

Name:

# Mid-Term Examination 2

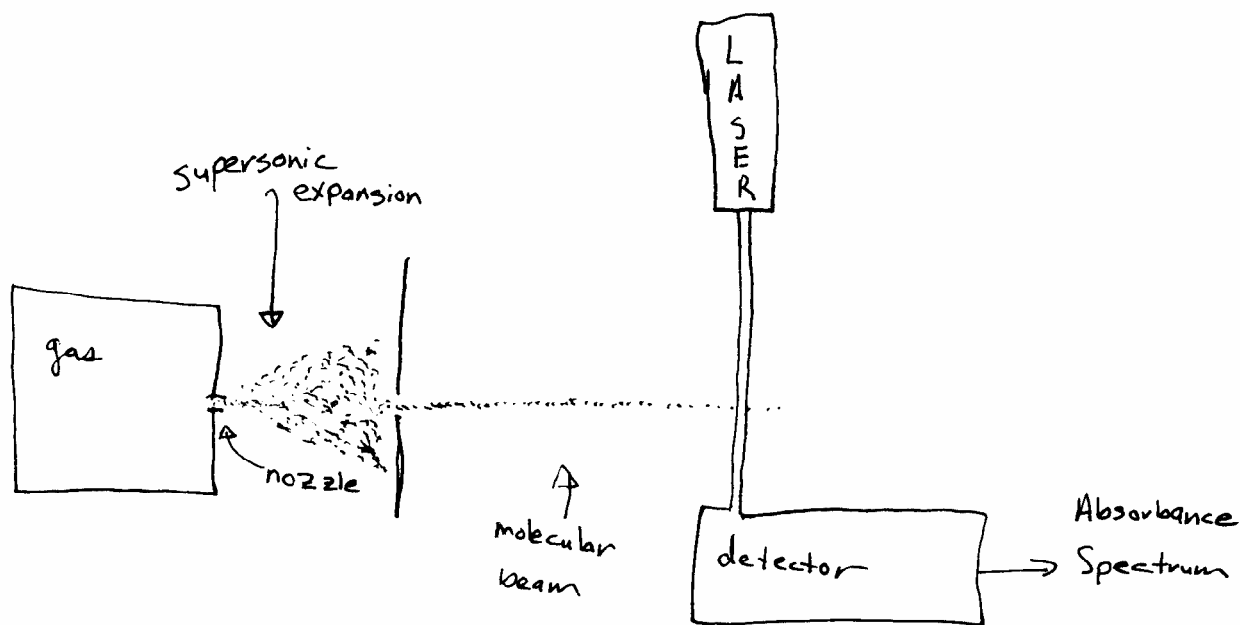
Chemistry 3BB3; Winter 2004

## Part 1. “Thinking Problems” (21 points; 3 points each)

Don't let yourself get frustrated on these. If you find something you can't work, move on. (These are not in increasing order of difficulty or anything like that.)

### 1. Transit-Time Broadening

Consider the following apparatus, which is typical of those used to measure high-resolution spectra. Molecules are confined to a high-pressure “oven”, which has a pin-hole “nozzle” that opens into a vacuum chamber. According to the Joule-Thompson effect, the molecules are cooled dramatically as they pass through the nozzle, typically to about 10 Kelvin. The molecules are also moving very quickly (this is often called a supersonic expansion, and the molecules are often moving faster than the speed of sound). Molecules moving “out of the beam” are split off; this effectively eliminates any Doppler broadening, since no molecules are moving “into” the laser beam. Pressure broadening is also small, and lifetime effects are small if the final state is long-lived. The dominant effect is often called “transit-time broadening”, which is a third type of effect —distinct from both inhomogeneous and homogeneous broadening.



Name:

- (a) Suppose that the molecule is out of the laser field from  $t = -\infty$  to  $t = 0$ , in a homogeneous laser field from  $t = 0$  to  $t = \tau$ , and out of the laser field from  $t = \tau$  to  $t \rightarrow \infty$ . Explain why the observed rate of transition is:

$$W_{fi}(\tau) = \frac{\left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 4V^2 g(\hbar\omega_{fi}) \left[ \frac{\sin^2((\omega_{fi} - \omega)\tau/2)}{\tau(\omega_{fi} - \omega)^2} \right]}{\hbar^2}$$

You can assume that the laser is monochromatic.

We have that the radiation acts on our molecule for a time  $\tau$ . We need to know what the probability that, at the end of that time, the molecule is in the “final” state,  $f$ . So, let’s rob the expression from the spectroscopy chapter: we have that (cf. Eq. (55)),

$$P_f(\tau) = \frac{\left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 V^2 \tau^2}{\hbar^2} \left[ \text{sinc}^2((\omega_{fi} + \omega)\tau/2) + \text{sinc}^2((\omega_{fi} - \omega)\tau/2) \right]$$

Now, since the system is so cold, we are justified in assuming that the molecule will be in the ground state. Consequently, we need only consider the absorption case, so the first sinc term is thus rather small. (It is, in any event, smaller than the last term in Eq. (54), which we have neglected.

$$\begin{aligned} P_f(\tau) &= \frac{\left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 V^2 \tau^2}{\hbar^2} \text{sinc}^2((\omega_{fi} - \omega)\tau/2) \\ &= \frac{\left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 V^2 \tau^2}{\hbar^2} \left( \frac{\sin((\omega_{fi} - \omega)\tau/2)}{(\omega_{fi} - \omega)\tau/2} \right)^2 \\ &= \frac{\left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 4V^2}{\hbar^2} \left( \frac{\sin^2((\omega_{fi} - \omega)\tau/2)}{(\omega_{fi} - \omega)^2} \right) \end{aligned}$$

To this point we neglected the intensity of the source. The source is assumed to be monochromatic and tuned to the transition frequency, the energy density of the source is  $g(\hbar\omega_{fi})$  then

$$P_f(\tau) = \frac{\left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 4V^2 g(\hbar\omega_{fi})}{\hbar^2} \left( \frac{\sin^2((\omega_{fi} - \omega)\tau/2)}{(\omega_{fi} - \omega)^2} \right)$$

Now, we recall that the rate of transition is the transition per unit time, or  $W_{fi} = \frac{P_f(t)}{t}$ . So we have that

$$\begin{aligned} W_{fi}(\tau) &= \frac{P_f(\tau)}{\tau} \\ &= \frac{\left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 4V^2 g(\hbar\omega_{fi})}{\hbar^2} \left( \frac{\sin^2((\omega_{fi} - \omega)\tau/2)}{\tau(\omega_{fi} - \omega)^2} \right) \end{aligned}$$

Name:

(b) What is the full-width at half-maximum? You may find it helpful to know that the solution to

$$\sin(x) - \frac{x\sqrt{2}}{2} = 0$$

is  $x = 1.392 \approx \frac{7}{5}$ .

The full-width at half maximum is independent of the peak height. Consequently, we can neglect all the “factors” in from of the rate expressions, since they only adjust the intensity of the absorbance, not its line width. So the line-shape is

$$I(\omega) = A \left[ \frac{\sin^2 \left( (\omega_{fi} - \omega) \tau / 2 \right)}{(\omega_{fi} - \omega)^2} \right]$$

where  $A$  is the amplitude. Redefine the amplitude as  $\mathcal{A} = \left( \frac{2}{\tau} \right)^2 A$ . Then

$$I(\omega) = \mathcal{A} \left( \frac{2}{\tau} \right)^2 \left[ \frac{\sin^2 \left( (\omega_{fi} - \omega) \tau / 2 \right)}{(\omega_{fi} - \omega)^2} \right] = \mathcal{A} \left[ \frac{\sin^2 \left( (\omega_{fi} - \omega) \tau / 2 \right)}{\left( (\omega_{fi} - \omega) \left( \frac{\tau}{2} \right) \right)^2} \right] = \mathcal{A} \text{sinc}^2 \left( (\omega_{fi} - \omega) \tau / 2 \right)$$

The sinc function has a maximum at  $(\omega_{fi} - \omega) \frac{\tau}{2}$  equals zero, and its value at this point is 1. So we want to find the place where

$$I(\omega) = \frac{\mathcal{A}}{2} = \mathcal{A} \text{sinc}^2 \left( (\omega_{fi} - \omega) \tau / 2 \right)$$

This occurs where

$$\begin{aligned} \text{sinc}^2 \left( (\omega_{fi} - \omega) \tau / 2 \right) &= \frac{1}{2} \\ \sin^2 \left( (\omega - \omega_{fi}) \tau / 2 \right) &= \frac{1}{2} \left( (\omega - \omega_{fi}) \tau / 2 \right)^2 \\ \sin \left( (\omega - \omega_{fi}) \tau / 2 \right) &= \frac{1}{\sqrt{2}} \left( (\omega - \omega_{fi}) \tau / 2 \right) \end{aligned}$$

This has the general form of the equation

$$\sin x = x \sqrt{\frac{1}{2}}$$

In general, this must be solved numerically. This gives the form of the equation we have above, so we know that  $x \approx \frac{7}{5}$ . So

$$\begin{aligned} (\omega - \omega_{fi}) \tau / 2 &\approx 7/5 \\ (\omega - \omega_{fi}) &\approx 14/5\tau \end{aligned}$$

This is the “half-width and half-maximum”. The full width at half maximum will then be about  $\frac{28}{5\tau}$ .

Name:

## 2. Term Symbols for Diatomics

Just as we did for atoms, we can derive term symbols for homonuclear diatomic molecules. We have build up the term symbols from the molecular orbitals just as we built up the atomic term symbols from the atomic orbitals. The term symbol for a homonuclear diatomic molecule has the general form

$$^{2S+1}\Lambda_{\nu_g, J}^{\pm}$$

where  $2S + 1$  is the spin-multiplicity,  $\Lambda = \Sigma, \Pi, \Delta, \Phi, \dots$  correspond to the amount of orbital angular momentum about the bonding axis,  $\pm$  corresponds to whether or not the *molecule's* wave function is symmetric with respect to reflection in the  $xz$  plane (- for symmetric, + for nonsymmetric), the  $\nu$  and  $g$  correspond to whether the wave function is symmetric with respect to inversion about the bond midpoint, and  $J$  is the total (spin + orbital) angular momentum about the internuclear axis.

To show how this works, we consider the Oxygen molecule. The electron configuration is

$$(\sigma_g^2(1s))^2 (\sigma_u(1s))^2 (\sigma_g(2s))^2 (\sigma_u(2s))^2 (\pi_u^+(2p))^2 (\pi_u^-(2p))^2 (\sigma_g(2p))^2 (\pi_g^+(2p))(\pi_g^-(2p))$$

The “closed subshells” do not matter. We have two orbitals with the same energy; we can fill them with electrons with the same spin ( $2S + 1 = 3$ , triplet) or opposite spin ( $2S + 1 = 1$ , singlet). The electrons can move around the axis in the same direction or in opposite directions. If they move in the same direction,

there are two possibilities,  $|\psi_{\pi_g^+(2p)}(\mathbf{r}_1)\alpha(1) \psi_{\pi_g^+(2p)}(\mathbf{r}_1)\beta(1)|, |\psi_{\pi_g^-(2p)}(\mathbf{r}_1)\alpha(1) \psi_{\pi_g^-(2p)}(\mathbf{r}_1)\beta(1)|$ . In both cases,  $\Lambda = 1 + 1 = 2$ , since both electrons are moving around the internuclear axis with  $m_l = 1$ . So we have two  $^1\Delta$  terms. The rule for assigning  $\nu$ 's and  $g$ 's is

$$u + u = g$$

$$g + g = g$$

$$u + g = u$$

That is, if two orbitals have the same inversion symmetry, they cancel out. (It would be better to write the previous formula in terms of multiplication, since it resembles the multiplication table for  $-1$  and  $1$ .) So we have two  $^1\Delta_g$  terms. The two terms do, however, have different inversion symmetry. We have a  $\Delta_g^+$  and a  $\Delta_g^-$  term. The rule for assigning  $J$  values is analogous to that for atoms,  $J = |\Lambda + S|, |\Lambda + S - 1|, \dots, |\Lambda - S|$ . This gives the terms as  $^1\Delta_{g,2}^+, ^1\Delta_{g,2}^-$ .

Corresponding to the term with spins-paired but the electrons in different orbitals, we have two terms,  $|\psi_{\pi_g^+(2p)}(\mathbf{r}_1)\alpha(1) \psi_{\pi_g^-(2p)}(\mathbf{r}_1)\beta(1)|, |\psi_{\pi_g^+(2p)}(\mathbf{r}_1)\beta(1) \psi_{\pi_g^-(2p)}(\mathbf{r}_1)\alpha(1)|$ . This gives  $^1\Sigma_{g,0}^+, ^1\Sigma_{g,0}^-$  terms. Finally, we have the ground-state term, with the electrons paired. This gives  $^3\Sigma_{g,1}^+, ^3\Sigma_{g,1}^-$  terms. Because the electrons are equivalent, some of these terms are not allowed; for  $O_2$ , the  $^1\Sigma_{g,0}^-$  and  $^3\Sigma_{g,1}^+$  are not allowed.

**(a) Singlet oxygen is an important intermediate in many chemical reactions. Which singlet term do you *expect* to have the lowest energy.**

Well, Hund's rule for atoms suggested that states with higher orbital angular momentum were lower in energy. So, given a choice between the  $^1\Sigma_g^+$  and the  $^1\Delta_g^+$ , the latter ( $^1\Delta_g^+$ ) seems most likely to be lower in energy.

Name:

**(b) The terms associated with a  $\pi^1\delta^1$  electron configuration are  $^1\Pi, ^3\Pi, ^3\Phi, ^1\Phi$ . Explain why, and fill in the other parts of these term symbols.**

The spins can be paired (forming singlets) or unpaired (forming triplets). In addition, we can have the electronic motion in the  $\pi$  orbital “with” or “against” that in the  $\delta$  orbital. Thus, the orbital angular momentum can be  $|\Lambda_{\pi_u^\pm} + \Lambda_{\delta_g^\pm}| = |1 + 2| = 3$  (with) or  $|\Lambda_{\pi_u^\pm} - \Lambda_{\delta_g^\pm}| = |1 - 2| = 1$  (against). There are thus  $^1\Phi, ^3\Phi$  and  $^1\Pi, ^3\Pi$  states. The  $\pm$  combinations are all possible (since I did not specify which specific orbitals; similarly, all the  $u, g$  combinations are possible. The only thing left to is what are the possible values of  $J$ . Possible values of  $J$  are  $|\Lambda + S|, \dots, |\Lambda - S|$ , which gives

$$^3\Phi: \quad J = |3 + 1|, |3 + 1 - 1|, |3 - 1| = 4, 3, 2$$

$$^1\Phi: \quad J = |3 + 0| = 3$$

$$^3\Pi: \quad J = |1 + 1|, |1 + 1 - 1|, |1 - 1| = 2, 1, 0$$

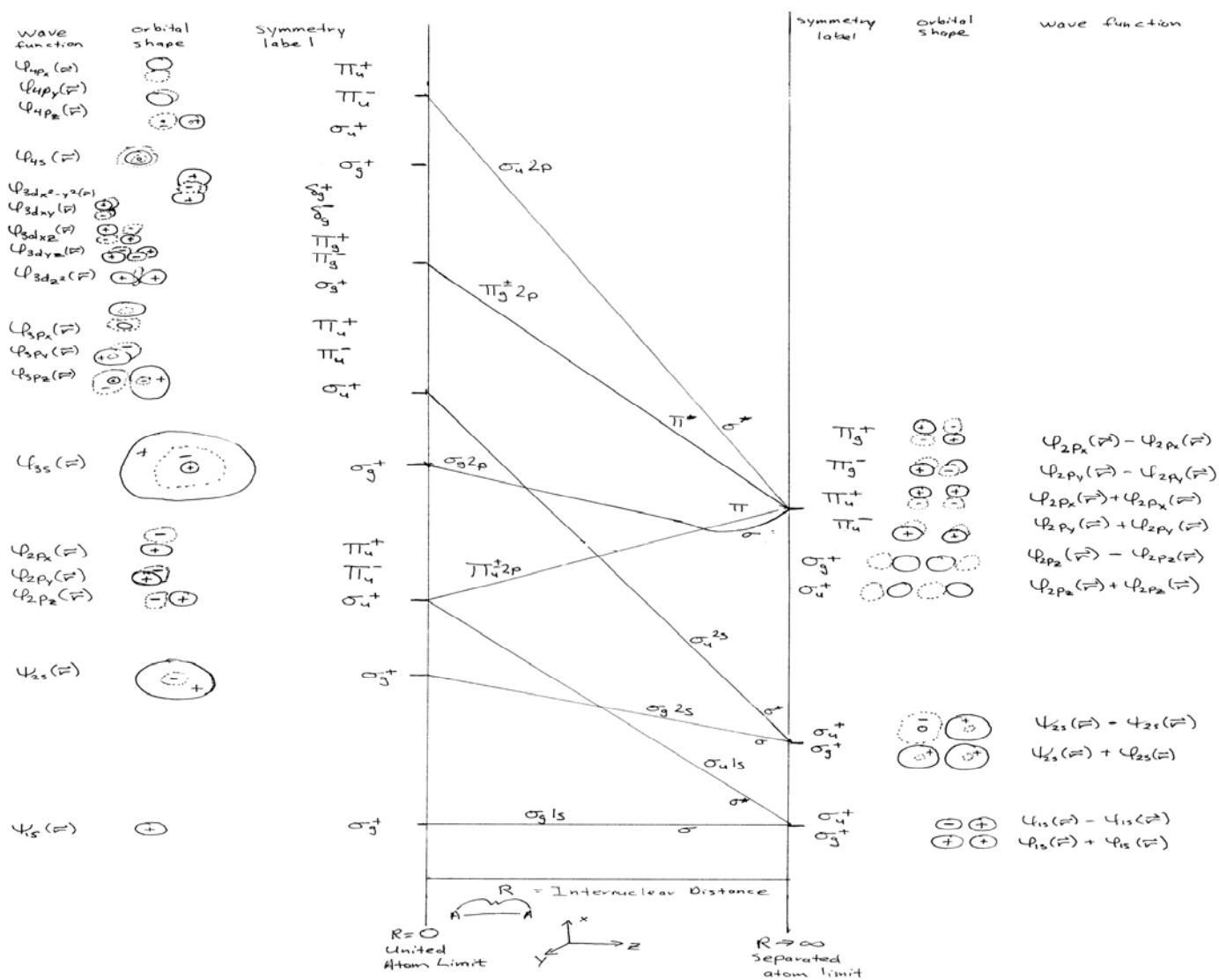
$$^1\Pi: \quad J = |1 + 0| = 1$$

The terms are then

$$\begin{aligned} &^3\Phi_{u/g,4}^\pm, ^3\Phi_{u/g,3}^\pm, ^3\Phi_{u/g,2}^\pm \\ &^1\Phi_{u/g,3}^\pm \\ &^3\Pi_{u/g,2}^\pm, ^3\Pi_{u/g,1}^\pm, ^3\Pi_{u/g,0}^\pm \\ &^1\Pi_{u/g,1}^\pm \end{aligned}$$

**(c) Draw the continuation of the correlation diagram for homonuclear diatomics, so that you can decide which MO's are occupied for the 3<sup>rd</sup>-row homonuclear diatomic molecules ( $Na_2, \dots, Ar_2$ ). (See the next page.)**

Name:



Name:

Use the correlation diagram to address the following questions:

(d)  $Al_2$  has  $^3\Pi_u^\pm$  ground states. Which molecular orbitals are occupied? What are the permissible values of  $J$ ?

Well, the first state that will be occupied is the combination of the  $3s$  orbitals  $(\sigma_g(3s))^2(\sigma_u(3s))^2$ . But  $Al_2$  has two remaining valence electrons. Hmm...where to put them. Well, we have a triplet state, so the two electrons must go into different orbitals. However, if we put one in the  $\pi_u^+$  orbital and one in the  $\pi_u^-$  orbital, then we'd have a total orbital angular momentum of zero (one electron revolves clockwise, and one revolves anticlockwise); we end up with a  $^3\Sigma_g^-$  state then, just like for  $O_2$ . So it must be that, for  $Al_2$ , the  $\sigma_g(3p)$  orbital lies lower in energy than the  $\pi_u^\pm(3p)$  orbitals. (Remember that the  $\sigma_g(2p)$  orbital was only a little higher in energy than the  $\pi_u^\pm(2p)$  orbitals for boron and carbon.) However, if the  $\sigma_g(2p)$  orbital was actually doubly occupied, then...well, in that case we'd have that the term would be  $^1\Sigma$ . So, it must be that the fact that electrons want to have opposite spin (maximum multiplicity, as per Hund's rules) is a favorable enough effect to take one electron from the  $\sigma_g(2p)$  and promote it to either the  $\pi_u^+(2p)$  or the  $\pi_u^-(2p)$ . The ground state will be degenerate, then, with the electron configurations being:

$$\begin{aligned} &(\sigma_g(3s))^2(\sigma_u(3s))^2(\sigma_g(2p))^1(\pi_u^+(2p))^1 \\ &(\sigma_g(3s))^2(\sigma_u(3s))^2(\sigma_g(2p))^1(\pi_u^-(2p))^1 \end{aligned}$$

The possible values of  $J$  are

$$|\Lambda + S|, |\Lambda + S - 1|, \dots, |\Lambda - S| = |1 + 1|, |1 + 1 - 1|, |1 - 1| = 2, 1, 0.$$

(e)  $Si_2$  has a ground state term of  $^3\Pi_u$ . Which molecular orbitals are occupied? What are the permissible values of  $J$ ?

In this case the analysis is similar. We need to distribute 4 electrons between the  $\sigma_g(2p), \pi_u^+(2p), \pi_u^-(2p)$  orbitals. Possible electron configurations are

$$\begin{aligned} &(\sigma_g(3s))^2(\sigma_u(3s))^2(\sigma_g(2p))^2(\pi_u^+(2p))^1(\pi_u^-(2p))^1 \rightarrow ^3\Sigma^- \\ &(\sigma_g(3s))^2(\sigma_u(3s))^2(\sigma_g(2p))^1(\pi_u^+(2p))^2(\pi_u^-(2p))^1 \rightarrow ^3\Pi_g^+ \\ &(\sigma_g(3s))^2(\sigma_u(3s))^2(\sigma_g(2p))^1(\pi_u^+(2p))^1(\pi_u^-(2p))^2 \rightarrow ^3\Pi_g^- \end{aligned}$$

Name:

The first is, again, like in  $O_2$ . It doesn't agree with the experimental facts you were provided with. The other terms are  $\Pi$  terms, as required, so the last two electron-configurations are what we are looking for.

The possible  $J$  values are the same as before,  $J = 2, 1, 0$ .



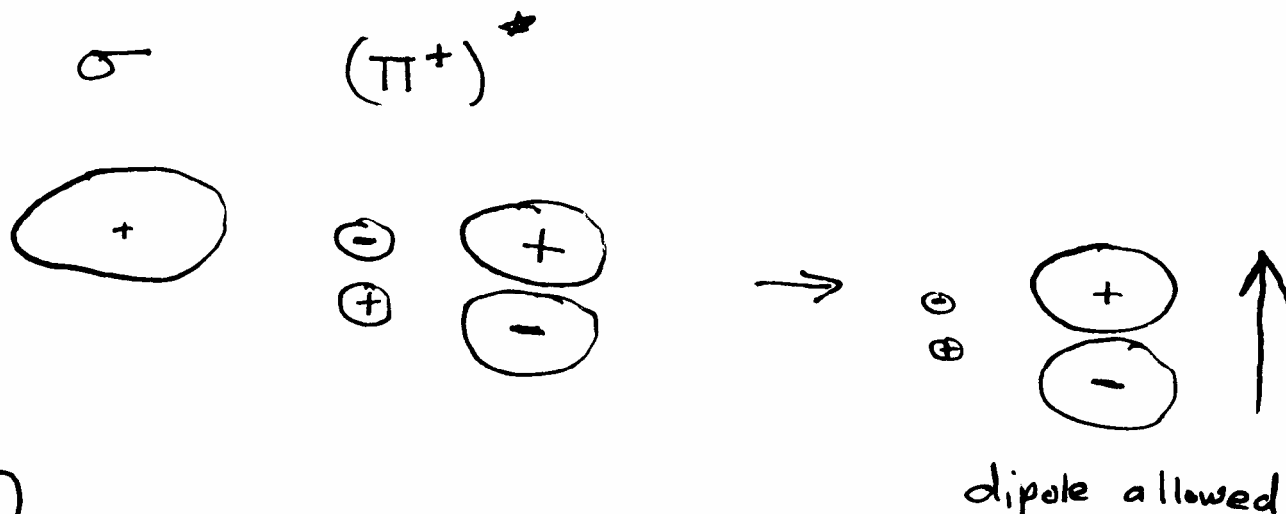
Name:

## Part 2: Closed-Book Derivations and Problems. (39 points; 3 points each)

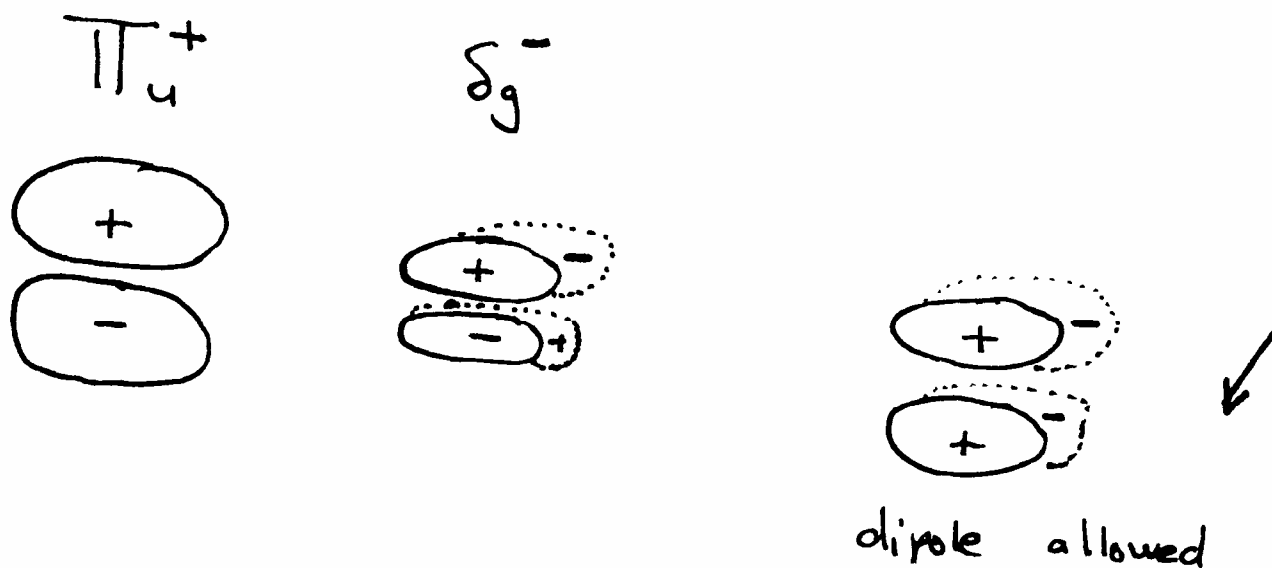
### 1. Selection Rules

For each of the following transitions, decide whether it is allowed or forbidden *and describe why*.

- (a) Excitation of an electron from a  $\sigma$ -bonding MO to a  $\pi^*$ -antibonding MO in a *heteronuclear* diatomic molecule



- (b) Excitation of an electron from a  $\pi_u^+$  MO to a  $\delta_g^-$  MO in a *homonuclear* diatomic molecule



Name:

(c) The terms associated with the  $1s^1 2p^1$  and  $2p^2$  electron configurations of He are listed below.

Which transitions are allowed? Why? Forbidden? Why?

$1s^1 2p^1$  :  $^3P, ^1P$

$2p^2$  :  $^1S, ^1D, ^3P$

$^3P \rightarrow ^3P$  allowed because  $L = 1 \rightarrow L' = 1$  is allowed.

$^1P \rightarrow ^1S, ^1D$  is allowed because

$$|L' - L| = |2 - 1| = 1 \quad ({}^1P \rightarrow {}^1D)$$

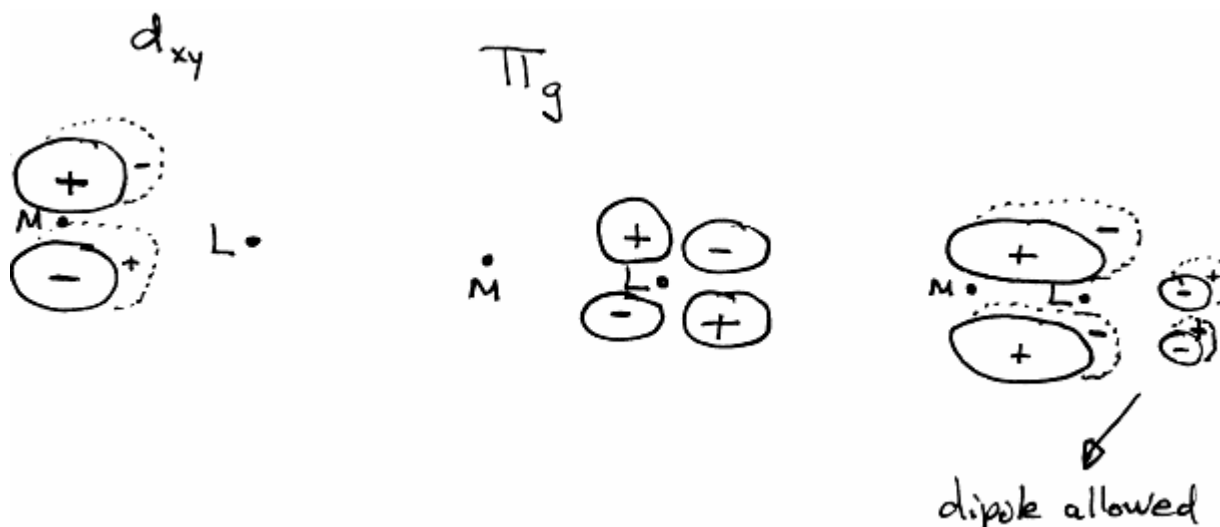
$$|L' - L| = |0 - 1| = 1 \quad ({}^1P \rightarrow {}^1S)$$

$^3P \rightarrow ^1S, ^1D$  are forbidden (spin-forbidden, allowed when spin-orbit effects are included) because the multiplicity changes.

$^1P \rightarrow ^3P$  is forbidden because the multiplicity changes.

**Bonus (5 pts.):** One of the most important spectroscopic signatures of transition metals are metal-to-ligand charge-transfer excitations. One of the most common is the  $d$ -to- $\pi^*$  transitions. Explain why the transition between a  $d$ -orbital on the metal and a  $\pi_g^\pm$  orbital on the ligand is not only allowed, but intense.

The key is that the ligand-centered  $\pi_g^\pm$  and the metal-centered  $d$ -orbitals are not located at the same point in space. So the “transition dipole” (which were were examining by multiplying the two orbitals together) is centered between the two orbitals.



Name:

## 2. Franck-Condon Factors

(a) Write the general form of Fermi's Golden rule.

$$W_{fi} = \frac{2\pi V^2 g(\hbar\omega_{fi}) \left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2}{\hbar}$$

(b) Starting from the previous expression, derive the expression for the rate of transitions from the  $\nu^{th}$  vibrational state of the  $i^{th}$  excited state to the  $\mu^{th}$  vibrational state of the  $f^{th}$  excited state,  $W_{\mu f, \nu i}$ .

We start by analyzing the integral in Fermi's Golden Rule. We write the wave function as a product of electronic and nuclear wave functions, as per the Born-Oppenheimer approximation. Thus,

$$\begin{aligned}\Phi_{\nu i}(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_P) &= \xi_i(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_P) \chi_{\nu i}(\mathbf{R}_1, \dots, \mathbf{R}_P) \\ \Phi_{\mu f}(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_P) &= \xi_f(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_P) \chi_{\mu f}(\mathbf{R}_1, \dots, \mathbf{R}_P)\end{aligned}$$

We have, then, that

$$\begin{aligned}\langle \Phi_{\mu f} | \hat{\mu}_x | \Phi_{\nu i} \rangle_{1\dots N, 1\dots P} &= \left\langle \Phi_{\mu f} \left| \sum_{i=1}^N -ex_i + \sum_{\alpha=1}^P Z_{\alpha} eX_{\alpha} \right| \Phi_{\nu i} \right\rangle_{1\dots N, 1\dots P} \\ &= \left\langle \chi_{\mu f} \xi_f \left| \sum_{i=1}^N -ex_i \right| \chi_{\nu i} \xi_i \right\rangle_{1\dots N, 1\dots P} + \left\langle \chi_{\mu f} \xi_f \left| \sum_{\alpha=1}^P Z_{\alpha} eX_{\alpha} \right| \chi_{\nu i} \xi_i \right\rangle_{1\dots N, 1\dots P} \\ &= \left\langle \chi_{\mu f} \xi_f \left| \sum_{i=1}^N -ex_i \right| \chi_{\nu i} \xi_i \right\rangle_{1\dots N, 1\dots P} + \left\langle \chi_{\mu f} \left| \left( \langle \xi_f | \xi_i \rangle_{1\dots N} \right) \sum_{\alpha=1}^P Z_{\alpha} eX_{\alpha} \right| \chi_{\nu i} \right\rangle_{1\dots P}\end{aligned}$$

In the last line we have used the fact that the nuclear wave functions do not depend on the electronic coordinates, and integrated over the electronic coordinates,  $\mathbf{r}_1, \dots, \mathbf{r}_N$ . The subscripts on the bra-kets denote whether we integrate with respect to the electronic coordinates (1,2,...N) or the nuclear coordinates (1,2,...P) or both. Since the electronic wave functions of different electronic states are orthogonal, we have that  $\langle \xi_f | \xi_i \rangle_{1\dots N} = 0$  for electronic excitations. (This is not true for ro-vibrational spectroscopy.) So we need only worry about the first term. Now, let's define the transition dipole for a specific nuclear configuration using,

$$\mu_{fi}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) \equiv \left\langle \xi_f \left| \sum_{i=1}^N -ex_i \right| \xi_i \right\rangle_{1\dots N}.$$

We have, then, that

Name:

$$\begin{aligned}\langle \Phi_{\mu_f} | \hat{\mu}_x | \Phi_{\nu_i} \rangle_{1...N, 1...P} &= \left\langle \chi_{\mu_f} \left| \sum_{i=1}^N -ex_i \right| \chi_{\nu_i} \right\rangle_{1...N, 1...P} \\ &= \left\langle \chi_{\mu_f} \left| \mu_{f_i}(\mathbf{R}_1, \dots, \mathbf{R}_P) \right| \chi_{\nu_i} \right\rangle_{1...P}\end{aligned}$$

Now, we know that the electrons move much faster than the nuclei. So, when we perform an electronic excitation there is scarcely any nuclear motion. So let's use a Taylor series to expand out  $\mu_{f_i}(\mathbf{R}_1, \dots, \mathbf{R}_P)$  around the equilibrium nuclear positions in the initial state,  $(\mathbf{R}_1^{(i)}, \dots, \mathbf{R}_P^{(i)})$ . Using the Taylor series, we have that

$$\mu_{f_i}(\mathbf{R}_1, \dots, \mathbf{R}_P) = \mu_{f_i}(\mathbf{R}_1^{(i)}, \dots, \mathbf{R}_P^{(i)}) + \sum_{k=1}^P (\mathbf{R}_k - \mathbf{R}_k^{(i)}) \cdot \nabla_k \mu_{f_i}(\mathbf{R}_1^{(i)}, \dots, \mathbf{R}_P^{(i)}) + \dots$$

We substitute into the expression above, obtaining

$$\begin{aligned}\langle \Phi_{\mu_f} | \hat{\mu}_x | \Phi_{\nu_i} \rangle_{1...N, 1...P} &= \left\langle \chi_{\mu_f} \left| \mu_{f_i}(\mathbf{R}_1, \dots, \mathbf{R}_P) \right| \chi_{\nu_i} \right\rangle_{1...P} \\ &= \left\langle \chi_{\mu_f} \left| \mu_{f_i}(\mathbf{R}_1^{(i)}, \dots, \mathbf{R}_P^{(i)}) + \sum_{\alpha=1}^P (\mathbf{R}_\alpha - \mathbf{R}_\alpha^{(i)}) \cdot \nabla_\alpha \mu_{f_i}(\mathbf{R}_1^{(i)}, \dots, \mathbf{R}_P^{(i)}) + \dots \right| \chi_{\nu_i} \right\rangle_{1...P} \\ &= \mu_{f_i}(\mathbf{R}_1^{(i)}, \dots, \mathbf{R}_P^{(i)}) \langle \chi_{\mu_f} | \chi_{\nu_i} \rangle + \sum_{\alpha=1}^P \left\langle \chi_{\mu_f} \left| (\mathbf{R}_\alpha - \mathbf{R}_\alpha^{(i)}) \cdot \nabla_\alpha \mu_{f_i}(\mathbf{R}_1^{(i)}, \dots, \mathbf{R}_P^{(i)}) \right| \chi_{\nu_i} \right\rangle_{1...P} + \dots\end{aligned}$$

In the Condon approximation, we assume that the second and higher order terms are small compared to the first term. These terms couple the motion of the nuclei to the motion of the electrons, leading to “vibronic coupling” between the electronic excitation and the vibrational motion. These effects are neglected in the Condon approximation. Thus, we have that

$$\begin{aligned}\langle \Phi_{\mu_f} | \hat{\mu}_x | \Phi_{\nu_i} \rangle_{1...N, 1...P} &= \left\langle \chi_{\mu_f} \left| \mu_{f_i}(\mathbf{R}_1, \dots, \mathbf{R}_P) \right| \chi_{\nu_i} \right\rangle_{1...P} \\ &\approx \mu_{f_i}(\mathbf{R}_1^{(i)}, \dots, \mathbf{R}_P^{(i)}) \langle \chi_{\mu_f} | \chi_{\nu_i} \rangle \quad (\text{Condon approximation})\end{aligned}$$

Substituting this into the equation from part (a), we have that

$$\begin{aligned}W_{\mu_f, \nu_i} &= \frac{2\pi V^2 g(\hbar\omega_{\mu_f, \nu_i}) \left| \langle \Phi_{\mu_f} | \hat{\mu}_x | \Phi_{\nu_i} \rangle \right|^2}{\hbar} \\ &= \frac{2\pi V^2 g(\hbar\omega_{\mu_f, \nu_i}) \left| \mu_{f_i}(\mathbf{R}_1^{(i)}, \dots, \mathbf{R}_P^{(i)}) \right|^2 \left| \langle \chi_{\mu_f} | \chi_{\nu_i} \rangle \right|^2}{\hbar}\end{aligned}$$

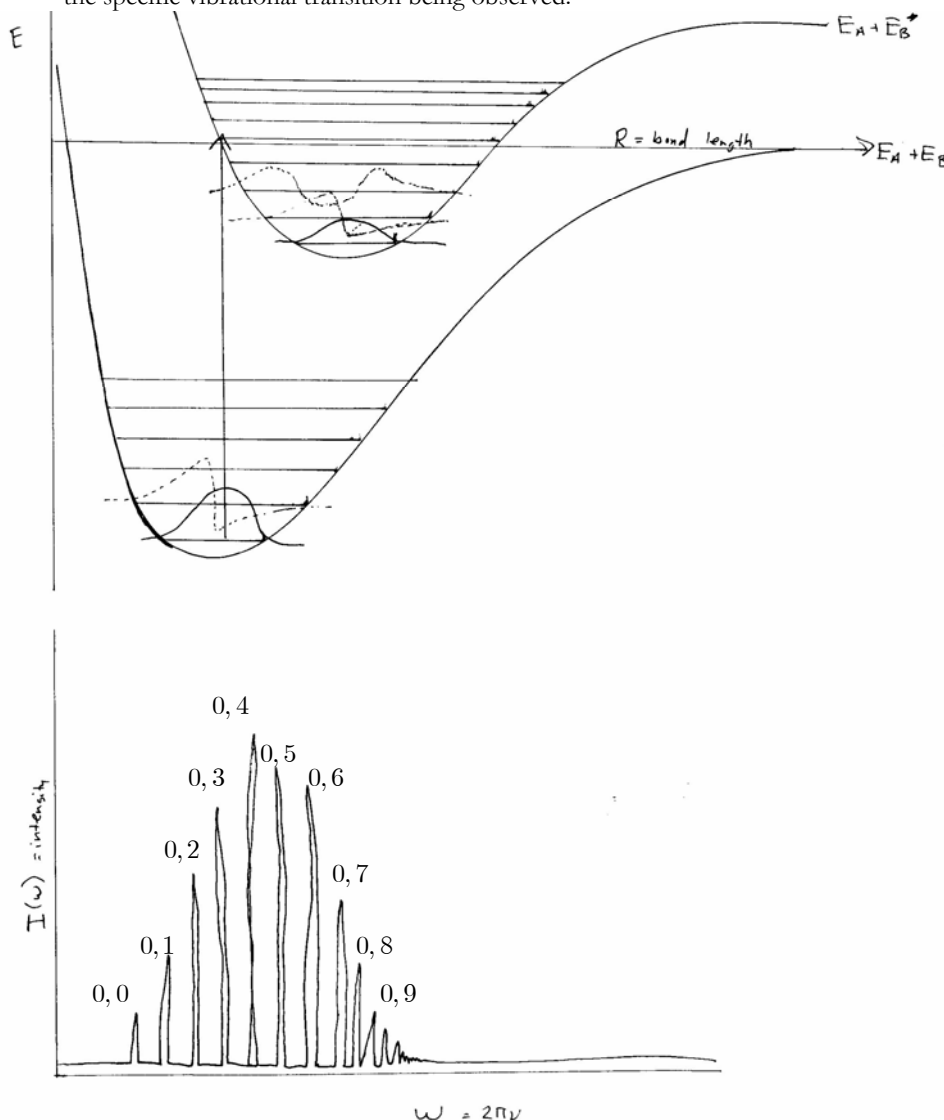
The  $\left| \langle \chi_{\mu_f} | \chi_{\nu_i} \rangle \right|^2$  term is called the Franck-Condon factor.

Name:

- (c) Referring to your work in part (b), what is the Condon approximation? What is the rationale behind this approximation?

The Condon approximation is associated with neglecting terms that depend on the way  $\mu_{fi}(\mathbf{R}_1, \dots, \mathbf{R}_p)$  changes with respect to the nuclear positions. The rationale is that the nuclei move very little in the time it takes for a molecule to move from one electronic state to another, so that we can effectively predict the electronic spectroscopy of a molecule by keeping the nuclei “clamped” still while we analyze the electronic transition.

- (d) Draw potential energy surfaces for a case where the final state has a somewhat larger equilibrium bond length than the ground state. Draw in the vibrational energy levels. Sketch the spectrum, labeling each spectral line with the specific vibrational transition being observed.



Here the numbers indicate that the excitation proceeds from the ground vibration state (state 0) of the lower electronic state to the ground (or excited) states (states 0,1,2,...) of the higher potential energy surface.

Name:

### 3. Chemical Binding

In class we discussed what makes a chemical bond. We considered 2-atoms,  $A$  and  $B$ , with bonding orbitals  $\phi_A(\mathbf{r})$  and  $\phi_B(\mathbf{r})$ . Then, we considered a Hartree-Fock (or Kohn-Sham) Hamiltonian for the orbitals,

$$\hat{h}_{A,B}(\mathbf{r}) = -\frac{\nabla^2}{2} + v_{A,B}(\mathbf{r})$$

Define the Hamiltonian for the diatomic as

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + v_A(\mathbf{r}_1) + v_B(\mathbf{r}_1) + v_A(\mathbf{r}_2) + v_B(\mathbf{r}_2)$$

and consider the molecular orbitals of the diatomic to be given by

$$\psi(\mathbf{r}) = c\phi_A(\mathbf{r}) + \sqrt{1-c^2}\phi_B(\mathbf{r}).$$

Denote the integrals

$$\int \phi_A^*(\mathbf{r}) \left( -\frac{\nabla^2}{2} + v_A(\mathbf{r}) \right) \phi_A(\mathbf{r}) d\mathbf{r} = \varepsilon_A$$

$$\int \phi_B^*(\mathbf{r}) \left( -\frac{\nabla^2}{2} + v_B(\mathbf{r}) \right) \phi_B(\mathbf{r}) d\mathbf{r} = \varepsilon_B$$

$$\int \phi_A^*(\mathbf{r}) \left( -\frac{\nabla^2}{2} + v_A(\mathbf{r}) + v_B(\mathbf{r}) \right) \phi_A(\mathbf{r}) d\mathbf{r} = \alpha_A$$

$$\int \phi_B^*(\mathbf{r}) \left( -\frac{\nabla^2}{2} + v_A(\mathbf{r}) + v_B(\mathbf{r}) \right) \phi_B(\mathbf{r}) d\mathbf{r} = \alpha_B$$

$$\int \phi_A^*(\mathbf{r}) \left( -\frac{\nabla^2}{2} + v_A(\mathbf{r}) + v_B(\mathbf{r}) \right) \phi_B(\mathbf{r}) d\mathbf{r} = \beta = \beta^*$$

$$\int \phi_A^*(\mathbf{r}) \phi_B(\mathbf{r}) d\mathbf{r} = 0 = \int \phi_B^*(\mathbf{r}) \phi_A(\mathbf{r}) d\mathbf{r}$$

$$\int \phi_B^*(\mathbf{r}) \phi_B(\mathbf{r}) d\mathbf{r} = 1 = \int \phi_A^*(\mathbf{r}) \phi_A(\mathbf{r}) d\mathbf{r}$$

(a) In terms of  $\alpha_A, \alpha_B$ , and  $\beta$ , what are the energy levels in the diatomic molecule?

Note that the molecular Hamiltonian is separable. That is, it can be written as a sum of two terms. So we write the wave function as a product of two molecular orbitals— $\Psi(\mathbf{r}_1, \mathbf{r}_2) \propto \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$ . Doing the separation of variables yields the one-electron Schrödinger equation for the molecular orbital,

$$\left( -\frac{\nabla^2}{2} + v_A(\mathbf{r}) + v_B(\mathbf{r}) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Now, we know that  $\psi(\mathbf{r}) = c\phi_A(\mathbf{r}) + d\phi_B(\mathbf{r})$ . (It is easier to not set  $d = \sqrt{1-c^2}$  quite yet.) Substitute this in. We get

$$\left( -\frac{\nabla^2}{2} + v_A(\mathbf{r}) + v_B(\mathbf{r}) \right) (c\phi_A(\mathbf{r}) + d\phi_B(\mathbf{r})) = E(c\phi_A(\mathbf{r}) + d\phi_B(\mathbf{r}))$$

Cross multiply by  $\phi_A^*(\mathbf{r})$  and integrate. You get the equation

$$\int \phi_A^*(\mathbf{r}) \left( -\frac{\nabla^2}{2} + v_A(\mathbf{r}) + v_B(\mathbf{r}) \right) (c\phi_A(\mathbf{r}) + d\phi_B(\mathbf{r})) d\mathbf{r} = \int \phi_A^*(\mathbf{r}) E(c\phi_A(\mathbf{r}) + d\phi_B(\mathbf{r})) d\mathbf{r}$$

$$\alpha_A c + \beta d = Ec$$

Similarly, multiply through by  $\phi_B^*(\mathbf{r})$  and integrate; you get

Name:

$$\int \phi_B^*(\mathbf{r}) \left( \frac{-\nabla^2}{2} + v_A(\mathbf{r}) + v_B(\mathbf{r}) \right) (c\phi_A(\mathbf{r}) + d\phi_B(\mathbf{r})) d\mathbf{r} = \int \phi_B^*(\mathbf{r}) E (c\phi_A(\mathbf{r}) + d\phi_B(\mathbf{r})) d\mathbf{r}$$

$$\beta c + \alpha_B d = E d$$

This is equivalent to the matrix eigenvalue problem,

$$\begin{bmatrix} \alpha_A & \beta \\ \beta & \alpha_B \end{bmatrix} \begin{bmatrix} c \\ d \end{bmatrix} = E \begin{bmatrix} c \\ d \end{bmatrix}$$

$$\left( \begin{bmatrix} \alpha_A & \beta \\ \beta & \alpha_B \end{bmatrix} - E \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \right) \begin{bmatrix} c \\ d \end{bmatrix} = 0$$

$$\begin{bmatrix} \alpha_A - E & \beta \\ \beta & \alpha_B - E \end{bmatrix} \begin{bmatrix} c \\ d \end{bmatrix} = 0$$

The eigenvalues are found by solving the determinant equation

$$\begin{vmatrix} \alpha_A - E & \beta \\ \beta & \alpha_B - E \end{vmatrix} = 0$$

So we have

$$(\alpha_A - E)(\alpha_B - E) - \beta^2 = E^2 - (\alpha_A + \alpha_B)E + \alpha_A\alpha_B - \beta^2 = 0$$

$$E = \frac{\alpha_A + \alpha_B}{2} \pm \frac{\sqrt{(\alpha_A + \alpha_B)^2 - 4(\alpha_A\alpha_B - \beta^2)}}{2}$$

$$= \frac{\alpha_A + \alpha_B}{2} \pm \frac{\sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2}}{2}$$

These values are the energy levels for the orbitals.

Name:

(b) In terms of  $\varepsilon_A, \varepsilon_B, \alpha_A, \alpha_B$ , and  $\beta$ , what is the formula for the binding energy?

The electrons in the “unbound” molecules have energies  $\varepsilon_A$  and  $\varepsilon_B$ . The electrons in the bound molecule each have energy

$$E = \frac{\alpha_A + \alpha_B}{2} - \frac{\sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2}}{2}.$$

(The positive sign corresponds to the antibonding orbital, since it is the orbital with higher energy.) Since there are 2 electrons in this orbital, the energy of the electrons in the molecule is approximate  $\alpha_A + \alpha_B - \sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2}$ . Subtracting, we get that the “energy of reaction” is about

$$E_{\text{rxn}} = \left( \alpha_A + \alpha_B - \sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2} \right) - (\varepsilon_A + \varepsilon_B)$$

This is an approximation to the binding energy. You could also consider the “separated atoms state” consisting of a cation and an anion. In that case,

$$E_{\text{rxn}} = \left( \alpha_A + \alpha_B - \sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2} \right) - (2 \cdot \min(\varepsilon_A, \varepsilon_B))$$

because the anion should consist of both electrons should be in the atomic orbital with lower energy. Either answer is OK.

(c) In terms of  $\alpha_A, \alpha_B$ , and  $\beta$ , what is the formula for the binding molecular orbital?

The binding molecular orbital is found by solving for the coefficients of the eigenfunction. Taking the first equation, we have

$$\alpha_A c + \beta d = E c$$

$$\alpha_A c + \beta \sqrt{1 - c^2} = E c$$

$$\beta \sqrt{1 - c^2} = (E - \alpha_A) c$$

$$\beta^2 (1 - c^2) = (E - \alpha_A)^2 c^2$$

$$\beta^2 = ((E - \alpha_A)^2 + \beta^2) c^2$$

$$\frac{\beta^2}{(E - \alpha_A)^2 + \beta^2} = c^2$$

$$\sqrt{\frac{\beta^2}{(E - \alpha_A)^2 + \beta^2}} = c$$

$$\sqrt{\frac{\beta^2}{\left( \frac{\alpha_A + \alpha_B}{2} - \frac{\sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2}}{2} - \alpha_A \right)^2 + \beta^2}} = c$$

$$\sqrt{\frac{\beta^2}{\left( \frac{\alpha_B - \alpha_A}{2} - \frac{\sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2}}{2} - \alpha_A \right)^2 + \beta^2}} = c$$



Name:

## 4. MO and VB Theory

- (a) Write a Molecular-Orbital-theory wave function for the Hydrogen molecule,  $H_2$ . Include configuration interaction with the antibonding orbital, and weight the coefficient of the antibonding orbital with  $\kappa$ .

$$\Psi^{MO+CI}(\mathbf{r}_1, \mathbf{r}_2) \propto \left[ \left( \psi_{1s}^{(l)}(\mathbf{r}_1) + \psi_{1s}^{(r)}(\mathbf{r}_1) \right) \left( \psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_2) \right) \right. \\ \left. + \kappa \left( \psi_{1s}^{(l)}(\mathbf{r}_1) - \psi_{1s}^{(r)}(\mathbf{r}_1) \right) \left( \psi_{1s}^{(l)}(\mathbf{r}_2) - \psi_{1s}^{(r)}(\mathbf{r}_2) \right) \right] (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

- (b) Write a Valence-Bond-theory wave function for the Hydrogen molecule,  $H_2$ . Include ionic contribution, and weight the coefficient of the ionic contribution with  $\delta$ .

$$\Psi^{VB+ionic}(\mathbf{r}_1, \mathbf{r}_2) \propto \left( \psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) \right) + \delta \left( \psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) \right)$$

- (c) Show that the MO+CI and the VB+ionic wave functions are equivalent by deriving a relationship between  $\kappa$  and  $\delta$ .

$$\Psi^{MO+CI}(\mathbf{r}_1, \mathbf{r}_2) \propto \left[ \begin{aligned} &(1 + \kappa) \psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) + (1 - \kappa) \psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) \\ &+ (1 - \kappa) \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) + (1 + \kappa) \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) \end{aligned} \right] \\ \propto (1 - \kappa) \left( \psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) \right) \\ + (1 + \kappa) \left( \psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) \right) \\ \propto \left( \psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) \right) + \frac{1+\kappa}{1-\kappa} \left( \psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) \right)$$

Name:

## Part 3: Multiple-Choice; Short-Answer (35 points; 1 point each)

1-4. Write a representative molecular orbital for each of the following states.

Orbital Symmetry Label	Molecular Orbital
$\sigma_g^+$	$\psi_{1s}^{(l)}(\mathbf{r}) + \psi_{1s}^{(r)}(\mathbf{r})$
$\pi_g^+$	$\psi_{2p_x}^{(l)}(\mathbf{r}) - \psi_{2p_x}^{(r)}(\mathbf{r})$
$\pi_u^-$	$\psi_{2p_y}^{(l)}(\mathbf{r}) + \psi_{2p_y}^{(r)}(\mathbf{r})$
$\delta_u^+$	$\psi_{3d_{x^2-y^2}}^{(l)}(\mathbf{r}) - \psi_{3d_{x^2-y^2}}^{(r)}(\mathbf{r})$

5. Which of the following orbital types are “bonding” orbitals (as opposed to antibonding).

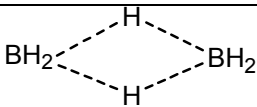
- (a)  $\sigma_u$  (c)  $\pi_u^+$  (e)  $\delta_u^+$   
 (b)  $\sigma_g$  (d)  $\pi_g^+$  (f)  $\delta_g^-$

6. Write the form of the Beryllium  $sp$  hybrid orbitals used to describe  $BeH_2$ .

$$\psi_{2s}(\mathbf{r}) + \psi_{2p_z}(\mathbf{r})$$

$$\psi_{2s}(\mathbf{r}) - \psi_{2p_z}(\mathbf{r})$$

7-8. For each of the following molecules, use Hund’s localization criteria to determine whether the molecular orbitals can be written in terms of localized orthogonal orbitals.

Molecule	Can Localized Orbitals be constructed (Yes/No)
$NH_3$ (ammonia)	Yes
 Diborane.	No

In  $LiF$ , the binding molecular orbital has the approximate form

$$c_{Li}\psi_{2s}^{Li}(\mathbf{r}) + c_F\psi_{2p_z}^F(\mathbf{r})$$

Here,  $c_F \approx .9$  and  $c_{Li} \approx .2$ .  $S \equiv \langle \psi_{2s}^{Li} | \psi_{2p_z}^F \rangle = .4$ .

9. The Lithium-Fluorine bond is directed along the

- (a)  $x$  axis. (b)  $y$  axis. (c)  $z$ -axis.

10. Using Mulliken population analysis, the estimated charge of the Fluorine atom is:

The “amount” of the orbital that is associated with the Fluorine atom is  $c_F^2 + \frac{1}{2}(2Sc_Fc_{Li}) = .81 + .2 \cdot .9 \cdot .4 = .81 + .072 = .882$ . Since the orbital is doubly occupied, this means that the Fluorine atom has  $2 \cdot .882 = 1.764$  bonding electrons on it, while it donates only one electron (the  $2p_z$  electron) to the bond. The net gain of electrons is .764, so the Fluorine atom has a  $-.764$  charge.

Name:

**11-13. For each of the following, indicate whether the statement pertains to molecular orbital (MO) or valence bond (VB) theory.**

  MO   In the simplest form, this theory gives a poor description of molecular dissociation.

  VB   This theory is associated with orbital hybridization.

  MO   Using this theory, it is easy to predict the results of electronic spectroscopy.

  VB   In this theory, the pairing of electrons to form lone pairs and chemical bonds is of primary importance.

  MO   Using this method, it is easy to predict the multiplicity and bond order of diatomic molecules.

  MO   This method is easier computationally.

  MO   In this theory, a simple wave function can usually be written as a single Slater determinant.

  VB   This theory is associated with the theory of resonance.

**14. You put a molecule in the presence of light. The light travels in the  $z$ -direction and the magnetic field oscillates in the  $x$ -direction. The electric field vector oscillates in the**

(a)  $x$ -direction.

(b)  $y$ -direction

(c)  $z$ -direction

**15. Which of the following are valid relationships for light/photons? Here  $c$  is the speed of light,  $h$  is Planck's constant, and  $\hbar \equiv \frac{h}{2\pi}$ .**

(a) wave number =  $2\pi$ (wavelength)

(e) angular frequency =  $2\pi$ (frequency)

(b) Energy =  $\hbar c$ (wave number)

(f) wavelength =  $c \cdot$  period

(c) momentum  $\cdot$  wavelength =  $h$

(g) wave number =  $c \cdot \frac{1}{\text{angular frequency}}$

(d) Energy =  $h \cdot$  (frequency)

**16. If  $\langle \Phi_1 | \hat{\mu}_x | \Phi_0 \rangle = 0$ , we say that the transition from the ground to first-excited state is:**

(a) electric dipole allowed.

(c) magnetic dipole allowed

(b) electric dipole forbidden.

(d) magnetic dipole forbidden

**17. Write down the time-dependent Schrödinger Equation.**

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Name:

18. In general, what is the relationship between the frequency of absorbed radiation and the difference in energy between the initial and final states?

$$\nu = \frac{E_f - E_i}{h}$$

19. Suppose  $\Psi_k$  is the eigenfunction for a stationary state. We can write the time-dependent eigenfunction as

$$\Psi_k(\mathbf{r}_1, \dots, \mathbf{r}_N; t) \equiv \Phi_k(\mathbf{r}_1, \dots, \mathbf{r}_N) \cdot \chi(t)$$

where  $\Phi_k(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is an eigenfunction of the time-independent Schrödinger equation,

$$\hat{H}\Phi_k(\mathbf{r}_1, \dots, \mathbf{r}_N) = E_k\Phi_k(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

What is  $\chi(t)$ ?

$$\chi(t) = e^{-iE_k t/\hbar}$$

- 20-22. Describe why the long-wavelength approximation is usually valid. What types of transitions are forbidden in the limit of infinitely long wavelength, but allowed for “real” systems with finite wavelength?

The long-wavelength approximation is based on the fact that the wavelength of the light used in electronic spectroscopy is usually much larger than the size of the molecule. Consequently, the molecule just sees an oscillating electric dipole—it does not see the “curvature” of the light wave. I would explain this with the trigonometric analysis:

$$\begin{aligned} E_x(\mathbf{r}, t) &= 2V \sin(\omega t - kz) \\ &= 2V \sin(\omega t) \cos(kz) - 2V \cos(\omega t) \sin(kz) \\ &= 2V \sin(\omega t) \cos\left(\frac{\omega z}{c}\right) - 2V \cos(\omega t) \sin\left(\frac{\omega z}{c}\right) \\ &\approx 2V \sin(\omega t) \left(1 + \frac{\omega^2 z^2}{2c^2} + \dots\right) - 2V \cos(\omega t) \left(\frac{\omega z}{c} - \frac{\omega^3 z^3}{6c^3} + \dots\right) \end{aligned}$$

where I have used the Taylor series in the last step. Clearly, for small displacements,  $2\pi \frac{z}{\lambda} \approx 0$ , only the  $2V \sin(\omega t)$  is relevant.

The other terms we have neglected have factors of  $\frac{\omega}{c} = \frac{2\pi}{\lambda} = k$ . For large wave lengths, they are forbidden. But for “real” wavelengths we can observe magnetic dipole, electric quadrupole, magnetic quadrupole, electric octopole, etc. transitions.

Name:

**23-25. Describe the weak-field approximation. Why is it usually valid? Give an example of a phenomenon that would be forbidden for light with an infinitely weak field (so  $V(\mathbf{r}, t) = 2V \sin(\omega t - kz)$  with  $V \rightarrow 0$ ).**

The weak-field approximation is behind our decision to use perturbation theory. It suggests that the response of the wave function (and energy) to the radiation is linear. That is, when we expand the wave function and the energy in terms of the field strength,  $V$ , we assume that  $V$  is small compared to the fields felt by the electrons in the molecule, so that the “perturbation” is small. This is true because the fields inside molecules are gigantic: the electrons and nuclei are so close together that, even though their charge is relatively small, the fields are *enormous* compared to that of almost any light source we can apply. So it is a good approximation to truncate the Taylor (= perturbation) series after first-order,

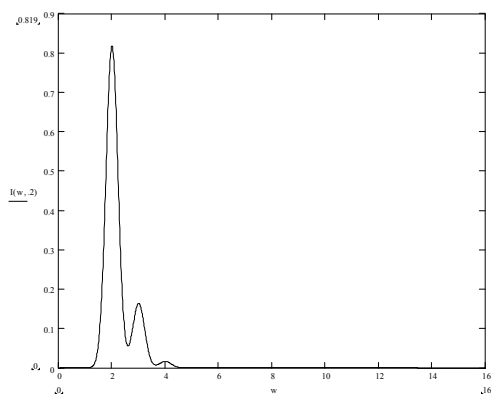
$$E(V) = E + V \frac{\partial E}{\partial V} + \dots$$

$$\Psi(V) = \Psi + V \frac{\partial \Psi}{\partial V} + \dots$$

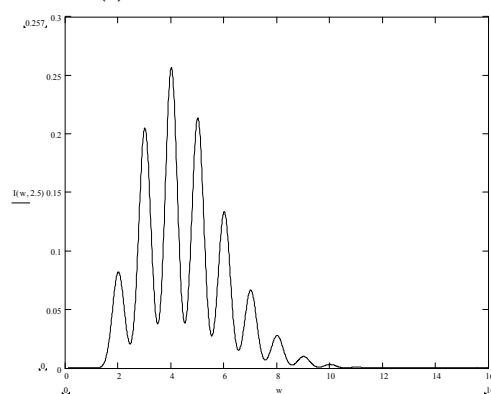
Still, we do not *have* to do this. There are nonlinear optical effects which are described by the higher order terms in the perturbation series. Two of the most important are resonant Raman spectroscopy and multi-photon excitations. In each case, two (rather than just one) photon is involved in the process.

**26. The  $C_2$  cation is associated with the formation of carbon nanotubes and fullerenes by from graphite. The lowest-lying dipole-allowed excitation is associated with a spectrum most resembling**

(a)



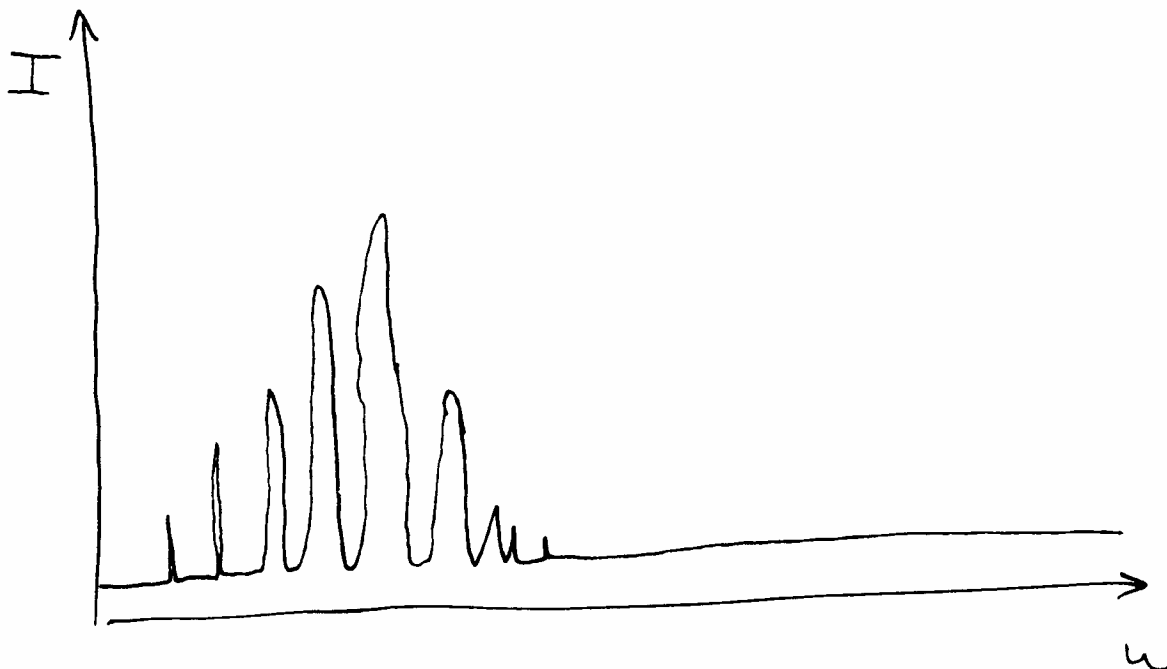
(b)



The lowest-lying excitation is from a  $\pi_u^\pm$  orbital to a  $\sigma_g$  orbital. This is a bonding-orbital to bonding-orbital transition, so we don't expect the bond length to change much. The answer is (a).

Name:

27. The following spectrum is associated with the phenomenon of predissociation.



28-32. Label each of the following according to the appropriate line shape. (“L” for Lorentzian or “G” for Gaussian.)

L This line shape has rather “long tails” extending from its peak frequency. In fact, its variance (the standard deviation squared) does not exist.

L High-resolution spectra usually have this line shape.

L Running reactions at high pressure is a useful technique for forcing a chemical equilibrium towards the products (via La Chatelier’s principle). Keeping the reaction vessel cold helps prevent “side-reactions” that would harm the product yield. If we monitor the reaction by observing the intensity a characteristic absorption of the product molecule, we would observe what type of lineshape?

G Spectra at high temperature (but low pressure) are usually associated with this line shape.

G This line shape is associated with inhomogeneous broadening

Name:

- 32,33. Write formulae for the Gaussian and Lorentzian lineshapes. You can omit the normalization constant.

$$I_{Lorentzian}(\omega) \propto \frac{1}{\left(\frac{\Gamma}{2}\right)^2 + (\omega - \omega_0)^2}$$

$$I_{Gaussian}(\omega) \propto e^{-4 \ln(2) \left(\frac{\omega - \omega_0}{\Gamma}\right)^2}$$

In the last five or so years, there has been increasing interest in doing chemistry in ionic liquids, which are “molten salts” that are still liquid at room temperature (usually because the ions are very bulky, which inhibits crystallization). We measure the spectrum of a molecule in (A) an ionic liquid and (B) in hexane (nonpolar solvent).

34. The absorption spectrum in the ionic liquid has a \_\_\_\_\_ line shape.  
(a) Gaussian (b) Lorentzian
35. For a characteristic absorption, we measure the full-width at half-maximum,  $\Gamma$ .  $\Gamma$  is larger for the  
(a) ionic liquid (b) hexane