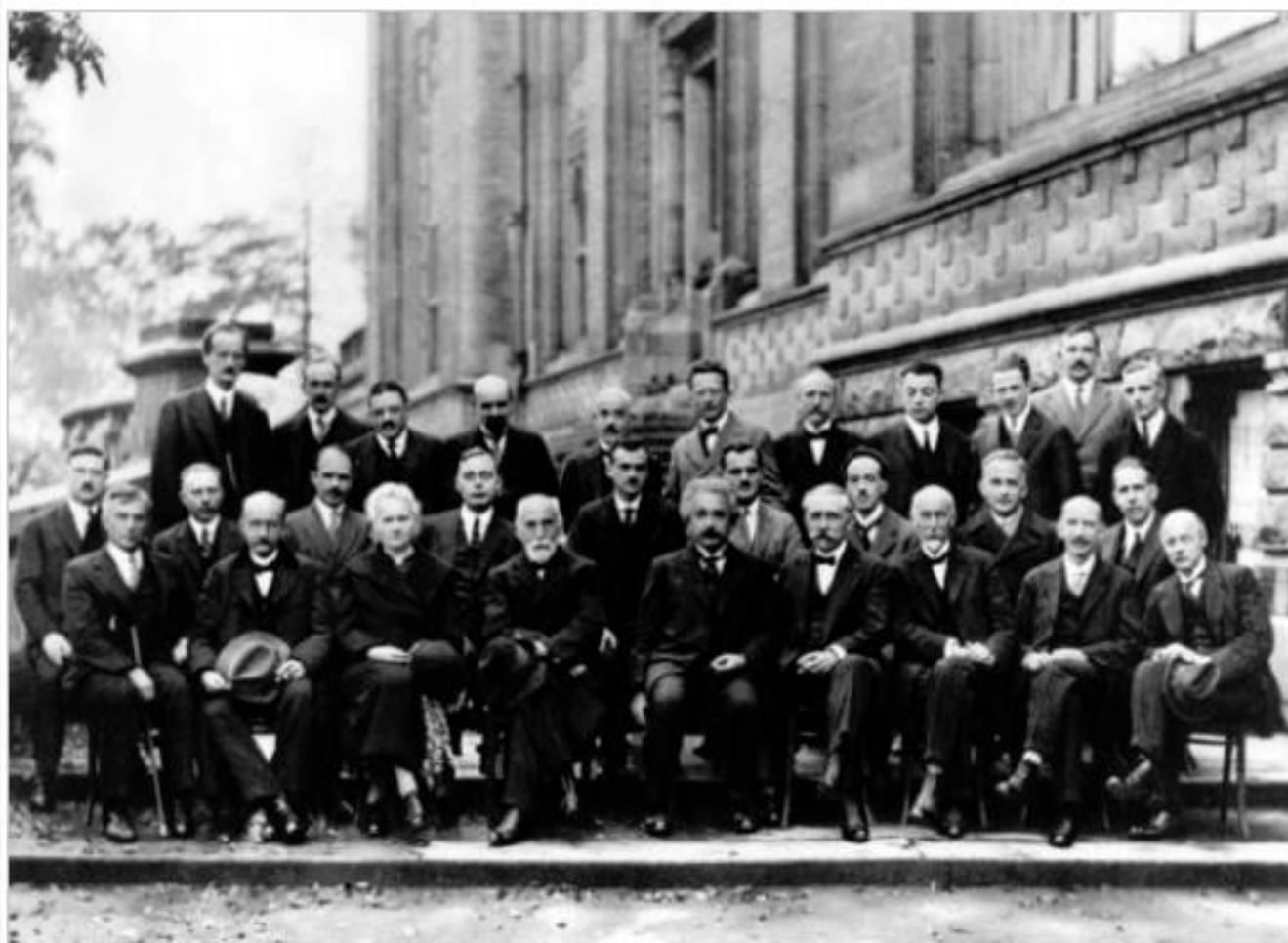So some of you are wondering why I was in Belgium last week. I was invited to the Solvay conference on Chemical Reactivity. While the group that was assembled is perhaps a little less prestigious than the group at the 1927 conference (I was invited, after all), this is still the sort of invitation that you don't turn down....

A. Piccard, E. Henriot, P. Ehrenfest, Ed. Herzen, Th. De Donder, E. Schrödinger, E. Verschaffelt, W. Pauli, W. Heisenberg, R.H. Fowler, L. Brillouin,
P. Debye, M. Knudsen, W.L. Bragg, H.A. Kramers, P.A.M. Dirac, A.H. Compton, L. de Broglie, M. Born, N. Bohr,
I. Langmuir, M. Planck, Mme. Curie, H.A. Lorentz, A. Einstein, P. Langevin, Ch. E. Guye, C.T.R. Wilson, O.W. Richardson

Fifth conference participants, 1927. Institut International de Physique Solvay.

17 of these people eventually won a Nobel Prize. That's atypical even of this conference, but the only other conference I have a picture of was pretty impressive too.

Photograph of the first conference in 1911.

Seated (L-R): W. Nernst, M. Brillouin, E. Solvay, H. Lorentz, E. Warburg, J. Perrin, W. Wien, M. Curie, and H. Poincaré.
Standing (L-R): R. Goldschmidt, M. Planck, H. Rubens, A. Sommerfeld, F. Lindemann, M. de Broglie, M. Knudsen, F. Hasenohrl, G. Hostelet, E. Hertzen, J.H. Jeans, E. Rutherford, H.K. Onnes, A. Einstein, and P. Langevin.

Final Examination

Chemistry 3BB3

Winter, 2006

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

Part 1. Multiple Choice/Short Answer (2 pts. each)

1. Write the electronic Hamiltonian for the Lithium Hydride <u>molecule</u> (LiH) in SI units, <u>showing the dependence on $\hbar$, e, m_e, etc.</u>. Be sure to include the appropriate values for the atomic numbers of the nuclei and the number of electrons. (I don't want Z_α and N hanging around in your equations; what are the values for Z_α and N for LiH?)

2. **The atomic unit of length is the**
    (a) Bohr.
    (b) Schrödinger.
    (c) Slater.
    (d) Oppenheimer.
    (e) Hartree
    (f) None of the above.

3. **Let $\Psi\left(r_1,\sigma_1;r_2,\sigma_2;\ldots;r_N,\sigma_N\right)$ be antisymmetric with respect to exchange of any two electronic coordinates. Show that the probability of two electrons with the same spin being at the same location is zero.**

4. **Suppose you are given the following information about the <u>probability of observing an electron</u> in the _Helium cation_ (with atomic number equal to two).**
    - very close to the nucleus, the probability of observing an electron is proportional to r^2.
    - very far from the nucleus, the probability of observing an electron decays as e^{-r}.

    The electron in He$^+$ is in what type of orbital.

5-8. You perform an experiment that measures the emission due to the 2p state in the Hydrogen atom.

5. What is the term symbol for the initial state of the system (the 2p state that fluoresces?)

6. What is the term symbol for the final state of the system (the lower-energy state that the system ends up in)?

7. What is the frequency of the fluorescence in SI units. (That is, show the dependence on $\hbar$, e, m_e, etc..

8. Fluorescence spectra are often plotted as intensity versus wave numbers. If you did this, this spectral line would correspond to an peak at how many wave numbers. (Your expression will include a dependence on fundamental constants like h, c, π .)

9-11. Hund's rules get the ground state term symbol for the Cerium atom (with a closed subshells $4f^1 5d^1$ configuration) incorrect. The true term symbol is $^1G_4$.

9. What is the term symbol predicted by Hund's rules?

10-12. Let $\Psi^{Ce}_{^1G_4} \tau$ is the ground state wave function for Cerium. Fill in the eigenvalues (where applicable) for the following operators. When more than one eigenvalue is possible, indicate *all* the possible values. Do not use atomic units.

$$\hat{L}^2 \Psi^{Ce}_{^1G_4} \tau = \qquad\qquad \Psi^{Ce}_{^1G_4} \tau$$

$$\hat{L}_z \Psi^{Ce}_{^1G_4} \tau = \qquad\qquad \Psi^{Ce}_{^1G_4} \tau$$

$$\hat{S}^2 \Psi^{Ce}_{^1G_4} \tau = \qquad\qquad \Psi^{Ce}_{^1G_4} \tau$$

$$\hat{S}_z \Psi^{Ce}_{^1G_4} \tau = \qquad\qquad \Psi^{Ce}_{^1G_4} \tau$$

$$\hat{J}^2 \Psi^{Ce}_{^1G_4} \tau = \qquad\qquad \Psi^{Ce}_{^1G_4} \tau$$

$$\hat{J}_z \Psi^{Ce}_{^1G_4} \tau = \qquad\qquad \Psi^{Ce}_{^1G_4} \tau$$

13-14. You perform a calculation for the Lithium atom by forming a Slater determinant of orbitals, $\left| \psi^{\alpha}_{1s} \alpha \quad \psi^{\beta}_{1s} \beta \quad \psi^{\alpha}_{2s} \alpha \right|$. You then choose the orbitals so that the energy,

$$\frac{\left\langle \left| \psi^{\alpha}_{1s} \alpha \quad \psi^{\beta}_{1s} \beta \quad \psi^{\alpha}_{2s} \alpha \right| \left| \hat{H} \right| \left| \psi^{\alpha}_{1s} \alpha \quad \psi^{\beta}_{1s} \beta \quad \psi^{\alpha}_{2s} \alpha \right| \right\rangle}{\left\langle \left| \psi^{\alpha}_{1s} \alpha \quad \psi^{\beta}_{1s} \beta \quad \psi^{\alpha}_{2s} \alpha \right| \left| \psi^{\alpha}_{1s} \alpha \quad \psi^{\beta}_{1s} \beta \quad \psi^{\alpha}_{2s} \alpha \right| \right\rangle}$$

is as small as possible.

13. **This computational method is called**
   (a) the Hartree method.
   (b) the Fermi-Amaldi method.
   (c) the restricted Hartree-Fock method
   (d) the unrestricted Hartree-Fock method
   (e) the Kohn-Sham DFT method
   (f) configuration interaction.

14. **The energy obtained from this calculation is** _____ **the true ground state energy.**
   (a) greater than
   (b) equal to
   (c) less than

15. **Suppose you are given an approximate valence bond wave function for a molecule and you want to improve its accuracy. You would**
    (a) add contributions from additional resonance structures
    (b) add contributions from the wave functions of electronic excited states.

16. **You want to form a strong covalent bond between two atoms. In order to do this, the atomic orbitals should _____. (List at least two properties of the atomic orbitals that are associated with the presence of a strong single bond between them.)**

17. **The $\psi^{left}_{y\ 5z^2-r^2}\ \boldsymbol{r}\ +\ \psi^{right}_{y\ 5z^2-r^2}\ \boldsymbol{r}$ molecular orbital (formed from two f orbitals) is a _____ molecular orbital. [Circle the appropriate choices in the form below.]**
$$\left[\sigma \text{ or } \pi \text{ or } \delta \text{ or } \phi\right]^{[+ \text{ or } -]}_{[u \text{ or } g]}$$

18. **Write down Fermi's Golden rule for dipole transitions. When you do this, write out the expression for the transition dipole for an atom. (That is, do not use $\hat{\mu}_x$ to represent the transition dipole; tell me what $\hat{\mu}_x$ means.)**

19. **For a molecule in the kth excited state of a system, the spatial part of the wave function solves $\hat{H}\psi_k = E_k\psi_k$. Complete the following equation by filling in the "time dependence" of the wave function.**

$$\Psi\ \boldsymbol{r}_1,...,\boldsymbol{r}_N;t\ =\ \psi_k\ \boldsymbol{r}_1,...,\boldsymbol{r}_k\ \times\left[\right]$$

20-21. For each of the following statements, indicate whether the result is associated with the weak-field approximation (W), long-time approximation (T), long-wavelength approximation (L), or the Condon approximation (C). (Select all that apply).

_____ "Magnetic dipole" allowed transitions are much weaker than "electric dipole" allowed transitions.

_____ In the absence of broadening, the absorption spectrum of a molecule is a collection of delta-function peaks.

_____ Multi-photon processes like frequency doubling (where two photons are absorbed by the system and one photon, with twice as much energy, is emitted) are negligible.

_____ Because the atomic nuclei do not move very much during the process of an electronic excitation, the way the transition dipole varies as the positions of the atoms changes can be neglected.

22-23. In molecular orbital theory, we often talk about the **HOMO** (highest occupied molecular orbital) and the **LUMO** (lowest unoccupied molecular orbital). Are the following transitions allowed or forbidden? **[Show your work; you will get partial credit if you figure out what the HOMO and LUMO are, even if you do not predict "allowed" or "forbidden" correctly.]**

22. The transition from the **HOMO** to the **LUMO** in the Fluorine dimer, F_2, is

(a) allowed   (b) forbidden

23. Suppose we take the CO molecule and compress it so much that the bond length tends to zero. (That is, we compress the carbon monoxide molecule so much that it begins to look like it is in the united atom limit.) The transition from the **HOMO** to the **LUMO** in the Carbon Monoxide molecule in the united atom limit is

(a) allowed   (b) forbidden

24-25. High resolution infrared spectra are often made using matrix isolation. In Matrix isolation, one makes a dilute solution of the analyte and then freezes the solution. Typically, the solvent interacts only very weakly with the solute that is being studied: the most common solvents are Argon [Argon matrix isolation spectroscopy] and Neon [Neon matrix isolation spectroscopy].

Suppose we take a dilute solution of Calcium Hydride (CaH$_2$) in Neon, and then freeze the solution. (Due to freezing point depression, the resulting solid will have a temperature less than the freezing point of Neon, which is 27 K.) Now we take a spectra of CaH$_2$ in the Neon matrix. There are usually a few different spectral lines, corresponding to different crystal environments for the analyte. However, we can say something about the shapes of the lines that occur, namely that:

24. The lineshapes in the spectra will be
    (a) Gaussian   (b) Lorentzian

25. The type of broadening will be
    (a) inhomogeneous
    (b) homogeneous

Part 2. Closed-Book Problems (50 points)

In some cases, there are "choices" for the questions. If you do both questions, then I will give you full credit for one question and bonus marks for the second question. The second question is worth ½ of the first question.

1. Determine the term symbols for the $1s^2 2s^2 2p^5 3s^2 3p^2$ excited state of Aluminum. (Note that there are only 5 electrons in the *2p* orbital and 2 electrons in the *3p* orbital.) [5 points]

2. Concavity of the Energy. [5 points]

The total energy of a system clearly depends on the Hamiltonian, and so we can say that the energy is a functional of the Hamiltonian, $E\left[\hat{H}\right]$. Suppose the Hamiltonian for a system can be written as the sum of two Hamiltonians,

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B$$

(a) Show that the ground state energy for the whole system "AB" is greater than the sum of the ground state energies of the two subsystems, "A" and "B". That is, show that

$$E\left[\hat{H}_{AB}\right] \geq E\left[\hat{H}_A\right] + E\left[\hat{H}_B\right]$$

3. Do one of the following: [5 points]

(a) Derive the Hellmann-Feynman Theorem

$$\frac{\partial E}{\partial \lambda} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle$$

(b) Derive the Hypervirial theorem. The Hypervirial theorem says that if $\hat{A}$ be a Hermitian operator that does not change with respect to time, then the time rate of change in the expectation value of $\hat{A}$ is then given by the formula

$$\frac{d\left\langle \Psi(\tau;t) \left| \hat{A}(\tau) \right| \Psi(\tau;t) \right\rangle}{dt} = \frac{i}{\hbar} \left\langle \Psi(\tau;t) \left\| \left[\hat{H}(\tau,t), \hat{A}(\tau) \right] \right\| \Psi(\tau;t) \right\rangle$$

Here, $H(\tau,t)$ is the Hamiltonian for the system and $\Psi(\tau,t)$ is the wave function for the system.

4. Do one of the following: [5 points]

(a) Start by writing the simplest valence bond wave function for the Hydrogen atom, including ionic corrections. (Neglect all contributions except those from the hydrogen 1s orbitals.) Show that this wave function can be rewritten in the form of the molecular orbital wave function, plus its correction due to configuration interaction. [1 point for writing down the VB+ionic wave function correction; 1 point for writing down the MO+CI wave function correctly, and 3 points for showing how they are related to each other.]

(b) Consider a molecular orbital wave function with the following form:

$$\Psi_{MO} = \left| \, \psi_{2s}^{Be} + \psi_{1s}^{left} + \psi_{1s}^{right} \quad \alpha \quad \psi_{2p_z}^{Be} - \psi_{1s}^{left} + \psi_{1s}^{right} \quad \alpha \, \right|$$

This wave function would occur, for example, as a highly excited state in BeH_2^{4+}. Show that this wave function can be rewritten in terms of *sp* hybrid orbitals.

5. Do one of the following: [5 points]

(a) **Starting from Fermi's golden rule, derive the expression for the transition rate, $W_{\mu f, \nu i}$, for a molecule that is initially in the νth rovibrational state of the ith electronic excited state and is, after exposure to radiation, in the μth rovibrational state of the fth 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

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

    where $\chi_{\mu f} \left(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_P \right)$ is the nuclear (i.e. rovibrational) wave function for the μth rovibrational state of the fth electronic excited state in the system.

(b) **Using the Born-Oppenheimer Approximation, derive**

    (i) the electronic Schrödinger equation for a LiH.

    (ii) the nuclear Schrödinger equation for LiH.

6. Do one of the following: [5 points]

(a) **Show that** $\hat{J}^2$ **and** $\hat{S}^2$ **commute.** *You cannot use results for commutators including* $\hat{\boldsymbol{J}}$. Instead, write $\hat{\boldsymbol{J}}$ in terms of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$, and then use commutator identities (e.g., formulae for $\left[\hat{A}, \hat{B}\hat{C}\right]$, $\left[\hat{A}\hat{B}, \hat{C}\right]$, $\left[\hat{A}, \hat{B}+\hat{C}\right]$, $\left[\hat{A}+\hat{B}, \hat{C}\right]$) and known commutator relationships for the orbital angular momentum ($\hat{\boldsymbol{L}} = \left[\hat{L}_x, \hat{L}_y, \hat{L}_z\right]$, $\hat{L}^2 = \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{L}}$) and the spin angular momentum ($\hat{\boldsymbol{S}} = \left[\hat{S}_x, \hat{S}_y, \hat{S}_z\right]$, $\hat{S}^2 = \hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{S}}$) of electrons to get the desired result.

(b) **We talked about how the time correlation function was related to the lineshape. Typically there are two decay processes, one of which is fast (e.g., collisions) and one of which is slower (e.g., spontaneous emission). In this case, the probability of observing they system in state the initial state "t" seconds after the experiment begins is**

$$p_i\left(t\right) = \tfrac{1}{2}\left(e^{-|t|/T_{\text{fast}}} + e^{-|t|/T_{\text{slow}}}\right) \qquad p_{j\neq i}\left(0\right) = 0$$

Here we are assuming that the system is entirely in state "*i*" at time zero.

What is the equation for the lineshape that corresponds to this expression? You will need to know that:

$$\tfrac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega_0 t} e^{-\alpha|t|} e^{-i\omega t}\,dt = \frac{1}{8\pi}\left(\frac{\alpha}{\alpha^2 + \left(\omega - \omega_0\right)^2} + \frac{\alpha}{\alpha^2 + \left(\omega + \omega_0\right)^2}\right).$$

7. Hole-Burning. In this problem you will explain how hole-burning works. [10 points]

(a) When you shine an intense light source with frequency ν on a sample, it becomes transparent to that frequency. (That is, the amount of emitted and absorbed radiation are the same or, equivalently, the amount of incident and transmitted light is the same). Explain why. (You will need to use Fermi's golden rule in this explanation.)

(b) How is the effect you described in part (a) used in hole-burning spectroscopy to tell whether a spectral line is homogeneously or inhomogeneously broadened? Be sure to (i) describe the idea behind hole-burning and (ii) explain why the results for inhomogeneously broadened and homogenously broadened lines are different.

Bonus (2 points): Hole-burning doesn't always work. Sometimes it is impossible to "burn" a hole into an inhomogeneously broadened spectrum. Can you think of why this might occur? Why would increasing the power of your laser help you observe hole burning?

8. Assume the molecule BH_2Li is in a planar geometry, with all of the bond angles equal.

    (a) Draw the molecular orbital diagram for this molecule. You can ignore the Lithium atom's and Boron atom's 1s orbitals, since they are not involved in bonding.
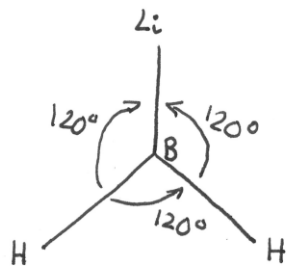
$$\left(\text{the } z\text{-axis is perpendicular to the paper.}\right)$$

(b) Number each of the orbitals in the diagram, 1, 2, 3 (for the occupied orbitals) and 4,5,6,7 (for the unoccupied orbitals). In the table below, indicate whether the transition from orbital "i" (i=1,2,3) to orbital "j" (j=4,5,6,7) is allowed or forbidden.

		ending orbitals			
		4	5	6	7
starting orbitals	1				
	2				
	3				

Bonus: (3 points) Bent's rule says that in a molecule where substituents have different electronegativity, the bond angle between the substituents with highest electronegativity is smaller than the bond angle between substituents with lower electronegativity. In this case, Lithium is less electronegative than Hydrogen and so we expect that the H-B-H angle to be smaller than the H-B-Li angle. Using arguments from *molecular orbital theory*, explain why.

Final Examination Key

Chemistry 3BB3

Winter, 2006

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

Part 1. Multiple Choice/Short Answer (2 pts. each)

1. **Write the electronic Hamiltonian for the Lithium Hydride <u>molecule</u> (LiH) in SI units, <u>showing the dependence on</u> $\hbar$, e, m_e, etc.. Be sure to include the appropriate values for the atomic numbers of the nuclei and the number of electrons. (I don't want Z_α and N hanging around in your equations; what are the values for Z_α and N for LiH?)**

$$\hat{H} = \sum_{i=1}^{4} \left(\frac{-\hbar^2}{2m_e} \nabla_i^2 \right) + \sum_{i=1}^{4} \left(\frac{-3e^2}{4\pi\varepsilon_0 \left| \boldsymbol{r}_i - \boldsymbol{R}_{Li} \right|} + \frac{-e^2}{4\pi\varepsilon_0 \left| \boldsymbol{r}_i - \boldsymbol{R}_{H} \right|} \right) + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \frac{e^2}{4\pi\varepsilon_i \left| \boldsymbol{r}_i - \boldsymbol{r}_j \right|}$$

2. **The atomic unit of length is the**
   (a) Bohr.
   (b) Schrödinger.
   (c) Slater.
   (d) Oppenheimer.
   (e) Hartree
   (f) None of the above.

3. **Let $\Psi\left(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_2, \sigma_2; \ldots; \boldsymbol{r}_N, \sigma_N \right)$ be antisymmetric with respect to exchange of any two electronic coordinates. Show that the probability of two electrons with the same spin being at the same location is zero.**

The wave function is antisymmetric with respect to simultaneous exchange of space and spin coordinates, so

$$\Psi\left(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_2, \sigma_2; \ldots; \boldsymbol{r}_N, \sigma_N \right) = -\Psi\left(\boldsymbol{r}_2, \sigma_2; \boldsymbol{r}_1, \sigma_1; \ldots; \boldsymbol{r}_N, \sigma_N \right)$$

If $\boldsymbol{r}_1 = \boldsymbol{r}_2$ and $\sigma_1 = \sigma_2$, then

$$\Psi\left(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_1, \sigma_1; \ldots; \boldsymbol{r}_N, \sigma_N \right) = -\Psi\left(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_1, \sigma_1; \ldots; \boldsymbol{r}_N, \sigma_N \right)$$
$$2\Psi\left(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_1, \sigma_1; \ldots; \boldsymbol{r}_N, \sigma_N \right) = 0$$
$$\Psi\left(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_1, \sigma_1; \ldots; \boldsymbol{r}_N, \sigma_N \right) = 0$$

Then

$$\left| \Psi\left(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_1, \sigma_1; \ldots; \boldsymbol{r}_N, \sigma_N \right) \right|^2 = 0$$

4. **Suppose you are given the following information about the <u>probability of observing an electron</u> in the _Helium cation_ (with atomic number equal to two).**

- very close to the nucleus, the probability of observing an electron is proportional to r^2.
- very far from the nucleus, the probability of observing an electron decays as e^{-r}.

The electron in He$^+$ is in what type of orbital.

$r^2 \rightarrow p$ orbital

$$e^{-\frac{Zr}{n}\,^2} = e^{-r} \qquad\qquad Z = 2 \text{ for He}$$

$$e^{-\frac{2\,2\,r}{n}} = e^{-r}$$

$$e^{-\frac{4r}{n}} = e^{-r}$$

$$n = 4$$

The electron is in a 4p orbital.

5-8.   You perform an experiment that measures the emission due to the 2p state in the Hydrogen atom.

5. **What is the term symbol for the initial state of the system (the 2p state that fluoresces?)**

$^2P_1$ **(one electron in a 2p orbital)**

6. **What is the term symbol for the final state of the system (the lower-energy state that the system ends up in)?**

$^2S_0$ **(one electron in a 1s orbital)**

7. **What is the frequency of the fluorescence in SI units. (That is, show the dependence on $\hbar$, _e, m_e_ , etc..**

The energy levels of the Hydrogen atom, in SI units, are $E_n = -\left(\dfrac{1}{2n^2}\right)\left(\dfrac{e^4 m_e}{4\pi\varepsilon_0\,^2\,\hbar^2}\right)$.

Using $\nu = \dfrac{\Delta E}{h}$, The frequency of the emission is then

$$\nu = \frac{\left(\dfrac{1}{2}-\dfrac{1}{8}\right)\left(\dfrac{e^4 m_e}{4\pi\varepsilon_0\,^2\,\hbar^2}\right)}{h} = \frac{3}{8}\left(\frac{e^4 m_e}{4\pi\varepsilon_0\,^2\,\hbar^2 h}\right) = \frac{3}{8}\left(\frac{2\pi\,^2\,e^4 m_e}{4\pi\varepsilon_0\,^2\,h^3}\right)$$

8. **Fluorescence spectra are often plotted as intensity versus wave numbers. If you did this, this spectral line would correspond to an peak at how many wave numbers. (Your expression will include a dependence on fundamental constants like _h, c,_ π .)**

$k = \dfrac{2\pi}{\lambda}$ and $\lambda = cT = \dfrac{c}{\nu}$. So $\dfrac{2\pi}{\lambda} = \dfrac{2\pi}{\frac{c}{\nu}} = \dfrac{2\pi\nu}{c}$. So

$$k = \frac{3}{8}\left(\frac{2\pi\,^3\,e^4 m_e}{4\pi\varepsilon_0\,^2\,ch^3}\right)$$

28

9-11. Hund's rules get the ground state term symbol for the Cerium atom (with a closed subshells $4f^1 5d^1$ configuration) incorrect. The true term symbol is $^1G_4$.

9. What is the term symbol predicted by Hund's rules?

$L = 3 + 2$ and $S = \frac{1}{2} + \frac{1}{2}$ would give the ground state term, which is $^3H_4$. (Small J is good for less than half-filled shells.)

10-12. Let $\Psi_{^1G_4}^{Ce}\ \tau$ is the ground state wave function for Cerium. Fill in the eigenvalues (where applicable) for the following operators. When more than one eigenvalue is possible, indicate **all** the possible values. Do not use atomic units.

$$\hat{L}^2 \Psi_{^1G_4}^{Ce}\ \tau\ =\ 20\hbar^2 \qquad\qquad \Psi_{^1G_4}^{Ce}\ \tau$$

$$\hat{L}_z \Psi_{^1G_4}^{Ce}\ \tau\ =\ \hbar\ -4 \text{ or -3 or -2 or -1 or 0 or 1 or 2 or 3 or 4 } \Psi_{^1G_4}^{Ce}\ \tau$$

$$\hat{S}^2 \Psi_{^1G_4}^{Ce}\ \tau\ = 0 \cdot \Psi_{^1G_4}^{Ce}\ \tau$$

$$\hat{S}_z \Psi_{^1G_4}^{Ce}\ \tau\ = 0 \cdot \Psi_{^1G_4}^{Ce}\ \tau$$

$$\hat{J}^2 \Psi_{^1G_4}^{Ce}\ \tau\ = 20\hbar^2 \Psi_{^1G_4}^{Ce}\ \tau$$

$$\hat{J}_z \Psi_{^1G_4}^{Ce}\ \tau\ = \hbar\ -4 \text{ or -3 or -2 or -1 or 0 or 1 or 2 or 3 or 4 } \Psi_{^1G_4}^{Ce}\ \tau$$

13-14. You perform a calculation for the Lithium atom by forming a Slater determinant of orbitals, $\left| \psi_{1s}^\alpha \alpha \quad \psi_{1s}^\beta \beta \quad \psi_{2s}^\alpha \alpha \right|$. You then choose the orbitals so that the energy,

$$\frac{\left\langle \left| \psi_{1s}^\alpha \alpha \quad \psi_{1s}^\beta \beta \quad \psi_{2s}^\alpha \alpha \right| \left| \hat{H} \right| \left| \psi_{1s}^\alpha \alpha \quad \psi_{1s}^\beta \beta \quad \psi_{2s}^\alpha \alpha \right| \right\rangle}{\left\langle \left| \psi_{1s}^\alpha \alpha \quad \psi_{1s}^\beta \beta \quad \psi_{2s}^\alpha \alpha \right| \left| \psi_{1s}^\alpha \alpha \quad \psi_{1s}^\beta \beta \quad \psi_{2s}^\alpha \alpha \right| \right\rangle}$$

is as small as possible.

13. This computational method is called
(a)   the Hartree method.
(b)   the Fermi-Amaldi method.
(c)   the restricted Hartree-Fock method

(d) the unrestricted Hartree-Fock method
(e)   the Kohn-Sham DFT method
(f)   configuration interaction.

14. The energy obtained from this calculation is _____ **the true ground state energy.**
(a) greater than
(b) equal to
(c) less than

15. Suppose you are given an approximate valence bond wave function for a molecule and you want to improve its accuracy. You would
(a) add contributions from additional resonance structures
(b)   add contributions from the wave functions of electronic excited states.

16. You want to form a strong covalent bond between two atoms. In order to do this, the atomic orbitals should _____. (List at least two properties of the atomic orbitals that are associated with the presence of a strong single bond between them.)

-- orbitals that are similar in size.

-- orbitals that are similar in energy.

-- good overlap between orbitals. (Orbitals in similar regions of space.)

-- "directionality" in orbitals (so that they "point at" each other).

-- smaller orbitals are (usually) better than bigger orbitals.

17. The $\psi_{y\,5z^2-r^2}^{left}\,r\;+\;\psi_{y\,5z^2-r^2}^{right}\,r$ molecular orbital (formed from two *f* orbitals) is a ____ molecular orbital. [Circle the appropriate choices in the form below.]

$$\overline{\pi}_{u}$$

18. Write down Fermi's Golden rule for dipole transitions. When you do this, write out the expression for the transition dipole for an atom. (That is, do not use $\hat{\mu}_x$ to represent the transition dipole; tell me what $\hat{\mu}_x$ *means*.)

$$W_{fi} = \frac{2\pi V^2}{\hbar} \left| \left\langle \Phi_f \left| \sum_{j=1}^{N} -e\left(\frac{x_j + y_j + z_j}{2}\right) + \sum_{\alpha=1}^{P} Z_\alpha e\left(\frac{X_\alpha + Y_\alpha + Z_\alpha}{2}\right) \right| \Phi_i \right\rangle \right|^2 \; g\; \hbar\omega_{fi} \; + g\; \hbar\omega_{if}$$

19. For a molecule in the kth excited state of a system, the spatial part of the wave function solves $\hat{H}\psi_k = E_k\psi_k$. Complete the following equation by filling in the "time dependence" of the wave function.

$$\Psi\;r_1,...,r_N;t \;=\; \psi_k\;r_1,...,r_k\;\times\left[e^{-\dfrac{iE_k t}{\hbar}}\right]$$

20-21. For each of the following statements, indicate whether the result is associated with the weak-field approximation (W), long-time approximation (T), long-wavelength approximation (L), or the Condon approximation (C). (Select all that apply).

___L____ "Magnetic dipole" allowed transitions are much weaker than "electric dipole" allowed transitions.

___T____ In the absence of broadening, the absorption spectrum of a molecule is a collection of delta-function peaks.

___W____ Multi-photon processes like frequency doubling (where two photons are absorbed by the system and one photon, with twice as much energy, is emitted) are negligible.

___C____ Because the atomic nuclei do not move very much during the process of an electronic excitation, the way the transition dipole varies as the positions of the atoms changes can be neglected.

22-23. In molecular orbital theory, we often talk about the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital). Are the following transitions allowed or forbidden? [Show your work; you will get partial credit if you figure out what the HOMO and LUMO are, even if you do not predict "allowed" or "forbidden" correctly.]

22. The transition from the HOMO to the LUMO in the Fluorine dimer, F_2, is
(a) allowed   (b) forbidden

This is a transition from a π_g orbital to a σ_u orbital. It is allowed.
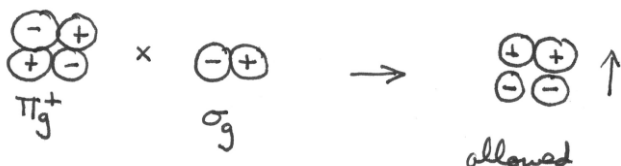
23. Suppose we take the CO molecule and compress it so much that the bond length tends to zero. (That is, we compress the carbon monoxide molecule so much that it begins to look like it is in the united atom limit.) The transition from the HOMO to the LUMO in the Carbon Monoxide molecule in the united atom limit is
(a) allowed   **(b) forbidden**

The united atom limit is the Silicon atom. The number of electrons is 14. The HOMO and LUMO are both "p" orbitals. Transitions from one p orbital to another are forbidden, in general, the "product" doesn't have a dipole. Alternatively, you might recall that the ground state terms for the

p^2 configuration is ^3P, ^1D and ^1S. Transitions from ^3P to either of the singlet states are forbidden because of spin-orbit effects. Transitions from ^1D to ^1S are dipole forbidden because $\Delta L = 2$

24-25. **High resolution infrared spectra are often made using matrix isolation. In Matrix isolation, one makes a dilute solution of the analyte and then freezes the solution. Typically, the solvent interacts only very weakly with the solute that is being studied: the most common solvents are Argon [Argon matrix isolation spectroscopy] and Neon [Neon matrix isolation spectroscopy].**

Suppose we take a dilute solution of Calcium Hydride (CaH$_2$) in Neon, and then freeze the solution. (Due to freezing point depression, the resulting solid will have a temperature less than the freezing point of Neon, which is 27 K.) Now we take a spectra of CaH$_2$ in the Neon matrix. There are usually a few different spectral lines, corresponding to different crystal environments for the analyte. However, we can say something about the shapes of the lines that occur, namely that:

24. The lineshapes in the spectra will be
(a) Gaussian   **(b) Lorentzian**

25. The type of broadening will be
(a) inhomogeneous
(b) homogeneous

Part 2. Closed-Book Problems (50 points)

In some cases, there are "choices" for the questions. If you do both questions, then I will give you full credit for one question and bonus marks for the second question. The second question is worth ½ of the first question.

1. **Determine the term symbols for the $1s^2 2s^2 2p^5 3s^2 3p^2$ excited state of Aluminum. (Note that there are only 5 electrons in the *2p* orbital and 2 electrons in the *3p* orbital.) [5 points]**

The *1s*, *2s*, and *3s* subshells are filled and do not contribute.

The $2p^5$ configuration has the same term as the $2p^1$ configuration, ^2P.

The $3p^2$ configuration has terms ^3P, ^1D, and ^1S. You can derive this using the "diagram" below:

M_S	M_L		
	2	1	0
1		$\left\|\psi_1\alpha \quad \psi_0\alpha\right\|$	$\left\|\psi_1\alpha \quad \psi_{-1}\alpha\right\|$
0	$\left\|\psi_1\alpha \quad \psi_1\beta\right\|$	$\left\|\psi_1\beta \quad \psi_0\alpha\right\|$ $\left\|\psi_1\alpha \quad \psi_0\beta\right\|$	$\left\|\psi_1\alpha \quad \psi_{-1}\beta\right\|$ $\left\|\psi_1\beta \quad \psi_{-1}\alpha\right\|$ $\left\|\psi_0\alpha \quad \psi_0\beta\right\|$

^3P, ^1D, and ^1S

Now we need to couple these states together. We get:

$$^3P + {}^2P \rightarrow {}^4D, {}^4P, {}^4S; {}^2D, {}^2P, {}^2S$$
$$^1D + {}^2P \rightarrow {}^2F, {}^2D, {}^2P$$
$$^1S + {}^2P \rightarrow {}^2P$$

I didn't require that you list the values of J, but they would be

$$^4D_{\frac{7}{2},\frac{5}{2},\frac{3}{2},\frac{1}{2}}, {}^4P_{\frac{5}{2},\frac{3}{2},\frac{1}{2}}, {}^4S_{\frac{3}{2}}; {}^2D_{\frac{5}{2},\frac{3}{2}}, {}^2P_{\frac{3}{2},\frac{1}{2}}, {}^2S_{\frac{1}{2}}$$
$$^1D + {}^2P \rightarrow {}^2F_{\frac{7}{2},\frac{5}{2}}, {}^2D_{\frac{5}{2},\frac{3}{2}}, {}^2P_{\frac{3}{2},\frac{1}{2}}$$
$$^1S + {}^2P \rightarrow {}^2P_{\frac{3}{2},\frac{1}{2}}$$

2.   Concavity of the Energy. [5 points]

The total energy of a system clearly depends on the Hamiltonian, and so we can say that the energy is a functional of the Hamiltonian, $E\left[\hat{H}\right]$. Suppose the Hamiltonian for a system can be written as the sum of two Hamiltonians,

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B$$

(a) Show that the ground state energy for the whole system "*AB*" is greater than the sum of the ground state energies of the two subsystems, "*A*" and "*B*". That is, show that

$$E\left[\hat{H}_{AB}\right] \geq E\left[\hat{H}_A\right] + E\left[\hat{H}_B\right]$$

This is a straightforward application of the variational principle. Let Ψ_{AB} denote the ground state eigenfunction for $\hat{H}_{AB}$, Ψ_A denote the ground state eigenfunction for $\hat{H}_A$, and Ψ_B denote the ground-state eigenfunction for Ψ_B. From the variational principle, we have that

$$\left\langle \Psi_A \left| \hat{H}_A \right| \Psi_A \right\rangle \leq \left\langle \Psi_{AB} \left| \hat{H}_A \right| \Psi_{AB} \right\rangle$$
$$\left\langle \Psi_B \left| \hat{H}_B \right| \Psi_B \right\rangle \leq \left\langle \Psi_{AB} \left| \hat{H}_B \right| \Psi_{AB} \right\rangle$$

Adding the two inequalities together we have

$$\left\langle \Psi_A \left| \hat{H}_A \right| \Psi_A \right\rangle + \left\langle \Psi_B \left| \hat{H}_B \right| \Psi_B \right\rangle \leq \left\langle \Psi_{AB} \left| \hat{H}_A + \hat{H}_B \right| \Psi_{AB} \right\rangle$$
$$\left\langle \Psi_A \left| \hat{H}_A \right| \Psi_A \right\rangle + \left\langle \Psi_B \left| \hat{H}_B \right| \Psi_B \right\rangle \leq \left\langle \Psi_{AB} \left| \hat{H}_{AB} \right| \Psi_{AB} \right\rangle$$
$$E\left[\hat{H}_A\right] + E\left[\hat{H}_B\right] \leq E\left[\hat{H}_{AB}\right]$$

3. Do one of the following: [5 points]

(a) Derive the Hellmann-Feynman Theorem

$$\frac{\partial E}{\partial \lambda} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle$$

(b) Derive the Hypervirial theorem. The Hypervirial theorem says that if $\hat{A}$ be a Hermitian operator that does not change with respect to time, then the time rate of change in the expectation value of $\hat{A}$ is then given by the formula

$$\frac{d\left\langle \Psi(\tau;t) \left| \hat{A}(\tau) \right| \Psi(\tau;t) \right\rangle}{dt} = \frac{i}{\hbar} \left\langle \Psi(\tau;t) \left\| \hat{H}(\tau,t), \hat{A}(\tau) \right\| \Psi(\tau;t) \right\rangle$$

Here, $H(\tau,t)$ is the Hamiltonian for the system and $\Psi(\tau,t)$ is the wave function for the system.

(a)

Let τ to denote the coordinate dependence of the wave function and the Hamiltonian.

$$\frac{\partial E_k}{\partial \lambda} \equiv \frac{\partial \left\langle \Psi_k(\lambda) \left| \hat{H}(\lambda) \right| \Psi_k(\lambda) \right\rangle}{\partial \lambda}$$

$$= \int \frac{\partial \Psi_k^*(\lambda,\tau) \hat{H}(\lambda,\tau) \Psi_k(\lambda,\tau)}{\partial \lambda} d\tau$$

$$= \int \left(\begin{array}{c} \frac{\partial \Psi_k^*(\lambda,\tau)}{\partial \lambda} \hat{H}(\lambda,\tau) \Psi_k(\lambda,\tau) \\ + \Psi_k^*(\lambda,\tau) \frac{\partial \hat{H}(\lambda,\tau)}{\partial \lambda} \Psi_k(\lambda,\tau) \\ + \Psi_k^*(\lambda,\tau) \hat{H}(\lambda,\tau) \frac{\partial \Psi_k(\lambda,\tau)}{\partial \lambda} \end{array} \right) d\tau$$

$$= \int \left(\begin{array}{c} \frac{\partial \Psi_k^*(\lambda,\tau)}{\partial \lambda} E_k(\lambda) \Psi_k(\lambda,\tau) \\ + \Psi_k^*(\lambda,\tau) \frac{\partial \hat{H}(\lambda,\tau)}{\partial \lambda} \Psi_k(\lambda,\tau) \\ + \hat{H}(\lambda,\tau) \Psi_k(\lambda,\tau) \left[\frac{\partial \Psi_k(\lambda,\tau)}{\partial \lambda}\right]^* \end{array} \right) d\tau$$

$$= \int \left(\begin{array}{c} \frac{\partial \Psi_k^*(\lambda,\tau)}{\partial \lambda} E_k(\lambda) \Psi_k(\lambda,\tau) \\ + \Psi_k^*(\lambda,\tau) \frac{\partial \hat{H}(\lambda,\tau)}{\partial \lambda} E_k(\lambda,\tau) \\ + E_k(\lambda) \Psi_k(\lambda,\tau) \frac{\partial \Psi_k^*(\lambda,\tau)}{\partial \lambda} \end{array} \right) d\tau$$

$$= E_k \oint \left(\frac{\partial \Psi_k^*(\lambda,\tau)}{\partial \lambda} \Psi_k(\lambda,\tau) \Psi_k^*(\lambda,\tau) \frac{\partial \Psi_k(\lambda,\tau)}{\partial \lambda} \right) d\tau + \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle$$

$$= E_k \frac{\partial}{\partial \lambda} \int \Psi_k^*(\lambda,\tau) \Psi_k(\lambda,\tau) d\tau + \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle$$

$$= E_k \frac{\partial}{\partial \lambda} \left[1 \right] + \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle$$

$$= \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle$$

(b)

This is a simple exercise using the definition of a commutator and the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \Psi(\tau,t)}{\partial t} = \hat{H}(\tau,t)\,\Psi(\tau,t)$$

Note that the form $\Psi(\tau,t) = \psi(\tau)\,e^{-iEt/\hbar}$ is **only** true for time-independent Hamiltonians, as will be obvious from the derivation (see the notes on spectroscopy or any good quantum book). If you write $\Psi(\tau,t) = \psi(\tau)\,e^{-i\hat{H}(\tau,t)\,t/\hbar}$ you are essentially using the Heisenberg picture of quantum mechanics, and the result can then be derived. However, I'll use the Schrödinger form, mostly because it is more "standard" and because none of you used the Heisenberg form.

To the derivation:

$$\frac{d\left\langle \Psi(\tau;t)\left|\hat{A}(\tau)\right|\Psi(\tau;t)\right\rangle}{dt} = \left\langle \frac{\partial \Psi(\tau;t)}{\partial t}\left|\hat{A}(\tau)\right|\Psi(\tau;t)\right\rangle + \left\langle \Psi(\tau;t)\left|\hat{A}(\tau)\right|\frac{\partial \Psi(\tau;t)}{\partial t}\right\rangle$$
$$+ \left\langle \Psi(\tau;t)\left|\frac{\partial \hat{A}(\tau)}{\partial t}\right|\Psi(\tau;t)\right\rangle$$

The term on the second line is clearly zero: the operator $\hat{A}(\tau)$ is time-independent.

Next, we rewrite the time-dependent Schrödinger equation in the form

$$\frac{\partial \Psi(\tau,t)}{\partial t} = \frac{1}{i\hbar}\hat{H}(\tau,t)\,\Psi(\tau,t)$$
$$= \frac{-i}{\hbar}\hat{H}(\tau,t)\,\Psi(\tau,t)$$

and take the complex conjugate, which shows that

$$\frac{\partial \Psi^{*}(\tau,t)}{\partial t} = \left[\frac{-i}{\hbar}\hat{H}(\tau,t)\,\Psi(\tau,t)\right]^{*}$$
$$= \left[\frac{-i}{\hbar}\right]^{*}\left[\hat{H}(\tau,t)\,\Psi(\tau,t)\right]^{*}$$
$$= \frac{i}{\hbar}\left[\hat{H}(\tau,t)\,\Psi(\tau,t)\right]^{*}$$

and substitute these last two expressions into the formula for $\frac{\partial \langle A \rangle}{\partial t}$ to get

$$\frac{d\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle}{dt} = \left\langle \frac{\partial\Psi(\boldsymbol{\tau};t)}{\partial t}\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle + \left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\frac{\partial\Psi(\boldsymbol{\tau};t)}{\partial t}\right\rangle$$

$$= \frac{i}{\hbar}\left\langle \hat{H}(\boldsymbol{\tau};t)\Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle$$

$$- \frac{i}{\hbar}\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\hat{H}(\boldsymbol{\tau};t)\Psi(\boldsymbol{\tau};t)\right\rangle.$$

From the properties of Hermitian operators (particularly $\left\langle \hat{Q}\Psi\middle|\Psi\right\rangle = \left\langle \Psi\middle|\hat{Q}\middle|\Psi\right\rangle = \left\langle \Psi\middle|\hat{Q}\Psi\right\rangle$), we have

$$\frac{d\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle}{dt} = \frac{i}{\hbar}\left\langle \hat{H}(\boldsymbol{\tau};t)\Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle$$

$$- \frac{i}{\hbar}\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\hat{H}(\boldsymbol{\tau};t)\Psi(\boldsymbol{\tau};t)\right\rangle$$

$$= \frac{i}{\hbar}\left(\begin{array}{l}\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{H}(\boldsymbol{\tau};t)\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle \\ -\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\hat{H}(\boldsymbol{\tau};t)\right|\Psi(\boldsymbol{\tau};t)\right\rangle\end{array}\right)$$

$$= \frac{i}{\hbar}\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{H}(\boldsymbol{\tau};t)\hat{A}(\boldsymbol{\tau}) - \hat{A}(\boldsymbol{\tau})\hat{H}(\boldsymbol{\tau};t)\right|\Psi(\boldsymbol{\tau};t)\right\rangle$$

$$= \frac{i}{\hbar}\left\langle \Psi(\boldsymbol{\tau};t)\left|\left[\hat{H}(\boldsymbol{\tau};t),\hat{A}(\boldsymbol{\tau})\right]\right|\Psi(\boldsymbol{\tau};t)\right\rangle$$

4. Do one of the following: [5 points]

(a) Start by writing the simplest molecular orbital wave function for the Hydrogen atom, including configuration interaction corrections. (Neglect all contributions except those from the hydrogen 1s orbitals.) Show that this wave function can be rewritten in the form of the valence bond wave function, plus its correction due to ionic configurations. [1 point for writing down the VB+ionic wave function correction; 1 point for writing down the MO+CI wave function correctly, and 3 points for showing how they are related to each other.]

(b) Consider a molecular orbital wave function with the following form:

$$\Psi_{MO} = \left| \; \psi_{2s}^{Be} + \psi_{1s}^{left} + \psi_{1s}^{right} \quad \alpha \qquad \psi_{2p_z}^{Be} - \psi_{1s}^{left} + \psi_{1s}^{right} \quad \alpha \; \right|$$

This wave function would occur, for example, as a highly excited state in BeH_2^{4+}.
Show that this wave function can be rewritten in terms of *sp* hybrid orbitals.

(a)

$$\Psi^{MO+CI} \; (r_1, r_2) \; \propto \; \left(\begin{array}{cc} \psi_{1s}^{l} \; (r_1) + \psi_{1s}^{r} \; (r_1) & \psi_{1s}^{l} \; (r_2) + \psi_{1s}^{r} \; (r_2) \\ +\kappa \; \psi_{1s}^{l} \; (r_1) - \psi_{1s}^{r} \; (r_1) & \psi_{1s}^{l} \; (r_2) - \psi_{1s}^{r} \; (r_2) \end{array} \right) \; \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

$$\propto \; \left(\begin{array}{cc} 1+\kappa \; \psi_{1s}^{l} (r_1) \psi_{1s}^{l} (r_2) + 1-\kappa \; \psi_{1s}^{l} (r_1) \psi_{1s}^{r} (r_2) \\ + \; 1-\kappa \; \psi_{1s}^{r} (r_1) \psi_{1s}^{l} (r_2) + 1+\kappa \; \psi_{1s}^{r} (r_1) \psi_{1s}^{r} (r_2) \end{array} \right) \; \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

$$\propto \; \left[\begin{array}{c} 1-\kappa \; \psi_{1s}^{l}(r_1)\psi_{1s}^{r}(r_2) + \psi_{1s}^{r}(r_1)\psi_{1s}^{l}(r_2) \\ + \kappa \; \psi_{1s}^{l}(r_1)\psi_{1s}^{l}(r_2) + \psi_{1s}^{r}(r_1)\psi_{1s}^{r}(r_2) \end{array} \right] \; \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

$$\propto \; \left[\begin{array}{c} \psi_{1s}^{l}(r_1)\psi_{1s}^{r}(r_2) + \psi_{1s}^{r}(r_1)\psi_{1s}^{l}(r_2) \\ + \dfrac{1+\kappa}{1-\kappa} \; \psi_{1s}^{l}(r_1)\psi_{1s}^{l}(r_2) + \psi_{1s}^{r}(r_1)\psi_{1s}^{r}(r_2) \end{array} \right] \; \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

$$\propto \; \Psi^{VB+ionic} \; (r_1, r_2)$$

(b)

The following are key identities about determinants:

1. Addition of a multiple of any row/column to any other row or column of the matrix does not change the determinant

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = \begin{vmatrix} a_{11} & a_{12} + ka_{11} \\ a_{21} & a_{22} + ka_{21} \end{vmatrix} = \begin{vmatrix} a_{11} + ka_{12} & a_{12} \\ a_{21} + ka_{22} & a_{22} \end{vmatrix}$$

2. Multiplication of a row or column by a constant multiplies the who determinant by that constant.

$$k\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = \begin{vmatrix} a_{11} & ka_{12} \\ a_{21} & ka_{22} \end{vmatrix}$$

So, we add the second column of the determinant to the first column to obtain

$$\begin{vmatrix} \psi_{2s}^{Be} + \psi_{1s}^{left} + \psi_{1s}^{right} & \alpha & \psi_{2p_z}^{Be} - \psi_{1s}^{left} + \psi_{1s}^{right} & \alpha \end{vmatrix}$$

$$= \begin{vmatrix} \psi_{2s}^{Be} + \psi_{1s}^{left} + \psi_{1s}^{right} + \psi_{2p_z}^{Be} - \psi_{1s}^{left} + \psi_{1s}^{right} & \alpha & \psi_{2p_z}^{Be} - \psi_{1s}^{left} + \psi_{1s}^{right} & \alpha \end{vmatrix}$$

$$= \begin{vmatrix} \psi_{2s}^{Be} + \psi_{2p_z}^{Be} + 2\psi_{1s}^{right} & \alpha & \psi_{2p_z}^{Be} - \psi_{1s}^{left} + \psi_{1s}^{right} & \alpha \end{vmatrix}$$

Then we subtract ½ times the first column to the second column to get

$$\begin{vmatrix} \psi_{2s}^{Be} + \psi_{1s}^{left} + \psi_{1s}^{right} & \alpha & \psi_{2p_z}^{Be} - \psi_{1s}^{left} + \psi_{1s}^{right} & \alpha \end{vmatrix}$$

$$= \begin{vmatrix} \psi_{2s}^{Be} + \psi_{2p_z}^{Be} + 2\psi_{1s}^{right} & \alpha & \psi_{2p_z}^{Be} - \psi_{1s}^{left} + \psi_{1s}^{right} - \frac{1}{2}\ \psi_{2s}^{Be} + \psi_{2p_z}^{Be} + 2\psi_{1s}^{right} & \alpha \end{vmatrix}$$

$$= \begin{vmatrix} \psi_{2s}^{Be} + \psi_{2p_z}^{Be} + 2\psi_{1s}^{right} & \alpha & -\frac{1}{2}\ \psi_{2s}^{Be} - \psi_{2p_z}^{Be} - 2\psi_{1s}^{left} & \alpha \end{vmatrix}$$

Next we multiply the determinant by $\frac{-1}{2}$, so that

$$\frac{-1}{2}\begin{vmatrix} \psi_{2s}^{Be} + \psi_{1s}^{left} + \psi_{1s}^{right} & \alpha & \psi_{2p_z}^{Be} - \psi_{1s}^{left} + \psi_{1s}^{right} & \alpha \end{vmatrix}$$

$$= \frac{-1}{2}\begin{vmatrix} \psi_{2s}^{Be} + \psi_{2p_z}^{Be} + 2\psi_{1s}^{right} & \alpha & -1\left(\left\{\frac{\psi_{2s}^{Be} - \psi_{2p_z}^{Be}}{2}\right\} - \psi_{1s}^{left}\right)\alpha \end{vmatrix}$$

$$= \frac{1}{2}\begin{vmatrix} \psi_{2s}^{Be} + \psi_{2p_z}^{Be} + 2\psi_{1s}^{right} & \alpha & \left(\left\{\frac{\psi_{2s}^{Be} - \psi_{2p_z}^{Be}}{2}\right\} - \psi_{1s}^{left}\right)\alpha \end{vmatrix}$$

$$= \begin{vmatrix} \left(\left\{\frac{\psi_{2s}^{Be} + \psi_{2p_z}^{Be}}{2}\right\} + \psi_{1s}^{right}\right)\alpha & \left(\left\{\frac{\psi_{2s}^{Be} - \psi_{2p_z}^{Be}}{2}\right\} - \psi_{1s}^{left}\right)\alpha \end{vmatrix}$$

The terms in   are the *sp* hybrid orbitals.

5. Do one of the following: [5 points]

(a) Starting from Fermi's golden rule, derive the expression for the transition rate, $W_{\mu f, \nu i}$, for a molecule that is initially in the νth rovibrational state of the ith electronic excited state and is, after exposure to radiation, in the μth rovibrational state of the fth electronic excited state. Your discussion should be detailed and neat, and needs to contain the following key pieces of information to obtain full credit.

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

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

where $\chi_{\mu f}\left(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_P\right)$ is the nuclear (i.e. rovibrational) wave function for the μth rovibrational state of the fth electronic excited state in the system.

(b) **Using the Born-Oppenheimer Approximation, derive**
- **(i)** the electronic Schrödinger equation for a LiH.
- **(ii)** the nuclear Schrödinger equation for LiH.

(a)

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,

$$\Phi_{\nu i}\left(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \boldsymbol{R}_1, \ldots, \boldsymbol{R}_P\right) = \xi_i\left(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \boldsymbol{R}_1, \ldots, \boldsymbol{R}_P\right) \chi_{\nu i}\left(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_P\right)$$
$$\Phi_{\mu f}\left(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \boldsymbol{R}_1, \ldots, \boldsymbol{R}_P\right) = \xi_f\left(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \boldsymbol{R}_1, \ldots, \boldsymbol{R}_P\right) \chi_{\mu f}\left(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_P\right)$$

We have, then, that

$$
\begin{aligned}
\left\langle \Phi_{\mu f} \middle| \hat{\mu}_x \middle| \Phi_{\nu i} \right\rangle_{\substack{1\ldots N \\ 1\ldots P}} &= \left\langle \Phi_{\mu f} \middle| \sum_{i=1}^{N} -e x_i + \sum_{\alpha=1}^{P} Z_\alpha e X_i \middle| \Phi_{\nu i} \right\rangle_{\substack{1\ldots N \\ 1\ldots P}} \\
&= \left\langle \chi_{\mu f} \xi_f \middle| \sum_{i=1}^{N} -e x_i \middle| \chi_{\nu i} \xi_i \right\rangle_{\substack{1\ldots N \\ 1\ldots P}} + \left\langle \chi_{\mu f} \xi_f \middle| \sum_{\alpha=1}^{P} Z_\alpha e X_i \middle| \chi_{\nu i} \xi_i \right\rangle_{\substack{1\ldots N \\ 1\ldots P}} \\
&= \left\langle \chi_{\mu f} \xi_f \middle| \sum_{i=1}^{N} -e x_i \middle| \chi_{\nu i} \xi_i \right\rangle_{\substack{1\ldots N \\ 1\ldots P}} + \left\langle \chi_{\mu f} \middle| \left\langle \xi_f \middle| \xi_i \right\rangle_{1\ldots N} \sum_{\alpha=1}^{P} Z_\alpha e X_i \middle| \chi_{\nu i} \right\rangle_{1\ldots P}
\end{aligned}
$$

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, $r_1, ..., r_N$. 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 $\langle \xi_f | \xi_i \rangle_{1...N} = 0$ 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 $\langle \xi_i | \xi_i \rangle_{1...N} = 1$. Similarly, we have that

$$\left\langle \chi_{\mu f} \xi_f \left| \sum_{k=1}^{N} -ex_k \right| \chi_{\nu i} \xi_i \right\rangle_{\substack{1...N \\ 1...P}} = \left\langle \chi_{\mu i} \xi_i \left| \sum_{k=1}^{N} -ex_k \right| \chi_{\nu i} \xi_i \right\rangle_{\substack{1...N \\ 1...P}}$$

$$= 0 \qquad \text{unless } \mu = \nu$$

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

$$\left\langle \Phi_{\mu f} \left| \hat{\mu}_x \right| \Phi_{\nu i} \right\rangle_{\substack{1...N \\ 1...P}} = \left\langle \chi_{\mu i} \left| \sum_{\alpha=1}^{P} Z_\alpha e X_i \right| \chi_{\nu i} \right\rangle_{1...P}$$

and so Fermi's Golden rule reduces to

$$W_{\mu i, \nu i} = \frac{2\pi V^2 \ g \ \hbar\omega_{\mu i, \nu i} \ + g \ -\hbar\omega_{\mu i, \nu i}}{\hbar} \left| \left\langle \Phi_{\mu i} \left| \hat{\mu} \right| \Phi_{\nu i} \right\rangle \right|^2$$

$$= \frac{2\pi V^2 \ g \ \hbar\omega_{\mu i, \nu i} \ + g \ -\hbar\omega_{\mu i, \nu i}}{\hbar} \left| \left\langle \chi_{\mu i} \left| \sum_{\alpha=1}^{P} Z_\alpha e X_i \right| \chi_{\nu i} \right\rangle_{1...P} \right|^2$$

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

Returning to our derivation, we need only worry about the first term in the equation for $\left\langle \Phi_{\mu f} \left| \hat{\mu}_x \right| \Phi_{\nu i} \right\rangle_{\substack{1...N \\ 1...P}}$. Now, let's define the transition dipole for a specific nuclear configuration using,

$$\mu_{fi} \ R_1, R_2, ... R_P \ \equiv \left\langle \xi_f \left| \sum_{i=1}^{N} -ex_i \right| \xi_i \right\rangle_{1...N}.$$

We have, then, that

41

$$\left\langle \Phi_{\mu f} \left| \hat{\mu}_x \right| \Phi_{\nu i} \right\rangle_{\substack{1...N \\ 1...P}} = \left\langle \chi_{\mu f} \xi_f \left| \sum_{i=1}^{N} -e x_i \right| \chi_{\nu i} \xi_i \right\rangle_{\substack{1...N \\ 1...P}}$$

$$= \left\langle \chi_{\mu f} \left| \mu_{fi} \left(\boldsymbol{R}_1, ..., \boldsymbol{R}_P \right) \right| \chi_{\nu i} \right\rangle_{1...P}$$

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 $\mu_{fi}\left(\boldsymbol{R}_1, ..., \boldsymbol{R}_P \right)$ around the equilibrium nuclear positions in the initial state, $\boldsymbol{R}_1^{\,i}, ... \boldsymbol{R}_P^{\,i}$. Using the Taylor series, we have that

$$\mu_{fi}\left(\boldsymbol{R}_1, ..., \boldsymbol{R}_P \right) = \mu_{fi}\left(\boldsymbol{R}_1^{\,i}, ... \boldsymbol{R}_P^{\,i} \right) + \sum_{k=1}^{P} \left(\boldsymbol{R}_k - \boldsymbol{R}_k^{\,i} \right) \cdot \nabla_k \mu_{fi}\left(\boldsymbol{R}_1^{\,i}, ... \boldsymbol{R}_P^{\,i} \right) + ...$$

We substitute into the expression above, obtaining

$$\left\langle \Phi_{\mu f} \left| \hat{\mu}_x \right| \Phi_{\nu i} \right\rangle_{\substack{1...N \\ 1...P}} = \left\langle \chi_{\mu f} \left| \mu_{fi}\left(\boldsymbol{R}_1, ..., \boldsymbol{R}_P \right) \right| \chi_{\nu i} \right\rangle_{1...P}$$

$$= \left\langle \chi_{\mu f} \left| \mu_{fi}\left(\boldsymbol{R}_1^{\,i}, ... \boldsymbol{R}_P^{\,i} \right) + \sum_{\alpha=1}^{P} \left(\boldsymbol{R}_\alpha - \boldsymbol{R}_\alpha^{\,i} \right) \cdot \nabla_\alpha \mu_{fi}\left(\boldsymbol{R}_1^{\,i}, ... \boldsymbol{R}_P^{\,i} \right) + ... \right| \chi_{\nu i} \right\rangle_{1...P}$$

$$= \left. \begin{array}{l} \mu_{fi}\left(\boldsymbol{R}_1^{\,i}, ... \boldsymbol{R}_P^{\,i} \right) \left\langle \chi_{\mu f} \middle| \chi_{\nu i} \right\rangle \\ + \sum_{\alpha=1}^{P} \left\langle \chi_{\mu f} \left| \left(\boldsymbol{R}_k - \boldsymbol{R}_k^{\,i} \right) \cdot \nabla_\alpha \mu_{fi}\left(\boldsymbol{R}_1^{\,i}, ... \boldsymbol{R}_P^{\,i} \right) \right| \chi_{\nu i} \right\rangle_{1...P} \\ + ... \end{array} \right\} \begin{array}{l} \text{Condon approx.} \\ \text{vibronic coupling} \end{array}$$

(iii)   The Condon approximation is associated with neglecting terms that depend on the way $\mu_{fi}\left(\boldsymbol{R}_1, ..., \boldsymbol{R}_P \right)$ changes with respect to the nuclear positions. (These terms are represented by the second and higher order terms in the last equality in the preceding equation.) 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

$$\left\langle \Phi_{\mu f} \left| \hat{\mu}_x \right| \Phi_{\nu i} \right\rangle_{\substack{1...N \\ 1...P}} = \left\langle \chi_{\mu f} \left| \mu_{fi}\left(\boldsymbol{R}_1, ..., \boldsymbol{R}_P \right) \right| \chi_{\nu i} \right\rangle_{1...P}$$

$$\approx \mu_{fi}\left(\boldsymbol{R}_1^{\,i}, ... \boldsymbol{R}_P^{\,i} \right) \left\langle \chi_{\mu f} \middle| \chi_{\nu i} \right\rangle \qquad \text{Condon approximation}$$

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

$$W_{\mu f,\nu i} = \frac{2\pi V^2 \; g\left(\hbar\omega_{\mu f,\nu i}\right) + g\left(-\hbar\omega_{\mu f,\nu i}\right) \; \left|\left\langle \Phi_{\mu f}\left|\hat{\mu}_x\right|\Phi_{\nu i}\right\rangle\right|^2}{\hbar}$$

$$= \frac{2\pi V^2 \; g\left(\hbar\omega_{\mu f,\nu i}\right) + g\left(-\hbar\omega_{\mu f,\nu i}\right) \; \left|\mu_{fi}\left(\boldsymbol{R}_1^{\,i},\dots\boldsymbol{R}_P^{\,i}\right)\right|^2 \left|\left\langle \chi_{\mu f}\left|\chi_{\nu i}\right.\right\rangle\right|^2}{\hbar}$$

(iv) The term

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

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

$$W_{\mu f,\nu i} = \frac{2\pi V^2 \; g\left(\hbar\omega_{\mu f,\nu i}\right) + g\left(-\hbar\omega_{\mu f,\nu i}\right) \; \left|\left\langle \Phi_{\mu f}\left|\hat{\mu}_x\right|\Phi_{\nu i}\right\rangle\right|^2}{\hbar}$$

$$= \frac{2\pi V^2 \; g\left(\hbar\omega_{\mu f,\nu i}\right) + g\left(-\hbar\omega_{\mu f,\nu i}\right) \; \left|\mu_{fi}\left(\boldsymbol{R}_1^{\,i},\dots\boldsymbol{R}_P^{\,i}\right)\right|^2 F_{\mu f,\nu i}}{\hbar}$$

(b)

The Schrodinger equation, in atomic units, is

$$\left(\begin{array}{c} -\dfrac{\nabla_A^2}{2m_H} - \dfrac{\nabla_B^2}{2m_{Li}} + \sum_{i=1}^{4} -\dfrac{\nabla_i^2}{2} \\ -\sum_{i=1}^{4}\dfrac{1}{|\boldsymbol{r}_i - \boldsymbol{R}_H|} - \sum_{i=1}^{4}\dfrac{3}{|\boldsymbol{r}_i - \boldsymbol{R}_{Li}|} \\ +\sum_{i=1}^{3}\sum_{j=i+1}^{4}\dfrac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \dfrac{3}{|\boldsymbol{R}_H - \boldsymbol{R}_{Li}|} \end{array}\right)\Psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,...,\boldsymbol{r}_4;\boldsymbol{R}_H,\boldsymbol{R}_{Li}\right) = E\Psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,...,\boldsymbol{r}_4;\boldsymbol{R}_H,\boldsymbol{R}_{Li}\right)$$

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:

$$\Psi_{k\nu}\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\boldsymbol{r}_4,\boldsymbol{R}_H,\boldsymbol{R}_{Li}\right) = \psi_k\left(\boldsymbol{r}_1,...,\boldsymbol{r}_4;\boldsymbol{R}_H,\boldsymbol{R}_{Li}\right)\chi_{k\nu}\left(\boldsymbol{R}_H,\boldsymbol{R}_{Li}\right)$$

We substitute into part (b) and use the identity

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

to obtain

$$\left\{-\frac{\nabla_H^2}{2m_H} + \frac{-\nabla_{Li}^2}{2m_{Li}} + \sum_{i=1}^{4} -\frac{\nabla_i^2}{2} - \frac{1}{|r_i - R_H|} - \frac{3}{|r_i - R_{Li}|} \\ + \sum_{i=1}^{3}\sum_{j=i+1}^{4} \frac{1}{|r_i - r_j|} + \frac{3}{|R_H - R_{Li}|}\right\} \psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\chi_{k\nu}\left(R_H, R_{Li}\right)$$

$$= E_{k\nu}^{exact}\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\chi_{k\nu}\left(R_H, R_{Li}\right)$$

$$-\frac{\nabla_H^2}{2m_H} - \frac{\nabla_{Li}^2}{2m_{Li}}\,\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\chi_{k\nu}\left(R_H, R_{Li}\right)$$

$$+\left(\sum_{i=1}^{4}\left(\frac{\nabla_i^2}{2} - \frac{1}{|r_i - R_H|} - \frac{3}{|r_i - R_{Li}|}\right)\sum_{i=1}^{3}\sum_{j=i+1}^{4}\frac{1}{|r_i - r_j|} + \frac{3}{|R_H - R_{Li}|}\right)\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\chi_{k\nu}\left(R_H, R_{Li}\right)$$

$$= E_{k\nu}^{exact}\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\chi_{k\nu}\left(R_H, R_{Li}\right)$$

$$\left(\frac{-1}{2m_H}\right)\left\{\chi_{k\nu}\left(R_H, R_{Li}\right)\nabla_H^2\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right) + \psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\nabla_H^2\chi_{k\nu}\left(R_H, R_{Li}\right) \\ + 2\nabla_H\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\nabla_H\chi_{k\nu}\left(R_H, R_{Li}\right)\right\}$$

$$+\left(\frac{-1}{2m_{Li}}\right)\left\{\chi_{k\nu}\left(R_H, R_{Li}\right)\nabla_{Li}^2\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right) + \psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\nabla_{Li}^2\chi_{k\nu}\left(R_H, R_{Li}\right) \\ + 2\nabla_{Li}\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\nabla_{Li}\chi_{k\nu}\left(R_H, R_{Li}\right)\right\}$$

$$+\chi_{k\nu}\left(R_A, R_B\right)\left\{\sum_{i=1}^{4}\left(\frac{\nabla_i^2}{2} - \frac{1}{|r_i - R_H|} - \frac{3}{|r_i - R_{Li}|}\right)\sum_{i=1}^{3}\sum_{j=i+1}^{4}\frac{1}{|r_i - r_j|} + \frac{3}{|R_H - R_{Li}|}\right\}\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)$$

$$= E_{k\nu}^{exact}\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\chi_{k\nu}\left(R_H, R_{Li}\right)$$

$$\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\left(\frac{\nabla_H^2}{2m_H} + \frac{-\nabla_{Li}^2}{2m_{Li}}\right)\chi_{k\nu}\left(R_H, R_{Li}\right)$$

$$\color{blue}{- \frac{\nabla_H\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\nabla_H\,\chi_{k\nu}\left(R_H, R_{Li}\right)}{m_H} - \frac{\nabla_{Li}\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\nabla_{Li}\,\chi_{k\nu}\left(R_H, R_{Li}\right)}{m_{Li}}}$$

$$\color{blue}{+\chi_{k\nu}\left(R_H, R_{Li}\right)\left(\frac{\nabla_H^2}{2m_H} + \frac{-\nabla_{Li}^2}{2m_{Li}}\right)\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)}$$

$$+\chi_{k\nu}\left(R_H, R_{Li}\right)\left\{\sum_{i=1}^{4}\left(\frac{\nabla_i^2}{2} - \frac{1}{|r_i - R_H|} - \frac{3}{|r_i - R_{Li}|}\right)\sum_{i=1}^{3}\sum_{j=i+1}^{4}\frac{1}{|r_i - r_j|} + \frac{3}{|R_H - R_{Li}|}\right\}\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)$$

$$= E_{k\nu}^{exact}\psi_k\left(r_1, \ldots, r_4; R_H, R_{Li}\right)\chi_{k\nu}\left(R_H, R_{Li}\right)$$

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

$$\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)\left(\frac{-\nabla_H^2}{2m_H}+\frac{-\nabla_{Li}^2}{2m_{Li}}\right)\chi_{k\nu}\left(R_H,R_{Li}\right)$$

$$+\chi_{k\nu}\left(R_H,R_{Li}\right)\left(\sum_{i=1}^{4}-\frac{\nabla_i^2}{2}-\frac{1}{|r_i-R_H|}-\frac{3}{|r_i-R_{Li}|}+\sum_{i=1}^{3}\sum_{j=i+1}^{4}\frac{1}{|r_i-r_j|}+\frac{3}{|R_H-R_{Li}|}\right)\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)$$

$$=E_{k\nu}^{BO}\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)\chi_{k\nu}\left(R_H,R_{Li}\right)$$

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

$$\left(\sum_{i=1}^{4}-\frac{\nabla_i^2}{2}-\frac{1}{|r_i-R_H|}-\frac{3}{|r_i-R_{Li}|}+\sum_{i=1}^{3}\sum_{j=i+1}^{4}\frac{1}{|r_i-r_j|}+\frac{3}{|R_H-R_{Li}|}\right)\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)$$

$$\equiv U_k^{BO}\left(R_H,R_{Li}\right)\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)$$

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

$$\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)\left(\frac{-\nabla_H^2}{2m_H}+\frac{-\nabla_{Li}^2}{2m_{Li}}\right)\chi_{k\nu}\left(R_H,R_{Li}\right)+\chi_{k\nu}\left(R_H,R_{Li}\right)U_k^{BO}\left(R_H,R_{Li}\right)\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)$$

$$=E_{k\nu}^{BO}\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)\chi_{k\nu}\left(R_H,R_{Li}\right)$$

$$\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)\left(\frac{-\nabla_H^2}{2m_H}+\frac{-\nabla_{Li}^2}{2m_{Li}}+U_k^{BO}\left(R_H,R_{Li}\right)\right)\chi_{k\nu}\left(R_H,R_{Li}\right)$$

$$=E_{k\nu}^{BO}\psi_k\left(r_1,\ldots,r_4;R_H,R_{Li}\right)\chi_{k\nu}\left(R_H,R_{Li}\right)$$

$$\left(\frac{-\nabla_H^2}{2m_H}+\frac{-\nabla_{Li}^2}{2m_{Li}}+U_k^{BO}\left(R_H,R_{Li}\right)\right)\chi_{k\nu}\left(R_H,R_{Li}\right)=E_{k\nu}^{BO}\chi_{k\nu}\left(R_H,R_{Li}\right)$$

which gives the interpretation of the nuclei moving on the potential energy surface, $U_k^{BO}\left(R_1,R_2\right)$ due to the electrons in the system.

6. Do one of the following: [5 points]

(a) **Show that $\hat{J}^2$ and $\hat{S}^2$ commute.** *You cannot use results for commutators including $\hat{J}$.* Instead, write $\hat{\boldsymbol{J}}$ in terms of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$, and then use commutator identities (e.g., formulae for $\left[\hat{A}, \hat{B}\hat{C}\right]$, $\left[\hat{A}\hat{B}, \hat{C}\right]$, $\left[\hat{A}, \hat{B} + \hat{C}\right]$, $\left[\hat{A} + \hat{B}, \hat{C}\right]$) and known commutator relationships for the orbital angular momentum ($\hat{\boldsymbol{L}} = \left[\hat{L}_x, \hat{L}_y, \hat{L}_z\right]$, $\hat{L}^2 = \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{L}}$) and the spin angular momentum ($\hat{\boldsymbol{S}} = \left[\hat{S}_x, \hat{S}_y, \hat{S}_z\right]$, $\hat{S}^2 = \hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{S}}$) of electrons to get the desired result.

(b) **We talked about how the time correlation function was related to the lineshape. Typically there are two decay processes, one of which is fast (e.g., collisions) and one of which is slower (e.g., spontaneous emission). In this case, the probability of observing they system in state the initial state "t" seconds after the experiment begins is**

$$p_i\ t\ = \tfrac{1}{2}\ e^{-|t|/T_{\text{fast}}} + e^{-|t|/T_{\text{slow}}} \qquad\qquad p_{j\neq i}\ 0\ = 0$$

Here we are assuming that the system is entirely in state "i" at time zero.
   What is the equation for the lineshape that corresponds to this expression? You will need to know that:

$$\tfrac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega_0 t} e^{-\alpha|t|} e^{-i\omega t}\, dt = \frac{1}{8\pi}\left(\frac{\alpha}{\alpha^2 + \ \omega - \omega_0\ ^2} + \frac{\alpha}{\alpha^2 + \ \omega + \omega_0\ ^2}\right).$$

(a)

$$\left[\hat{J}^2, \hat{S}^2\right] = \left[\hat{\boldsymbol{J}} \cdot \boldsymbol{J}, \hat{S}^2\right]$$

$$= \left[\ \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}\ \cdot\ \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}\ , \hat{S}^2\right]$$

$$= \left[\hat{L}^2 + \hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{L}} + \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} + \hat{S}^2, \hat{S}^2\right]$$

$$= \left[\hat{L}^2 + 2\hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{L}} + \hat{S}^2, \hat{S}^2\right] \qquad \left(\begin{array}{l}\text{because spin and orbital angular}\\ \text{momenta commute}\end{array}\right)$$

$$= \left[\hat{L}^2, \hat{S}^2\right] + \left[2\hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{L}}, \hat{S}^2\right] + \left[\hat{S}^2, \hat{S}^2\right] \qquad \left(\begin{array}{l}\text{because the commutator of a sum}\\ \text{is the sum of the commutators}\end{array}\right)$$

$$= 0 + \left[2\hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{L}}, \hat{S}^2\right] + \left[\hat{S}^2, \hat{S}^2\right] \qquad \left(\text{ and } S \text{ are both good quantum numbers!}\right)$$

$$= 0 + \left[2\hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{L}}, \hat{S}^2\right] + 0 \qquad \left(\text{very operator commutes with itself}\right)$$

$$= 2\hat{\boldsymbol{S}} \cdot \left[\hat{\boldsymbol{L}}, \hat{S}^2\right] + 2\left[\hat{\boldsymbol{S}}, \hat{S}^2\right] \cdot \hat{\boldsymbol{L}} \qquad \left(\text{se identity for the commutator of a product}\right)$$

$$= 0 + 2\left[\hat{\boldsymbol{S}}, \hat{S}^2\right] \cdot \hat{\boldsymbol{L}} \qquad \left(\begin{array}{l}\text{because spin and orbital angular}\\ \text{momenta commute}\end{array}\right)$$

$$= 2\left[\hat{S}_x, \hat{S}^2\right]\hat{L}_x + 2\left[\hat{S}_y, \hat{S}^2\right]\hat{L}_y \qquad \left(\text{efinition of the dot product}\right)$$
$$+ 2\left[\hat{S}_z, \hat{S}^2\right]\hat{L}_z$$

$$= 2\ \ 0\ \hat{L}_x + 2\ \ 0\ \hat{L}_y + 2\ \ 0\ \hat{L}_z \qquad \left(\begin{array}{l}\hat{S}^2 \text{ commutes with every component of the spin}\\ \text{angular momentum}\end{array}\right)$$

$$= 0$$

(b)

We can write the formula for the lineshape as

$$I\left(\omega\right) \equiv \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i\left(t\right) \left\langle \Phi_i \left|\hat{\mu}_x\left(0\right) \hat{\mu}_x\left(t\right)\right| \Phi_i \right\rangle e^{-i\omega t} dt$$

or, alternatively, as

$$I\left(\omega\right) \equiv \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i\left(t\right) \left|\left\langle \Phi_f \left|\hat{\mu}_x\right| \Phi_i \right\rangle\right|^2 e^{i\omega_{fi} t} e^{-i\omega t} dt$$

Inserting the expression for $p_i\left(t\right)$ we have, for example,

$$I\left(\omega\right) \equiv \int_{-\infty}^{\infty} \sum_{f=0}^{\infty} \tfrac{1}{2}\left(e^{-t/\tau_{\text{fast}}} + e^{-t/\tau_{\text{fast}}}\right) \left|\left\langle \Phi_f \left|\hat{\mu}_x\right| \Phi_i \right\rangle\right|^2 e^{i\omega_{fi} t} e^{-i\omega t} dt$$

This gives back a lineshape that is the sum of two Lorentzians. The result is

$$I\left(\omega\right) = \sum_{f=0}^{\infty} \frac{\left|\left\langle \Phi_f \left|\hat{\mu}_x\right| \Phi_i \right\rangle\right|^2}{2} \left(\frac{\dfrac{1}{2\pi\tau_{\text{fast}}}}{\left(\dfrac{1}{2\tau_{\text{fast}}}\right)^2 + \left(\omega - \omega_{if}\right)^2} + \frac{\dfrac{1}{2\pi\tau_{\text{slow}}}}{\left(\dfrac{1}{2\tau_{\text{slow}}}\right)^2 + \left(\omega - \omega_{if}\right)^2} \right. $$
$$\left. + \frac{\dfrac{1}{2\pi\tau_{\text{fast}}}}{\left(\dfrac{1}{2\tau_{\text{fast}}}\right)^2 + \left(\omega + \omega_{if}\right)^2} + \frac{\dfrac{1}{2\pi\tau_{\text{slow}}}}{\left(\dfrac{1}{2\tau_{\text{slow}}}\right)^2 + \left(\omega + \omega_{if}\right)^2} \right)$$

The terms on the second line are negligible as long as you are considering absorption, rather than stimulation emission.

7.   Hole-Burning. In this problem you will explain how hole-burning works. [10 points]

(a) **When you shine an intense light source with frequency ν on a sample, it becomes transparent to that frequency. (That is, the amount of emitted and absorbed radiation are the same or, equivalently, the amount of incident and transmitted light is the same). Explain why. (You will need to use Fermi's golden rule in this explanation.)**
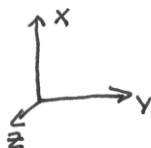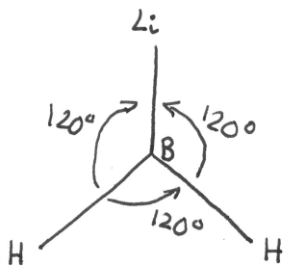
(b) How is the effect you described in part (a) used in hole-burning spectroscopy to tell whether a spectral line is homogeneously or inhomogeneously broadened? Be sure to (i) describe the idea behind hole-burning and (ii) explain why the results for inhomogeneously broadened and homogenously broadened lines are different.

Bonus (2 points): Hole-burning doesn't always work. Sometimes it is impossible to "burn" a hole into an inhomogeneously broadened spectrum. Can you think of why this might occur? Why would increasing the power of your laser help you observe hole burning?
Two cases are relevant. The first is when the rate of spontaneous emission is very, very fast. This can make it difficult to shine enough photons on the molecule so that the "rate of stimulated emission" is much faster than the "rate of spontaneous emission." The second case is when the system rearranges very quickly. That is, if the characteristic absorbance frequency of the molecules changes very rapidly (typically because the molecules' surroundings changes very fast, typically due to rapid solvent rearrangements) then it is possible that the molecules with a given absorbance frequency are "replenished" due to solvent rearrangements even faster than they can be depleted. This second case is rarer than the first case, though, because the rate of spontaneous emission is usually much faster than any molecular process that changes the characteristic absorbantion frequency of the molecule.

8. Assume the molecule BH_2Li is in a planar geometry, with all of the bond angles equal.

    (a) Draw the molecular orbital diagram for this molecule. You can ignore the Lithium atom's and Boron atom's 1s orbitals, since they are not involved in bonding.

(b) Number each of the orbitals in the diagram, 1, 2, 3 (for the occupied orbitals) and 4,5,6,7
   (for the unoccupied orbitals). In the table below, indicate whether the transition from
   orbital "i" (i=1,2,3) to orbital "j" (j=4,5,6,7) is allowed or forbidden.

		ending orbitals			
		4	5	6	7
starting orbitals	1				
	2				
	3				

Bonus: (3 points) Bent's rule says that in a molecule where substituents have different
   electronegativity, the bond angle between the substituents with highest electronegativity is
   smaller than the bond angle between substituents with lower electronegativity. In this
   case, Lithium is less electronegative than Hydrogen and so we expect that the H-B-H
   angle to be smaller than the H-B-Li angle. Using arguments from *molecular orbital theory*,
   explain why.