

Name:

# Mid-Term Examination

## Chemistry 3BB3

Winter, 2005

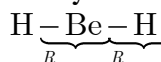
### Part 1. Thinking Problems.

#### Correlation Diagrams for Triatomic Molecules and Walsh's Rules

#### Part A. (4 points)

In class (and also in the notes) the  $BeH_2$  molecule was considered.

- Draw the correlation diagram for the symmetric stretch of this molecule



from the united atom limit ( $R = 0$ ) to the separated atom limit ( $R = \infty$ ). To get you started, the united atom states are drawn. You need only include the first seven states of the separated atoms.

- Make sure you sketch the orbitals in the separated atom limit and label all the orbitals (in both the united and separated atom limits!) with the appropriate symmetry labels for a  $D_{\infty h}$  molecule.

$$\text{H} - \text{A} - \text{H}$$

R      R



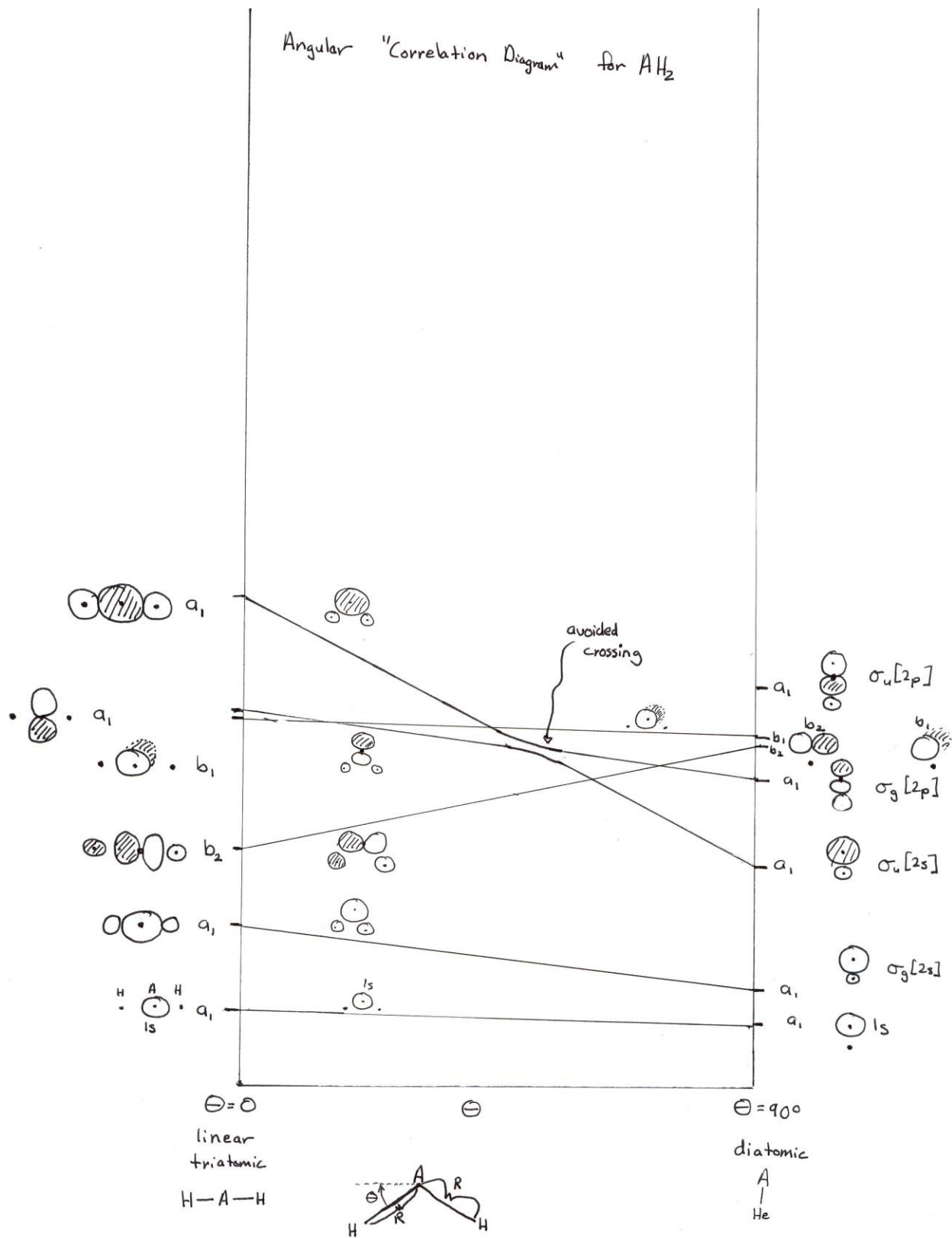
## Part B. (4 points)

Now, let's consider what happens if we bend the bond, so that we have only  $C_{2v}$  symmetry.

- Draw the correlation diagram for the states of this molecule. To get you started, the states for the  $\theta = 0^\circ$  case are drawn.
- What molecule does this resemble when  $\theta = 90^\circ$ ?
- Sketch the orbitals in the  $\theta = 90^\circ$  limit.
- Label the symmetry of each orbital (the  $\theta = 0^\circ$  limit is done as an example). For a molecule with  $C_{2v}$  symmetry, we have only two symmetry elements to use in labeling the orbitals
  - Rotation about the  $C_2$  axis, which lies in the molecular plane and passes through the non-hydrogen atom. If the orbital is symmetric with respect to rotation by  $180^\circ$ , then it is labeled with an "a". If the orbital is antisymmetric with respect to rotation by  $180^\circ$ , then it is labeled with a "b."
  - Reflection through the mirror plane that lies along the  $C_2$  axis and is perpendicular to the molecular plane. If the orbital is symmetric with respect to reflection through this plane, it is labeled with a subscript "1." Otherwise it is labeled with a subscript "2."
- Connect the states in the correlation diagram.

Molecular orbitals are labeled as  $n$  symmetry label, where  $n$  is the number you attain by counting--starting the lowest valence orbital, so the  $a_1$  orbital associated with the  $1s$  on the central atom doesn't count—towards higher-energy orbitals. So the  $3a_1$  orbital is the highest-energy orbital in the linear conformation. As one bends the molecule, the  $3a_1$  in the  $\theta = 0$  limit starts to resemble the  $\sigma_g 2s$  (which is the  $2a_1$  orbital) in the "bent" limit. Since we cannot connect the  $3a_1$  orbital with  $\theta = 0$  with the  $2a_1$  orbital with  $\theta = 90^\circ$  without violating the non-crossing rule, we have an avoided crossing.

# Angular "Correlation Diagram" for $\text{AH}_2$



### Part C. (2 points)

The correlation diagram you constructed in Part “B” is often called a “Walsh” diagram. The idea is that bending the molecule lowers the orbital energy of some orbitals and raises the energy of others. Usually, if the highest occupied molecular orbital is stabilized by bending, then the molecule will be bent to lower the energy of this orbital. (Lower energy orbitals are less diffuse, and thus less sensitive to minor changes in molecular conformation.) More generally, we have

**Walsh’s rule:** *If bending the molecule away from the linear conformation stabilizes the sum of orbital energies, then the molecule will be bent.*

**Based on your answer in part “B”, which of the following molecules will be bent?**

- |                    |                   |
|--------------------|-------------------|
| (a) $\text{LiH}_2$ | (c) $\text{BH}_2$ |
| (b) $\text{BeH}_2$ | (d) $\text{NH}_2$ |

$\text{LiH}_2$  and  $\text{BeH}_2$  have 5 and 6 electrons, respectively. The HOMO orbital of the linear molecules is the  $1b_2$  orbital, which is destabilized by bending. So these are linear molecules.  $\text{BH}_2$  and  $\text{NH}_2$  have 7 and 9 electrons, respectively. The HOMO orbitals of the linear molecules is either the  $2a_1$  or the  $1b_1$ . By bending the molecule, the  $2a_1$  orbital is stabilized, so it is favorable to bend these molecules.

**Which molecule do you expect to be more bent,  $\text{BH}_2$  or  $\text{NH}_2$ ?**

- |                   |                   |
|-------------------|-------------------|
| (a) $\text{BH}_2$ | (b) $\text{NH}_2$ |
|-------------------|-------------------|

$\text{BH}_2$  will have one electron in the  $2a_1$  orbital and  $\text{NH}_2$  will have two electrons in this orbital. Bending the molecule stabilizes this orbital and, since  $\text{NH}_2$  has more electrons in the  $2a_1$  orbital, this is more important for  $\text{NH}_2$ . Thus  $\text{NH}_2$ , with two electrons in an orbital that favors the bent structure, is more bent than  $\text{BH}_2$ , with only one electron in that orbital.

## Part D. (4 points)

In the long-wavelength and Condon approximations, which of the following transitions will be allowed.

- |  |   |
|--|---|
| (a) transitions from an $a_1$ orbital to an $a_1$ orbital. | (f) transitions from an $a_2$ orbital to a $b_1$ orbital. |
| (b) transitions from an $a_1$ orbital to an $a_2$ orbital. | (g) transitions from an $a_2$ orbital to a $b_2$ orbital. |
| (c) transitions from an $a_1$ orbital to a $b_1$ orbital.  | (h) transitions from a $b_1$ orbital to a $b_1$ orbital.  |
| (d) transitions from an $a_1$ orbital to a $b_2$ orbital.  | (i) transitions from a $b_1$ orbital to a $b_2$ orbital.  |
| (e) transitions from an $a_2$ orbital to an $a_2$ orbital. | (j) transitions from a $b_2$ orbital to a $b_2$ orbital.  |

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

Because we are using the Condon approximation and the long-wavelength approximation, we need only worry about (a) the shape of the electronic orbitals (nuclear motions/vibronic coupling can be neglected; Condon approximation) and (b) electric dipole allowed transitions (electric quadrupole and magnetic dipole transitions can be neglected; long-wavelength approximation).

There are two ways to work this problem. First, we can use the character table from group theory. In this case, multiply the entries in the character table to see what the symmetry of the “product” orbital is. Then, see if one of the Cartesian coordinates (i.e., the dipole in some direction) transforms in the same way as the product orbital.

For example:

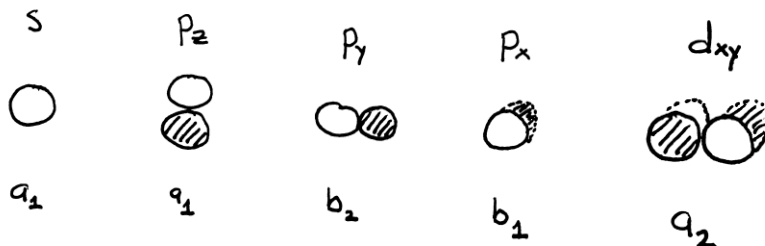
$$\begin{aligned}\psi_{b_1} \quad \psi_{b_2} &\rightarrow \begin{bmatrix} 1 & -1 & 1 & -1 \end{bmatrix} \begin{bmatrix} 1 & -1 & -1 & 1 \end{bmatrix} \\ &\rightarrow \begin{bmatrix} 1 \cdot 1 & -1 \cdot -1 & 1 \cdot -1 & -1 \cdot 1 \end{bmatrix} \\ &\rightarrow \begin{bmatrix} 1 & 1 & -1 & -1 \end{bmatrix} \\ &\rightarrow A_2\end{aligned}$$

no dipole component

$$\begin{aligned}\psi_{a_2} \quad \psi_{b_2} &\rightarrow \begin{bmatrix} 1 & 1 & -1 & -1 \end{bmatrix} \begin{bmatrix} 1 & -1 & -1 & 1 \end{bmatrix} \\ &\rightarrow \begin{bmatrix} 1 & -1 & 1 & -1 \end{bmatrix} \\ &\rightarrow B_1\end{aligned}$$

transforms the same way as the  $x$  Cartesian coordinate

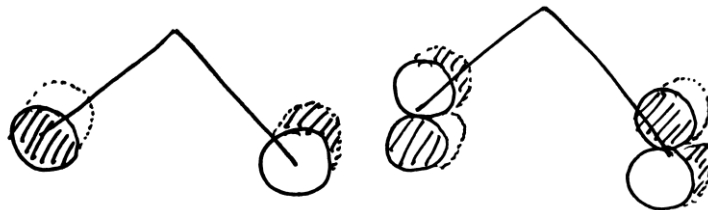
We can also do this problem using our standard “multiply” method. (The “multiply” method is really just symmetry without the group theory.) First, consider which orbitals on the “heavy atom” will transform with each symmetry, e.g.:



These symmetry labels assume that the molecule is in the plane of the paper and the  $z$  axis is the  $C_2$  axis.

Next, “multiply” these orbitals together in the standard way to find which are allowed/forbidden. Since any molecular orbital with these symmetry can mix with these atomic orbitals (and no molecular orbital with a different symmetry can mix with these atomic orbitals), if transitions between these orbitals is allowed, then that is sufficient to show that the transition is allowed. (The converse is not quite true, but it is usually so.)

- Clearly, because of the usual fact that  $s \rightarrow p$  is allowed, we have that  $a_1 \rightarrow a_1$ ,  $a_1 \rightarrow b_1$ , and  $a_1 \rightarrow b_2$  are dipole allowed.
- The “multiplication” method in the notes also shows that  $p_y \rightarrow d_{xy}$  and  $p_x \rightarrow d_{xy}$  are allowed ( $p_z \rightarrow d_{xy}$  is only electric quadrupole allowed, not electric dipole allowed). Thus  $b_2 \rightarrow a_2$  and  $b_1 \rightarrow a_2$  are allowed.
- $b_1 \rightarrow b_1$  and  $b_2 \rightarrow b_2$  are allowed because the  $d$  orbitals,  $3d_{xz}$  and  $3d_{yz}$  have  $b_1$  and  $b_2$  symmetry, respectively.
- Finally, we can show that  $a_2 \rightarrow a_2$  is allowed using an  $f$  orbital, but it is much more convenient to use the two  $a_2$  orbitals formed from the  $p_x$  and  $d_{xz}$  orbitals on the hydrogen atoms:





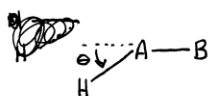
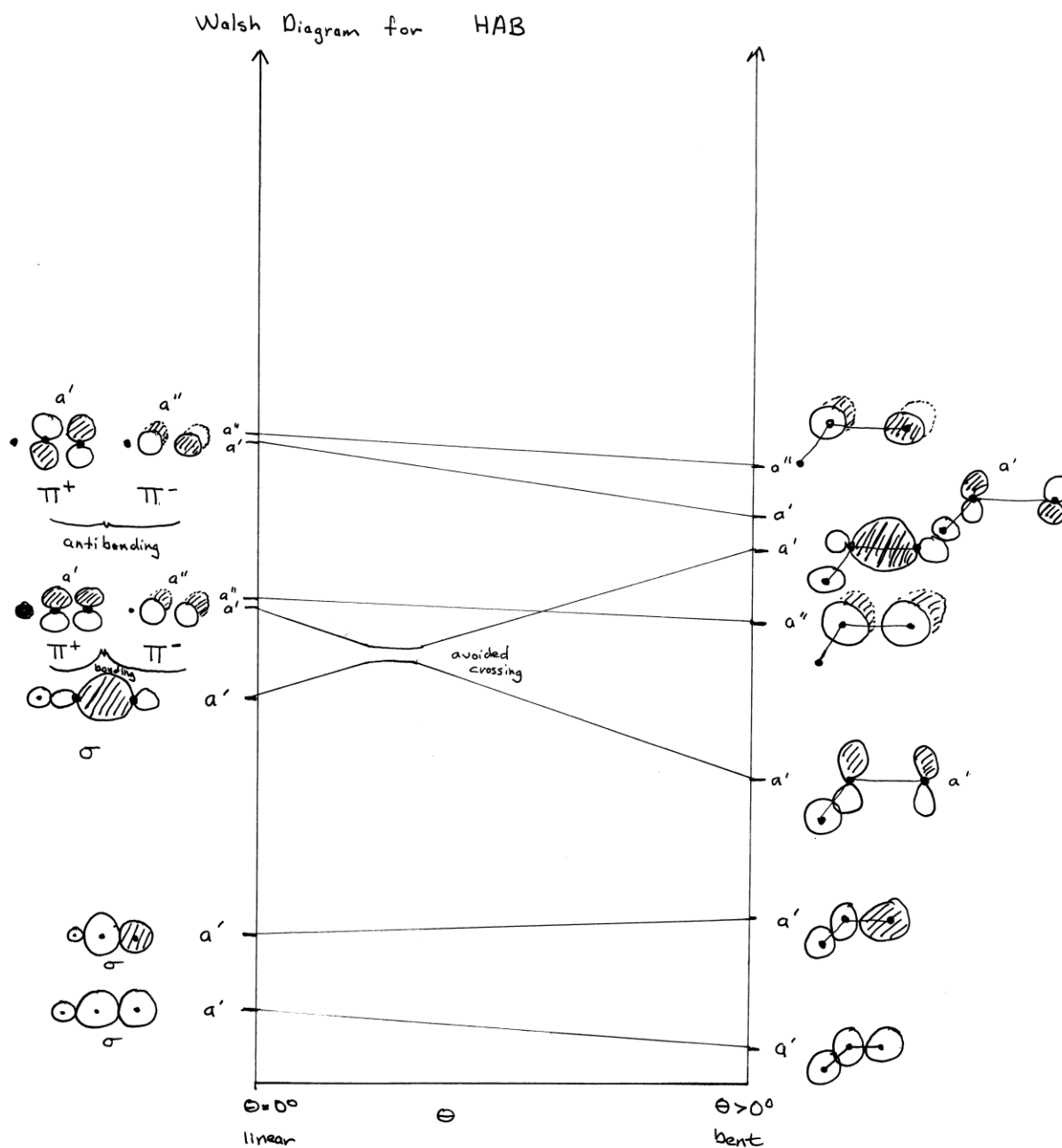
### Part E. (4 points)

Now we consider a HAB system, which has  $C_{\infty v}$  symmetry in the linear geometry and  $C_s$  symmetry when bent. The only symmetry in this system is reflection in the molecular plane.

- If the orbital is *symmetric* with respect to reflection in the molecular plane, it is labeled as a’.
- If the orbital is *antisymmetric* with respect to reflection in the molecular plane, it is labeled as a”.

A partial correlation diagram is reproduced below.

- **Label the symmetry of each state.**
- **Connect the “bent” and “linear” states.**



The molecule is in the plane of the paper!

only valence orbitals ( $2s+2p$  on A+B;  $1s$  on H) are included

The avoided crossing arises because as the molecule bends ( $\theta$  increases) the fourth  $a'$  orbital in the linear conformation starts to look more and more like the third  $a'$  orbital in the bent conformation. Similarly, the third  $a'$  orbital in the linear conformation begins to look more like the fourth  $a'$  orbital for the linear conformation. However, the non-crossing rule says we can't connect these states! So, instead, there is an "avoided" crossing—the states can't "go where they want to go" and so they try to do so, and then swerve.

## Part F. (2 points)

Using this correlation diagram, we can determine whether a molecule of the type HAB is bent or linear.

Is the first excited state of HCN linear or bent?

(a) linear

**(b) bent**

HCN has  $(1+4+5=10)$  valence electrons, so the ground state electron configuration is  $1a'^2 2a'^2 3a'^2 4a'^2 1a''^2$ . Thus, HCN is linear: the highest occupied orbital is nonbonding (there is no strong preference for the bent or linear geometry from this orbital) and the next two highest orbitals roughly “cancel each other out,” but tend towards linearity. The first excited state has the  $1a'^2 2a'^2 3a'^2 4a'^2 1a''^1 5a'^1$  geometry; the energy of the fifth lowest  $a'$  orbital ( $5a'$ ) is lowered by bending the molecule, so the first excited state of HCN is bent.

Is the first excited state of HBeLi linear or bent?

**(a) linear**

(b) bent

HBeLi has  $1+2+1 = 4$  valence electrons, so the electron configuration of the ground state is  $1a'^2 2a'^2$ . The molecule is linear in the ground state since the second-lowest orbital of  $a'$  symmetry (denoted  $2a'$ ) is destabilized by angle bending. The excited-state electron configuration is  $1a'^2 2a' 3a'$  and the  $3a'$  orbital is also destabilized by bending the molecule, so HBeLi is linear in its first excited state.

## Part 2. Multiple Choice/Short Answer

Except when noted otherwise, you should use the Born-Oppenheimer approximation and atomic units throughout Parts 2 and 3 of this exam.

1. Write the Wave Function for the Hydrogen molecule,  $H_2$ , that arises in Valence-Bond Theory with a correction due to ionic terms.

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

2. Which of the following diatomic molecules *do not* have a singlet ground state?

- |             |                |                 |
|-------------|----------------|-----------------|
| (a) $B_2$   | (d) $N_2$      | (g) $F_2$       |
| (b) $C_2^+$ | (e) $O_2$      | (h) $Ne_2^{+2}$ |
| (c) $C_2$   | (f) $F_2^{+2}$ |                 |

3. You are given a heteronuclear diatomic molecule,  $AB$ . Which of the following properties are most strongly associated with the presence of a strong covalent bond (with minimal ionic character)?

- (a) Strong orbital overlap between the bonding orbitals.
- (b) Weak orbital overlap between the bonding orbitals.
- (c) A large difference in orbital energies of the bonding orbitals.
- (d) A small difference in the orbital energies of the bonding orbitals.
- (e) Both of the bonding orbitals have orbital energies that are very small (extremely negative).
- (f) Both of the bonding orbitals have orbital energies that are rather large (barely negative).

4. You are given two molecular orbitals,  $\psi_1(\mathbf{r})$  and  $\psi_2(\mathbf{r})$ , of a heteronuclear diatomic molecule. The chemical bond (which defines  $C_\infty$  molecular symmetry axis) is directly along the  $z$  axis. The orbital angular momenta of each orbital about the symmetry axis is measured, giving (in atomic units)

$$\langle \psi_1 | \hat{L}_z | \psi_1 \rangle = -2 \qquad \langle \psi_2 | \hat{L}_z | \psi_2 \rangle = 1$$

- (a)  $\psi_1(\mathbf{r})$  is a  $\sigma^+$  orbital and  $\psi_2(\mathbf{r})$  is a  $\pi^-$  orbital.
- (b)  $\psi_1(\mathbf{r})$  is a  $\pi^-$  orbital and  $\psi_2(\mathbf{r})$  is a  $\sigma^+$  orbital.
- (c)  $\psi_1(\mathbf{r})$  is a  $\delta^+$  orbital and  $\psi_2(\mathbf{r})$  is a  $\pi^+$  orbital.
- (d)  $\psi_1(\mathbf{r})$  is a  $\pi^+$  orbital and  $\psi_2(\mathbf{r})$  is a  $\delta^+$  orbital.
- (e)  $\psi_1(\mathbf{r})$  is a  $\delta^-$  orbital and  $\psi_2(\mathbf{r})$  is a  $\pi^-$  orbital.
- (f)  $\psi_1(\mathbf{r})$  is a  $\pi^-$  orbital and  $\psi_2(\mathbf{r})$  is a  $\delta^-$  orbital.
- (g)  $\psi_1(\mathbf{r})$  is a  $\delta^-$  orbital and  $\psi_2(\mathbf{r})$  is a  $\pi^+$  orbital.**
- (h)  $\psi_1(\mathbf{r})$  is a  $\pi^+$  orbital and  $\psi_2(\mathbf{r})$  is a  $\delta^-$  orbital.
- (i)  $\psi_1(\mathbf{r})$  is a  $\phi^+$  orbital and  $\psi_2(\mathbf{r})$  is a  $\pi^-$  orbital.
- (j)  $\psi_1(\mathbf{r})$  is a  $\pi^-$  orbital and  $\psi_2(\mathbf{r})$  is a  $\phi^+$  orbital.

5. A reasonable approximation to the bond length of  $H_2^+$  could be obtained by assuming that the wave function was a linear combination of  $1s$  orbitals, provided the  $1s$  orbitals

(a) were mixed with  $2p$  orbitals directed along the chemical bond.

**(b) were scaled using an effective nuclear charge.**

(c) neither approximation is sufficient alone, but making both approximations together suffices.

(d) even with both approximations together, the predicted bond length is still in error by more than .02 Bohr.

6. A reasonable approximation to the bond dissociation energy,  $D_e$ , of  $H_2^+$  could be obtained by assuming that the wave function was a linear combination of  $1s$  orbitals, provided the  $1s$  orbitals

(a) were mixed with  $2p$  orbitals directed along the chemical bond.

(b) were scaled using an effective nuclear charge.

**(c) neither approximation is sufficient alone, but making both approximations together suffices.**

(d) even with both approximations together, the predicted bond dissociation energy is still in error by more than .01 Hartree.

7-11. For each of the following statements, indicate whether the statement is more strongly associated with molecular-orbital theory (MO) and/or valence-bond theory (VB).

\_\_VB\_\_ Even in its simplest form, this theory tends to describe molecular dissociation properly.

\_\_VB,MO\_\_ By adding suitable corrections, this theory can approach the exact solution to the Schrödinger equation.

\_\_VB,MO\_\_ In its simplest form, this theory overestimates the energy of the chemical system.

\_\_MO\_\_ Approximate implementation of this theory is easier computationally.

\_\_MO\_\_ This theory is associated with linear combinations of atomic orbitals.

\_\_MO\_\_ In this theory, molecular excitation can be described by promotion of an electron from an occupied to an unoccupied orbital.

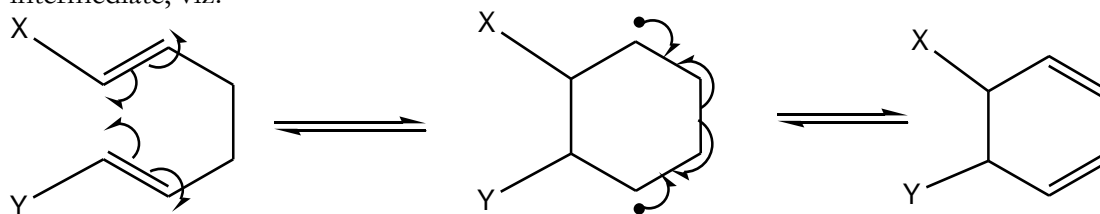
\_\_VB\_\_ Hybridized atomic orbitals are commonly used in this theory.

\_\_MO\_\_ Even in its simplest form, this theory can describe the tendency of bonds in heteronuclear diatomics to “polarize” towards the most electronegative atoms.

\_\_VB\_\_ The Heitler-London wave function is associated with this theory.

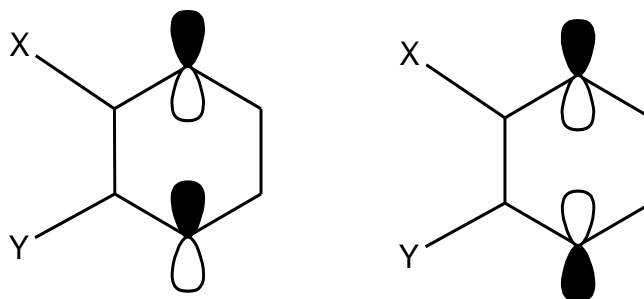
\_\_VB\_\_ This theory is associated with the perfect-pairing wave function.

12-13. One of the proposed mechanisms for the Cope rearrangement goes through a diyl intermediate, viz.



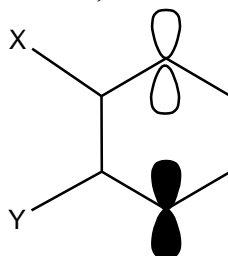
diyl intermediate

The highest-occupied molecular orbital and lowest-unoccupied molecular orbitals, respectively, in the diyl intermediate are sketched below<sup>1</sup>



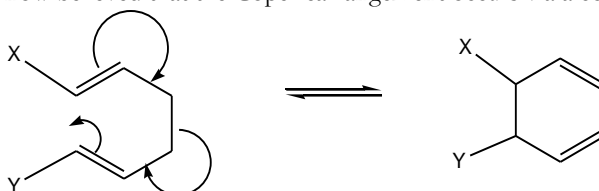
Could the excitation from the HOMO orbital (on the left) to the LUMO orbital (on the right) be observed spectroscopically?<sup>2</sup> Justify your answer.

This excitation is allowed, and should be spectroscopically observable. Multiplying the HOMO times the LUMO orbital of the diyl intermediate, we obtain a state like



<sup>1</sup> Here, the p-orbitals are perpendicular to the ring system. (Thus, if the ring system is in the plane of the paper, the p-orbitals are perpendicular to the plane of the paper.)

<sup>2</sup> The diyl intermediate, if it exists at all, will be very short-lived. Thus, there will at most a very small amount of the diyl intermediate present in solution at any one point in time. It is worth noting that, for most choices of the substituents X and Y, it is now believed that the Cope rearrangement occurs via a concerted process,



14. Write down the time-dependent Schrödinger Equation.

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

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

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

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

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

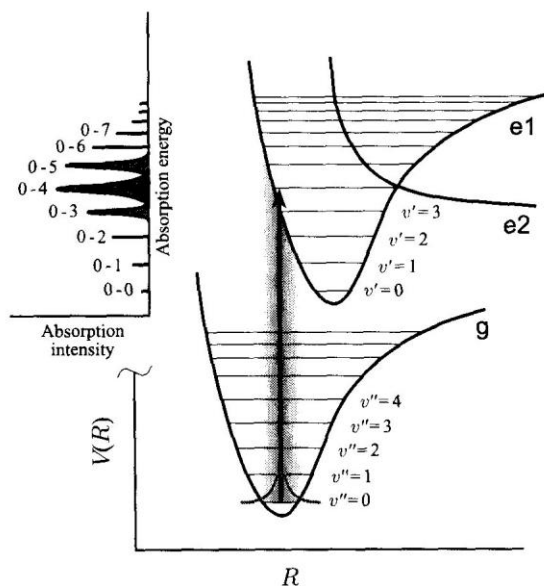
where  $\Phi_k(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is an eigenfunction of the time-independent Schrödinger equation,

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

What is  $\chi(t)$ ?

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

- 17-18. Sketch the potential energy surfaces, along with the associated electronic spectrum, for predissociation.



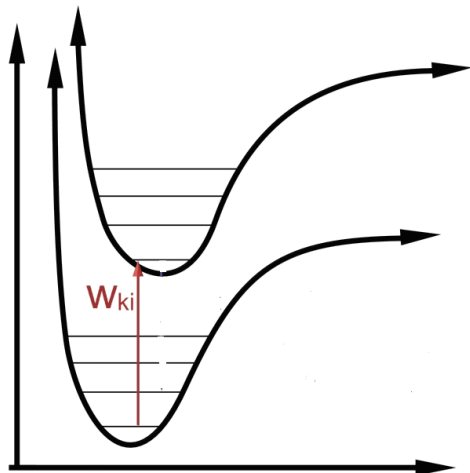
**Figure 11.11.** Potential energy surfaces leading to predissociation.

You should have a figure something like this one, though you'll probably draw the spectra below (rather than beside) the potential energy surface).

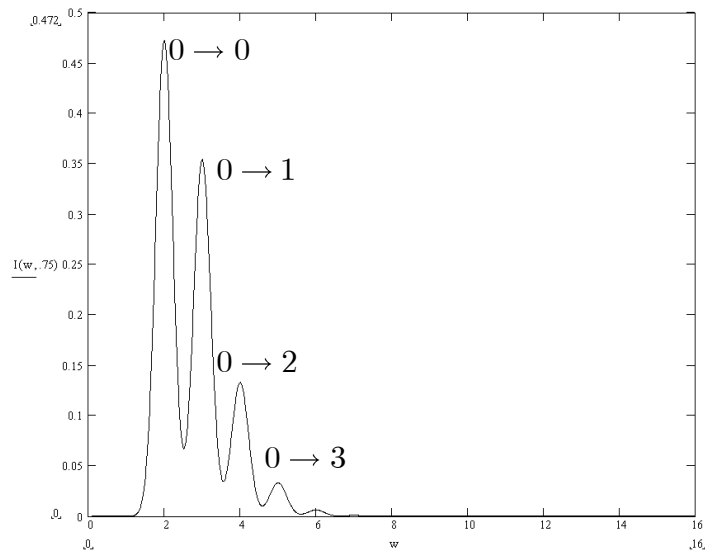
19-20. Consider the lowest-energy dipole-allowed excitation of the  $C_2^-$  molecule.

- Sketch the potential energy surfaces corresponding to the ground and first dipole-allowed excited-state potential energy surfaces of this system.
- Assuming the molecule is initial in the ground vibrational state, sketch the spectrum, labeling your axes and clearly denoting the final vibrational states corresponding to each spectral line you draw.

The excitation in question would be the excitation from the  $\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \pi_u^{+2} \pi_u^{-2} \sigma_g^1$  electron configuration to the  $\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \pi_u^{+2} \pi_u^{-1} \sigma_g^2$  or the  $\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \pi_u^{+1} \pi_u^{-2} \sigma_g^2$  electron configuration. (The  $\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \pi_u^{+2} \pi_u^{-2} \sigma_g^1$  to  $\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \pi_u^{+2} \pi_u^{-2} \pi_g^{\pm 1}$  excitation is forbidden.) Consequently, we are promoting electrons from a bonding orbital to another bonding orbital, and we do not expect the bond length to change very much, though it might lengthen slightly since the  $\sigma_g$  orbital is a bit higher in energy. This gives potential energy surfaces (vs. bond length) similar to:



and a spectrum (absorption intensity vs. frequency) similar to:



Here we have indicated the initial vibrational state (ground vibrational state,  $\nu = 0$ ) and final vibrational state  $\nu = 0, 1, 2, 3, \dots$



21. The momentum of a photon can be expressed in terms of the period of the light,  $T$ .

What is this relationship?

Start with:

$$p = \hbar k = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \frac{h}{\lambda}$$

then use

$$\lambda = cT$$

to obtain

$$p = \frac{h}{cT}$$

22. The energy of a photon can be expressed in terms of the period of the light,  $T$ . What is this relationship?

Start with:

$$E = h\nu$$

then use

$$\nu = \frac{1}{T}$$

to obtain

$$E = \frac{h}{T}.$$

23. We expect magnetic dipole-allowed (but electric dipole-forbidden) transitions to be most intense when

(a) the difference in energy between the ground and excited states is large.

(b) the difference in energy between the ground and excited states is small.

24. Which of the following orbitals is associated with a  $\phi$  bond? Here the atoms in the diatomic molecule lie along the  $z$  axis.

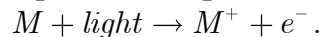
(a)  $\psi_{4f_z^3} \mathbf{r} + \psi_{4f_z^3} \mathbf{r}$

(b)  $\psi_{4f_x^3} \mathbf{r} + \psi_{4f_x^3} \mathbf{r}$

(c)  $\psi_{4f_{yz}} \mathbf{r} + \psi_{4f_{yz}} \mathbf{r}$

(d)  $\psi_{4f_{x^2-y^2}} \mathbf{r} + \psi_{4f_{x^2-y^2}} \mathbf{r}$

25. In photoelectron spectroscopy, we perform the process



The kinetic energy of the ionized electron can then be measured to obtain information about the energy levels of the cation. Resonance-enhanced multiphoton ionization (REMPI) spectroscopy is a popular technique for measure photoelectron spectra of molecules with high resolution. The most distinctive feature of this technique is that the molecule is ionized by light with frequency

$$\omega_{\text{light}} < \frac{I}{\hbar},$$

where  $I$  denotes the ionization potential of the molecule in question. REMPI spectroscopy works best when

**(a) the incident light has high intensity.**

(b) the incident light has low intensity.

## Part 3. Closed-Book Derivation

### 1. Molecular Orbital Theory for the Hydrogen Molecule

- (a) We wrote a simple molecular-orbital wave function for the Hydrogen molecule in terms of linear combinations of  $1s$  orbitals. What was this wave function? (2 points)

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

- (b) We said that simple molecular-orbital theory was not very good at modeling dissociation. Using your wave function from part (a), explain why. (5 points)

Expand this wave function as

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

Note that as the bond length approaches infinity, this wave function becomes associated with

- two ionic terms (on the first line of the preceding equation) which correspond to dissociation into a hydride anion and a proton
- two covalent terms (on the second line of the preceding equation) which correspond to dissociation into two neutral hydrogen atoms

However, when the hydrogen molecule dissociates,  $H_2 \rightarrow 2H$  (and not  $H_2 \rightarrow H^- + H^+$ ). The terms of the first line are thus spurious, and by averaging the energy of the hydride anion in with the energy of the appropriate dissociation state (two hydrogen atoms), one finds much too high an energy. (A full discussion can be found in the notes, but the preceding is more than adequate for these purposes.)

## 2. Franck-Condon Factors and Fermi's Golden Rule

- (a) Write Fermi's Golden Rule for Dipole Transitions. (3 points)

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

- (b) Starting from the expression in part (a), derive the expression for the transition rate,  $W_{\mu f, \nu i}$ , for a molecule that is initially in the  $\nu^{th}$  rovibrational state of the  $i^{th}$  electronic excited state and is, after exposure to radiation, in the  $\mu^{th}$  rovibrational state of the  $f^{th}$  electronic excited state. Your discussion should be detailed and neat, and needs to contain the following key pieces of information to obtain full credit.

- (i) identify which term(s) are associated with rovibrational spectroscopy (without concomitant electronic transitions, so  $i = f$ ).
- (ii) identify which term(s) are neglected because they are associated with vibronic coupling.
- (iii) clearly identify the Condon approximation and discuss why it is usually valid.
- (iv) write your final answer in terms of the Franck-Condon factor

$$F_{\mu f, \nu i} = \left| \langle \chi_{\mu f} | \chi_{\nu i} \rangle \right|^2$$

where  $\chi_{\mu f} \mathbf{R}_1, \dots, \mathbf{R}_p$  is the nuclear (i.e. rovibrational) wave function for the  $\mu^{th}$  rovibrational state of the  $f^{th}$  electronic excited state in the system.

- (v) Explain why

$$\sum_{\mu=0}^{\infty} F_{\mu f, \nu i} = 1.$$

Each of the preceding portions of the problem should be *clearly* marked with the assigned number. Parts (i)-(v) are worth 3 points each and the overall derivation is worth 5 points. [For example, if you cannot complete the derivation but you can complete, say, part (iv), then you could earn 3 points by writing down the final expression and defining the Franck-Condon factor.]

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

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

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  $(1, 2, \dots, N)$  or the nuclear coordinates  $(1, 2, \dots, P)$  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.*

- (i) The last statement (in italics) is not true for ro-vibrational spectroscopy. Instead, for rovibrational spectra, we have that  $f = i$  and so  $\langle \xi_i | \xi_i \rangle_{1\dots N} = 1$ . Similarly, we have that

$$\begin{aligned}
\left\langle \chi_{\mu f} \xi_f \left| \sum_{k=1}^N -ex_k \right| \chi_{\nu i} \xi_i \right\rangle_{1\dots N, 1\dots P} &= \left\langle \chi_{\mu i} \xi_i \left| \sum_{k=1}^N -ex_k \right| \chi_{\nu i} \xi_i \right\rangle_{1\dots N, 1\dots P} \\
&= 0 \quad \text{unless } \mu = \nu
\end{aligned}$$

So if we are doing a rovibrational transition without a concomitant electronic transition, then  $i = f$  but  $\mu \neq \nu$ . In this case, then,

$$\langle \Phi_{\mu f} | \hat{\mu}_x | \Phi_{\nu i} \rangle_{1\dots N, 1\dots P} = \left\langle \chi_{\mu i} \left| \sum_{\alpha=1}^P Z_{\alpha} eX_i \right| \chi_{\nu i} \right\rangle_{1\dots P}$$

and so Fermi's Golden rule reduces to

$$\begin{aligned}
W_{\mu i, \nu i} &= \frac{2\pi V^2}{\hbar} \frac{g \hbar \omega_{\mu i, \nu i} + g - \hbar \omega_{\mu i, \nu i}}{\hbar} \left| \langle \Phi_{\mu i} | \hat{\mu} | \Phi_{\nu i} \rangle \right|^2 \\
&= \frac{2\pi V^2}{\hbar} \frac{g \hbar \omega_{\mu i, \nu i} + g - \hbar \omega_{\mu i, \nu i}}{\hbar} \left| \left\langle \chi_{\mu i} \left| \sum_{\alpha=1}^P Z_{\alpha} eX_i \right| \chi_{\nu i} \right\rangle_{1\dots P} \right|^2
\end{aligned}$$

This term is associated with rovibrational spectroscopy. (That said, if you just said that the second term in Eq. (1) was the term of interest, you would get full credit.)

Returning to our derivation, we need only worry about the first term in Eq. (1). Now, let's define the transition dipole for a specific nuclear configuration using,

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

We have, then, that

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

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

$$\begin{aligned} \langle \Phi_{\mu_f} | \hat{\mu}_x | \Phi_{\nu_i} \rangle_{1\dots N} &= \left\langle \chi_{\mu_f} \left| \mu_{f_i} \mathbf{R}_1, \dots, \mathbf{R}_P \right| \chi_{\nu_i} \right\rangle_{1\dots P} \\ &= \left\langle \chi_{\mu_f} \left| \mu_{f_i} \mathbf{R}_1^i, \dots, \mathbf{R}_P^i + \sum_{\alpha=1}^P \mathbf{R}_\alpha - \mathbf{R}_\alpha^i \cdot \nabla_\alpha \mu_{f_i} \mathbf{R}_1^i, \dots, \mathbf{R}_P^i + \dots \right| \chi_{\nu_i} \right\rangle_{1\dots P} \quad (2) \\ &= \left. \begin{aligned} &\mu_{f_i} \mathbf{R}_1^i, \dots, \mathbf{R}_P^i \left\langle \chi_{\mu_f} \left| \chi_{\nu_i} \right\rangle \\ &+ \sum_{\alpha=1}^P \left\langle \chi_{\mu_f} \left| \mathbf{R}_\alpha - \mathbf{R}_\alpha^i \cdot \nabla_\alpha \mu_{f_i} \mathbf{R}_1^i, \dots, \mathbf{R}_P^i \right| \chi_{\nu_i} \right\rangle_{1\dots P} \\ &+ \dots \end{aligned} \right\} \begin{array}{l} \text{Condon approx.} \\ \text{vibronic coupling} \end{array} \end{aligned}$$

- (iii) The Condon approximation is associated with neglecting terms that depend on the way  $\mu_{f_i} \mathbf{R}_1, \dots, \mathbf{R}_P$  changes with respect to the nuclear positions. (These terms are represented by the second and higher order terms in the last equality in Eq. (2)) 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.

- (ii) 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.

Again returning to our derivation and working within the Condon approximation, we have

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

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

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

- (iv) The term

$$F_{\mu f, \nu i} \equiv \left| \langle \chi_{\mu f} | \chi_{\nu i} \rangle \right|^2$$

is called the Franck-Condon factor. In terms of the Franck-Condon Factor, we have

$$\begin{aligned} W_{\mu f, \nu i} &= \frac{2\pi V^2 g \hbar \omega_{\mu f, \nu i} + g - \hbar \omega_{\mu f, \nu i} \left| \langle \Phi_{\mu f} | \hat{\mu}_x | \Phi_{\nu i} \rangle \right|^2}{\hbar} \\ &= \frac{2\pi V^2 g \hbar \omega_{\mu f, \nu i} + g - \hbar \omega_{\mu f, \nu i} \left| \mu_{f_i} \mathbf{R}_1^i, \dots, \mathbf{R}_P^i \right|^2 F_{\mu f, \nu i}}{\hbar} \end{aligned} \quad (3)$$

This completes the main derivation. Part (v) follows:

- (v) To do part (v), we need to recall that  $\chi_{\mu f} \mathbf{R}_1, \dots, \mathbf{R}_P$  is a complete set of eigenstates.

Therefore, any function can be expanded in terms of this set of states. Specifically, we can write

$$\chi_{\nu i} \mathbf{R}_1, \dots, \mathbf{R}_P = \sum_{\mu=0}^{\infty} c_{\mu} \chi_{\mu f} \mathbf{R}_1, \dots, \mathbf{R}_P \quad (4)$$

Recalling that the expansion coefficients are given by the formula<sup>3</sup>

$$c_{\mu} = \langle \chi_{\mu f} | \chi_{\nu i} \rangle$$

and so

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<sup>3</sup> This formula can be derived by multiplying both sides of Eq. (4) by  $\chi_{\mu f} \mathbf{R}_1, \dots, \mathbf{R}_P$  \*

$\chi_{\nu i} \mathbf{R}_1, \dots, \mathbf{R}_P = \sum_{\mu=0}^{\infty} c_{\mu} \chi_{\mu f} \mathbf{R}_1, \dots, \mathbf{R}_P$  and integrating.

$$\sum_{\mu=0}^{\infty} F_{\mu f, \nu i} = \sum_{\mu=0}^{\infty} |c_{\mu}|^2 = 1.$$

An alternative proof uses the relation

$$\chi_{\nu i} \mathbf{R}_1, \dots, \mathbf{R}_P = \sum_{\mu=0}^{\infty} \langle \chi_{\mu f} | \chi_{\nu i} \rangle \chi_{\mu f} \mathbf{R}_1, \dots, \mathbf{R}_P$$

and notes that

$$\begin{aligned} 1 &= \langle \chi_{\nu i} | \chi_{\nu i} \rangle \\ &= \left\langle \chi_{\nu i} \left| \sum_{\mu=0}^{\infty} \langle \chi_{\mu f} | \chi_{\nu i} \rangle \chi_{\mu f} \mathbf{R}_1, \dots, \mathbf{R}_P \right. \right\rangle \\ &= \sum_{\mu=0}^{\infty} \langle \chi_{\mu f} | \chi_{\nu i} \rangle \langle \chi_{\nu i} | \chi_{\mu f} \rangle \\ &= \sum_{\mu=0}^{\infty} |\langle \chi_{\mu f} | \chi_{\nu i} \rangle|^2 \\ &= \sum_{\mu=0}^{\infty} F_{\mu f, \nu i} \end{aligned}$$