

# Mathematical Methods, the Born-Oppenheimer Approximation, and the One-Electron Atom

You can choose to omit one problem from numbers III-VI.

## I. The Dirac Delta Function

On the first day of class, I talked about the Dirac Delta function. The defining relation of the Dirac delta function is that

$$\int_{-\infty}^{\infty} f(x) \delta(x - x_0) dx \equiv f(x_0) \quad (1.1)$$

A. Show that the Dirac delta function is normalized. That is, show that

$$\int_{-\infty}^{\infty} \delta(x - x_0) dx \equiv 1 \quad (1.2)$$

Next, recall that any function can be expanded in terms of a complete set of orthonormal basis functions—for instance, the eigenfunctions of the harmonic oscillator Hamiltonian (or, for that matter, any Hamiltonian).

B. Let  $\{\psi_n(x)\}_{n=0}^{\infty}$  be a complete set of orthonormal functions. Show that the Dirac delta function is given by

$$\sum_{n=0}^{\infty} \psi_n(x_0) \psi_n(x) \equiv \delta(x - x_0). \quad (1.3)$$

The left-hand-side of Eq. (1.3) is called the Poisson kernel. If the sum doesn't extend all the way to infinity, it is called the Christoffel-Darboux kernel.

C. Use integration by parts to show that

$$\int_{-\infty}^{\infty} f(x) \frac{d(\delta(x - x_0))}{dx} dx \equiv - \left. \frac{df(x)}{dx} \right|_{x=x_0} = -f'(x_0) \quad (1.4)$$

In three dimensions, we have

$$\delta(\mathbf{r} - \mathbf{r}_0) \equiv \delta(x - x_0) \delta(y - y_0) \delta(z - z_0) \quad (1.5)$$

D. Confirm that

$$\int f(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_0) d\mathbf{r} = f(\mathbf{r}_0). \quad (1.6)$$

(Here, and in the following, integrations without limits are assumed to be over all space. So

$$\int f(\mathbf{r}) d\mathbf{r} \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y, z) dx dy dz \quad (1.7)$$

E. In Spherical coordinates,

$$\delta(\mathbf{r} - \mathbf{r}_0) = \frac{1}{r^2 \sin \theta} \delta(r - r_0) \delta(\theta - \theta_0) \delta(\phi - \phi_0) \quad (1.8)$$

**Explain why the  $\frac{1}{r^2 \sin \theta}$  term is needed.**

When I introduced the Dirac delta function, I said that

$$\int \rho(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_0) d\mathbf{r} = \rho(\mathbf{r}_0) \quad (1.9)$$

represented the probability of observing an electron at  $\mathbf{r}_0$ , if  $\rho(\mathbf{r})$  is the electron density—the distribution function for electrons.

**F. Let  $P(\mathbf{r})$  be the charge density for a single classical particle. What sort of physical system is characterized by**

$$P(\mathbf{r}) \equiv Ze\delta(\mathbf{r} - \mathbf{r}_0)? \quad (1.10)$$

The Dirac delta function is usually constructed using “delta function sequences”. The simplest such sequence is the function

$$f_a(x) = \begin{cases} 0 & x < -a \\ \frac{1}{2a} & -a \leq x \leq a \\ 0 & x > a \end{cases} \quad (1.11)$$

**G. Show that**

$$\lim_{a \rightarrow 0^+} f_a(x) \rightarrow \delta(x) \quad (1.12)$$

**by showing that this function satisfies the key relation, Eq. (1.1).**

From this result, do you see why I said that Eq. (1.9) represents the “expectation value” for observing an electron at the point  $\mathbf{r}_0$ ?

Hint for part **G**: Remember, from calculus, that the average value of a function on an interval is

$$\text{average value of } f \text{ in the interval } [a, b] \equiv \bar{f} \equiv \frac{1}{b-a} \int_a^b f(x) dx \quad (1.13)$$

Equation (1.13) is easy to remember: it is just the continuous version of the formula for the mean of a data set,

$$\bar{f} = \frac{1}{N} \sum_{n=1}^N f_n \quad (1.14)$$

## II. The Born-Oppenheimer Approximation

The goal of this exercise is to show that the ground state total energy computed using the Born-Oppenheimer approximation is a lower bound to the true energy.

Let's consider the exact ground state wave function,  $\Psi_{\text{exact}}(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\})$ , which solves

$$(\hat{T}_n + \hat{T}_e + V(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\})) \Psi_{\text{exact}} = E_{\text{exact}} \Psi_{\text{exact}}. \quad (11.1)$$

From the variational principle, the ground state energy could also be found by

$$E_{\text{exact}} = \min_{\Psi} \frac{\langle \Psi | \hat{T}_n + \hat{T}_e + V(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) | \Psi \rangle_{\mathbf{r}, \mathbf{R}}}{\langle \Psi | \Psi \rangle_{\mathbf{r}, \mathbf{R}}}. \quad (11.2)$$

The notation  $\langle \cdot \rangle_{\mathbf{r}, \mathbf{R}}$  indicates that the integration variables include both the electronic and the nuclear coordinates.

By comparison, in the Born-Oppenheimer approximation, we approximate the wave function with

$$\Psi^{BO} \equiv \psi_e^{BO}(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) \chi_n^{BO}(\{\mathbf{R}_\alpha\}) \quad (11.3)$$

and determine  $\psi_e$  using the “electronic Schrödinger equation”

$$(T_e + V(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}))\psi_e^{BO}(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) = U^{BO}(\{\mathbf{R}_\alpha\})\psi_e^{BO}(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}). \quad (\text{II.4})$$

For any given set of nuclear positions,  $\{\mathbf{R}_\alpha\}$  is constant, and we could use the variational principle to determine the potential energy surface,  $U(\{\mathbf{R}_\alpha\})$ ,

$$U^{BO}(\{\mathbf{R}_\alpha\}) = \min_{\psi_e} \frac{\langle \psi_e | \hat{T}_e + V(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) | \psi_e \rangle_r}{\langle \psi_e | \psi_e \rangle_r} \quad (\text{II.5})$$

Unlike the case in Eq. (II.2), here the notation,  $\langle | \rangle_r$ , indicates that the expression is only integrated with respect to electronic coordinates.

We can consider  $\Psi_{exact}(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\})$  to be an “approximate wave function” for the electronic Hamiltonian.

Then, from Eq. (II.5), we have that

$$\frac{\langle \Psi | \hat{T}_e + V(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) | \Psi \rangle_r}{\langle \Psi | \Psi \rangle_r} \geq \frac{\langle \psi_e | \hat{T}_e + V(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) | \psi_e \rangle_r}{\langle \psi_e | \psi_e \rangle_r} = U(\{\mathbf{R}_\alpha\}) \quad (\text{II.6})$$

and so

$$\langle \Psi | \hat{T}_e + V(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) | \Psi \rangle_r \geq U(\{\mathbf{R}_\alpha\}) \langle \Psi | \Psi \rangle_r. \quad (\text{II.7})$$

Now, using the fact that

$$E_{exact} = \frac{\langle \Psi_{exact} | \hat{T}_n + \hat{T}_e + V(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) | \Psi_{exact} \rangle_{\mathbf{r}, \mathbf{R}}}{\langle \Psi_{exact} | \Psi_{exact} \rangle_{\mathbf{r}, \mathbf{R}}}, \quad (\text{II.8})$$

#### A. Show that

$$E_{exact} \langle \Psi_{exact} | \Psi_{exact} \rangle_{\mathbf{r}, \mathbf{R}} \geq \langle \Psi_{exact} | \hat{T}_n + U^{BO}(\{\mathbf{R}_\alpha\}) | \Psi_{exact} \rangle_{\mathbf{r}, \mathbf{R}} \quad (\text{II.9})$$

(Hint: use Eqs. (II.7) and (II.8).)

Now, recall that the nuclear wave function in the Born-Oppenheimer approximation is determined from the Schrödinger equation,

$$(\hat{T}_n + U^{BO}(\{\mathbf{R}_\alpha\}))\chi_n^{BO}(\{\mathbf{R}_\alpha\}) = E^{BO}\chi_n^{BO}(\{\mathbf{R}_\alpha\}). \quad (\text{II.10})$$

#### B. Write the variational principle corresponding to Eq. (II.10).

#### C. Use Equation (II.9) and the result from part B to show that

$$E_{exact} \geq E^{BO}. \quad (\text{II.11})$$

### III. Mass Effects in One Electron atoms

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

$$V(r) \equiv \frac{-GM_H m_e}{r} \quad (\text{III.1})$$

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

$$\mathbf{X} \equiv \frac{M\mathbf{R} + m\mathbf{r}}{m + M} \quad (\text{III.2})$$

and a relative position coordinate

$$\mathbf{x} = \mathbf{r} - \mathbf{R}. \quad (\text{III.3})$$

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

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

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,  $\Psi(\mathbf{x}, \mathbf{X}) = \psi(\mathbf{x})\phi(\mathbf{X})$ , 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)?**

## IV. Expectation Values in the Hydrogen Atom

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:

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

You will have to evaluate numerous integrals with of the form

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

To evaluate this integral, note that

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

Then, one has that

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

so

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

- 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<sub>z</sub>-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

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

- 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,

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

Often one defines the “radius” of an orbital in a many-electron atom using either Equation (IV.6) or Eq. (IV.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

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

The energy of an electron very far from a many-electron atom is equal to minus the ionization potential of that atom.

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

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

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

We can state the Heisenberg Uncertainty principle as

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

where

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

and

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

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

- I.** Show that Eq. (IV.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).

## V. More on Expectation Values

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

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

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

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

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

$$\frac{\lambda+1}{n^2} Z^2 \langle r^\lambda \rangle - Z(2\lambda+1) \langle r^{\lambda-1} \rangle + \lambda[l(l+1) - \frac{1}{4}(\lambda+1)(\lambda-1)] \langle r^{\lambda-2} \rangle = 0 \quad (\text{V.3})$$

(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,  $\langle r^0 \rangle = 1$ .)

## VI. Wintner's Nodal Theorem

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

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

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

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

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  $\Omega_\beta$ .

### 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

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

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

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

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

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

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

Let us assume that  $\Psi_l(\tau)$  does not change sign in  $\Omega_\alpha$ . 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. (VI.4) is

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

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

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

where we have assumed that  $(E_k - v(\tau)) - (\mathcal{E}_l - \mathcal{V}(\tau))$  does not change sign in the region  $\Omega_\alpha$ . The key to deriving Eqs. (VI.6) and (VI.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. (VI.6) and (VI.7) we deduce that

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

whence

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

(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 (VI.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,  $\Phi_k$ , of a system with energy  $E_k$ . Let  $\Phi_{l < k}$  be any state with lower energy,  $E_l < E_k$ . Let  $\Omega_\alpha$  be any “nodal region” of  $\Phi_l$ . Then  $\Phi_k$  must have a node in  $\Omega_\alpha$ .**

**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. (VI.9) also. For instance, using inequalities like

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

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



The Following Problems are Not Assigned Problems. However, you should read through the problems and ensure that you understand them, as they are important and/or fundamental. The first problem should be familiar from 3BA3; the second is just a suggestion of a good exercise. Of course, either of these would count as “extra credit” if you actually decided to perform them.

## VII. Perturbation Theory for Degenerate States

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 principal 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

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

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

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

form a  $g$ -fold degenerate state, so that

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

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

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

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,

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

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

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

where

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

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 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. (VII.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  $\lambda$ ,

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

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

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

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

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

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

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

and

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

The “perturbed Hamiltonian”,

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

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

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

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

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

Equations (VII.11) and (VII.14) are our working equations. The choice of notation is such that a superscript  $(\mu)$  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  $\hat{H}^{(\mu)}$  form a complete set, we can write  $\Psi_n^{(0)}$  as

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

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

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

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

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

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

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

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

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

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,

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

we must have that  $l_n = r_n$ . (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  $\mu^0 = 1$ ,  $\mu$ ,  $\mu^2$ , etc. on the left-hand-side and right-hand-side of Eq. (VII.20) must be equal.

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

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

Let us first consider the case where  $E_n^{(\mu)}$  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  $E_n^{(\mu)}$  is a non-degenerate state.

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

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

That is,  $c_{in} = 0$  unless  $\Psi_i^{(\mu)}$  and  $\Psi_n^{(\mu)}$  have the same energy. Recalling that the Kronecker delta,  $\delta_{ij}$ , is zero unless its arguments are equal ( $i = j$ ), we can summarize the consequences of Eq. (VII.23) with

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

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

**A. Show that Eq. (VII.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. (VII.20).

**B. When you equate the coefficients of  $\mu$  in Eq. (VII.20), show that you obtain the equation**

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

The easiest way to solve Eq. (VII.26) is to multiply both sides by  $\Psi_m^{(\mu)}$  and integrate. We obtain

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

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

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

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

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

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  $\mathbf{c}_n \equiv [c_{k+1,n}^{(\mu)}, c_{k+2,n}^{(\mu)}, \dots, c_{k+g,n}^{(\mu)}]$  is an eigenvector of**

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

then Eq. (VII.29) is satisfied.

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

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

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

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

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

and

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

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

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

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

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

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

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

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

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

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

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

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.