

Final Examination

Chemistry 3BB3; Winter, 2005

2-choice multiple choice. 1 point each.

1. Is

$$\Psi(r_1, \sigma(1), r_2, \sigma(2)) \propto e^{-\zeta_1} e^{-\zeta_2} (1 + b|r_1 - r_2| + c|r_1 - r_2|^2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

an acceptable approximate wave function for the Helium atom?

- (a) yes
- (b) no

2. To separate atoms with different amounts of spin-angular momentum about the z -axis, we could pass the atoms through a

- (a) electric field.
- (b) magnetic field.

3. In the Hydrogen atom, which transition do you expect to be more intense based on the size of the transition dipole, $\langle \phi_f | \hat{\mu} | \phi_i \rangle$.

- (a) a transition from the $1s$ orbital to the $2p$ orbital.
- (b) a transition from the $1s$ orbital to the $6p$ orbital.

4. Linear combinations of atomic orbitals are most strongly associated with

- (a) molecular-orbital theory.
- (b) valence-bond theory.

5. Suppose you use linear combinations of occupied atomic orbitals to describe a diatomic molecule. If you want to make sure that you obtain a good approximation for the equilibrium bond length, it is most effective to

- (a) generalize the atomic orbitals by introducing "effective nuclear charges."
- (b) mix unoccupied orbitals, especially p orbitals. (For example, you might include a contribution from the $2p$ orbital in the wave function for the hydrogen molecule.)

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12. For a homonuclear diatomic molecule, transitions from a π_u^+ orbital to a π_u^- orbital are
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13. For a homonuclear diatomic molecule, transitions from a π_u^+ orbital to a π_g^- orbital are
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14. In interstellar space, molecules are very far apart (the density can be measured in molecules per cubic meter) and very, very, cold (2.7 Kelvin). The lineshape of their observed spectra will be best approximated by
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15. In the corona of the sun, the gasses are *very hot*, but the density of the gasses is still rather low. If we observe the spectra of the sun's corona, the lineshapes will be best approximated by
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16. Suppose we take the spectrum of a cheap American beer (essentially, we are interested in a damnably dilute solution of ethanol molecules in water). We expect that lineshape of the absorptions associated with the ethanol molecules will be
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Multiple Choice and Short-Answer: (2 points each)

One of the most important reasons why the Bohr model for the Hydrogen atom was accepted is because it correctly predicted the *Rydberg* formula, which encapsulates the transition frequency of *all* the observed spectral lines for the Hydrogen atom. Rydberg was a mere high school teacher (well, maybe not a “mere” high school teacher) when he derived this formula. In addition, you have a big advantage, of course, because quantum mechanics has been invented now (and all Rydberg had was a bunch of spectra to stare at).

17. So, Hydrogen atoms are observed to absorb at frequencies of

$$\omega_{fi} =$$

Your formula should be written in terms of the principle quantum numbers of the initial and final states.

18. The wave function is required to be an eigenfunction of the molecular Hamiltonian and also an eigenfunction of \hat{J}^2 . We can choose Ψ_J so that it is also an eigenfunction of:

- | | | | |
|-----------------|-----------------|-----------------|-----------------|
| (a) \hat{L}_z | (c) \hat{S}_z | (e) \hat{J}_x | (g) \hat{S}_y |
| (b) \hat{L}^2 | (d) \hat{S}^2 | (f) \hat{L}_x | (h) \hat{S}_x |

19. Write a Slater determinant for the triplet excited state of the Beryllium atom with the $1s^2 2p^1 3d^1$ electron configuration. Choose the Slater determinant so that it corresponds to the greatest possible magnetic quantum number, M_L . Write this *as a determinant of a matrix*, and not using our shorthand “one-line” notation.

20. For the Slater determinant in the previous problem, what are the expectation values of the following operators? (List all possibilities when multiple possibilities exist.)

$$\hat{L}^2$$

$$\hat{J}_z$$

Determine the ground state term symbols associated with Germanium, which has the $[Ar]4s^23d^{10}4p^2$ electron configuration.

21. List the term symbols in order of increasing energy (e.g., lowest energy first) using Hund's rules. You can ignore the dependence on J in this case.
22. Circle all the terms for which a Slater determinant wave function can be written. (That is, circle all the terms for which a Slater determinant representation, Φ , that is an eigenfunction of \hat{L}^2 and \hat{S}^2 with the appropriate value of L and S exists.)
23. For the ground-state term, the value of J associated with the ground state is

24. How many σ_g orbitals are occupied in the B_2 molecule?

(a) one

(b) two

(c) three

Suppose we consider the hydrogen molecule, H_2 , at very large distances, where the energy from simple molecular-orbital theory is much too high. Recall that when this occurs, it is because the simple-molecular orbital theory wave function has significantly higher energy than the “true” wave function, which is accurately described by valence-bond theory.

25. What is the simplest valence-bond wave function. (This is the Heitler-London wave function.)

26. Write the Heitler-London + ionic wave function; that is, write the Heitler-London wave function, including the contribution from ionic terms.

27. The *restricted* Hartree-Fock approximation gives back the very bad molecular-orbital theory result for the dissociation of H_2 . The *unrestricted* Hartree-Fock approximation actually does much better, and correctly predicts that the separated-atom limit of the hydrogen molecule. Explain why.

28. We discussed various approximations when deriving Fermi's Golden Rule. When these approximations were not true, "exotic" or "rare" phenomena are observed. Match each approximation listed below to the phenomenon that is observed when it does not hold

Phenomena:

- (i) electric quadrupole transitions
- (ii) nonlinear optical effects (e.g., more than one photon is absorbed at the same time)
- (iii) vibronic coupling
- (iv) light is absorbed even though the energy of the photons, $E = \hbar\omega$ doesn't match the energy of the transitions.

Approximations:

_____ long-wavelength approximation.

_____ weak-field approximation.

29. Write the general form of a Lorentzian lineshape with peak absorbance at ω_0 and full-width at half maximum given by Γ . (If you forget some of the dependencies, do the best you can.)

In discussing broadening, a key quantity was the time-correlation function, $C(t)$, which expressed the relationship between the “transition dipole” moment at time t to the “transition dipole moment” at time zero.

30. What was the expression for the dipole moment operator at time t ? (Recall that we could consider the *Heisenberg* picture, where the operators depend on time, or the *Schrödinger* picture, where the wave function depend on time. This question relates to the *Heisenberg picture*.)

$$\hat{\mu}(t) \equiv$$

31. What was the expression for the time-correlation function?

$$C(t) \equiv$$

32. The lineshape function, $I(\omega)$, is proportional to the Fourier transform of the time-correlation function. Specifically,

$$I(\omega) \equiv 2\pi\hat{C}(\omega)$$

What is the formula for $\hat{C}(\omega)$, in terms of $C(t)$. (This just tests whether you know what the definition of the Fourier Transform is.)

In predissociation, we said that the progression of spectral lines associated with the vibrational fine structure of the electronic transition started off sharp, then became broader, and then became sharp again.

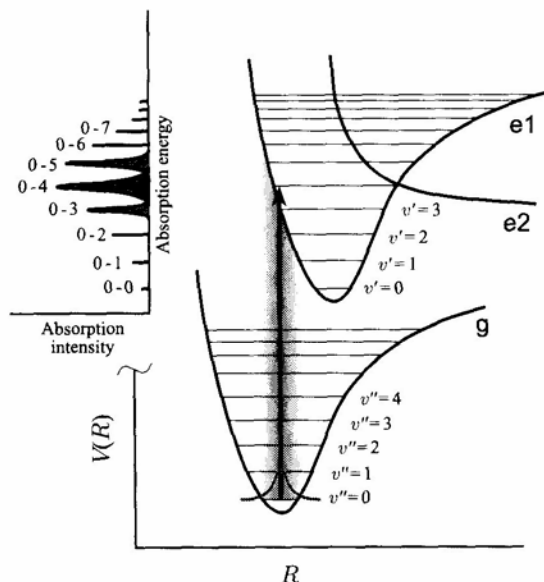


Figure 11.11. Potential energy surfaces leading to predissociation.

Your experimentalist friends decide to test whether this is homogeneous broadening or inhomogeneous broadening by engaging in a “hole-burning” experiment on one of the broad spectral lines. You tell them that they are idiots, and you already know how the experiment will turn out. In fact, you even sketch the results of the experiment for them.

33. Sketch the absorption spectrum with and without hole-burning. For simplicity, you can consider only the peak that corresponds to transitions from the ground vibrational state (of the ground electronic state) to the fourth excited vibrational state (of the excited electronic state).

Derivation Portion (40 points; Choose 5 of 6):

1. Using the Born-Oppenheimer Approximation, derive

- (a) the electronic Schrödinger equation for a LiH.
- (b) the nuclear Schrödinger equation for LiH.

(The derivation is worth 3 points. Writing the electronic and nuclear Schrodinger equations correctly worth 2 points each. Labeling the “physical interpretation” of each term (e.g., appropriately labeling the term that corresponds to the electronic kinetic energy) is worth 1 point.

2. Expectation values for the Hydrogen atom. You will find it helpful to recall that

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

- (a) For a given principle quantum number, n , write a wave function for the state that has the highest possible magnetic quantum number, m , that is consistent with n . (Do not forget the angular portion of the wave function. I don't expect you to know the normalization constant.) (2 points)

$$\Psi_{n,l,m}(r, \theta, \phi) = N_{n,l,m} \cdot \left[\right] \quad (2)$$

- (b) What is the most probable distance from the nucleus for an electron in this state? (2 points)

- (c) What is the average (mean) distance of an electron from the nucleus for these states? (Include the appropriate dependence on the normalization constant, $N_{n,l,m}$, in your answer.) (2 points)

- (d) Based on your intuition, is distance of the electron from the nucleus in these states (with the maximum value of m) *greater than* or *smaller than* the distance of the electron from the nucleus in states with smaller total angular momentum? (1 point)
- (a) greater than
(b) smaller than

The root-mean-square (rms) distance of the electron from the nucleus is related to the expectation value of $\langle r^2 \rangle$. Specifically, we have

$$r_{\text{rms}} \equiv \sqrt{\langle r^2 \rangle} \quad (3)$$

- (e) Again, based on your intuition, which of the following is true (1 point)

- (a) $r_{\text{most probable}} < r_{\text{rms}} < r_{\text{mean}}$ (c) $r_{\text{mean}} < r_{\text{most probable}} < r_{\text{rms}}$ (e) $r_{\text{rms}} < r_{\text{mean}} < r_{\text{most probable}}$
 (b) $r_{\text{most probable}} < r_{\text{mean}} < r_{\text{rms}}$ (d) $r_{\text{mean}} < r_{\text{rms}} < r_{\text{most probable}}$ (f) $r_{\text{rms}} < r_{\text{most probable}} < r_{\text{mean}}$

3. For the Helium atom, we considered a wave function with the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2) \left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right) \quad (4)$$

where

$$\phi_{1s}(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}. \quad (5)$$

We found that the energy of this wave function was given by the form,

$$\begin{aligned} E(\zeta) &\equiv \langle \Psi(\mathbf{r}_1, \mathbf{r}_2) | \hat{H} | \Psi(\mathbf{r}_1, \mathbf{r}_2) \rangle \\ &= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - 2) \end{aligned} \quad (6)$$

where the Hamiltonian of the Helium atom has the form

$$\hat{H} \equiv \frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (7)$$

- (a) Suppose we approximate the energy of the Helium atom by using first-order perturbation theory, where the electron-electron repulsion term in Eq. (7) is treated as a perturbation. What is the approximate energy? (4 points)

- (b) Suppose we approximate the energy of the Helium atom using the variational principle, using trial wave functions with the form given by Eqs. (4) and (5). What is the approximate energy? (4 points)

4. Molecular-Orbital Theory for the Heteronuclear Diatomic Molecule

Consider a heteronuclear diatomic molecule, CD . Assume that the bond between atoms C and D can be well described as a linear combination of an atomic orbital, $\phi_C(\mathbf{r})$ centered on atom C and an atomic orbital, $\phi_D(\mathbf{r})$, centered on atom D . These orbitals are eigenfunctions of the “effective” Schrodinger equations for the atoms,

$$\left(\frac{-\nabla^2}{2} + v_C(\mathbf{r})\right)\phi_C(\mathbf{r}) = \varepsilon_C\phi_C(\mathbf{r}) \quad (8)$$

and

$$\left(\frac{-\nabla^2}{2} + v_D(\mathbf{r})\right)\phi_D(\mathbf{r}) = \varepsilon_D\phi_D(\mathbf{r}) \quad (9)$$

The molecular orbital related to bonding/antibonding are eigenfunctions of the equation

$$\left(-\frac{\nabla^2}{2} + v_C(\mathbf{r}) + v_D(\mathbf{r})\right)\psi(\mathbf{r}) = E_{MO}\psi(\mathbf{r}) \quad (10)$$

and, as stated before, the molecular orbital can be approximated as a linear combination of the atomic orbitals, $\phi_C(\mathbf{r})$ and $\phi_D(\mathbf{r})$.

In order to solve this problem, we made several assumptions, which you may make again here. We assumed that the overlap between the atomic orbitals was zero

$$S_{CD} \equiv \langle \psi_C | \psi_D \rangle = \int \psi_C^*(\mathbf{r}) \psi_D(\mathbf{r}) d\mathbf{r} \approx 0 \quad (11)$$

and we “named” the resonance integral β ,

$$\beta = \langle \psi_C | \hat{h} | \psi_D \rangle \quad (12)$$

- (a) Show that, in this model, the energy of the bonding and antibonding molecular orbitals is (4 points)

$$E_{MO} = \frac{\varepsilon_C + \varepsilon_D}{2} \pm \frac{\varepsilon_C - \varepsilon_D}{2} \sqrt{1 + \frac{4|\beta|^2}{(\varepsilon_C - \varepsilon_D)^2}} \quad (13)$$

(b) Suppose ε_C is an acid and ε_D is a base. Does the antibonding molecular orbital correspond to the positive sign or the negative sign in Eq. (13). (1 point)

(c) The antibonding molecular orbital can be written as (1 point)

$$\psi(\mathbf{r}) = k_C \psi_C(\mathbf{r}) + k_D \psi_D(\mathbf{r}) \quad (14)$$

(a) $|k_C| < |k_D|$

(b) $|k_C| > |k_D|$

(d) We said that the resonance integral could be written in the form

$$\beta = S_{CD} \left(\frac{\varepsilon_C + \varepsilon_D}{2} \right) + \frac{\langle \psi_C | v_D(\mathbf{r}) | \psi_D \rangle + \langle \psi_C | v_C(\mathbf{r}) | \psi_D \rangle}{2}. \quad (15)$$

Derive this result. (2 points)

5. Time-Dependent Perturbation Theory

When we performed time-dependent perturbation theory, we expanded the energy and wave function in a Taylor series expansion with respect to the amplitude of the applied field, V .

$$E(t) = E_i + V \left. \frac{\partial E(t)}{\partial V} \right|_{V=0} + \frac{V^2}{2!} \left. \frac{\partial^2 E(t)}{\partial V^2} \right|_{V=0} + \dots \quad (16)$$

$$\Psi(t) = \Psi_i + V \left. \frac{\partial \Psi(t)}{\partial V} \right|_{V=0} + \frac{V^2}{2!} \left. \frac{\partial^2 \Psi(t)}{\partial V^2} \right|_{V=0} + \dots \quad (17)$$

Substituting these results into the time-dependent Schrödinger equation and grouping terms with the same order, we obtained:

$$\begin{aligned} \hat{H}_{molecule} \Psi_i &= i\hbar \frac{\partial \Psi_i}{\partial t} \\ \hat{H}_{molecule} \left(V \left. \frac{\partial \Psi(t)}{\partial V} \right|_{V=0} \right) + \hat{V} \Psi_i &= i\hbar \left(V \left. \frac{\partial^2 \Psi(t)}{\partial V \partial t} \right|_{V=0} \right) \\ \hat{H}_{molecule} \left(\frac{V^2}{2!} \left. \frac{\partial^2 \Psi(t)}{\partial V^2} \right|_{V=0} \right) + \hat{V} \left(V \left. \frac{\partial \Psi(t)}{\partial V} \right|_{V=0} \right) &= i\hbar \left(\frac{V^2}{2!} \left. \frac{\partial^3 \Psi(t)}{\partial V^2 \partial t} \right|_{V=0} \right) \\ &\vdots \end{aligned} \quad (18)$$

(a) Derive Eq. (19) (3 points)

Solving the first equation in Eq. (18), we obtained

$$\Psi_i = \Phi_i e^{-iE_i t/\hbar}. \quad (19)$$

We then expanded the first-order change in the wave function in terms of the unperturbed wave functions,

$$\begin{aligned} V \left. \frac{\partial \Psi}{\partial V} \right|_{V=0} &= \sum_{k=0}^{\infty} c_k^{(1)} \Psi_k \\ &= \sum_{k=0}^{\infty} c_k^{(1)} \Phi_k e^{-iE_k t/\hbar}. \end{aligned} \quad (20)$$

and inserted this into the second equation (18), obtaining

$$\hat{V} \Phi_i e^{-iE_i t/\hbar} = i\hbar \sum_{k=0}^{\infty} \Phi_k e^{-iE_k t/\hbar} \frac{\partial c_k^{(1)}}{\partial t} \quad (21)$$

Assume that the perturbation in question is zero up to time t , and $Vf(t)$ thereafter. That is,

$$V(\mathbf{r}, t) = \begin{cases} 0 & t \leq 0 \\ Vf(t)g(x) & t > 0. \end{cases} \quad (22)$$

Suppose that, before the perturbation is turned on, only the ground state is occupied.

- (b) Show that the probability of finding an electron in the excited state τ seconds after the perturbation has been “turned on” is (5 points)

$$P_f(t) = \frac{\left| \langle \Phi_f | g(x) | \Phi_i \rangle \right|^2 V^2}{\hbar^2} \left| \int_0^t f(\tau) e^{i\omega_{fi}\tau} d\tau \right|^2 \quad (23)$$

6. When we were discussing collisional broadening, we derived a formula for the lineshape, namely

$$I(\omega) = \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i P_{none}(t) \langle \Phi_i | \hat{\mu}(0) \hat{\mu}(t) | \Phi_i \rangle e^{-i\omega t} dt \quad (24)$$

where $P_{none}(t)$ is the probability that the molecule has not undergone any collisions at time t and

$$\mu(t) = e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \quad (25)$$

If the pressure in our sample is very, very small, then we might approximate $P_{none}(t)$ as

$$P_{none}(t) = 1 \quad (26)$$

Using Eq. (26), derive the formula for the lineshape in this limit. (Hint: you should recover a formula that is familiar from our discussion of Fermi's Golden Rule, because this is precisely the case where broadening is negligible.)

Thinking Problem (10 points):

It is not uncommon to see an electronic excited state with a double minimum. The most famous case is the simple Hydrogen atom, wherein many of the bonding excited states (including the two with lowest energy) have double wells. The following curve, from [E. R. Davidson, *J. Chem. Phys.* 35 1189 (1965).] is a classic example. This problem will examine this phenomenon in more detail.

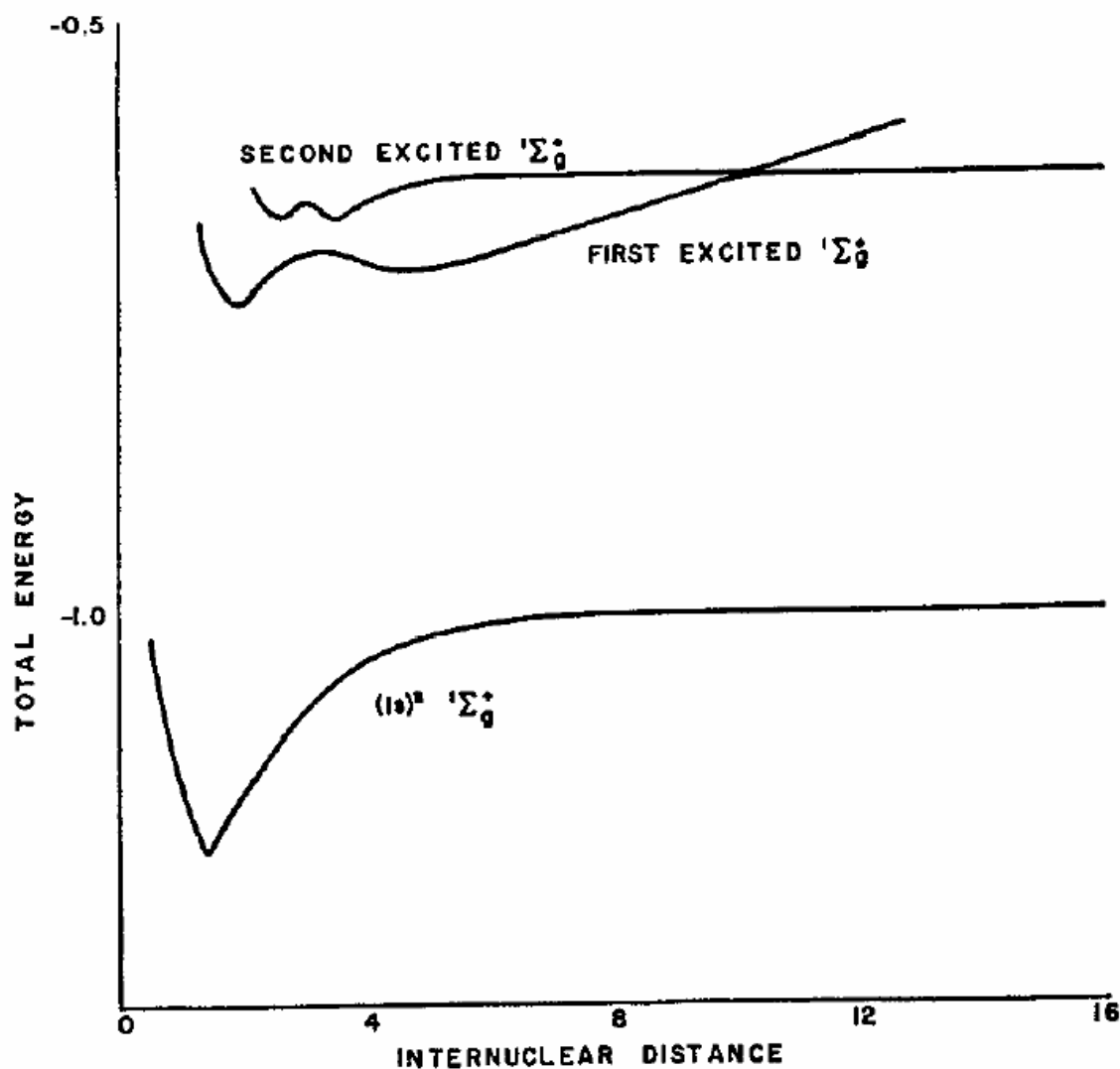
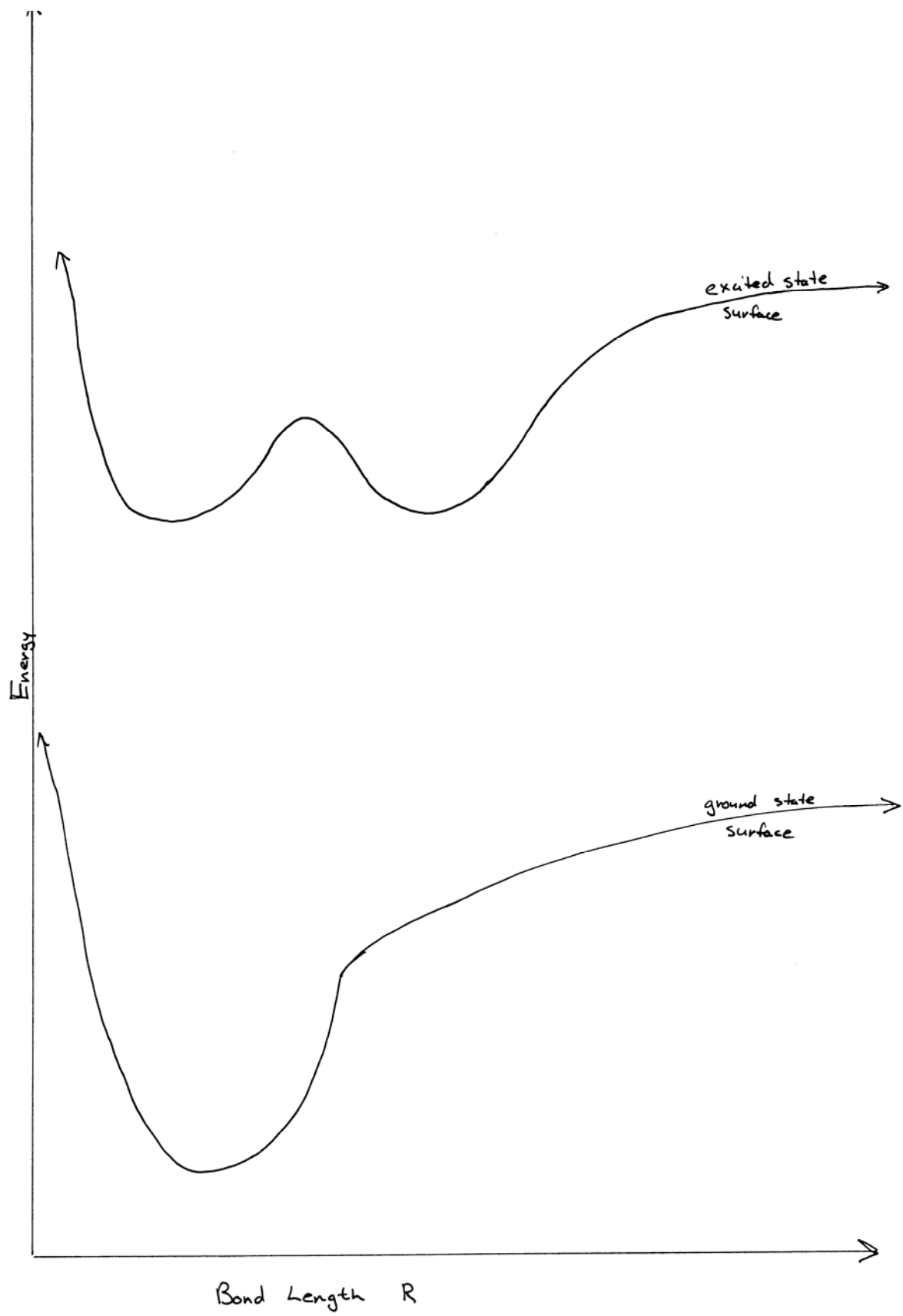


FIG. 2. A sketch of the potential curves for the first three $1\Sigma_g^+$ states of H_2 .



In parts B and C, we consider the absorption (part B) and emission (part C) spectrum that are characteristic of this molecule. In both problems, you can assume that

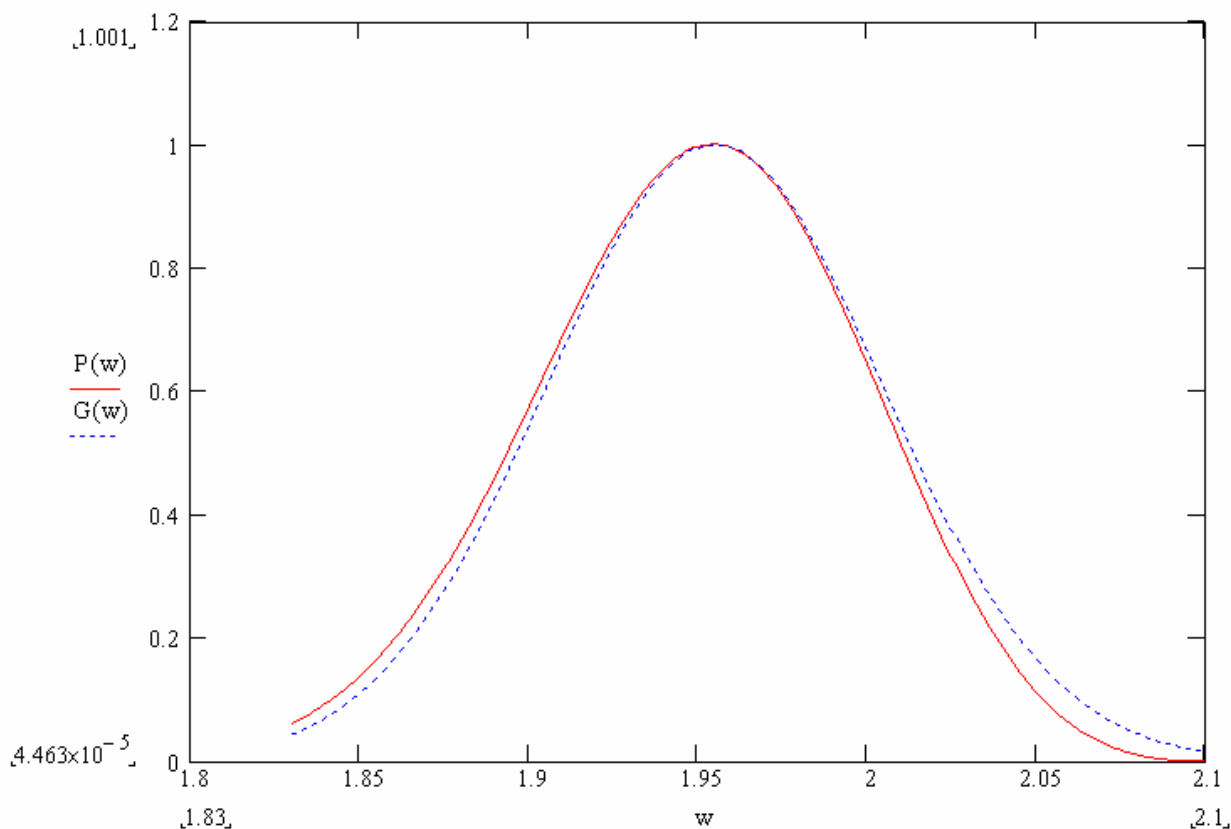
- (a) **the molecule is initially in the ground vibrational state.** (That is, absorption occurs from the ground vibrational state of the ground electronic state; emission occurs from the ground vibrational state of the excited electronic state. This is usually a reasonable assumption if the excited electronic state is long-lived).
- (b) **your experimental setup cannot resolve the vibrational fine-structure of the electronic transition.**
- (c) **vibronic coupling is negligible.**

B. Consider excitation from the ground electronic state to the electronic excited state shown here. Sketch the absorption spectrum. (2 points)

C. Sketch the emission spectrum from the excited electronic state to the ground electronic state. Use the same energy scale that you used in Part B. (2 points)

Due to anharmonicity in the potential energy surface, electronic spectral lines are often *not* symmetric. (Both the Gaussian and the Lorentzian lineshapes, on the contrary, are perfectly symmetric.) In this case, the probability that a molecule absorbs at frequency ω can be modeled with the expression

$$P(\omega) = \left(A + B(\omega - \omega_0 + \kappa_{shift})^2 \right) e^{-\alpha(\omega - \omega_0)^2} \quad (28)$$



- D. Suppose the probability that a molecule absorbs at frequency ω is given by Eq. (28). Does this describe homogeneous or inhomogeneous broadening? What is the formula for the spectral lineshape? (3 points)

Final Examination

Chemistry 3BB3; Winter, 2005

2-choice multiple choice. 1 point each.

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an acceptable approximate wave function for the Helium atom?

(a) yes

(b) no

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(a) electric field.

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Multiple Choice and Short-Answer: (2 points each)

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17. **So, Hydrogen atoms are observed to absorb at frequencies of**

$$\omega_{fi} = \frac{1}{2\hbar} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (\text{in atomic units})$$

Your formula should be written in terms of the principle quantum numbers of the initial and final states.

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| (b) \hat{L}^2 | (d) \hat{S}^2 | (f) \hat{L}_x | (h) \hat{S}_x |

19. Write a Slater determinant for the triplet excited state of the Beryllium atom with the $1s^2 2p^1 3d^1$ electron configuration. Choose the Slater determinant so that it corresponds to the greatest possible magnetic quantum number, M_L . Write this *as a determinant of a matrix*, and not using our shorthand “one-line” notation.

$$\Psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\alpha(1) & \psi_{1s}(\mathbf{r}_1)\beta(1) & \psi_{2p_1}(\mathbf{r}_1)\alpha(1) & \psi_{3d_2}(\mathbf{r}_1)\alpha(1) \\ \psi_{1s}(\mathbf{r}_2)\alpha(2) & \psi_{1s}(\mathbf{r}_2)\beta(2) & \psi_{2p_1}(\mathbf{r}_2)\alpha(2) & \psi_{3d_2}(\mathbf{r}_2)\alpha(2) \\ \psi_{1s}(\mathbf{r}_3)\alpha(3) & \psi_{1s}(\mathbf{r}_3)\beta(3) & \psi_{2p_1}(\mathbf{r}_3)\alpha(3) & \psi_{3d_2}(\mathbf{r}_3)\alpha(3) \\ \psi_{1s}(\mathbf{r}_4)\alpha(4) & \psi_{1s}(\mathbf{r}_4)\beta(4) & \psi_{2p_1}(\mathbf{r}_4)\alpha(4) & \psi_{3d_2}(\mathbf{r}_4)\alpha(4) \end{vmatrix}$$

20. For the Slater determinant in the previous problem, what are the expectation values of the following operators? (List all possibilities when multiple possibilities exist.)

$$\begin{aligned} \hat{L}^2 \Psi &= \hbar^2 (3)(4) \Psi \\ &= 12\hbar^2 \Psi \end{aligned}$$

$$\hat{J}_z \Psi = (\hat{L}_z + \hat{S}_z) \Psi = \hbar (3 + 1) \Psi = 4\hbar \Psi$$

Determine the ground state term symbols associated with Germanium, which has the $[Ar]4s^23d^{10}4p^2$ electron configuration.

21. List the term symbols in order of increasing energy (e.g., lowest energy first) using Hund's rules. You can ignore the dependence on J in this case.
22. Circle all the terms for which a Slater determinant wave function can be written. (That is, circle all the terms for which a Slater determinant representation, Φ , that is an eigenfunction of \hat{L}^2 and \hat{S}^2 with the appropriate value of L and S exists.)

3P , 1D , 1S ; The double-underlined terms are associated with Slater determinants.

23. For the ground-state term, the value of J associated with the ground state is

3P_0

24. How many σ_g orbitals are occupied in the B_2 molecule?

(a) one

(b) two

(c) three

Suppose we consider the hydrogen molecule, H_2 , at very large distances, where the energy from simple molecular-orbital theory is much too high. Recall that when this occurs, it is because the simple-molecular orbital theory wave function has significantly higher energy than the “true” wave function, which is accurately described by valence-bond theory.

25. What is the simplest valence-bond wave function. (This is the Heitler-London wave function.)

$$\Psi_{H_2}^{VB+ionic}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(\phi_{1s}^{(l)}(\mathbf{r}_1) \phi_{1s}^{(r)}(\mathbf{r}_2) + \phi_{1s}^{(r)}(\mathbf{r}_1) \phi_{1s}^{(l)}(\mathbf{r}_2) \right) \left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right)$$

26. Write the Heitler-London + ionic wave function; that is, write the Heitler-London wave function, including the contribution from ionic terms.

$$\Psi_{H_2}^{VB+ionic}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \left(c_{\text{covalent}} \left(\phi_{1s}^{(l)}(\mathbf{r}_1) \phi_{1s}^{(r)}(\mathbf{r}_2) + \phi_{1s}^{(r)}(\mathbf{r}_1) \phi_{1s}^{(l)}(\mathbf{r}_2) \right) + c_{\text{ionic}} \left(\phi_{1s}^{(l)}(\mathbf{r}_1) \phi_{1s}^{(l)}(\mathbf{r}_2) + \phi_{1s}^{(r)}(\mathbf{r}_1) \phi_{1s}^{(r)}(\mathbf{r}_2) \right) \right) \left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right)$$

27. The *restricted* Hartree-Fock approximation gives back the very bad molecular-orbital theory result for the dissociation of H_2 . The *unrestricted* Hartree-Fock approximation actually does much better, and correctly predicts that the separated-atom limit of the hydrogen molecule. Explain why.

In the unrestricted Hartree-Fock theory, orbitals with different spins can have different spatial parts. In the separated atom limit, the hydrogen atoms, which can be described well with the wave function

$$\Psi_{UHF} = \frac{1}{\sqrt{2}!} \begin{vmatrix} \psi_{1s}^{\text{left}}(\mathbf{r}_1) \alpha(1) & \psi_{1s}^{\text{right}}(\mathbf{r}_1) \beta(1) \\ \psi_{1s}^{\text{left}}(\mathbf{r}_2) \alpha(2) & \psi_{1s}^{\text{right}}(\mathbf{r}_2) \beta(2) \end{vmatrix}$$

This wave function can't be used with RHF (the orbitals with different spin have different spatial parts, since the β -spin electron is localized on the “right” atom and the α -spin electron is localized on the “left” atom. But it is fine in a UHF context. (For your own education: it is interesting to note that, when the bond distance is short enough, it *is* favorable for electrons with different spins to have the same spatial orbital, and then the UHF and RHF wave functions have the same energy. The point where the UHF wave function starts to give a lower energy is called the Coulson-Fisher point.)

28. We discussed various approximations when deriving Fermi's Golden Rule. When these approximations were not true, "exotic" or "rare" phenomena are observed. Match each approximation listed below to the phenomenon that is observed when it does not hold

Phenomena:

- (i) electric quadrupole transitions
- (ii) nonlinear optical effects (e.g., more than one photon is absorbed at the same time)
- (iii) vibronic coupling
- (iv) light is absorbed even though the energy of the photons, $E = \hbar\omega$ doesn't match the energy of the transitions.

Approximations:

____(i)____ long-wavelength approximation.

____(ii)____ weak-field approximation.

29. Write the general form of a Lorentzian lineshape with peak absorbance at ω_0 and full-width at half maximum given by Γ . (If you forget some of the dependencies, do the best you can.)

$$L(\omega, \Gamma) = \frac{\frac{\Gamma}{2\pi}}{\left(\frac{\Gamma}{2}\right)^2 + (\omega - \omega_{if})^2}$$

In discussing broadening, a key quantity was the time-correlation function, $C(t)$, which expressed the relationship between the “transition dipole” moment at time t to the “transition dipole moment” at time zero.

30. What was the expression for the dipole moment operator at time t ? (Recall that we could consider the *Heisenberg* picture, where the operators depend on time, or the *Schrödinger* picture, where the wave function depend on time. This question relates to the *Heisenberg picture*.)

$$\hat{\mu}(t) \equiv e^{i\hat{H}t/\hbar} \mu e^{-i\hat{H}t/\hbar}$$

31. What was the expression for the time-correlation function?

$$C(t) \equiv \sum_{i=0}^{\infty} p_i \langle \Phi_i | \hat{\mu}_x(0) \hat{\mu}_x(t) | \Phi_i \rangle$$

32. The lineshape function, $I(\omega)$, is proportional to the Fourier transform of the time-correlation function. Specifically,

$$I(\omega) \equiv 2\pi \hat{C}(\omega)$$

What is the formula for $\hat{C}(\omega)$, in terms of $C(t)$. (This just tests whether you know what the definition of the Fourier Transform is.)

$$\hat{C}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(t) e^{-i\omega t} dt$$

In predissociation, we said that the progression of spectral lines associated with the vibrational fine structure of the electronic transition started off sharp, then became broader, and then became sharp again.

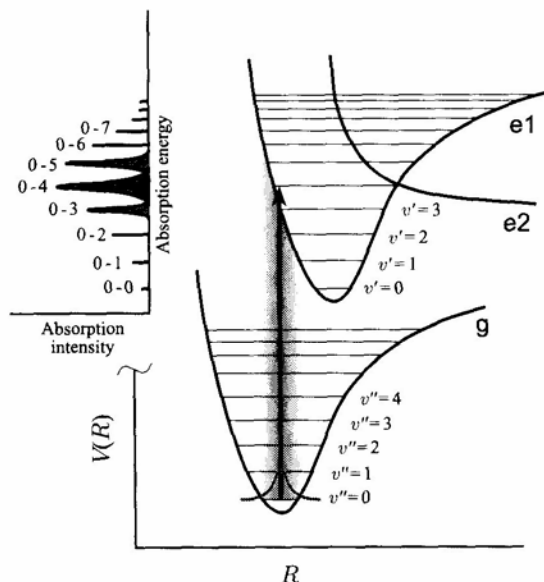
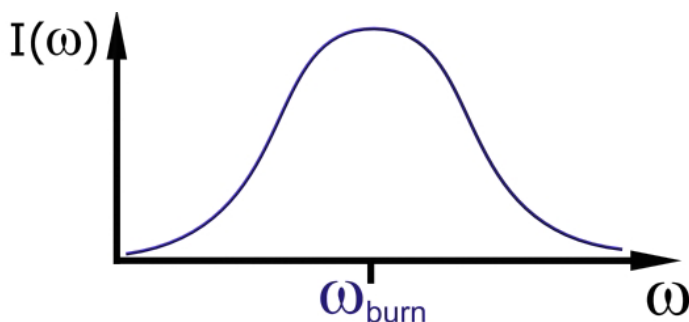


Figure 11.11. Potential energy surfaces leading to predissociation.

Your experimentalist friends decide to test whether this is homogeneous broadening or inhomogeneous broadening by engaging in a “hole-burning” experiment on one of the broad spectral lines. You tell them that they are idiots, and you already know how the experiment will turn out. In fact, you even sketch the results of the experiment for them.

33. Sketch the absorption spectrum with and without hole-burning. For simplicity, you can consider only the peak that corresponds to transitions from the ground vibrational state (of the ground electronic state) to the fourth excited vibrational state (of the excited electronic state).



This is lifetime broadening—due to the very short lifetime of the state (because it can cross over to the nearby excited state). Lifetime broadening is homogeneous—it affects all molecules in a given rovibrational state equally. Thus, hole-burning will have no effect, and the above picture is both before *and* after. (Even though the amplitude of the line will decrease slightly we turn on the second laser, the picture will be qualitatively (and often quantitatively) indistinguishable.

Derivation Portion (40 points; Choose 5 of 6):

1. Using the Born-Oppenheimer Approximation, derive

- (a) the electronic Schrödinger equation for a LiH.
- (b) the nuclear Schrödinger equation for LiH.

(The derivation is worth 3 points. Writing the electronic and nuclear Schrodinger equations correctly worth 2 points each. Labeling the “physical interpretation” of each term (e.g., appropriately labeling the term that corresponds to the electronic kinetic energy) is worth 1 point.

The Schrodinger equation, in atomic units, is

$$\left(-\frac{\nabla_A^2}{2m_H} - \frac{\nabla_B^2}{2m_{Li}} + \sum_{i=1}^4 -\frac{\nabla_i^2}{2} - \sum_{i=1}^4 \frac{1}{|\mathbf{r}_i - \mathbf{R}_H|} - \sum_{i=1}^4 \frac{1}{|\mathbf{r}_i - \mathbf{R}_{Li}|} + \sum_{i=1}^3 \sum_{j=i+1}^4 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{|\mathbf{R}_H - \mathbf{R}_{Li}|} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li})$$

Here we have two nuclei (with charges $Z_1 = 1$ and $Z_2 = 3$ and masses $m_1 = m_H$ and $m_2 = m_{Li}$).

The key idea is separation of variables, wherein the position of the electrons is considered to be dependent of the position of the nuclei, but not their motion. To this end, we write the wave function as the product of an electronic and nuclear component:

$$\Psi_{kv}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) = \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \chi_{kv}(\mathbf{R}_H, \mathbf{R}_{Li})$$

We substitute into part (b) and use the identity

$$\begin{aligned} \nabla_H^2 \psi(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \chi(\mathbf{R}_H, \mathbf{R}_{Li}) &= \chi(\mathbf{R}_H, \mathbf{R}_{Li}) \nabla_H^2 \psi(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \\ &+ \psi(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \nabla_H^2 \chi(\mathbf{R}_H, \mathbf{R}_{Li}) \\ &+ 2 \nabla_H \psi(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \cdot \nabla_H \chi(\mathbf{R}_H, \mathbf{R}_{Li}) \end{aligned}$$

to obtain

$$\begin{aligned}
& \left(-\frac{\nabla_H^2}{2m_H} + \frac{-\nabla_{L_i}^2}{2m_{L_i}} + \sum_{i=1}^4 \left(-\frac{\nabla_i^2}{2} - \frac{1}{|\mathbf{r}_i - \mathbf{R}_H|} - \frac{3}{|\mathbf{r}_i - \mathbf{R}_{L_i}|} \right) \right) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \\
& + \sum_{i=1}^3 \sum_{j=i+1}^4 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{3}{|\mathbf{R}_H - \mathbf{R}_{L_i}|} \Bigg) \\
& = E_{k\nu}^{exact} \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \\
& \left(-\frac{\nabla_H^2}{2m_H} - \frac{\nabla_{L_i}^2}{2m_{L_i}} \right) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \\
& + \left(\sum_{i=1}^4 \left(-\frac{\nabla_i^2}{2} - \frac{1}{|\mathbf{r}_i - \mathbf{R}_H|} - \frac{3}{|\mathbf{r}_i - \mathbf{R}_{L_i}|} \right) + \sum_{i=1}^3 \sum_{j=i+1}^4 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{3}{|\mathbf{R}_H - \mathbf{R}_{L_i}|} \right) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \\
& = E_{k\nu}^{exact} \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \\
& \left(\frac{-1}{2m_H} \right) \left(\chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \nabla_H^2 \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) + \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \nabla_H^2 \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \right) \\
& + 2 \nabla_H \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \cdot \nabla_H \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \\
& + \left(\frac{-1}{2m_{L_i}} \right) \left(\chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \nabla_{L_i}^2 \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) + \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \nabla_{L_i}^2 \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \right) \\
& + 2 \nabla_{L_i} \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \cdot \nabla_{L_i} \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \\
& + \chi_{k\nu}(\mathbf{R}_A, \mathbf{R}_B) \left(\sum_{i=1}^4 \left(-\frac{\nabla_i^2}{2} - \frac{1}{|\mathbf{r}_i - \mathbf{R}_H|} - \frac{3}{|\mathbf{r}_i - \mathbf{R}_{L_i}|} \right) + \sum_{i=1}^3 \sum_{j=i+1}^4 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{3}{|\mathbf{R}_H - \mathbf{R}_{L_i}|} \right) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \\
& = E_{k\nu}^{exact} \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \\
& \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \left(\frac{-\nabla_H^2}{2m_H} + \frac{-\nabla_{L_i}^2}{2m_{L_i}} \right) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \\
& \quad - \frac{\nabla_H \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \cdot \nabla_H \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i})}{m_H} - \frac{\nabla_{L_i} \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \cdot \nabla_{L_i} \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i})}{m_{L_i}} \\
& \quad + \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \left(\frac{-\nabla_H^2}{2m_H} + \frac{-\nabla_{L_i}^2}{2m_{L_i}} \right) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \\
& \quad + \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i}) \left(\sum_{i=1}^4 \left(-\frac{\nabla_i^2}{2} - \frac{1}{|\mathbf{r}_i - \mathbf{R}_H|} - \frac{3}{|\mathbf{r}_i - \mathbf{R}_{L_i}|} \right) + \sum_{i=1}^3 \sum_{j=i+1}^4 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{3}{|\mathbf{R}_H - \mathbf{R}_{L_i}|} \right) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \\
& = E_{k\nu}^{exact} \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{L_i}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{L_i})
\end{aligned}$$

Because the mass of the nuclei is much larger than the mass of the electron, the blue terms are quite small compared to those that come afterwards. We set the blue terms equal to zero, which amounts to assuming that because the nuclei move much more slowly than the electrons, the nuclei can be considered “fixed” on the time scale of electronic motion. Neglecting these terms, we obtain

$$\begin{aligned}
& \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \left(\frac{-\nabla_H^2}{2m_H} + \frac{-\nabla_{Li}^2}{2m_{Li}} \right) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li}) \\
& + \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li}) \left(\sum_{i=1}^4 \left(-\frac{\nabla_i^2}{2} - \frac{1}{|\mathbf{r}_i - \mathbf{R}_H|} - \frac{3}{|\mathbf{r}_i - \mathbf{R}_{Li}|} \right) + \sum_{i=1}^3 \sum_{j=i+1}^4 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{3}{|\mathbf{R}_H - \mathbf{R}_{Li}|} \right) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \\
& = E_k^{BO} \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li})
\end{aligned}$$

which is the classic form of the Schrödinger equation from separation of variables. We then solve the electronic Schrödinger equation

$$\begin{aligned}
& \left(\sum_{i=1}^4 \left(-\frac{\nabla_i^2}{2} - \frac{1}{|\mathbf{r}_i - \mathbf{R}_H|} - \frac{3}{|\mathbf{r}_i - \mathbf{R}_{Li}|} \right) + \sum_{i=1}^3 \sum_{j=i+1}^4 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{3}{|\mathbf{R}_H - \mathbf{R}_{Li}|} \right) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \\
& \equiv U_k^{BO}(\mathbf{R}_H, \mathbf{R}_{Li}) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li})
\end{aligned}$$

and substitute this result into the previous result, obtaining the nuclear Schrödinger equation

$$\begin{aligned}
& \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \left(\frac{-\nabla_H^2}{2m_H} + \frac{-\nabla_{Li}^2}{2m_{Li}} \right) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li}) + \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li}) U_k^{BO}(\mathbf{R}_H, \mathbf{R}_{Li}) \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \\
& = E_k^{BO} \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li}) \\
& \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \left(\frac{-\nabla_H^2}{2m_H} + \frac{-\nabla_{Li}^2}{2m_{Li}} + U_k^{BO}(\mathbf{R}_H, \mathbf{R}_{Li}) \right) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li}) \\
& = E_k^{BO} \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_4; \mathbf{R}_H, \mathbf{R}_{Li}) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li})
\end{aligned}$$

$$\left(\frac{-\nabla_H^2}{2m_H} + \frac{-\nabla_{Li}^2}{2m_{Li}} + U_k^{BO}(\mathbf{R}_H, \mathbf{R}_{Li}) \right) \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li}) = E_k^{BO} \chi_{k\nu}(\mathbf{R}_H, \mathbf{R}_{Li})$$

which gives the interpretation of the nuclei moving on the potential energy surface, $U_k^{BO}(\mathbf{R}_1, \mathbf{R}_2)$ due to the electrons in the system.

2. Expectation values for the Hydrogen atom. You will find it helpful to recall that

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

- (a) For a given principle quantum number, n , write a wave function for the state that has the highest possible magnetic quantum number, m , that is consistent with n . (Do not forget the angular portion of the wave function. I don't expect you to know the normalization constant.) (2 points)

$$\Psi_{n,l,m}(r, \theta, \phi) = N_{n,n-1,n-1} \cdot r^{n-1} e^{-\left(\frac{Z}{n}\right)r} Y_{n-1}^{n-1}(\theta, \phi)$$

- (b) What is the most probable distance from the nucleus for an electron in this state? (2 points)

The probability of observing an electron at the point r, θ, ϕ is

$$|\Psi_{n,l,m}(r, \theta, \phi)|^2 \propto r^{2(n-1)} e^{-\left(\frac{2Z}{n}\right)r} |Y_{n-1}^{n-1}(\theta, \phi)|^2$$

The most probable distance from the nucleus includes all the possible values of θ, ϕ that are associated with a given r . This produces a “ $4\pi r^2$ ” factor, in general, but due to the normalization of the spherical harmonic, it is only an r^2 factor. That is, the probability that we will observe an electron in the spherical shell between r and $r + dr$ is:

$$\begin{aligned} P(r) dr &= r^2 dr \left(N_{n,n-1,n-1} \right)^2 \int_0^{\pi} \int_0^{2\pi} r^{2(n-1)} e^{-\left(\frac{2Z}{n}\right)r} |Y_{n-1}^{n-1}(\theta, \phi)|^2 \sin \theta d\phi d\theta \\ &= \left(N_{n,n-1,n-1} \right)^2 r^{2n} e^{-\left(\frac{2Z}{n}\right)r} \end{aligned}$$

The highest probability density corresponds to the place where

$$\begin{aligned} 0 &= \frac{dP(r)}{dr} \\ 0 &= \left(N_{n,n-1,n-1} \right)^2 \left(2nr^{2n-1} e^{-\left(\frac{2Z}{n}\right)r} + r^{2n} \left(\frac{-2Z}{n} \right) e^{-\left(\frac{2Z}{n}\right)r} \right) \\ 0 &= 2n - \frac{2Z}{n} r \\ r &= \frac{n^2}{Z} \end{aligned}$$

- (c) What is the average (mean) distance of an electron from the nucleus for these states? (Include the appropriate dependence on the normalization constant, $N_{n,l,m}$, in your answer.) (2 points)

$$\begin{aligned}
 \langle r \rangle &= \left(N_{n,n-1,n-1} \right)^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} r^{2(n-1)} e^{-(2Z/n)r} \left| Y_{n-1}^{n-1}(\theta, \phi) \right|^2 r^2 \sin \theta d\phi d\theta dr \\
 &= \left(N_{n,n-1,n-1} \right)^2 \int_0^\infty r^{2n} e^{-(2Z/n)r} dr \\
 &= \left(N_{n,n-1,n-1} \right)^2 \int_0^\infty r^{2n} e^{-(2Z/n)r} dr \\
 &= \left(N_{n,n-1,n-1} \right)^2 \frac{(2n)!}{(2Z/n)^{2n+1}} \\
 &= \left(N_{n,n-1,n-1} \right)^2 \frac{(2n)! n^{2n+1}}{(2Z)^{2n+1}}
 \end{aligned}$$

- (d) Based on your intuition, is distance of the electron from the nucleus in these states (with the maximum value of m) *greater than* or *smaller than* the distance of the electron from the nucleus in states with smaller total angular momentum? (1 point)

(a) greater than

(b) smaller than

The root-mean-square (rms) distance of the electron from the nucleus is related to the expectation value of $\langle r^2 \rangle$. Specifically, we have

$$r_{\text{rms}} \equiv \sqrt{\langle r^2 \rangle} \quad (2)$$

- (e) Again, based on your intuition, which of the following is true (1 point)

- | | | |
|---|---|---|
| (a) $r_{\text{most probable}} < r_{\text{rms}} < r_{\text{mean}}$ | (c) $r_{\text{mean}} < r_{\text{most probable}} < r_{\text{rms}}$ | (e) $r_{\text{rms}} < r_{\text{mean}} < r_{\text{most probable}}$ |
| (b) $r_{\text{most probable}} < r_{\text{mean}} < r_{\text{rms}}$ | (d) $r_{\text{mean}} < r_{\text{rms}} < r_{\text{most probable}}$ | (f) $r_{\text{rms}} < r_{\text{most probable}} < r_{\text{mean}}$ |

3. For the Helium atom, we considered a wave function with the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2) \left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right) \quad (3)$$

where

$$\phi_{1s}(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}. \quad (4)$$

We found that the energy of this wave function was given by the form,

$$\begin{aligned} E(\zeta) &\equiv \langle \Psi(\mathbf{r}_1, \mathbf{r}_2) | \hat{H} | \Psi(\mathbf{r}_1, \mathbf{r}_2) \rangle \\ &= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - 2) \end{aligned} \quad (5)$$

where the Hamiltonian of the Helium atom has the form

$$\hat{H} \equiv \frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (6)$$

(a) Suppose we approximate the energy of the Helium atom by using first-order perturbation theory, where the electron-electron repulsion term in Eq. (7) is treated as a perturbation. What is the approximate energy? (4 points)

The zeroth-order wave function is the solution to the Schrödinger equation without the electron-electron repulsion term,

$$\left(\frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} \right) \Psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = E^{(0)} \Psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$$

Clearly the energy of this state is

$$E^{(0)} = 2(E_{He^+}) = 2 \left(\frac{-(2^2)}{2} \right) = -4 \text{ Hartree}$$

and the wave function is a simple product of wave functions for He^+ , i.e.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr_1} \right) \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr_2} \right) \left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right)$$

The correction from first-order perturbation theory is simply

$$E^{(1)} - E^{(0)} \equiv \langle \Psi^{(0)} | \text{perturbation} | \Psi^{(0)} \rangle = \left\langle \Psi^{(0)} \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \Psi^{(0)} \right\rangle.$$

Here $E^{(1)}$ is the energy from first-order perturbation theory, which is what we want to know. Using the result for $E^{(0)}$, it is clear that

$$\begin{aligned}
E^{(1)} &= E^{(0)} + \left\langle \Psi^{(0)} \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \Psi^{(0)} \right\rangle \\
&= \left\langle \Psi^{(0)} \left| \frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} \right| \Psi^{(0)} \right\rangle + \left\langle \Psi^{(0)} \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \Psi^{(0)} \right\rangle \\
&= \left\langle \Psi^{(0)} \left| \frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \Psi^{(0)} \right\rangle
\end{aligned}$$

and using the zeroth order wave function, it is clear that we are interested in the $\zeta = Z = 2$ case of Eq. (5). This gives

$$\begin{aligned}
E^{(1)} &= E(2) = -2^2 + \frac{5}{8}2 + 2(2)(2-2) \\
&= -4 + \frac{5}{4} \\
&= -2.75 \text{ Hartree}
\end{aligned}$$

- (b) Suppose we approximate the energy of the Helium atom using the variational principle, using trial wave functions with the form given by Eqs. (4) and (5). What is the approximate energy? (4 points)

The energy is found by minimizing Eq. (5) with respect to ζ to find the optimal effective nuclear charge, and then substituting back in. The optimum effective nuclear charge is then

$$\begin{aligned}
0 &= \frac{\partial}{\partial \zeta} \left(-\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - 2) \right) \\
&= -2\zeta + \frac{5}{8} + 4\zeta - 4 \\
&= 2\zeta - \frac{27}{8} \\
\zeta &= \frac{27}{16} = 1.6875
\end{aligned}$$

and substituting back in gives

$$\begin{aligned}
E &\rightarrow -\left(\frac{27}{16}\right)^2 + \frac{5}{8}\left(\frac{27}{16}\right) + 2\left(\frac{27}{16}\right)\left(\frac{27}{16} - 2\right) \\
&= \left(\frac{27}{16}\right)\left(-\frac{27}{16} + \frac{5}{8} - 2\left(\frac{5}{16}\right)\right) \\
&= \left(-\frac{27}{16}\right)^2 \\
&= -2.848 \text{ Hartree}
\end{aligned}$$

4. Molecular-Orbital Theory for the Heteronuclear Diatomic Molecule

Consider a heteronuclear diatomic molecule, CD . Assume that the bond between atoms C and D can be well described as a linear combination of an atomic orbital, $\phi_C(\mathbf{r})$ centered on atom C and an atomic orbital, $\phi_D(\mathbf{r})$, centered on atom D . These orbitals are eigenfunctions of the “effective” Schrodinger equations for the atoms,

$$\left(\frac{-\nabla^2}{2} + v_C(\mathbf{r})\right)\phi_C(\mathbf{r}) = \varepsilon_C\phi_C(\mathbf{r}) \quad (7)$$

and

$$\left(\frac{-\nabla^2}{2} + v_D(\mathbf{r})\right)\phi_D(\mathbf{r}) = \varepsilon_D\phi_D(\mathbf{r}) \quad (8)$$

The molecular orbital related to bonding/antibonding are eigenfunctions of the equation

$$\left(-\frac{\nabla^2}{2} + v_C(\mathbf{r}) + v_D(\mathbf{r})\right)\psi(\mathbf{r}) = E_{MO}\psi(\mathbf{r}) \quad (9)$$

and, as stated before, the molecular orbital can be approximated as a linear combination of the atomic orbitals, $\phi_C(\mathbf{r})$ and $\phi_D(\mathbf{r})$.

In order to solve this problem, we made several assumptions, which you may make again here. We assumed that the overlap between the atomic orbitals was zero

$$S_{CD} \equiv \langle \psi_C | \psi_D \rangle = \int \psi_C^*(\mathbf{r}) \psi_D(\mathbf{r}) d\mathbf{r} \approx 0 \quad (10)$$

and we “named” the resonance integral β ,

$$\beta = \langle \psi_C | \hat{h} | \psi_D \rangle \quad (11)$$

- (a) Show that, in this model, the energy of the bonding and antibonding molecular orbitals is (4 points)

$$E_{MO} = \frac{\varepsilon_C + \varepsilon_D}{2} \pm \frac{\varepsilon_C - \varepsilon_D}{2} \sqrt{1 + \frac{4|\beta|^2}{(\varepsilon_C - \varepsilon_D)^2}} \quad (12)$$

Start by writing the Schrödinger equation for the molecular orbital, namely

$$\hat{h}(c_C\phi_C(\mathbf{r}) + c_D\phi_D(\mathbf{r})) = E(c_C\phi_C(\mathbf{r}) + c_D\phi_D(\mathbf{r}))$$

Next, multiply, on the left, both sides of the equation by $\phi_C(\mathbf{r})$ and $\phi_D(\mathbf{r})$ and integrate. This gives us the equations

$$\begin{bmatrix} \langle \phi_C | \hat{h} | \phi_C \rangle & \langle \phi_C | \hat{h} | \phi_D \rangle \\ \langle \phi_D | \hat{h} | \phi_C \rangle & \langle \phi_D | \hat{h} | \phi_D \rangle \end{bmatrix} \begin{bmatrix} c_C \\ c_D \end{bmatrix} = E \begin{bmatrix} \langle \phi_C | \phi_C \rangle & \langle \phi_C | \phi_D \rangle \\ \langle \phi_D | \phi_C \rangle & \langle \phi_D | \phi_D \rangle \end{bmatrix} \begin{bmatrix} c_C \\ c_D \end{bmatrix}$$

Using Eq. (10) and the normalization of the atomic orbitals, we have

$$\begin{bmatrix} \langle \phi_C | \hat{h} | \phi_C \rangle & \langle \phi_C | \hat{h} | \phi_D \rangle \\ \langle \phi_D | \hat{h} | \phi_C \rangle & \langle \phi_D | \hat{h} | \phi_D \rangle \end{bmatrix} \begin{bmatrix} c_C \\ c_D \end{bmatrix} = E \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} c_C \\ c_D \end{bmatrix}$$

$$\begin{bmatrix} \langle \phi_C | \hat{h} | \phi_C \rangle & \langle \phi_C | \hat{h} | \phi_D \rangle \\ \langle \phi_D | \hat{h} | \phi_C \rangle & \langle \phi_D | \hat{h} | \phi_D \rangle \end{bmatrix} \begin{bmatrix} c_C \\ c_D \end{bmatrix} = E \begin{bmatrix} c_C \\ c_D \end{bmatrix}$$

This is the usual form of the eigenvalue problem. We examine the integrals,

$$\begin{aligned}
\langle \phi_C | \hat{h} | \phi_C \rangle &= \langle \phi_C | -\frac{\nabla^2}{2} + v_C(\mathbf{r}) + v_D(\mathbf{r}) | \phi_C \rangle \\
&= \langle \phi_C | -\frac{\nabla^2}{2} + v_C(\mathbf{r}) | \phi_C \rangle + \langle \phi_C | v_D(\mathbf{r}) | \phi_C \rangle \\
&= \langle \phi_C | \varepsilon_A | \phi_C \rangle + \langle \phi_C | v_D(\mathbf{r}) | \phi_C \rangle \\
&= \varepsilon_C \langle \psi_C | \psi_C \rangle + \langle \phi_C | v_D(\mathbf{r}) | \phi_C \rangle \\
&= \varepsilon_C + \langle \phi_C | v_D(\mathbf{r}) | \phi_C \rangle.
\end{aligned}$$

The last term is small (it is comparable to S_{CD}) and can be neglected. With this result and Eq. (11), we have

$$\begin{bmatrix} \varepsilon_C & \beta \\ \beta^* & \varepsilon_D \end{bmatrix} \begin{bmatrix} c_C \\ c_D \end{bmatrix} = E \begin{bmatrix} c_C \\ c_D \end{bmatrix}$$

The eigenvalues are found by solving the determinant

$$\begin{vmatrix} \varepsilon_C - E & \beta \\ \beta^* & \varepsilon_D - E \end{vmatrix} = 0$$

$$E^2 - (\varepsilon_C + \varepsilon_D)E + \varepsilon_C \varepsilon_D - |\beta|^2 = 0$$

and so

$$\begin{aligned}
E &= \frac{(\varepsilon_C + \varepsilon_D)}{2} \pm \frac{1}{2} \sqrt{(\varepsilon_C + \varepsilon_D)^2 - 4(\varepsilon_C \varepsilon_D - |\beta|^2)} \\
&= \frac{(\varepsilon_C + \varepsilon_D)}{2} \pm \frac{1}{2} \sqrt{\varepsilon_C^2 + \varepsilon_D^2 + 2\varepsilon_C \varepsilon_D - 4\varepsilon_C \varepsilon_D + 4|\beta|^2} \\
&= \frac{(\varepsilon_C + \varepsilon_D)}{2} \pm \frac{1}{2} \sqrt{\varepsilon_C^2 + \varepsilon_D^2 - 2\varepsilon_C \varepsilon_D + 4|\beta|^2} \\
&= \frac{(\varepsilon_C + \varepsilon_D)}{2} \pm \frac{1}{2} \sqrt{(\varepsilon_C - \varepsilon_D)^2 + 4|\beta|^2} \\
&= \frac{(\varepsilon_C + \varepsilon_D)}{2} \pm \frac{|\varepsilon_C - \varepsilon_D|}{2} \sqrt{1 + \frac{4|\beta|^2}{(\varepsilon_C - \varepsilon_D)^2}}
\end{aligned}$$

The absolute value sign is optional, though, as it only reorders (and does not change) the energy levels.

(b) Suppose ε_C is an acid and ε_D is a base. Does the antibonding molecular orbital correspond to the positive sign or the negative sign in Eq. (13). (1 point)

The antibonding orbital has higher energy than $\frac{\varepsilon_C + \varepsilon_D}{2}$. Since the ionization potential of the electron acceptor—the acid—will be greater than the ionization potential of the electron donor—the base), $\varepsilon_C \approx -I_C < -I_D \approx \varepsilon_D$. Since $\varepsilon_C - \varepsilon_D < 0$, the **negative** sign corresponds to the antibonding orbital.

(c) The antibonding molecular orbital can be written as (1 point)

$$\psi(\mathbf{r}) = k_C \psi_C(\mathbf{r}) + k_D \psi_D(\mathbf{r}) \quad (13)$$

(a) $|k_C| < |k_D|$. (The bonding orbital is mostly on the acid; the antibonding orbital will be mostly on the base.)

(b) $|k_C| > |k_D|$

(d) We said that the resonance integral could be written in the form

$$\beta = S_{CD} \left(\frac{\varepsilon_C + \varepsilon_D}{2} \right) + \frac{\langle \psi_C | v_D(\mathbf{r}) | \psi_D \rangle + \langle \psi_C | v_C(\mathbf{r}) | \psi_D \rangle}{2}. \quad (14)$$

Derive this result. (2 points)

$$\begin{aligned} \beta &= \langle \psi_B | \hat{h} | \psi_A \rangle \\ &= \langle \psi_B | -\frac{\nabla^2}{2} + v_A(\mathbf{r}) + v_B(\mathbf{r}) | \psi_A \rangle \\ &= \langle \psi_B | \frac{1}{2} \left(-\frac{\nabla^2}{2} + v_A(\mathbf{r}) \right) + \frac{1}{2} \left(-\frac{\nabla^2}{2} + v_B(\mathbf{r}) \right) + \frac{v_A(\mathbf{r}) + v_B(\mathbf{r})}{2} | \psi_A \rangle \\ &= \langle \psi_B | \frac{1}{2} \left(-\frac{\nabla^2}{2} + v_A(\mathbf{r}) \right) | \psi_A \rangle + \langle \psi_B | \frac{1}{2} \left(-\frac{\nabla^2}{2} + v_B(\mathbf{r}) \right) | \psi_A \rangle + \langle \psi_B | \frac{v_A(\mathbf{r}) + v_B(\mathbf{r})}{2} | \psi_A \rangle \\ &= \frac{1}{2} \langle \psi_B | \varepsilon_A | \psi_A \rangle + \frac{1}{2} \langle \left(-\frac{\nabla^2}{2} + v_B(\mathbf{r}) \right) \psi_B | \psi_A \rangle + \frac{1}{2} \langle \psi_B | v_A(\mathbf{r}) + v_B(\mathbf{r}) | \psi_A \rangle \\ &= \left(\frac{1}{2} \varepsilon_A S_{AB} + \frac{1}{2} \varepsilon_B S_{AB} \right) + \frac{1}{2} \left(\langle \psi_B | v_A(\mathbf{r}) | \psi_A \rangle + \langle \psi_B | v_B(\mathbf{r}) | \psi_A \rangle \right) \\ &= S_{AB} \left(\frac{\varepsilon_A + \varepsilon_B}{2} \right) + \frac{\langle \psi_B | v_A(\mathbf{r}) | \psi_A \rangle + \langle \psi_B | v_B(\mathbf{r}) | \psi_A \rangle}{2} \end{aligned}$$

5. Time-Dependent Perturbation Theory

When we performed time-dependent perturbation theory, we expanded the energy and wave function in a Taylor series expansion with respect to the amplitude of the applied field, V .

$$E(t) = E_i + V \left. \frac{\partial E(t)}{\partial V} \right|_{V=0} + \frac{V^2}{2!} \left. \frac{\partial^2 E(t)}{\partial V^2} \right|_{V=0} + \dots \quad (15)$$

$$\Psi(t) = \Psi_i + V \left. \frac{\partial \Psi(t)}{\partial V} \right|_{V=0} + \frac{V^2}{2!} \left. \frac{\partial^2 \Psi(t)}{\partial V^2} \right|_{V=0} + \dots \quad (16)$$

Substituting these results into the time-dependent Schrödinger equation and grouping terms with the same order, we obtained:

$$\begin{aligned} \hat{H}_{molecule} \Psi_i &= i\hbar \frac{\partial \Psi_i}{\partial t} \\ \hat{H}_{molecule} \left(V \left. \frac{\partial \Psi(t)}{\partial V} \right|_{V=0} \right) + \hat{V} \Psi_i &= i\hbar \left(V \left. \frac{\partial^2 \Psi(t)}{\partial V \partial t} \right|_{V=0} \right) \\ \hat{H}_{molecule} \left(\frac{V^2}{2!} \left. \frac{\partial^2 \Psi(t)}{\partial V^2} \right|_{V=0} \right) + \hat{V} \left(V \left. \frac{\partial \Psi(t)}{\partial V} \right|_{V=0} \right) &= i\hbar \left(\frac{V^2}{2!} \left. \frac{\partial^3 \Psi(t)}{\partial V^2 \partial t} \right|_{V=0} \right) \\ &\vdots \end{aligned} \quad (17)$$

(a) Derive Eq. (18) (3 points)

$$\begin{aligned} \hat{H}_{molecule} \Psi_i &= i\hbar \frac{\partial \Psi_i}{\partial t} \\ E_i \Phi_i \chi_i &= i\hbar \frac{\partial \Phi_i \chi_i}{\partial t} \\ E_i \Phi_i \chi_i &= i\hbar \Phi_i \frac{\partial \chi_i}{\partial t} \\ \frac{1}{i\hbar} E_i dt &= \frac{1}{\chi_i} d\chi_i \\ \frac{-i}{\hbar} \int E_i dt &= \int \frac{1}{\chi_i} d\chi_i \\ -\frac{iE_i t}{\hbar} &= \ln(\chi_i) + (\text{constant}) \\ \chi_i &= e^{-iE_i t/\hbar + \phi} \end{aligned}$$

The phase factor is arbitrary, and can be taken to be zero.

Solving the first equation in Eq. (18), we obtained

$$\Psi_i = \Phi_i e^{-iE_i t/\hbar}. \quad (18)$$

We then expanded the first-order change in the wave function in terms of the unperturbed wave functions,

$$\begin{aligned} V \left. \frac{\partial \Psi}{\partial V} \right|_{V=0} &= \sum_{k=0}^{\infty} c_k^{(1)} \Psi_k \\ &= \sum_{k=0}^{\infty} c_k^{(1)} \Phi_k e^{-iE_k t/\hbar}. \end{aligned} \quad (19)$$

and inserted this into the second equation (18), obtaining

$$\hat{V} \Phi_i e^{-iE_i t/\hbar} = i\hbar \sum_{k=0}^{\infty} \Phi_k e^{-iE_k t/\hbar} \frac{\partial c_k^{(1)}}{\partial t} \quad (20)$$

Assume that the perturbation in question is zero up to time t , and $Vf(t)$ thereafter. That is,

$$V(\mathbf{r}, t) = \begin{cases} 0 & t \leq 0 \\ Vf(t)g(x) & t > 0. \end{cases} \quad (21)$$

Suppose that, before the perturbation is turned on, only the ground state is occupied.

(b) Show that the probability of finding an electron in the excited state τ seconds after the perturbation has been “turned on” is (5 points)

$$P_f(t) = \frac{\left| \langle \Phi_f | g(x) | \Phi_i \rangle \right|^2 V^2}{\hbar^2} \left| \int_0^t f(\tau) e^{i\omega_f \tau} d\tau \right|^2 \quad (22)$$

We start with Eq. (20), and multiply the left-hand sides by Φ_f^* , and then integrate over the spatial coordinates. This gives

$$\begin{aligned} \langle \Phi_f | \hat{V} | \Phi_i \rangle e^{-iE_i t/\hbar} &= i\hbar \sum_{k=0}^{\infty} \langle \Phi_f | \Phi_k \rangle e^{-iE_k t/\hbar} \frac{\partial c_k^{(1)}}{\partial t} \\ \langle \Phi_f | \hat{V} | \Phi_i \rangle e^{-iE_i t/\hbar} &= i\hbar \sum_{k=0}^{\infty} \delta_{kf} e^{-iE_k t/\hbar} \frac{\partial c_k^{(1)}}{\partial t} \\ \langle \Phi_f | \hat{V} | \Phi_i \rangle e^{-iE_i t/\hbar} &= i\hbar e^{-iE_f t/\hbar} \frac{\partial c_f^{(1)}}{\partial t} \\ \frac{\partial c_f^{(1)}}{\partial t} &= \frac{1}{i\hbar} e^{i(E_f - E_i)t/\hbar} \langle \Phi_f | \hat{V} | \Phi_i \rangle \\ \frac{\partial c_f^{(1)}}{\partial t} &= \frac{1}{i\hbar} e^{i\omega_f t/\hbar} \langle \Phi_f | \hat{V} | \Phi_i \rangle \end{aligned}$$

Using the form of \hat{V} in Eq. (21), we have

$$\begin{aligned} \frac{\partial c_f^{(1)}}{\partial t} &= \frac{1}{i\hbar} e^{i\omega_f t/\hbar} \langle \Phi_f | V f(t) g(x) | \Phi_i \rangle \\ \frac{\partial c_f^{(1)}}{\partial t} &= \frac{V}{i\hbar} f(t) e^{i\omega_f t/\hbar} \langle \Phi_f | g(x) | \Phi_i \rangle \\ c_f^{(1)}(\tau) &= \frac{V \langle \Phi_f | g(x) | \Phi_i \rangle}{i\hbar} \left(\int_0^{\tau} f(t) e^{i\omega_f t/\hbar} dt + c_f^{(1)}(0) \right) \\ c_f^{(1)}(\tau) &= \frac{V \langle \Phi_f | g(x) | \Phi_i \rangle}{i\hbar} \left(\int_0^{\tau} f(t) e^{i\omega_f t/\hbar} dt \right) \end{aligned}$$

Finally, we have that

$$P_f(t) = |c_f^{(1)}(t)|^2 = \frac{V^2 \left| \langle \Phi_f | g(x) | \Phi_i \rangle \right|^2}{\hbar^2} \left| \int_0^{\tau} f(t) e^{i\omega_f t/\hbar} dt \right|^2$$

6. When we were discussing collisional broadening, we derived a formula for the lineshape, namely

$$I(\omega) = \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i P_{\text{none}}(t) \langle \Phi_i | \hat{\mu}(0) \hat{\mu}(t) | \Phi_i \rangle e^{-i\omega t} dt \quad (23)$$

where $P_{\text{none}}(t)$ is the probability that the molecule has not undergone any collisions at time t and

$$\mu(t) = e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \quad (24)$$

If the pressure in our sample is very, very small, then we might approximate $P_{\text{none}}(t)$ as

$$P_{\text{none}}(t) = 1 \quad (25)$$

Using Eq. (24), derive the formula for the lineshape in this limit. (Hint: you should recover a formula that is familiar from our discussion of Fermi's Golden Rule, because this is precisely the case where broadening is negligible.)

Starting from Eq. (23), we substitute in Eqs. (24) and (25) to obtain

$$\begin{aligned} I(\omega) &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| e^{i\hat{H}(0)/\hbar} \hat{\mu} e^{-i\hat{H}(0)/\hbar} e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \right| \Phi_i \right\rangle e^{-i\omega t} dt \\ &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| (1) \cdot \hat{\mu} \cdot (1) e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \right| \Phi_i \right\rangle e^{-i\omega t} dt \\ &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| \hat{\mu} e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \right| \Phi_i \right\rangle e^{-i\omega t} dt. \end{aligned}$$

Next, we recall that

$$\delta(\tau - \tau') = \sum_{f=0}^{\infty} \Phi_f^*(\tau) \Phi_f(\tau')$$

and so, since the delta function is normalized, we can write

$$\begin{aligned} I(\omega) &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| \hat{\mu} \left(\int \delta(\tau - \tau') d\tau \right) e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \right| \Phi_i \right\rangle e^{-i\omega t} dt \\ &= \int_{-\infty}^{\infty} \int \sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| \hat{\mu} [\delta(\tau - \tau')] e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \right| \Phi_i \right\rangle e^{-i\omega t} d\tau dt \\ &= \int_{-\infty}^{\infty} \int \sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| \hat{\mu} \left[\sum_{f=0}^{\infty} \Phi_f^*(\tau) \Phi_f(\tau') \right] e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \right| \Phi_i \right\rangle e^{-i\omega t} d\tau dt \\ &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \left\langle \Phi_i \left| \hat{\mu} \Phi_f(\tau') \Phi_f^*(\tau) e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \right| \Phi_i \right\rangle e^{-i\omega t} dt \\ &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \langle \Phi_i | \hat{\mu} | \Phi_f \rangle \left\langle \Phi_f \left| e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \right| \Phi_i \right\rangle e^{-i\omega t} dt \end{aligned}$$

Now, we use the fact that

$$e^{-\left(i\hat{H}t/\hbar\right)}\Phi_i = e^{-\left(iE_it/\hbar\right)}\Phi_i$$

and the fact that $e^{\frac{i\hat{\mu}}{\hbar}}$ is a Hermitian operator to obtain

$$\begin{aligned} I(\omega) &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \langle \Phi_i | \hat{\mu} | \Phi_f \rangle \left\langle e^{-i\hat{H}t/\hbar} \Phi_f | \hat{\mu} | e^{-i\hat{H}t/\hbar} \Phi_i \right\rangle e^{-i\omega t} dt \\ &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \langle \Phi_i | \hat{\mu} | \Phi_f \rangle \left\langle \Phi_f e^{-iE_ft/\hbar} | \hat{\mu} | \Phi_i e^{-iE_it/\hbar} \right\rangle e^{-i\omega t} dt \\ &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \langle \Phi_i | \hat{\mu} | \Phi_f \rangle \left\langle \Phi_f \left| e^{iE_ft/\hbar} \hat{\mu} e^{-iE_it/\hbar} \right| \Phi_i \right\rangle e^{-i\omega t} dt \\ &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \langle \Phi_i | \hat{\mu} | \Phi_f \rangle \left\langle \Phi_f | \hat{\mu} e^{i\omega_{fi}t} | \Phi_i \right\rangle e^{-i\omega t} dt \\ &= \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \langle \Phi_i | \hat{\mu} | \Phi_f \rangle \left\langle \Phi_f | \hat{\mu} | \Phi_i \right\rangle e^{i\omega_{fi}t} e^{-i\omega t} dt \\ &= \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \langle \Phi_i | \hat{\mu} | \Phi_f \rangle \left\langle \Phi_f | \hat{\mu} | \Phi_i \right\rangle \int_{-\infty}^{\infty} e^{i\omega_{fi}t} e^{-i\omega t} dt \end{aligned}$$

But we know that

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i(\omega - \omega_0)t} dt = \delta(\omega - \omega_0)$$

and so

$$I(\omega) = \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} 2\pi p_i \langle \Phi_i | \hat{\mu} | \Phi_f \rangle \left\langle \Phi_f | \hat{\mu} | \Phi_i \right\rangle \delta(\omega - \omega_{fi}).$$

Thinking Problem (10 points):

It is not uncommon to see an electronic excited state with a double minimum. The most famous case is the simple Hydrogen atom, wherein many of the bonding excited states (including the two with lowest energy) have double wells. The following curve, from [E. R. Davidson, *J. Chem. Phys.* 35 1189 (1965).] is a classic example. This problem will examine this phenomenon in more detail.

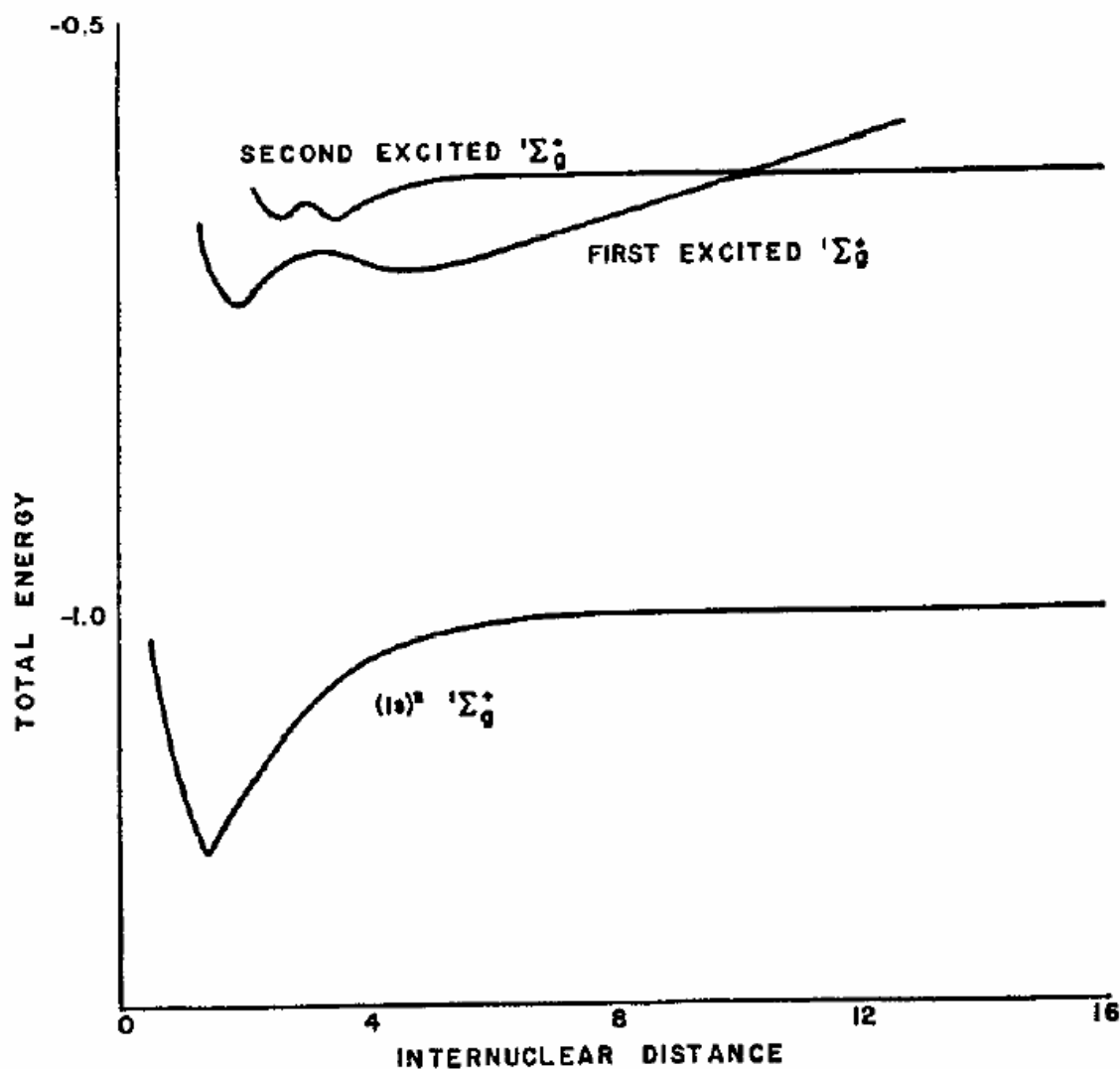


FIG. 2. A sketch of the potential curves for the first three $1\Sigma_g^+$ states of H_2 .

Let's consider two states of a diatomic molecule with potential energy curves that look like the following.

A. (3 points)

In order to describe the spectrum, we need to draw, qualitatively, the wave functions for the (a) ground and (b) excited-state potential energy curves. For the purposes of sketching the wave functions of the ground state, you can consider the state to be well modeled by a harmonic oscillator located at the minimum (this is sketched in the figure on the next page). The ground-state wave function for the Harmonic oscillator with force constant, k , centered at bond length R_0 , is

$$\chi(R) = \left(\frac{\sqrt{\mu k}}{\pi}\right)^{1/4} e^{-\frac{\sqrt{\mu k}}{2}(R-R_0)^2} \quad (26)$$

Here, μ is the reduced mass of the atomic nuclei.

Approximating the ground state of the excited-state is more difficult. We now discuss this:

- (i) **Suppose the two wells in the excited-state potential energy curve were very far apart. What is the wave function for the ground vibrational state in this limit? Is it degenerate?**

This is analogous to the “separated atom” limit. We can take linear combinations of the wave functions centered on the two “distant” wells. So an approximate wavefunction could be written as

$$\Psi_{\text{separated}} \propto \chi_1(R) \pm \chi_2(R)$$

where

$$\begin{aligned} \chi_1(R) &= \left(\frac{\sqrt{\mu k}}{\pi}\right)^{1/4} e^{-\frac{\sqrt{\mu k}}{2}(R-R_1)^2} \\ \chi_2(R) &= \left(\frac{\sqrt{\mu k}}{\pi}\right)^{1/4} e^{-\frac{\sqrt{\mu k}}{2}(R-R_2)^2} \end{aligned}$$

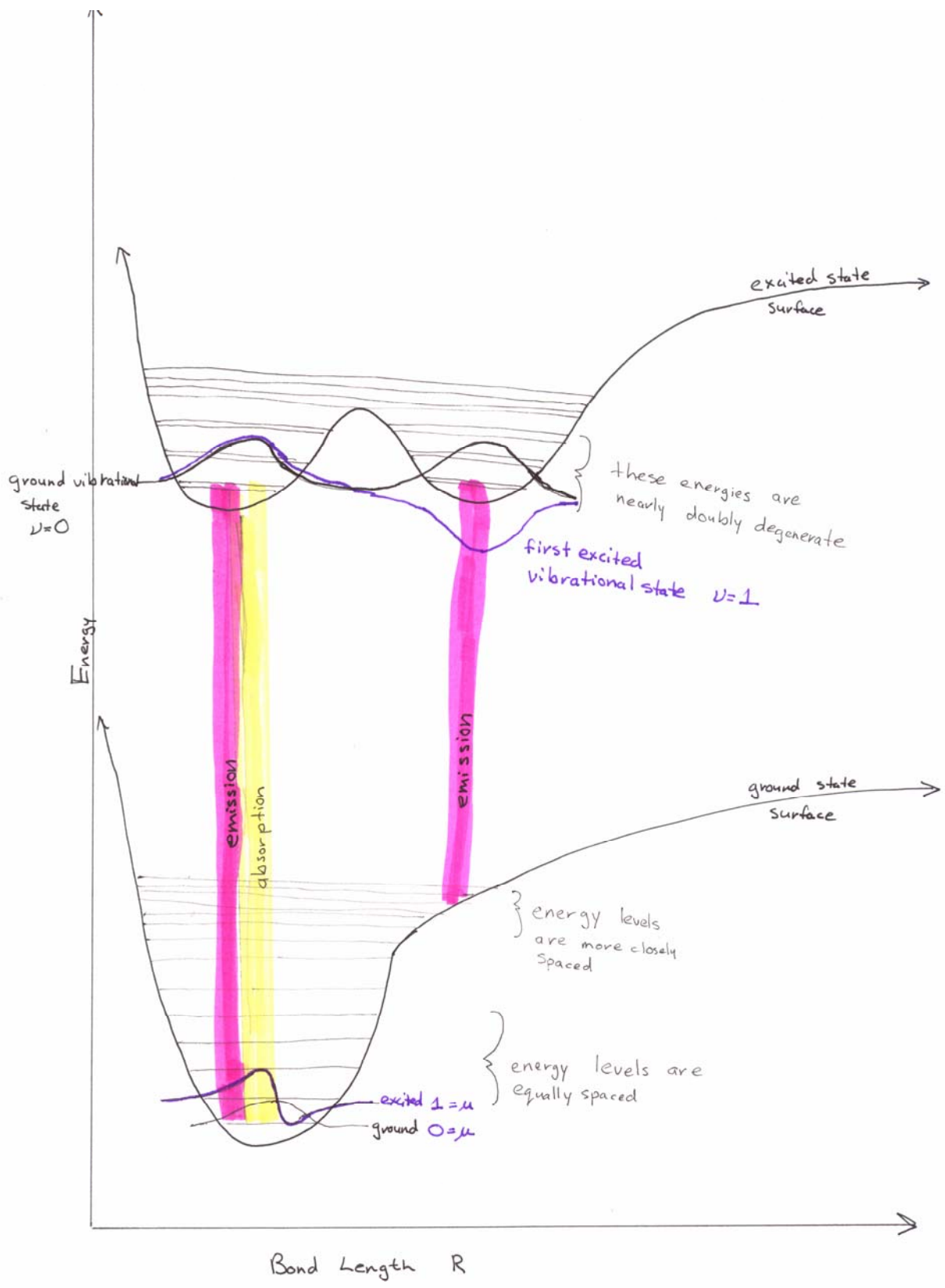
and $|R_2 - R_1| \rightarrow \infty$. The state is double degenerate.

- (ii) **Suppose the minimum points of the two wells were not separated very much—or even at all. What can you say about the wave function of the ground vibrational state in this limit? Is it degenerate?**

In this case there is only a single well, and the curvature of the well is twice what it normally would be (since $\frac{1}{2}kx^2 + \frac{1}{2}kx^2 = \frac{1}{2}(2k)x^2$), so

$$\chi_{\text{united}}(R) = \left(\frac{\sqrt{2\mu k}}{\pi}\right)^{1/4} e^{-\frac{\sqrt{2\mu k}}{2}(R-R_0)^2}$$

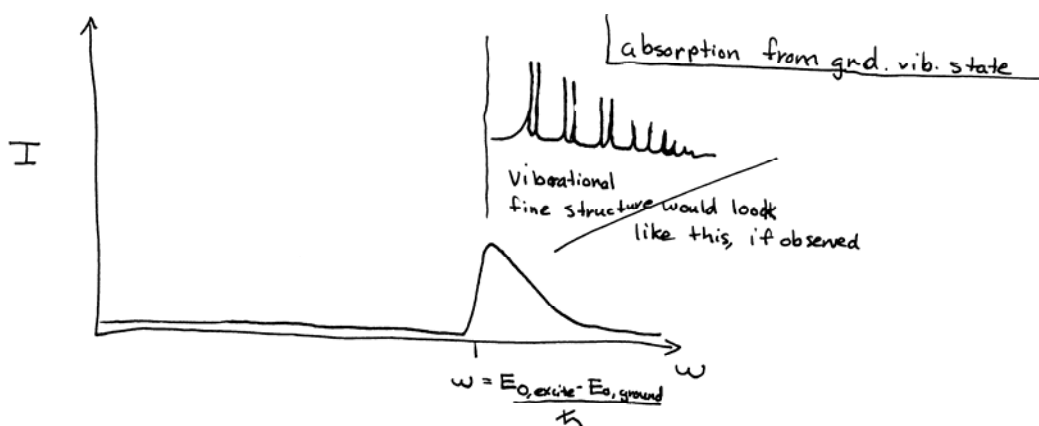
- (iii) **Using the figure on the next page, sketch the vibrational energy levels for the ground and excited vibrational states. Also, draw the wave functions for the lowest two energy states.**



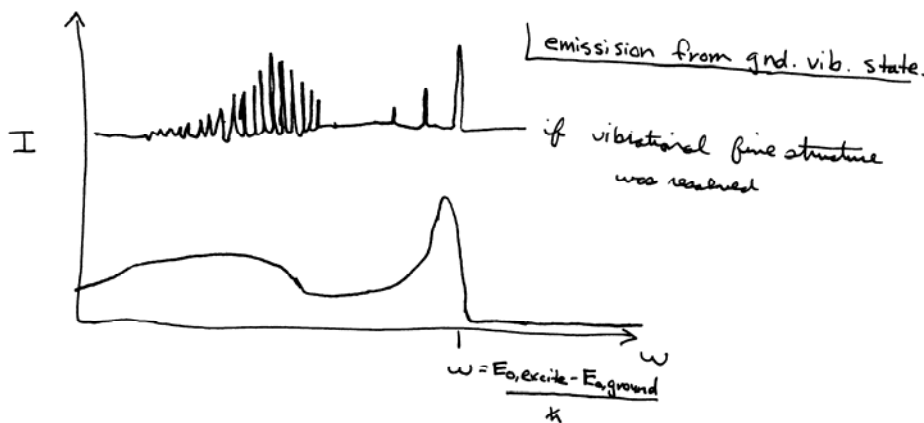
In parts B and C, we consider the absorption (part B) and emission (part C) spectrum that are characteristic of this molecule. In both problems, you can assume that

- (a) **the molecule is initially in the ground vibrational state.** (That is, absorption occurs from the ground vibrational state of the ground electronic state; emission occurs from the ground vibrational state of the excited electronic state. This is usually a reasonable assumption if the excited electronic state is long-lived).
- (b) **your experimental setup cannot resolve the vibrational fine-structure of the electronic transition.**
- (c) **vibronic coupling is negligible.**

B. Consider excitation from the ground electronic state to the electronic excited state shown here. Sketch the absorption spectrum. (2 points)

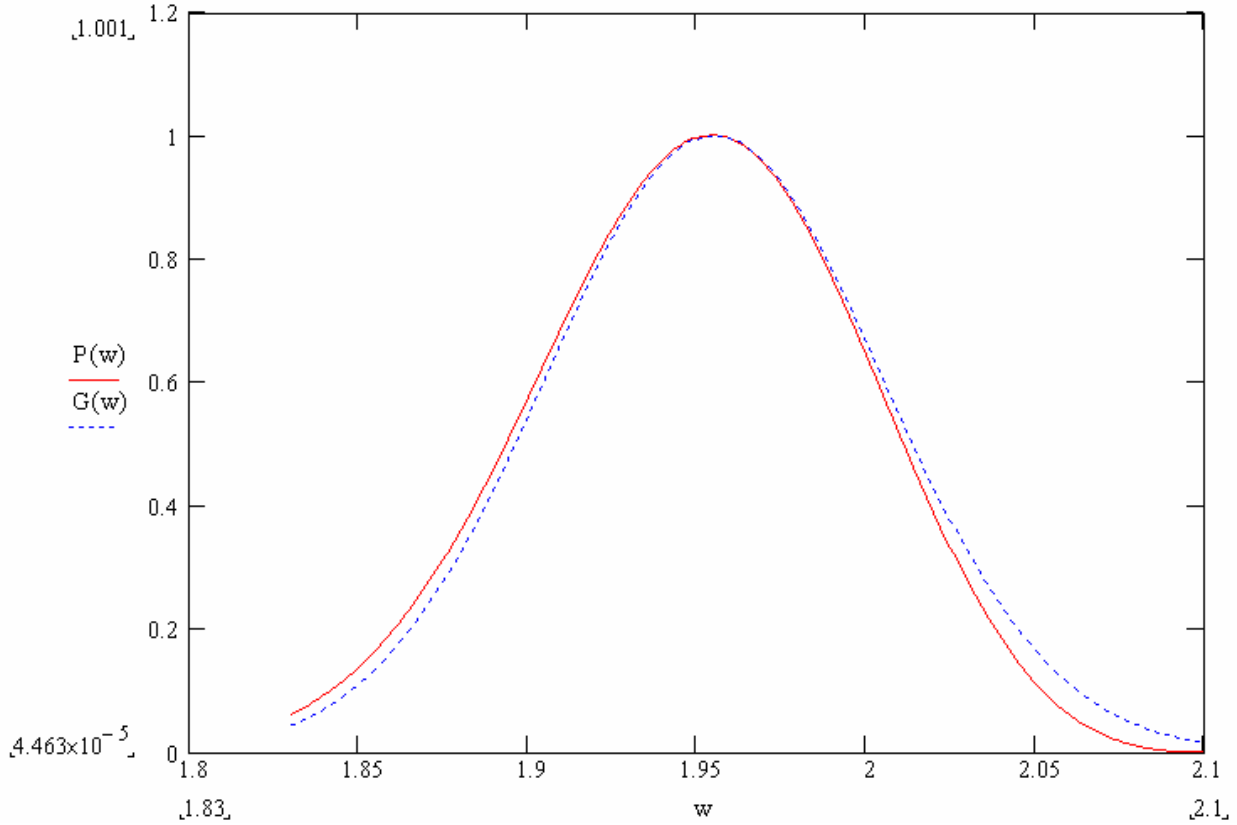


C. Sketch the emission spectrum from the excited electronic state to the ground electronic state. Use the same energy scale that you used in Part B. (2 points)



Due to anharmonicity in the potential energy surface, electronic spectral lines are often *not* symmetric. (Both the Gaussian and the Lorentzian lineshapes, on the contrary, are perfectly symmetric.) In this case, the probability that a molecule absorbs at frequency ω can be modeled with the expression

$$P(\omega) = \left(A + B(\omega - \omega_0 + \kappa_{shift})^2 \right) e^{-\alpha(\omega - \omega_0)^2} \quad (27)$$



- D.** Suppose the probability that a molecule absorbs at frequency ω is given by Eq. (28). Does this describe homogeneous or inhomogeneous broadening? What is the formula for the spectral lineshape? (3 points)

This is inhomogeneous broadening.

The lineshape is given by

$$I(\omega) \equiv \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 P(\omega)$$

where $P(\omega)$ is given by Eq. (27).