}). \quad (\text{XVI.3})$$

Here, $\mathcal{O}(d\mathbf{r} \cdot d\mathbf{r})$ denotes that the error in Eq. (XVI.3) is of the order $d\mathbf{r} \cdot d\mathbf{r}$ —in the limit of very small $d\mathbf{r}$ such terms are negligible.

We define the functional derivative in the same way—the functional derivative of $A[\Psi]$ with respect to Ψ is defined as that function, $\frac{\delta A[\Psi]}{\delta \Psi(\tau)}$, that maps changes in Ψ , $\delta\Psi$ to changes in $A[\Psi]$, $dA[\Psi]$ via the formula

$$dA[\Psi] \equiv A[\Psi + \delta\Psi] - A[\Psi] = \int \frac{\delta A[\Psi]}{\delta \Psi(\tau)} \delta\Psi(\tau) d\tau + \mathcal{O}(\langle \delta\Psi | \delta\Psi \rangle). \quad (\text{XVI.4})$$

A. Choose $\delta\Psi(\tau) = \varepsilon \cdot \delta(\tau - \tau_0)$ in Eq. (XVI.4). Show that

$$\frac{\delta A[\Psi]}{\delta \Psi(\tau_0)} = \lim_{\varepsilon \rightarrow 0} \frac{A[\Psi + \varepsilon \delta(\tau - \tau_0)] - A[\Psi]}{\varepsilon} = \left(\frac{dA[\Psi + \varepsilon \delta(\tau - \tau_0)]}{d\varepsilon} \right)_{\varepsilon=0} \quad (\text{XVI.5})$$

Equation (XVI.5) is a useful formula for computing functional derivatives. Another method follows directly from the definition: compute $A[\Psi + \delta\Psi] - A[\Psi]$ and write the result in the form of Eq. (XVI.4). The coefficient of $\delta\Psi(\tau)$ is the functional derivative. Yet another method follows when we write expand the wave function in a basis set,

$$\Psi[\tau] \equiv \sum_{n=0}^{\infty} k_n \Phi_n[\tau] \quad (\text{XVI.6})$$

$$\Psi[\tau] + \delta\Psi[\tau] \equiv \sum_{n=0}^{\infty} (k_n + \delta k_n) \Phi_n[\tau] \quad (\text{XVI.7})$$

so that

$$\delta\Psi[\tau] = \sum_{n=0}^{\infty} \delta k_n \Phi_n[\tau]. \quad (\text{XVI.8})$$

Using the relationship

$$\begin{aligned} A[\mathbf{k}] + dA - A[\mathbf{k}] &= \nabla_{\mathbf{k}} A[\mathbf{k}] \cdot d\mathbf{k} + \mathcal{O}(d\mathbf{k} \cdot d\mathbf{k}) \\ &= \sum_{n=0}^{\infty} \frac{\partial A}{\partial k_n} dk_n + \mathcal{O}(d\mathbf{k} \cdot d\mathbf{k}) \end{aligned} \quad (\text{XVI.9})$$

one finds that

$$\frac{\delta A[\Psi]}{\delta \Psi[\tau]} = \sum_{n=0}^{\infty} \frac{\partial A}{\partial k_n} \left(\frac{\delta k_n}{\delta \Psi[\tau]} \right) = \sum_{n=0}^{\infty} \frac{\partial A}{\partial k_n} \left(\frac{\delta \langle \Psi[\tau] | \Phi_n \rangle}{\delta \Psi[\tau]} \right) = \sum_{n=0}^{\infty} \frac{\partial A}{\partial k_n} \Phi_n. \quad (\text{XVI.10})$$

B. Show that Eq. (XVI.10) satisfies the definition of the functional derivative, Eq. (XVI.4).

We should say a few words about what a functional is. A functional is, as should be clear from the above, just a “function of a function.” For instance, the energy is a **functional** of the wave function, because it can be computed from the wave function using

$$E[\Psi] \equiv \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (\text{XVI.11})$$

To remove possible ambiguity, we denote the argument of a functional with in brackets, but the argument of a simple function in parentheses. Functionals and functions are closely related. For instance, introducing a basis set for the wave function reveals that the functional derivative is really just a generalization of the gradient (compare Eqs. (XVI.3) and (XVI.10)), and turns a functional into a function. For instance, we can write the energy as a function of the coefficients of a basis function expansion: using (XVI.6),

$$E[\mathbf{k}] = E[k_n]_{n=0}^{\infty} \equiv \frac{\sum_{l=0}^{\infty} \sum_{m=0}^{\infty} k_l^* k_m \langle \Phi_l | \hat{H} | \Phi_m \rangle}{\sum_{l=0}^{\infty} \sum_{m=0}^{\infty} k_l^* k_m \langle \Phi_l | \Phi_m \rangle}. \quad (\text{XVI.12})$$

The Schrödinger equation,

$$\hat{H}\Psi_k = E_k \Psi_k \quad (\text{XVI.13})$$

can be derived from the requirement that $\frac{\delta E[\Psi]}{\delta \Psi} = 0$. This is a more fundamental “derivation” of the Schrödinger equation than most (though one can do much by forcing a functional called the “action” to be stationary instead focusing on the energy). This is important, since it reveals that the eigenvectors and eigenvalues of the Hamiltonian operator represent stationary, or stable, states of the system.

C. Show that the Schrödinger Equation is equivalent to principle of stationary energy, $\frac{\delta E}{\delta \Psi} = 0$. (Read the following hint.)

(I know of two straightforward ways to perform the derivation. One is to use Eq. (XVI.5), but this is complicated by the fact that the kinetic energy operator will operate on the delta function. However, using the three-dimension generalization of problem I.C allows one to perform the analysis. The most straightforward approach is to calculate $E \Psi + \delta \Psi - E \Psi$ and rearrange the result into a form like

$$E \Psi + \delta \Psi - E \Psi = \int A \Psi \delta \Psi \, d\tau + \mathcal{O} |\delta \Psi|^2 \quad (\text{XVI.14})$$

Again, the analysis is a bit complicated because of the kinetic energy operator. The key is to use Green's theorem (cf. Eq. III.8 in problem set 1) to write integrals like $\langle \Psi | \nabla^2 \delta \Psi \rangle$ in terms of integrals like $\langle \nabla^2 \Psi | \delta \Psi \rangle$. In expanding the denominator you might want to use the geometric series, namely

$$1 + x^k \equiv 1 + k \cdot x + \frac{k(k-1)}{2!} x^2 + \dots + \binom{k}{n} x^n + \dots \quad (\text{XVI.15})$$

What is a stationary state? The following analysis might be helpful. Consider what happens when we change the wave function of a stationary state, Ψ_k , by a small amount, $\varepsilon \phi$. We can assume that ϕ and Ψ_k are orthogonal and normalized. Then (you will need to use the geometric series again),

D. Show that

$$E \Psi_k + \varepsilon \phi \equiv E_k + \varepsilon^2 E_\phi - E_k - \varepsilon^4 E_\phi - E_k^2 + \dots \quad (\text{XVI.16})$$

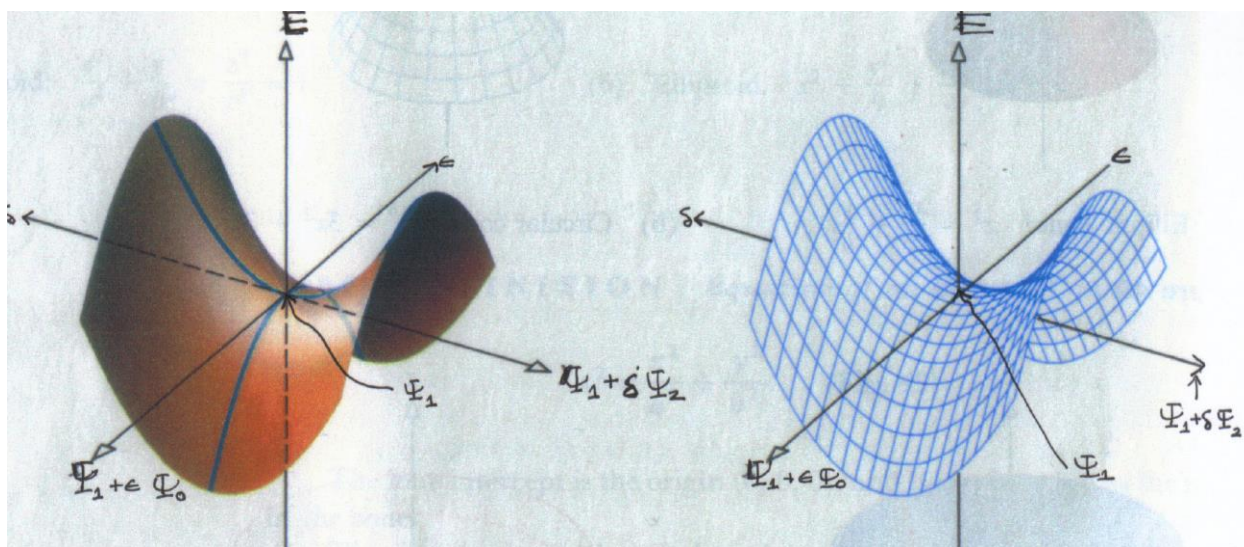
where E_k is the energy of the stationary state, Ψ_k , and

$$E_\phi \equiv \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \langle \phi | \hat{H} | \phi \rangle. \quad (\text{XVI.17})$$

The interpretation is that stationary states of systems are “saddle points”; the first order change in energy is zero, but the second order change is negative if ϕ has a lower energy than Ψ_k but positive if ϕ has a larger energy than Ψ_k . The ground state is the absolute minimum energy state (and is thus a simple minimum, and not a maximum), but the k^{th} excited state is a true saddle point—one can lower the energy by moving in a k directions (take $\phi = \sum_{n=0}^{k-1} c_n \Psi_n$) but other directions (take

$\phi = \sum_{n=k+1}^{\infty} c_n \Psi_n$) raise the energy.

The following figure depicts the situation for the first excited state of a system.



The stability of a stationary state is related to “how broad” the saddle point is, since this determines “how big” a perturbation is needed to a system away from its “stationary state” and force a transition to a lower-energy state. Thus, from Eq. (XVI.16), one might expect that the rate at which a molecule spontaneously decays from an excited state, E_k , to a lower-energy stationary state, $E_{l < k}$, would be proportional to $E_k - E_l$. This gives the right trend (higher excited states are inherently less stable and transitions from excited states to lower-energy states are favored. But the assumption of a linear dependence is wrong (for rather subtle reasons); the lifetime of excited states is proportional to $E_k - E_l$ ³.

XVII. 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

$$\Psi_{Hartree}(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N) = \prod_{i=1}^N \phi_i(\mathbf{r}_i, \sigma_i) \quad (XVII.1)$$

would be, where the orbitals are constrained to be orthonormal

$$\langle \phi_i \sigma_i | \phi_j \sigma_j \rangle = \delta_{ij}. \quad (XVII.2)$$

Here σ_i denotes the spin (α or β) for the i^{th} electron; equation (XVII.2) indicates that non-orthogonal orbitals must have different spin.

Equation (XVII.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 Vladimir 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

$$E_{Hartree} \left[\phi_i, \sigma_i \right]_{i=1}^N = \left\langle \prod_{m=1}^N \phi_m \mathbf{r}_m \sigma_m \middle| \sum_{i=1}^N -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \middle| \prod_{n=1}^N \phi_n \mathbf{r}_n \sigma_n \right\rangle \quad (XVII.3)$$

$$= \sum_{i=1}^N \left\langle \phi_i \mathbf{r} \middle| -\frac{\nabla^2}{2} - \frac{Z}{r} \middle| \phi_i \mathbf{r} \right\rangle + \sum_{i=1}^N \sum_{j=i+1}^N \left\langle \phi_i \mathbf{r} \phi_j \mathbf{r}' \middle| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \middle| \phi_i \mathbf{r} \phi_j \mathbf{r}' \right\rangle$$

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

$$h \mathbf{r} \equiv -\frac{\nabla^2}{2} - \frac{Z}{r}. \quad (XVII.4)$$

B. What is the interpretation of the second term in Eq. (XVII.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. (XVII.3), subject to the orthonormality constraint, Eq. (XVII.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, $\phi_\alpha \mathbf{r}$, when all the other orbitals are fixed, do not lead to a change in the energy. This ensures that $\phi_\alpha \mathbf{r}$ is the “best possible” orbital.

$$\frac{\delta E \left[\phi_i \right]_{i=1}^N}{\delta \phi_\alpha \mathbf{r}} = 0. \quad (XVII.5)$$

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,

$$\frac{\delta F \phi \mathbf{r} + G \phi \mathbf{r}}{\delta \phi \mathbf{r}} = \frac{\delta F \phi \mathbf{r}}{\delta \phi \mathbf{r}} + \frac{\delta G \phi \mathbf{r}}{\delta \phi \mathbf{r}} \quad (XVII.6)$$

Another useful relation is the “product rule”.

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

$$\frac{\delta F \phi \mathbf{r} G \phi \mathbf{r}}{\delta \phi \mathbf{r}} = G \phi \mathbf{r} \frac{\delta F \phi \mathbf{r}}{\delta \phi \mathbf{r}} + F \phi \mathbf{r} \frac{\delta G \phi \mathbf{r}}{\delta \phi \mathbf{r}} \quad (XVII.7)$$

There are several chain rules also. Notably

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

$$\frac{\delta f F \phi}{\delta \phi \mathbf{r}} = \frac{df}{dF} \cdot \frac{\delta F \phi}{\delta \phi \mathbf{r}} \quad (XVII.8)$$

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

$$\frac{\delta F \phi f; \mathbf{r}}{\delta f \mathbf{r}} = \int \frac{\delta F \phi}{\delta \phi \mathbf{r}'} \cdot \frac{\delta \phi \mathbf{r}'}{\delta f \mathbf{r}} d\mathbf{r}' \quad (XVII.9)$$

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

$$\frac{dF(\phi, \zeta, \mathbf{r})}{d\zeta} = \int \frac{\delta F(\phi)}{\delta \phi(\mathbf{r}')} \cdot \frac{d\phi(\mathbf{r}')}{d\zeta} d\mathbf{r}' \quad (\text{XVII.10})$$

Equation (XVII.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 (XVII.10) is used, for instance, to describe how the energy depends on the effective nuclear charge for each orbital.

The chain rules can be derived directly from Eq. (XVI.5) and the “usual chain rule.”

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,

$$F(\phi, \mathbf{r}) \equiv \int f(\phi(\mathbf{r}), \nabla \phi(\mathbf{r}), \nabla^2 \phi(\mathbf{r}), \dots) d\mathbf{r}, \quad (\text{XVII.11})$$

then

$$\frac{\delta F(\phi)}{\delta \phi(\mathbf{x})} = \frac{\partial f}{\partial \phi(\mathbf{x})} - \nabla \cdot \frac{\partial f}{\partial \nabla \phi(\mathbf{x})} + \nabla^2 \frac{\partial f}{\partial \nabla^2 \phi(\mathbf{x})} - \nabla \cdot \nabla^2 \frac{\partial f}{\partial \nabla^3 \phi(\mathbf{x})} + \dots \quad (\text{XVII.12})$$

Equation (XVII.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 it’s preferable to the way you worked problem IV.

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

$$E_{\text{Hartree}}[\phi_i, \sigma_i, N] = \sum_{i=1}^N \frac{\langle \phi_i(\mathbf{r}) | \hat{h}(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle}{\langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle} + \sum_{i=1}^N \sum_{j=i+1}^N \frac{\langle \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \rangle}{\langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle \langle \phi_j(\mathbf{r}) | \phi_j(\mathbf{r}) \rangle} \quad (\text{XVII.13})$$

So

$$\begin{aligned} 0 &= \frac{\delta E_{\text{Hartree}}}{\delta \phi_\alpha(\mathbf{x})} \\ &= \frac{\delta}{\delta \phi_\alpha(\mathbf{x})} \left[\sum_{i=1}^N \frac{\langle \phi_i(\mathbf{r}) | \hat{h}(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle}{\langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle} + \sum_{i=1}^N \sum_{j=i+1}^N \frac{\langle \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \rangle}{\langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle \langle \phi_j(\mathbf{r}) | \phi_j(\mathbf{r}) \rangle} \right] \\ &\stackrel{\text{Eq. (V.6)}}{=} \frac{\delta}{\delta \phi_\alpha(\mathbf{x})} \left[\sum_{i=1}^N \frac{\langle \phi_i(\mathbf{r}) | \hat{h}(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle}{\langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle} \right] \\ &\quad + \frac{\delta}{\delta \phi_\alpha(\mathbf{x})} \sum_{i=1}^N \sum_{j=i+1}^N \frac{\langle \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \rangle}{\langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle \langle \phi_j(\mathbf{r}) | \phi_j(\mathbf{r}) \rangle} \end{aligned} \quad (\text{XVII.14})$$

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

$$\begin{aligned}
0 = & \frac{\delta}{\delta\phi_\alpha \mathbf{x}} \left[\frac{\langle \phi_\alpha \mathbf{r} | \hat{h} \mathbf{r} | \phi_\alpha \mathbf{r} \rangle}{\langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle} \right] + \frac{\delta}{\delta\phi_\alpha \mathbf{x}} \sum_{j=\alpha+1}^N \frac{\langle \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' \rangle}{\langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle \langle \phi_j \mathbf{r} | \phi_j \mathbf{r} \rangle} \\
& + \frac{\delta}{\delta\phi_\alpha \mathbf{x}} \sum_{i=1}^{\alpha-1} \frac{\langle \phi_i \mathbf{r} \phi_\alpha \mathbf{r}' | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_i \mathbf{r} \phi_\alpha \mathbf{r}' \rangle}{\langle \phi_i \mathbf{r} | \phi_i \mathbf{r} \rangle \langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle}
\end{aligned} \quad (\text{XVII.15})$$

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

$$\frac{\delta}{\delta\phi_\alpha \mathbf{x}} \left[\frac{\langle \phi_\alpha \mathbf{r} | \hat{h} \mathbf{r} | \phi_\alpha \mathbf{r} \rangle}{\langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle} \right] = 2\hat{h}\phi_\alpha \mathbf{x} - 2\langle \phi_\alpha \mathbf{r} | \hat{h} \mathbf{r} | \phi_\alpha \mathbf{r} \rangle \phi_\alpha \mathbf{x} \quad (\text{XVII.16})$$

(you may assume the orbital is real).

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

$$\begin{aligned}
& \frac{\delta}{\delta\phi_\alpha \mathbf{x}} \frac{\langle \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' \rangle}{\langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle \langle \phi_j \mathbf{r} | \phi_j \mathbf{r} \rangle} \\
&= \frac{1}{\langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle \langle \phi_j \mathbf{r} | \phi_j \mathbf{r} \rangle} \left(\frac{\delta}{\delta\phi_\alpha \mathbf{x}} \langle \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' \rangle \right) \\
&+ \langle \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' \rangle \frac{\delta}{\delta\phi_\alpha \mathbf{x}} \frac{1}{\langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle \langle \phi_j \mathbf{r} | \phi_j \mathbf{r} \rangle} \\
&= \frac{1}{1 \cdot 1} \left(\frac{\delta}{\delta\phi_\alpha \mathbf{x}} \iint \phi_\alpha^2 \mathbf{r} \frac{\phi_j^2 \mathbf{r}'}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}' d\mathbf{r} \right) \\
&+ \iint \phi_\alpha^2 \mathbf{r} \frac{\phi_j^2 \mathbf{r}'}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}' d\mathbf{r} \frac{\delta}{\delta\phi_\alpha \mathbf{x}} \frac{1}{\langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle} \cdot 1 \\
&= \left(\int \phi_\alpha^2 \frac{\phi_j^2}{|\mathbf{r}'-\mathbf{x}|} d\mathbf{r}' \right) \\
&+ \iint \phi_\alpha^2 \frac{\phi_j^2}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}' d\mathbf{r} \left(\frac{-1}{\langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle} \frac{\delta}{\delta\phi_\alpha \mathbf{x}} \langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle \right) \\
&= \left(2 \int \frac{\phi_j^2}{|\mathbf{r}'-\mathbf{x}|} d\mathbf{r}' \right) \phi_\alpha \iint \phi_\alpha^2 \frac{\phi_j^2}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}' d\mathbf{r} \left(\frac{-1}{\langle \phi_\alpha \mathbf{r} | \phi_\alpha \mathbf{r} \rangle} \frac{\delta}{\delta\phi_\alpha \mathbf{x}} \int \phi_\alpha^2 d\mathbf{r} \right) \\
&= 2 \left(\int \frac{\phi_j^2}{|\mathbf{r}'-\mathbf{x}|} d\mathbf{r}' \right) \phi_\alpha \cdot 2 \langle \phi_\alpha \mathbf{r} | \phi_j \mathbf{r}' | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' \rangle \phi_\alpha
\end{aligned} \quad (\text{XVII.17})$$

Using these results, you can:

E. Show that the orbital, $\phi_\alpha \mathbf{r}$ satisfies a one-electron Schrödinger equation, namely

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

where

$$\begin{aligned} \varepsilon_\alpha &\equiv \left\langle \psi_\alpha \mathbf{r} \left| \hat{h} \mathbf{r} + \sum_{i \neq \alpha}^N \int \frac{|\psi_i \mathbf{r}'|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right| \psi_\alpha \mathbf{r} \right\rangle \\ &= \left\langle \psi_\alpha \mathbf{r} \left| \hat{h} \mathbf{r} \right| \psi_\alpha \mathbf{r} \right\rangle + \sum_{\substack{i=1; \\ i \neq \alpha}}^N \left\langle \phi_\alpha \mathbf{r} \phi_i \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_\alpha \mathbf{r} \phi_i \mathbf{r}' \right\rangle. \end{aligned} \quad (\text{XVII.19})$$

There is an equation like (XVII.18) for each value of α , $\alpha = 1, 2, \dots, N, N+1, N+2, \dots$. When $\alpha > N$, we say $\phi_\alpha \mathbf{r}$ 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. (XVII.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. (XVII.18) for $\psi_\alpha \mathbf{r}$. Call this $\psi_\alpha^0 \mathbf{r}$. This changes the value of the Hartree potential,

$$v_\beta^{\text{Hartree}} \mathbf{r} \equiv \sum_{i \neq \beta}^N \int \frac{|\psi_i \mathbf{r}'|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (\text{XVII.20})$$

for all the other orbitals, $\phi_{\beta \neq \alpha} \mathbf{r}$. Solving the Hartree equation for the other orbitals, one obtains $\psi_\beta^0 \mathbf{r}$. Substituting the revised orbitals, $\psi_{\beta \neq \alpha}^0 \mathbf{r}$, into the expression for $v_\alpha^{\text{Hartree}} \mathbf{r}$ gives one a new equation for the α^{th} orbital, yielding $\psi_\alpha^1 \mathbf{r}$. 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. (XVII.18)? Why do we leave out the $i = \alpha$ term?

We wish to clarify the interpretation of the quantities ε_α . Because Eq. (XVII.19) looks like an energy expression, we call ε_α the “orbital energy” of the α^{th} 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

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

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

Consider solving Eq. (XVII.18) for an unoccupied orbital, $\phi_\beta \mathbf{r}$ with $\beta > N$. ($\phi_\beta \mathbf{r}$ 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 (XVII.18) becomes

$$\left(\hat{h} \mathbf{r} + \sum_{i=1}^N \int \frac{|\psi_i \mathbf{r}'|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) \phi_\beta \mathbf{r} = \varepsilon_\beta \phi_\beta \mathbf{r} \quad (\text{XVII.22})$$

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

$$\Psi_{\alpha}^{\beta} \uparrow \mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N = \left(\prod_{i \neq \alpha}^N \phi_i \mathbf{r}_i \sigma_i \right) \phi_\beta \mathbf{r}_\alpha \sigma_\beta \quad (\text{XVII.23})$$

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

$$\begin{aligned} E_{\alpha}^{\beta} &= \left\langle \left(\prod_{i \neq \alpha}^N \phi_i \mathbf{r}_i \sigma_i \right) \phi_\beta \mathbf{r}_\alpha \sigma_\beta \left| \sum_{i=1}^N \hat{h} \mathbf{r}_i + \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \left(\prod_{i \neq \alpha}^N \phi_i \mathbf{r}_i \sigma_i \right) \phi_\beta \mathbf{r}_\alpha \sigma_\beta \right. \right\rangle \\ &= \sum_{i=1}^N \left\langle \phi_i \mathbf{r} \left| \hat{h} \mathbf{r} \right| \phi_i \mathbf{r} \right\rangle + \left\langle \phi_\beta \mathbf{r} \left| \hat{h} \mathbf{r} \right| \phi_\beta \mathbf{r} \right\rangle \\ &\quad + \sum_{i=1}^N \sum_{j=i+1}^N \left\langle \phi_i \mathbf{r} \phi_j \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_i \mathbf{r} \phi_j \mathbf{r}' \right\rangle + \sum_{i=1}^N \left\langle \phi_i \mathbf{r} \phi_\beta \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_i \mathbf{r} \phi_\beta \mathbf{r}' \right\rangle \\ &= \sum_{i=1}^N \left\langle \phi_i \mathbf{r} \left| \hat{h} \mathbf{r} \right| \phi_i \mathbf{r} \right\rangle + \left\langle \phi_\beta \mathbf{r} \left| \hat{h} \mathbf{r} \right| \phi_\beta \mathbf{r} \right\rangle - \left\langle \phi_\alpha \mathbf{r} \left| \hat{h} \mathbf{r} \right| \phi_\alpha \mathbf{r} \right\rangle \\ &\quad + \sum_{i=1}^N \sum_{j=i+1}^N \left\langle \phi_i \mathbf{r} \phi_j \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_i \mathbf{r} \phi_j \mathbf{r}' \right\rangle - \sum_{i=1}^{\alpha-1} \left\langle \phi_i \mathbf{r} \phi_\alpha \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_i \mathbf{r} \phi_\alpha \mathbf{r}' \right\rangle \\ &\quad - \sum_{j=\alpha+1}^N \left\langle \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_\alpha \mathbf{r} \phi_j \mathbf{r}' \right\rangle \\ &\quad + \sum_{i=1}^N \left\langle \phi_i \mathbf{r} \phi_\beta \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_i \mathbf{r} \phi_\beta \mathbf{r}' \right\rangle - \left\langle \phi_\alpha \mathbf{r} \phi_\beta \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_\alpha \mathbf{r} \phi_\beta \mathbf{r}' \right\rangle \\ &= \sum_{i=1}^N \left\langle \phi_i \mathbf{r} \left| \hat{h} \mathbf{r} \right| \phi_i \mathbf{r} \right\rangle + \sum_{i=1}^N \sum_{j=i+1}^N \left\langle \phi_i \mathbf{r} \phi_j \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_i \mathbf{r} \phi_j \mathbf{r}' \right\rangle \\ &\quad + \left\langle \phi_\beta \mathbf{r} \left| \hat{h} \mathbf{r} \right| \phi_\beta \mathbf{r} \right\rangle + \sum_{i=1}^N \left\langle \phi_i \mathbf{r} \phi_\beta \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_i \mathbf{r} \phi_\beta \mathbf{r}' \right\rangle \\ &\quad - \left\langle \phi_\alpha \mathbf{r} \left| \hat{h} \mathbf{r} \right| \phi_\alpha \mathbf{r} \right\rangle - \sum_{i \neq \alpha}^N \left\langle \phi_i \mathbf{r} \phi_\alpha \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_i \mathbf{r} \phi_\alpha \mathbf{r}' \right\rangle \\ &\quad - \left\langle \phi_\alpha \mathbf{r} \phi_\beta \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_\alpha \mathbf{r} \phi_\beta \mathbf{r}' \right\rangle \\ &= E_{\text{Hartree}} + \varepsilon_\beta - \varepsilon_\alpha - \left\langle \phi_\alpha \mathbf{r} \phi_\beta \mathbf{r}' \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_\alpha \mathbf{r} \phi_\beta \mathbf{r}' \right\rangle \end{aligned} \quad (\text{XVII.24})$$

It follows that the excitation energy is

$$E_{\uparrow \alpha}^{\beta} - E_{Hartree} \approx \varepsilon_{\beta} - \varepsilon_{\alpha} - \left\langle \phi_{\alpha} \mathbf{r} \phi_{\beta} \mathbf{r}' \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| \phi_{\alpha} \mathbf{r} \phi_{\beta} \mathbf{r}' \right\rangle \quad (\text{XVII.25})$$

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

$$\int \frac{-|\phi_{\alpha} \mathbf{r}|^2}{|\mathbf{r}-\mathbf{x}|} d\mathbf{r} \quad (\text{XVII.26})$$

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. (XVII.26), we estimate to be

$$E_{e^-,h^+} = \iint \frac{-|\phi_{\alpha} \mathbf{r}|^2 |\phi_{\beta} \mathbf{x}|}{|\mathbf{r}-\mathbf{x}|} d\mathbf{r} d\mathbf{x} < 0 \quad (\text{XVII.27})$$

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

$$\Psi_{free}^{\beta} \mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N = \left(\prod_{i=1}^N \phi_i \mathbf{r}_i \sigma_i i \right) \phi_{\beta} \mathbf{r}_{\alpha} \sigma_{\beta} \alpha \quad (\text{XVII.28})$$

H. Show that the electron affinity is simply

$$EA_{\beta} \equiv E_{neutral} - E_{\uparrow}^{\beta}_{free} = -\varepsilon_{\beta} \quad (\text{XVII.29})$$

By the same sort of derivation, we find that the energy required to remove an electron from the α^{th} orbital to form the cation wavefunction,

$$\Psi_{\alpha}^{free} \mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N = \prod_{i \neq \alpha}^N \phi_i \mathbf{r}_i \sigma_i i. \quad (\text{XVII.30})$$

is

$$IP_{\alpha} \approx E_{\uparrow \alpha}^{free} - E_{neutral} = -\varepsilon_{\alpha}. \quad (\text{XVII.31})$$

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

- I. Explain why Eqs. (XVII.23), (XVII.28), and (XVII.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. (XVII.25) greater than or less than the exact excitation energy that would be computed with

the Hartree approximation? What about the electron affinity, Eq. (XVII.29) and the ionization potential, Eq. (XVII.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

$$\begin{aligned}\varepsilon_{2s} &\approx -\frac{Z^2}{8} + \frac{23}{54}Z \\ \varepsilon_{2p} &\approx -\frac{Z^2}{8} + \frac{118}{243}Z\end{aligned}\tag{XVII.32}$$

- 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?

XVIII. 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,

$$\psi_{1s}(\mathbf{r}; \zeta) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}\tag{XVIII.1}$$

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

$$\Psi_{\zeta}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\zeta, \mathbf{r}_1) \psi_{1s}(\zeta, \mathbf{r}_2)\tag{XVIII.2}$$

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

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

We find the optimum value of ζ from

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

which gives

$$\begin{aligned}\zeta &= 1.6875 = \frac{27}{16} \\ E &= -2.848.\end{aligned}\tag{XVIII.5}$$

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

$$\psi_{1s}^a(\mathbf{r}; \zeta) = \sqrt{\frac{\zeta_a^3}{\pi}} e^{-\zeta_a r} \quad (\text{XVIII.6})$$

$$\psi_{1s}^b(\mathbf{r}; \zeta) = \sqrt{\frac{\zeta_b^3}{\pi}} e^{-\zeta_b r}. \quad (\text{XVIII.7})$$

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

$$\Psi_{\zeta_a, \zeta_b}(\mathbf{r}_1, \mathbf{r}_2) \propto \psi_{1s}^a(\mathbf{r}_1) \psi_{1s}^b(\mathbf{r}_2) + \psi_{1s}^b(\mathbf{r}_1) \psi_{1s}^a(\mathbf{r}_2) \quad (\text{XVIII.8})$$

They he evaluated

$$E_{\zeta_a, \zeta_b} = \frac{\langle \Psi_{\zeta_a, \zeta_b} | \hat{H} | \Psi_{\zeta_a, \zeta_b} \rangle}{\langle \Psi_{\zeta_a, \zeta_b} | \Psi_{\zeta_a, \zeta_b} \rangle} \quad (\text{XVIII.9})$$

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

$$\begin{aligned} \zeta_a &= 1.19 \\ \zeta_b &= 2.18 \\ E &= -2.876 \end{aligned} \quad (\text{XVIII.10})$$

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

$$\Psi_{\zeta_a, \zeta_b}(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) \propto \psi_{1s}^a(\mathbf{r}_1) \psi_{1s}^b(\mathbf{r}_2) + \psi_{1s}^b(\mathbf{r}_1) \psi_{1s}^a(\mathbf{r}_2) \alpha(1) \beta(2) - \alpha(2) \beta(1). \quad (\text{XVIII.11})$$

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,

$$\begin{aligned} \Psi_{\zeta_a, \zeta_b}(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) &\propto \begin{vmatrix} \psi_{1s}^a(\mathbf{r}_1) \alpha(1) & \psi_{1s}^a(\mathbf{r}_2) \alpha(2) \\ \psi_{1s}^b(\mathbf{r}_1) \beta(1) & \psi_{1s}^b(\mathbf{r}_2) \beta(2) \end{vmatrix} + \begin{vmatrix} \psi_{1s}^b(\mathbf{r}_1) \alpha(1) & \psi_{1s}^b(\mathbf{r}_2) \alpha(2) \\ \psi_{1s}^a(\mathbf{r}_1) \beta(1) & \psi_{1s}^a(\mathbf{r}_2) \beta(2) \end{vmatrix} \\ &= \psi_{1s}^a(\mathbf{r}_1) \alpha(1) \psi_{1s}^b(\mathbf{r}_2) \beta(2) + \psi_{1s}^b(\mathbf{r}_1) \alpha(1) \psi_{1s}^a(\mathbf{r}_2) \beta(2) \\ &\quad - \psi_{1s}^a(\mathbf{r}_2) \alpha(2) \psi_{1s}^b(\mathbf{r}_1) \beta(1) - \psi_{1s}^b(\mathbf{r}_2) \alpha(2) \psi_{1s}^a(\mathbf{r}_1) \beta(1) \\ &= \psi_{1s}^a(\mathbf{r}_1) \psi_{1s}^b(\mathbf{r}_2) + \psi_{1s}^b(\mathbf{r}_1) \psi_{1s}^a(\mathbf{r}_2) \alpha(1) \beta(2) - \alpha(2) \beta(1) \end{aligned} \quad (\text{XVIII.12})$$

While Eq. (XVIII.12) is a Slater determinate, it is not really an orbital product wave function because the $\psi_{1s}^a(\mathbf{r})$ and $\psi_{1s}^b(\mathbf{r})$ are not orthogonal. However,

$\psi_{1s}^a(\mathbf{r}) + \psi_{1s}^b(\mathbf{r})$ and $\psi_{1s}^a(\mathbf{r}) - \psi_{1s}^b(\mathbf{r})$ are orthogonal since

$$\begin{aligned} &\int (\psi_{1s}^a(\mathbf{r}) + \psi_{1s}^b(\mathbf{r}))^* (\psi_{1s}^a(\mathbf{r}) - \psi_{1s}^b(\mathbf{r})) d\mathbf{r} \\ &= \int \psi_{1s}^a(\mathbf{r})^* \psi_{1s}^a(\mathbf{r}) d\mathbf{r} + \int \psi_{1s}^b(\mathbf{r})^* \psi_{1s}^a(\mathbf{r}) d\mathbf{r} \\ &\quad - \int \psi_{1s}^a(\mathbf{r})^* \psi_{1s}^b(\mathbf{r}) d\mathbf{r} - \int \psi_{1s}^b(\mathbf{r})^* \psi_{1s}^b(\mathbf{r}) d\mathbf{r} \\ &= 0 \end{aligned} \quad (\text{XVIII.13})$$

and we can

A. Show that

$$\Psi_{\zeta_a, \zeta_b} \mathbf{r}_1, s_1; \mathbf{r}_2, s_2 \propto \frac{1}{2} \begin{vmatrix} \psi_{1s}^a \mathbf{r}_1 + \psi_{1s}^b \mathbf{r}_1 & \alpha 1 & \psi_{1s}^a \mathbf{r}_2 + \psi_{1s}^b \mathbf{r}_2 & \alpha 2 \\ \psi_{1s}^a \mathbf{r}_1 + \psi_{1s}^b \mathbf{r}_1 & \beta 1 & \psi_{1s}^a \mathbf{r}_2 + \psi_{1s}^b \mathbf{r}_2 & \beta 2 \end{vmatrix} - \frac{1}{2} \begin{vmatrix} \psi_{1s}^a \mathbf{r}_1 - \psi_{1s}^b \mathbf{r}_1 & \alpha 1 & \psi_{1s}^a \mathbf{r}_2 - \psi_{1s}^b \mathbf{r}_2 & \alpha 2 \\ \psi_{1s}^a \mathbf{r}_1 - \psi_{1s}^b \mathbf{r}_1 & \beta 1 & \psi_{1s}^a \mathbf{r}_2 - \psi_{1s}^b \mathbf{r}_2 & \beta 2 \end{vmatrix}. \quad (\text{XVIII.14})$$

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

$$\begin{aligned} \Psi_{k_{1s^2}, k_{2s^2}, k_{1s2s}} \mathbf{r}_1, s_1; \mathbf{r}_2, s_2 &\propto k_{1s^2} \begin{vmatrix} \psi_{1s}^a \mathbf{r}_1 + \psi_{1s}^b \mathbf{r}_1 & \alpha 1 & \psi_{1s}^a \mathbf{r}_2 + \psi_{1s}^b \mathbf{r}_2 & \alpha 2 \\ \psi_{1s}^a \mathbf{r}_1 + \psi_{1s}^b \mathbf{r}_1 & \beta 1 & \psi_{1s}^a \mathbf{r}_2 + \psi_{1s}^b \mathbf{r}_2 & \beta 2 \end{vmatrix} \\ &+ k_{2s^2} \begin{vmatrix} \psi_{1s}^a \mathbf{r}_1 - \psi_{1s}^b \mathbf{r}_1 & \alpha 1 & \psi_{1s}^a \mathbf{r}_2 - \psi_{1s}^b \mathbf{r}_2 & \alpha 2 \\ \psi_{1s}^a \mathbf{r}_1 - \psi_{1s}^b \mathbf{r}_1 & \beta 1 & \psi_{1s}^a \mathbf{r}_2 - \psi_{1s}^b \mathbf{r}_2 & \beta 2 \end{vmatrix} \\ &+ k_{1s2s} \left(\begin{vmatrix} \psi_{1s}^a \mathbf{r}_1 + \psi_{1s}^b \mathbf{r}_1 & \alpha 1 & \psi_{1s}^a \mathbf{r}_2 + \psi_{1s}^b \mathbf{r}_2 & \alpha 2 \\ \psi_{1s}^a \mathbf{r}_1 - \psi_{1s}^b \mathbf{r}_1 & \alpha 1 & \psi_{1s}^a \mathbf{r}_2 - \psi_{1s}^b \mathbf{r}_2 & \alpha 2 \\ \psi_{1s}^a \mathbf{r}_1 + \psi_{1s}^b \mathbf{r}_1 & \beta 1 & \psi_{1s}^a \mathbf{r}_2 + \psi_{1s}^b \mathbf{r}_2 & \beta 2 \\ \psi_{1s}^a \mathbf{r}_1 - \psi_{1s}^b \mathbf{r}_1 & \beta 1 & \psi_{1s}^a \mathbf{r}_2 - \psi_{1s}^b \mathbf{r}_2 & \beta 2 \end{vmatrix} \right) \end{aligned} \quad (\text{XVIII.15})$$

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. (XVIII.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

$$\psi_{1s}^{a,b} \mathbf{r} = \psi_{1s}^a \mathbf{r} + c_b \psi_{1s}^b \mathbf{r}; \quad (\text{XVIII.16})$$

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

$$\Psi_{c_b} \mathbf{r}_1, \mathbf{r}_2 \propto \psi_{1s}^{a,b} \mathbf{r}_1 \psi_{1s}^{a,b} \mathbf{r}_2 \quad (\text{XVIII.17})$$

calculate

$$E_{c_b} = \frac{\langle \Psi_{c_b} | \hat{H} | \Psi_{c_b} \rangle}{\langle \Psi_{c_b} | \Psi_{c_b} \rangle} \quad (\text{XVIII.18})$$

and calculate c_b from

$$\frac{\partial E}{\partial c_b} = 0 \quad (\text{XVIII.19})$$

B. Use Eq. (XVIII.19) to determine c_b . Evaluate E_{c_b} .

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

$$\psi_{2s}^{a,b}(\mathbf{r}) = \psi_{1s}^a(\mathbf{r}) + d_b \psi_{1s}^b(\mathbf{r}) \quad (\text{XVIII.20})$$

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

$$\langle \psi_{1s}^a(\mathbf{r}) + c_b \psi_{1s}^b(\mathbf{r}) | \psi_{1s}^a(\mathbf{r}) + d_b \psi_{1s}^b(\mathbf{r}) \rangle = 0 \quad (\text{XVIII.21})$$

This gives (if I did my math right)

$$d_b = \frac{c_b \langle \psi_{1s}^a(\mathbf{r}) | \psi_{1s}^b(\mathbf{r}) \rangle - 1}{c_b + \langle \psi_{1s}^a(\mathbf{r}) | \psi_{1s}^b(\mathbf{r}) \rangle} \quad (\text{XVIII.22})$$

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

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. (XVIII.17) gives a probability distribution function,

$$|\Psi_{c_b}(\mathbf{r}_1, \mathbf{r}_2)|^2 \propto |\psi_{1s}^{a,b}(\mathbf{r}_1)|^2 |\psi_{1s}^{a,b}(\mathbf{r}_2)|^2 = \begin{vmatrix} \psi_{1s}^{a,b}(\mathbf{r}_1) & \alpha & 1 & \psi_{1s}^{a,b}(\mathbf{r}_2) & \alpha & 2 \\ \psi_{1s}^{a,b}(\mathbf{r}_1) & \beta & 1 & \psi_{1s}^{a,b}(\mathbf{r}_2) & \beta & 2 \end{vmatrix} \quad (\text{XVIII.23})$$

which is a product of two one-electron distribution functions. If the probability of two events, say, an electron being at \mathbf{r}_1 and an electron being at \mathbf{r}_2 , is the product of the probabilities of the two events occurring separately (cf. Eq. (XVIII.23)), then those two events are “independent”—they are uncorrelated. We say that Eq. (XVIII.17) (and also Eq. (XVIII.2)) neglect electron correlation. Moreover, by definition, no Slater determinant includes electron correlation (although, for more than two electrons, Eqs. like (XVIII.23) no longer hold). The Eckhart function however crudely, accounts for electron correlation. In particular, Eq. (XVIII.11) describes radial (or “in-out”) correlation, because a function like $\psi_{1s}^a(\mathbf{r}_1) \psi_{1s}^b(\mathbf{r}_2)$ 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. (XVIII.11), $\psi_{1s}^b(\mathbf{r}_1) \psi_{1s}^a(\mathbf{r}_2)$, 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. (XVIII.15).

D. Write a linear combination of the Slater determinants (cf. Eq. (XVIII.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

$$E_{exact}^{He} = -2.9037 \text{ Hartree} \quad (\text{XVIII.24})$$

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,

$$\psi_{1s}^{15}(\mathbf{r}) = \sum_{i=1}^{15} c_i \sqrt{\frac{\zeta_i^3}{\pi}} e^{-\zeta_i r} \quad (\text{XVIII.25})$$

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.

radial correlation

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

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

Angular correlation

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

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

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

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

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

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

$$= \left[c_{1s} \psi_{1s}^{TP} \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \begin{pmatrix} \uparrow \downarrow \end{pmatrix} + c_{2p} \begin{pmatrix} \psi_{2p_x}^{TP} \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \\ \psi_{2p_y}^{TP} \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \\ \psi_{2p_z}^{TP} \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \end{pmatrix} \right] \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \alpha \begin{pmatrix} \uparrow \downarrow \end{pmatrix} \begin{pmatrix} \uparrow \downarrow \end{pmatrix}$$

where

$$\psi_{1s}^{TP} \mathbf{r} = \sqrt{\frac{1.69^3}{\pi}} e^{-1.69r} \quad (\text{XVIII.27})$$

$$\psi_{2p_{x,y,z}}^{TP} \mathbf{r} = \sqrt{\frac{5^3}{32\pi}} \cdot 5 \cdot x, y, z e^{-5r/2}.$$

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

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned} \quad (\text{XVIII.28})$$

and simplifying.

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

$$\Psi_{c_{1s}, c_{2p}} \mathbf{r}_1, \mathbf{r}_2 = c_{1s} \left(\frac{4.83}{\pi} e^{-1.69 r_1 + r_2} \right) + c_{2p} \left(\frac{3125}{32\pi} r_1 r_2 e^{-5(r_1 + r_2)/2} \left(\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi_1 - \phi_2 \right) \right) \quad (\text{XVIII.29})$$

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

Next we evaluate

$$E_{c_{1s}, c_{2p}} = \frac{\langle \Psi_{c_{1s}, c_{2p}} | \hat{H} | \Psi_{c_{1s}, c_{2p}} \rangle}{\langle \Psi_{c_{1s}, c_{2p}} | \Psi_{c_{1s}, c_{2p}} \rangle} \Psi_{c_{1s}, c_{2p}} \mathbf{r}_1, \mathbf{r}_2 \quad (\text{XVIII.30})$$

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

$$\begin{aligned}\frac{\partial E}{\partial c_{1s}} &= 0 \\ \frac{\partial E}{\partial c_{2s}} &= 0\end{aligned}\tag{XVIII.31}$$

For convenience, we define

$$\begin{aligned}\Psi_{1s}^{TP}(\mathbf{r}_1, \mathbf{r}_2) &\equiv \left(\frac{4.83}{\pi} e^{-1.69(r_1+r_2)} \right) \\ \Psi_{2p}^{TP}(\mathbf{r}_1, \mathbf{r}_2) &\equiv \left(\frac{3125}{32\pi} r_1 r_2 e^{-\left(\frac{5}{2}(r_1+r_2)\right)} \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi_1 - \phi_2 \right) \\ \varepsilon_{1s} &\equiv \langle \Psi_{1s}^{TP}(\mathbf{r}_1, \mathbf{r}_2) | \hat{H} | \Psi_{1s}^{TP}(\mathbf{r}_1, \mathbf{r}_2) \rangle \\ \varepsilon_{2p} &\equiv \langle \Psi_{2p}^{TP}(\mathbf{r}_1, \mathbf{r}_2) | \hat{H} | \Psi_{2p}^{TP}(\mathbf{r}_1, \mathbf{r}_2) \rangle \\ \beta_{1s,2p} = \beta_{2p,1s} &\equiv \langle \Psi_{1s}^{TP}(\mathbf{r}_1, \mathbf{r}_2) | \hat{H} | \Psi_{2p}^{TP}(\mathbf{r}_1, \mathbf{r}_2) \rangle\end{aligned}\tag{XVIII.32}$$

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

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

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

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

$$\begin{aligned}\frac{\partial E}{\partial c_{2p}} &= \frac{2c_{1s} \varepsilon_{1s} + 2c_{2p} \beta_{1s,2p}}{c_{1s}^2 + c_{2p}^2} - \frac{2c_{1s} c_{1s}^2 \varepsilon_{1s} + c_{2p}^2 \varepsilon_{2p} + 2c_{1s} c_{2p} \beta_{1s,2p}}{(c_{1s}^2 + c_{2p}^2)^2} \\ 0 &= \frac{2c_{1s} \varepsilon_{1s} + 2c_{2p} \beta_{1s,2p}}{c_{1s}^2 + c_{2p}^2} - \frac{2c_{1s} E(c_{1s}, c_{2p})}{c_{1s}^2 + c_{2p}^2} \\ 0 &= \varepsilon_{1s} - E(c_{1s}, c_{2p}) \frac{c_{1s}}{c_{1s} + c_{2p} \beta_{1s,2p}} \\ c_{1s} &= \left(\frac{\beta_{1s,2p}}{E(c_{1s}, c_{2p}) - \varepsilon_{1s}} \right) c_{2p}\end{aligned}\tag{XVIII.34}$$

and similarly

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

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

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

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

$$1 = \frac{\beta_{1s,2p}^2}{E - \epsilon_{1s} \quad E - \epsilon_{2p}}$$
(XVIII.36)

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

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

If we assume that $2\beta \ll |\alpha_a - \alpha_b|$, then we can use the geometric series

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

to obtain

$$E \approx \epsilon_{1s} - \frac{\beta^2}{\epsilon_{2p} - \epsilon_{1s}}$$
(XVIII.39)

as an approximation to the ground state energy.

H. Derive Eq. (XVIII.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. (XVIII.11) and (XVIII.26). This gives a wave function of the form

$$\Psi_{c_{1s}, c_{2p}}(\mathbf{r}_1, \mathbf{r}_2) = \left[c_{1s} \psi_{1s}^a(\mathbf{r}_1) \psi_{1s}^b(\mathbf{r}_2) + \psi_{1s}^b(\mathbf{r}_1) \psi_{1s}^a(\mathbf{r}_2) + c_{2p} \left(\psi_{2p_x}^{TP}(\mathbf{r}_1) \psi_{2p_x}^{TP}(\mathbf{r}_2) + \psi_{2p_y}^{TP}(\mathbf{r}_1) \psi_{2p_y}^{TP}(\mathbf{r}_2) + \psi_{2p_z}^{TP}(\mathbf{r}_1) \psi_{2p_z}^{TP}(\mathbf{r}_2) \right) \right] \alpha(1) \beta(2) - \alpha(2) \beta(1) \quad \text{(XVIII.40)}$$

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

I. Referring to Eq. (XVIII.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. (XVIII.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 ($\epsilon_{1s} - E \approx .0464$) as the atomic number goes to infinity, and the relative size of the correlation energy ($\frac{\epsilon_{1s} - E}{E}$) approaches zero.

XIX. Exchange Integrals are Positive (.9)

When we were discussing Hund's first rule for a 2-electron atom we indicated energy of the singlet state minus the energy of the triplet state was equal to $2K$,

$$2K = E^1\Lambda - E^3\Lambda, \quad (\text{XIX.1})$$

where

$$K \equiv \iint \frac{\psi_1^*(\mathbf{r}_1) \psi_2(\mathbf{r}_1) \psi_1^*(\mathbf{r}_2) \psi_2(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (\text{XIX.2})$$

$$> 0$$

Since $K > 0$, the energy of the singlet state was greater than that of the triplet state. This is a special case of the theorem that

For any well-behaved function, $f(\mathbf{r}_1)$,

$$\iint \frac{f(\mathbf{r}_1) f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \geq 0. \quad (\text{XIX.3})$$

If $f(\mathbf{r})$ is continuous and has continuous first derivatives then this is sufficient (but not necessary) for the theorem. Thus, most functions we'll be interested in will be "well-behaved."

Because we can always choose the wave functions in time-independent quantum mechanics to be real, we have opted to consider only the "real" case of the theorem. (The complex case—where $f(\mathbf{r}_2)$ is replaced by $f^*(\mathbf{r}_2)$ —is similar though.)

To prove Eq. (XIX.3), we first rewrite the equation as

$$\iint \frac{f(\mathbf{r}_1) f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \int f(\mathbf{r}_1) \left[\int \frac{f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] d\mathbf{r}_1 \quad (\text{XIX.4})$$

Now, we recognize that the innermost integral is just the electrostatic potential, $\Phi(\mathbf{r}_1)$, due to a charge distribution, $f(\mathbf{r}_2)$,

$$\Phi(\mathbf{r}_1) = \int \frac{f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \quad (\text{XIX.5})$$

Now, recall Poisson's equation; Poisson's equation says that the electrostatic potential due to a charge distribution satisfies the equation

$$\nabla^2 \Phi(\mathbf{r}_1) = -4\pi f(\mathbf{r}_1) \quad (\text{XIX.6})$$

This lets us write Eq. (XIX.4) as

$$\iint \frac{f(\mathbf{r}_1) f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \frac{-1}{4\pi} \int \nabla^2 \Phi(\mathbf{r}_1) \Phi(\mathbf{r}_1) d\mathbf{r}_1 \quad (\text{XIX.7})$$

We simplify this result using Green's first identity:

$$\iiint \phi(\mathbf{r}) \nabla^2 \psi(\mathbf{r}) + \nabla \phi(\mathbf{r}) \cdot \nabla \psi(\mathbf{r}) d\mathbf{r} \equiv \oint \phi(\mathbf{r}) \nabla \psi(\mathbf{r}) \cdot \mathbf{n} da \quad (\text{XIX.8})$$

A. Show that

$$\iint \frac{f(\mathbf{r}_1) f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{4\pi} \iiint \nabla \Phi(\mathbf{r}) \cdot \nabla \Phi(\mathbf{r}) d\mathbf{r} - \frac{1}{4\pi} \oint \Phi(\mathbf{r}) \nabla \Phi(\mathbf{r}) \cdot \mathbf{n} da \quad (\text{XIX.9})$$

The integral on the right-hand-side is over the "surface" of the volume of integration. If the volume of integration is all of space, then the surface integral can be evaluated on a sphere of infinite radius, which we can evaluate using

$$\begin{aligned}
\oint_{R \rightarrow \infty} \phi \mathbf{r} \cdot \nabla \psi \mathbf{r} \cdot \mathbf{n} da &= \int_0^\pi \int_0^{2\pi} \lim_{r \rightarrow \infty} \left[\phi \mathbf{r} \cdot \nabla \psi \mathbf{r} \cdot \hat{\mathbf{r}} r^2 \right] \sin \theta d\theta d\phi \\
&= \int_0^\pi \int_0^{2\pi} \lim_{r \rightarrow \infty} \left[\phi \mathbf{r} \cdot \frac{\partial \psi \mathbf{r}}{\partial r} r^2 \right] \sin \theta d\theta d\phi
\end{aligned}
\tag{XIX.10}$$

We can always write the electrostatic potential in terms of what is termed a multipole expansion. That is, the electrostatic potential can be expressed as a sum of the electrostatic potential due to the charge of a distribution, plus that from the dipole moment of the distribution, plus that of the quadrupole moment of the distribution. . . . Since we are integrating over a sphere, it is most convenient to express the multipole moments using the spherical harmonics.

B. Show that

$$\begin{aligned}
\Phi \mathbf{r} &\equiv \int \frac{f \mathbf{x}}{|\mathbf{r} - \mathbf{x}|} d\mathbf{x} \\
&= \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} \frac{4\pi}{2l+1} \frac{Y_l^m \theta, \phi}{r^{l+1}} \int f \mathbf{x} Y_l^m \theta_x, \phi_x d\mathbf{x}
\end{aligned}
\tag{XIX.11}$$

The numbers

$$\int f \mathbf{x} Y_l^m \theta_x, \phi_x d\mathbf{x}
\tag{XIX.12}$$

are called the multipole moments. In the convention used here,

$$Y_0^0 \theta, \phi = \frac{1}{\sqrt{4\pi}}.
\tag{XIX.13}$$

C. Show that the first multipole moment is just $\frac{1}{\sqrt{4\pi}}$ times the total charge in the distribution,

$$q = \int f \mathbf{x} d\mathbf{x}.
\tag{XIX.14}$$

For exchange integrals, the total charge is zero. For Coulomb integrals, the total charge is negative.

D. Use Eq. (XIX.11) to evaluate Eq. (XIX.9).

The equation you derive in part D completes the proof of the theorem. Specifically, we have that

$$\frac{1}{4\pi} \iiint \nabla \Phi \mathbf{r} \cdot \nabla \Phi \mathbf{r} d\mathbf{r} = \frac{1}{4\pi} \iiint |\nabla \Phi \mathbf{r}|^2 d\mathbf{r},
\tag{XIX.15}$$

which is positive (unless $\nabla \Phi \mathbf{r} = 0$ over all space) since the integral of a positive function is always positive.

XX. Atomic Orbital Radii and Effective Nuclear Charges

[Do not do this problem until I revise it; there is an error in the data.] (1.2)

For the Hydrogen atom, a popular definition of the atomic radius is the classical turning point of the electron. Consider that if the electron was a classical particle moving in a potential, $V(r)$, then it could never be located at a region where

$$V(r) > E
\tag{XX.1}$$

because, if it were, it would have negative kinetic energy. Thus, solving

$$V(r_{cl}) = E
\tag{XX.2}$$

gives a “radius” of the atom. Now, let us substitute in for the general hydrogenic atom. We have

$$-\frac{Z}{r_{cl}} = E_{electron} . \quad (XX.3)$$

The picture here is that we have an electron which is bound a distance, r_{cl} , from an ion with charge Z .

A. Show that for the Hydrogen atom,

$$r_{cl} = \frac{2n^2}{Z} \quad (XX.4)$$

In addition, we said that we could consider electrons to be subject to an effective nuclear charge, due to nuclear shielding. This gives, as a more general formula,

$$r_{cl} = \frac{2n^2}{Z_{eff}} \quad (XX.5)$$

Now, the amount of energy it takes to extract an electron from an orbital is equal to the ionization potential,

$$IP = E \left(\begin{array}{c} \text{system with electron} \\ \text{removed from the orbital} \end{array} \right) - E \left(\begin{array}{c} \text{system with electron} \\ \text{in the orbital} \end{array} \right) = -E_{electron} \quad (XX.6)$$

Equation (XX.3) then gives

$$r_{cl} = \frac{Z_{eff}}{IP} \quad (XX.7)$$

The radius of an atom or ion is often consider to be equal to the radius of the outermost orbital (the orbital with the largest value of n).

B. Explain why the size of atoms increases as you move down the periodic table.

C. Explain why the size of an atom decreases as you remove electrons to form the cation, dication, etc..

D. Why do you think the atomic radii of the lanthanides does not systematically increase with increasing atomic number?

One can approximate the shielding constants from Eq. (XX.5). For example, consider an atom with a $1s^2$ configuration. Using Eqs. (XX.5) and (XX.7) one finds that

$$IP = \frac{Z_{eff}^2}{2n^2} \quad (XX.8)$$

(This is eminently reasonable.) Express

$$Z_{eff} = Z - s , \quad (XX.9)$$

where s is a shielding constant.

E. Write an expression for s in terms of the Ionization Potential

The ionization potentials for the process



can be found in the CRC handbook. I've excerpted from this on the next page.

- F. Compute the shielding constants (you'll want to use a spreadsheet).
- G. Compare these shielding constants to the shielding constant for the 1s electrons in the hydride ion, which you can compute from
- $$H^- 1s^2 \rightarrow H \quad \Delta E = .027751 \text{ Hartree} \quad (\text{XX.11})$$
- H. How do the shielding constants change as the charge of the atom increases? Can you explain (in words) this result?
- I. Compute the radii of the 1s orbital for the 2-electron and 1-electron systems. What happens to the size of the orbital when you ionize the system?

In the limit of large atomic number (see problem V), the energy of a 2-electron atom is exactly

$$E_{Z \rightarrow \infty} = -Z^2 + \frac{5}{8} Z - .1576664295 \quad (\text{XX.12})$$

- J. Derive a formula for the shielding constant valid for large atomic numbers. What is the value of the shielding constant in the limit of large atomic number?

The commonly used shielding constant rules generally give shielding constants about half this size. The justification there is that one 1s electron (the second one to be ionized) feels the full nuclear charge (ergo $Z_{\text{eff}} = Z$) while the first 1s electron feels the shielded charge, $Z - s$. In order to describe both well, we average the two shielding constants; this provides a good compromise whereby electrons both close to and far away from the nucleus will be well described.

For systems with electrons in both the 1s and the 2s orbitals, we can compute shielding constants using the formula

$$Z_{\text{eff}}^{1s} = Z - n_{1s}^{1s} - \frac{1}{2} s_{1s}^{1s} - n_{2s}^{1s} s_{2s}^{1s} \quad (\text{XX.13})$$

$$Z_{\text{eff}}^{2s} = Z - n_{1s}^{2s} s_{1s}^{2s} - n_{2s}^{2s} - \frac{1}{2} s_{2s}^{2s} \quad (\text{XX.14})$$

where n_{1s} and n_{2s} are the number of electrons in the 1s and 2s orbitals and s_i^k denotes the shielding of the i th orbital by the k th orbital. You will find the following data useful for the next few problems:

$$\begin{aligned} \text{Li } 1s^2 2s^1 &\rightarrow \text{Li}^+ 1s^2 + e^- & IP &= 5.392 \text{ eV} \\ \text{Li } 1s^2 2s^1 &\rightarrow \text{Li}^+ 1s^1 2s^2 + e^- & IP &= 64.83 \text{ eV} \\ \text{Li}^+ 1s^2 &\rightarrow \text{Li}^{2+} 1s^1 + e^- & IP &= 75.638 \text{ eV} \\ \text{Be } 1s^2 2s^2 &\rightarrow \text{Be}^+ 1s^2 2s^1 + e^- & IP &= 9.322 \text{ eV} \\ \text{Be } 1s^2 2s^2 &\rightarrow \text{Be}^+ 1s^1 2s^2 + e^- & IP &= 123.56 \text{ eV} \\ \text{Be}^+ 1s^2 2s^1 &\rightarrow \text{Be}^{2+} 1s^2 + e^- & IP &= 127.43 \text{ eV} \\ \text{Be}^{2+} 1s^2 &\rightarrow \text{Be}^{3+} (s^1) e^- & IP &= 153.90 \text{ eV} \end{aligned} \quad (\text{XX.15})$$

- K. How much do the 1s electrons shield the 2s electron in Lithium? In Beryllium?
- L. How much does the 2s electron shield the 1s electron in Lithium? In Beryllium?
- M. How much do the 2s electrons shield each other in Beryllium?

Atomic Number	Ionization Potential (in eV)
2	24.587
3	75.64
4	153.897
5	259.375
6	392.087
7	552.0718
8	739.29
9	953.9112
10	1195.8286
11	1465.121
12	1761.805
13	2085.98
14	2437.63
15	2816.91
16	3223.78
17	3658.521
18	4120.8857
19	4610.8
20	5128.8
21	5674.8
22	6249
23	6851.3
24	7481.7
25	8140.6
26	8828
27	9544.1
28	10288.8
29	11062.38

XXI. 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.

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.

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

$$\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}) \quad (\text{XXI.1})$$

where $\Phi(\mathbf{r})$ is the electrostatic potential. An electron at \mathbf{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

$$\Phi(\mathbf{r}) = \frac{Z}{r} + \sum_{i=1}^{N-1} \frac{-1}{|\mathbf{r} - \mathbf{r}_i|} \quad (\text{XXI.2})$$

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. (XXI.2). (That is, we are neglecting the so-called “orbit-orbit” interaction, which couples the orbital angular momenta of the electrons together.) This gives

$$\begin{aligned} \Phi(\mathbf{r}) &= \frac{Z}{r} \\ \mathbf{E}(\mathbf{r}) &= -\frac{Z}{r^2} \hat{\mathbf{r}} \end{aligned} \quad (\text{XXI.3})$$

where $\hat{\mathbf{r}}$ 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

$$\begin{aligned} \mathbf{E}'(\mathbf{r}) &= \frac{1}{\sqrt{1 - \frac{|\mathbf{v} \times \mathbf{r}|^2}{c^2}}} \left(\mathbf{E}(\mathbf{r}) - \frac{\mathbf{v} \times \mathbf{r} \times \mathbf{B}(\mathbf{r})}{c} \right) - \frac{1}{1 + \sqrt{1 - \frac{|\mathbf{v} \times \mathbf{r}|^2}{c^2}}} \left(\frac{\mathbf{v} \times \mathbf{r}}{c} \right) \left(\frac{\mathbf{v} \cdot \mathbf{E}(\mathbf{r})}{c} \right) \\ \mathbf{B}'(\mathbf{r}) &= \frac{1}{\sqrt{1 - \frac{|\mathbf{v} \times \mathbf{r}|^2}{c^2}}} \left(\mathbf{B}(\mathbf{r}) - \frac{\mathbf{v} \times \mathbf{r} \times \mathbf{E}(\mathbf{r})}{c} \right) - \frac{1}{1 + \sqrt{1 - \frac{|\mathbf{v} \times \mathbf{r}|^2}{c^2}}} \left(\frac{\mathbf{v} \times \mathbf{r}}{c} \right) \left(\frac{\mathbf{v} \cdot \mathbf{B}(\mathbf{r})}{c} \right) \end{aligned} \quad (\text{XXI.4})$$

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

$$\begin{aligned} \mathbf{E}'(\mathbf{r}) &= \frac{1}{\sqrt{1 - \frac{|\mathbf{v} \times \mathbf{r}|^2}{c^2}}} \left(\mathbf{E}(\mathbf{r}) - \frac{1}{1 + \sqrt{1 - \frac{|\mathbf{v} \times \mathbf{r}|^2}{c^2}}} \left(\frac{\mathbf{v} \times \mathbf{r}}{c} \right) \left(\frac{\mathbf{v} \cdot \mathbf{E}(\mathbf{r})}{c} \right) \right) \\ \mathbf{B}'(\mathbf{r}) &= \frac{-1}{\sqrt{1 - \frac{|\mathbf{v} \times \mathbf{r}|^2}{c^2}}} \frac{\mathbf{v} \times \mathbf{r} \times \mathbf{E}(\mathbf{r})}{c} \end{aligned} \quad (\text{XXI.5})$$

³ This, of course, is not strictly true. The nuclear spin produces a magnetic moment, and this enters into Eq. (XXI.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-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.

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

$$\begin{aligned} \mathbf{E}' \cdot \mathbf{r} &= \mathbf{E} \cdot \mathbf{r} + \mathcal{O} \frac{v^2}{c^2} \\ \mathbf{B}' \cdot \mathbf{r} &= -\frac{\mathbf{v} \cdot \mathbf{r} \times \mathbf{E}}{c} + \mathcal{O} \frac{v^3}{c^3} \end{aligned} \quad (\text{XXI.6})$$

Here $v = |\mathbf{v}|$ is the speed and $\mathcal{O} \frac{v^k}{c^k}$ 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

$$E_{\text{magnetic}} \equiv -\boldsymbol{\mu}_S \cdot \mathbf{B}. \quad (\text{XXI.7})$$

Also, recall that the angular momentum operator is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (\text{XXI.8})$$

B. Show that

$$\begin{aligned} E_{\text{magnetic}} &= -\boldsymbol{\mu}_S \cdot \frac{Z}{cr^3} \mathbf{L} \\ &= \frac{gZ}{2c^2 r^3} \mathbf{S} \cdot \mathbf{L} \\ &\approx \frac{Z}{c^2 r^3} \mathbf{S} \cdot \mathbf{L}. \end{aligned} \quad (\text{XXI.9})$$

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 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

$$E_{\text{magnetic}}^{\text{correct}} \approx \frac{Z}{2c^2 r^3} \mathbf{S} \cdot \mathbf{L}. \quad (\text{XXI.10})$$

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

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

XXII. The Form of the Wave Function Close to the Nucleus of an Atom (.7)

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

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

Now, suppose that

$$\begin{aligned} |\mathbf{r}_1 - \mathbf{R}_1| &\ll |\mathbf{r}_k - \mathbf{R}_\alpha| & k \text{ and } \alpha \text{ are not both equal to } 1. \\ |\mathbf{r}_1 - \mathbf{R}_1| &\ll |\mathbf{r}_i - \mathbf{r}_j| & 1 \leq i, j \leq N \end{aligned} \quad (\text{XXII.2})$$

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

$$\begin{aligned} \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} &\gg \frac{1}{|\mathbf{r}_k - \mathbf{R}_\alpha|} & k, \alpha \neq 1 \\ \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} &\gg \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} & 1 \leq i, j \leq N \end{aligned} \quad (\text{XXII.3})$$

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

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

$$\left(-\frac{\nabla_1^2}{2} - \frac{Z_1}{r_1} - \sum_{\alpha=2}^P \frac{Z_\alpha}{|\mathbf{r}_1 - \mathbf{R}_\alpha|} + \sum_{j=2}^N \frac{1}{|\mathbf{r}_j - \mathbf{r}_1|} + \sum_{i=2}^N \left(-\frac{\nabla_i^2}{2} - \sum_{\alpha=1}^P \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right) + \sum_{i=2}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (\text{XXII.4})$$

B. Derive the next two equations:

$$\begin{aligned} \left(-\frac{\nabla_1^2}{2} - \frac{Z_1}{r_1} - \sum_{\alpha=2}^P \frac{Z_\alpha}{R_\alpha} + \sum_{j=2}^N \frac{1}{r_j} + \sum_{\alpha=2}^P \mathcal{O}\left(\frac{r_1}{R_\alpha}\right) + \sum_{j=2}^N \mathcal{O}\left(\frac{r_1}{r_j}\right) + \sum_{i=2}^N \left(-\frac{\nabla_i^2}{2} - \sum_{\alpha=1}^P \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right) + \sum_{i=2}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \\ \left(-\frac{\nabla_1^2}{2} - \frac{Z_1}{r_1} - \mathcal{O}\left(\frac{r_1^0}{r_1}\right) + \mathcal{O}\left(\frac{r_1}{r_1}\right) \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 0 \end{aligned} \quad (\text{XXII.5})$$

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

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{n=0}^{\infty} \frac{r_1^n}{n!} \frac{\partial^n \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{\partial^n r_1} \bigg|_{r_1=0} \quad (\text{XXII.6})$$

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

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi(\mathbf{0}, \mathbf{r}_2, \dots, \mathbf{r}_N) \left(1 - Z_1 r_1 + \mathcal{O}(r_1^2) \right). \quad (\text{XXII.7})$$

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

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi(\mathbf{0}, \mathbf{r}_2, \dots, \mathbf{r}_N) e^{-Z_1 r_1} + \mathcal{O}(r_1^2). \quad (\text{XXII.8})$$

Equation (XXII.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. (XXII.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

$$Z_1 = - \left. \frac{d \ln \Psi \mathbf{r}_1, \dots, \mathbf{r}_N}{dr_1} \right|_{r_1=0} \quad (\text{XXII.9})$$

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

XXIII. 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

$$\Psi \mathbf{r} \propto \sqrt{\frac{Z^3}{\pi}} e^{-Zr} \quad (\text{XXIII.1})$$

Thus, if we were to change variables to

$$\mathbf{x} = Z\mathbf{r} \quad (\text{XXIII.2})$$

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;

$$\left(\sum_{i=1}^N \left(-\frac{\nabla_{\mathbf{x}_i}^2}{2} - \frac{1}{x_i} \right) + \frac{1}{Z} \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \right) \Psi \mathbf{x}_1, \dots, \mathbf{x}_N = \frac{E}{Z^2} \Psi \mathbf{x}_1, \dots, \mathbf{x}_N \quad (\text{XXIII.3})$$

A. Derive Eq. (XXIII.3)

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

$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{x_1} - \frac{1}{x_2} + \frac{1}{Z|\mathbf{x}_1 - \mathbf{x}_2|} \right) \Psi \mathbf{x}_1, \dots, \mathbf{x}_N = \frac{E}{Z^2} \Psi \mathbf{x}_1, \dots, \mathbf{x}_N \quad (\text{XXIII.4})$$

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

$$\begin{aligned} E/Z &= Z^2 \sum_{n=0}^{\infty} \varepsilon_n \left(\frac{1}{Z} \right)^n \\ &= \sum_{n=0}^{\infty} \varepsilon_n \left(\frac{1}{Z} \right)^{n-2} \end{aligned} \quad (\text{XXIII.5})$$

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

$$\mathcal{E}_0 = \sum_{n=0}^{\infty} \varepsilon_n \left(\frac{1}{Z} \right)^n = \frac{E}{Z^2} \quad (\text{XXIII.6})$$

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

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

Inspecting Eq. (XXIII.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. (XXIII.5) fails to converge when

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.

$$\frac{1}{Z} < \frac{1}{Z_{critical}} = 1.09766 \quad (XXIII.7)$$

This implies that

$$Z_{critical} = .911029. \quad (XXIII.8)$$

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

$$E_{critical} = -\frac{Z_{critical}^2}{2}. \quad (XXIII.9)$$

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

$$f(x) \propto \lambda - x^\kappa, \quad (XXIII.10)$$

then the Taylor series,

$$f(x) = \sum_{n=0}^{\infty} f_n x^n \quad (XXIII.11)$$

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

$$\frac{f_{n+1}}{f_n} \sim \frac{1}{\lambda} \left(1 - \frac{1+\kappa}{n} \right) \quad (XXIII.12)$$

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. (XXIII.12) when $f(x)$ is given by Eq. (XXIII.10).

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

$$E \propto f(Z) \left(\frac{1}{.8941} - \frac{1}{Z} \right)^{6/5} \quad (XXIII.13)$$

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 $\frac{1}{\sqrt{n}}$, which was neglected in Stillinger's work. This led to the improved estimate for $Z_{critical}$ in Eq. (XXIII.8).

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

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

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

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

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

$$\begin{aligned}
 E_{Z,N} &= Z^{7/3} \left(\sum_{m=0}^{\infty} a_{0m} \left(\frac{N}{Z} \right)^{m+1/3} \right) + Z^2 \left(\sum_{m=0}^{\infty} a_{1m} \left(\frac{N}{Z} \right)^m \right) + Z^{5/3} \left(\sum_{m=0}^{\infty} a_{2m} \left(\frac{N}{Z} \right)^{m-1/3} \right) + \dots \\
 &= \sum_{n=0}^{\infty} \left[\left(\sum_{m=0}^{\infty} a_{nm} \left(\frac{N}{Z} \right)^{m-n/3} \right) Z^{7-n/3} \right] \\
 &= \sum_{n=0}^{\infty} \phi_n \frac{N}{Z} Z^{7-n/3}
 \end{aligned} \tag{XXIII.16}$$

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

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

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

G. Show that

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

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. (XXIII.18) to argue that for neutral atoms in the limit of large atomic number, the electronegativity should be (very roughly) proportional to $Z^{-1/3}$.

Along any given column of the periodic table, one does indeed find that the electronegativity reduces (roughly) as $Z^{-1/3}$. Clearly higher order effects ($Z^{-2/3}$ 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.

XXIV. Derivation of Hund's Rules [This problem is not yet completed; when it is finished, it will be worth 2.0 points]

We are going to derive Hund's rules for a closed subshells p^2 electron configuration. First, let's suppose the p orbitals we are considering have the following properties:

$$\begin{aligned}
 \psi_0(r, \theta, \phi) &= r \cdot f(r) Y_1^0(\theta, \phi) \\
 \psi_{\pm 1}(r, \theta, \phi) &= r \cdot \frac{f(r)}{\sqrt{2}} Y_1^{\pm 1}(\theta, \phi).
 \end{aligned} \tag{XXIV.1}$$

A. Show that

$$\psi_0(r) = \psi_z(r) = z f(r) \tag{XXIV.2}$$

$$\frac{\psi_1(r) + \psi_{-1}(r)}{\sqrt{2}} = \psi_x(r) = x f(r) \tag{XXIV.3}$$

$$\frac{\psi_1 \mathbf{r} - \psi_{-1} \mathbf{r}}{i\sqrt{2}} = \psi_y \mathbf{r} = yf \mathbf{r} \quad (\text{XXIV.4})$$

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

C. Show that

$$\Phi \mathbf{r}_1, \mathbf{r}_2 \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{-1} \mathbf{r}_1 & \alpha & 1 & \psi_1 \mathbf{r}_1 & \beta & 1 \\ \psi_{-1} \mathbf{r}_2 & \alpha & 2 & \psi_1 \mathbf{r}_2 & \beta & 2 \end{vmatrix} \quad (\text{XXIV.5})$$

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

D. The Slater determinant in Eq. (XXIV.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,

$$V \mathbf{r} = -\frac{Z}{r} + \int \frac{\rho_{core} \mathbf{x}}{|\mathbf{r} - \mathbf{x}|} d\mathbf{x} \quad (\text{XXIV.6})$$

where $\rho_{core} \mathbf{x}$ is the electron density associated with the closed subshells. Assume that

$$\left(-\frac{\nabla^2}{2} - \frac{Z}{r} + \int \frac{\rho \mathbf{x}}{|\mathbf{r} - \mathbf{x}|} d\mathbf{r} \right) \psi_m \mathbf{r} = \varepsilon \psi_m \mathbf{r} \quad (\text{XXIV.7})$$

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

$$\hat{h} \mathbf{r} = -\frac{\nabla^2}{2} + V \mathbf{r}, \quad (\text{XXIV.8})$$

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

$$\left(\hat{h} \mathbf{r}_1 + \hat{h} \mathbf{r}_2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \Psi \mathbf{r}_1, \mathbf{r}_2 = E \Psi \mathbf{r}_1, \mathbf{r}_2. \quad (\text{XXIV.9})$$

We want to show that

$$\frac{E^1S - E^1D}{E^1D - E^3P} = \frac{3}{2} \quad (\text{XXIV.10})$$

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

$$J_{ij} = \iint \frac{|\psi_i \mathbf{r}_1|^2 |\psi_j \mathbf{r}_2|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$K_{ij} = \iint \frac{\psi_i \mathbf{r}_1 \psi_j^* \mathbf{r}_1 \psi_i \mathbf{r}_2 \psi_j^* \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (\text{XXIV.11})$$

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

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

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