

One-Electron Atoms

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

I. 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

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

where the total mass is given by $M_{\text{total}} = m + M$ 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, $\Psi(x, X) = \psi(x)\phi(X)$, 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

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

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

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

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

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

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

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

(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

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

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 $r^{\lambda+1} \frac{d\phi_{n,l}(r)}{dr} - \frac{\lambda+1}{2} r^\lambda \phi_{n,l}(r)$ and integrate with respect to r from zero to infinity.

- A. Show that one can obtain the recurrence relation**

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

(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

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

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

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

Differentiating both sides by l we obtain

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

D. Show that

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

(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

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

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

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

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

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

(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

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

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

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

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

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

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

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

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

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

where

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

is the Coulomb potential due to the nucleus. Here

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

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

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

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

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

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

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

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, $\{f_n(x)\}_{n=0}^{\infty}$, 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

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

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

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

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,

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

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

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

$\rho(R)$ 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

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

To evaluate this integral, note that

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

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. (X.17)).

- H. Using Eq. (X.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

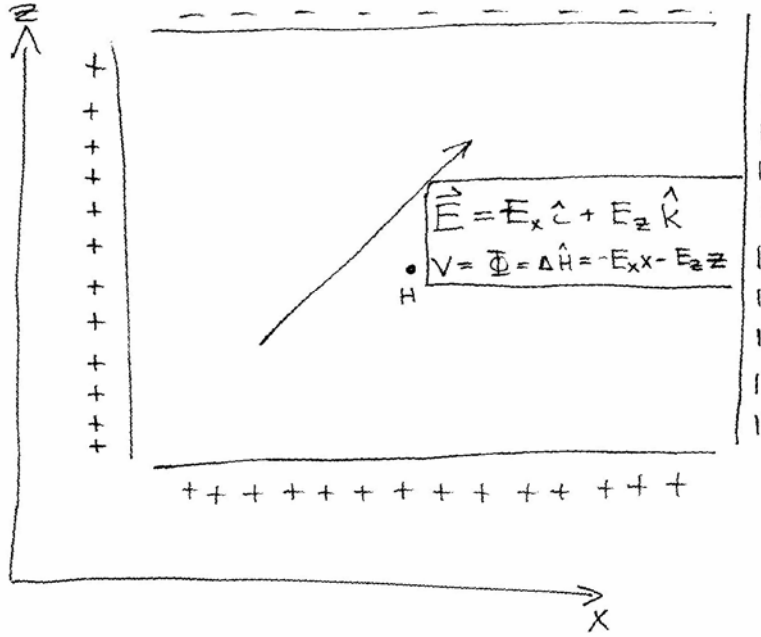
$$\sigma_p \equiv \sqrt{\langle \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} \rangle - \langle \hat{\mathbf{p}} \rangle \cdot \langle \hat{\mathbf{p}} \rangle} \quad (\text{VII.12})$$

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. 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,

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

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,

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

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,

$$\begin{aligned} V_{mn} &= \langle \psi_m | -E_x x - E_z z | \psi_n \rangle \\ &= \langle \psi_m | -E_x r \sin \theta \cos \phi - E_z r \cos \theta | \psi_n \rangle. \end{aligned} \quad (\text{VIII.3})$$

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)

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

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

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

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

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

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

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

- 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 $\psi_{2p_y}(\mathbf{r})$ 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

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

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

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

IX. 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, $\Phi_k(\boldsymbol{\tau})$. $\boldsymbol{\tau}$ can be \mathbf{r} , or even something in many more dimensions. Let's suppose that $\Phi_k(\boldsymbol{\tau})$ is an eigenfunction for a Hamiltonian,

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

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

$$\hat{\mathcal{H}}\Psi_l(\tau) = \left(-\frac{\nabla^2}{2} + \mathcal{V}(\tau)\right)\Psi_l(\tau) = \mathcal{E}_l\Psi_l(\tau). \quad (\text{IX.2})$$

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, $\{\Omega_\alpha\}_{\alpha=1}^{n_k+1}$, which are separated by nodal surfaces, $\{S_\beta\}_{\beta=1}^{n_k}$, 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

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

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. (IX.3) must be zero because, by definition, $\Phi_k(\tau)$ is zero on its nodal surface.

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

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

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

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

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. (IX.4) is

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

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

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

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. (IX.6) and (IX.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. (IX.6) and (IX.7) we deduce that

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

whence

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

(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 (IX.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. (IX.9) also. For instance, using inequalities like

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

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

X. 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

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

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),

$$\sum_{n=1}^N \left(-\frac{\nabla_n^2}{2} + \sum_{\alpha=1}^P -\frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} + \sum_{m=n+1}^N \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \Psi_k^N(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_P) = E_k^N(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) \Psi_k^N(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_P), \quad (\text{X.2})$$

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

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

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. (X.2). The Schrödinger equation for the molecule then becomes

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

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

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

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:

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

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 $|\Psi_0^{N-1}|^2$. The probability of observing electron N at \mathbf{r}_N is $|f_k(\mathbf{r}_N)|^2$. The probability of observing both events is given by Eq. (X.6).

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

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

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 Nth electron, namely:

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

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

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

where E_0^{N-1} is the ground state energy of the cation. Multiply this equation by $(\Psi_0^{N-1})^*$ and integrate over the first N-1 electronic positions. One obtains

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

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

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

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

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

where

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

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,

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

(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 (X.13) in Eq. (X.11), one obtains

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

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

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

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

$$\left(-\frac{\nabla_N^2}{2} - \frac{Q+1}{r_N} \right) f_{n,l}(\mathbf{r}_N) = (E_{n,l}^N - E_0^{N-1}) f_{n,l}(\mathbf{r}_N), \tag{X.17}$$

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

Equation (X.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

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

This gives, then

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

Equation (X.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 (X.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

$$f_{n,l}(\mathbf{r}) = A r^{\frac{Q+1}{\alpha}-1} e^{-\alpha r} \left(1 + \text{errors of order } \frac{1}{r}, \frac{1}{r^2}, \dots \right) \tag{X.20}$$

F. Show that

$$\alpha = \sqrt{2 \cdot IP_{n,l}} \tag{X.21}$$

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

$$e^{-\sqrt{-2E_{n,l}}r}, \tag{X.22}$$

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

$$\Delta_{n,l}^{(1)} \approx \left\langle f_{n,l}(\mathbf{r}_N) \left| \frac{-\sum_{\alpha=1}^P Z_{\alpha} R_{\alpha} A(\theta_{\alpha}, \phi_{\alpha}, \theta_N, \phi_N) + (N-1) \langle \Psi_0^{N-1} | A(\theta_1, \phi_1, \theta_N, \phi_N) \cdot r_1 | \Psi_0^{N-1} \rangle_{1 \dots N-1}}{r_N^2} \right| f_{n,l}(\mathbf{r}_N) \right\rangle \quad (\text{X.23})$$

Because the amount of positive charge, $\sum_{\alpha=1}^P Z_{\alpha}$, exceeds the amount of negative charge, $(N-1)$, the integrand in Eq. (X.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

$$\delta(l) \approx -\frac{n^3 \Delta_{n,l}^{(1)}}{(Q+1)^2}. \quad (\text{X.24})$$

Based on Eq. (X.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. (X.1) as

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

to find that we can identify

$$Z_{\text{eff}} \approx (Q+1) \left(1 + \frac{\delta(l)}{n}\right). \quad (\text{X.26})$$

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

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

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. (X.26) but because the ground state of an atom is not a Rydberg state, the approximation is usually very poor.

- I. Derive Eq. (X.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.

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

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

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

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

$$\left(\frac{-1}{2} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} \right) + \frac{A}{(1-r^2)^3} \right) S_{n,l}(r) = E_{n,l} S_{n,l}(r) \quad (\text{XI.2})$$

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.