Key for Final Examination

Chemistry 3BB3; Winter 2003

Part 1.   Multiple-Choice/Short Answer   (People in the second testing should read the questions carefully, as they differed *slightly*.)

1. Write the *electronic* Schrödinger equation for an *N*-electron *P*-atom molecule, where the electronic positions are denoted $\{r_i\}_{i=1}^{N}$ and the nuclear charges, masses, and positions are denoted $\{Z_\alpha\}_{\alpha=1}^{P}$, $\{M_\alpha\}_{\alpha=1}^{P}$ and $\{R_\alpha\}_{\alpha=1}^{P}$, respectively. You may use atomic units.

$$\sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2}+\sum_{\alpha=1}^{P}-\frac{Z_\alpha}{|r_i-R_\alpha|}+\sum_{j=i+1}^{N}\frac{1}{|r_i-r_j|}+\sum_{\alpha=1}^{P-1}\sum_{\beta=\alpha+1}^{P}\frac{Z_\alpha Z_\beta}{|R_\alpha-R_\beta|}\right)\psi_k(r_1,\ldots,r_N;R_1,\ldots,R_P)$$
$$\equiv U_k^{BO}(R_1,\ldots,R_P)\psi_k(r_1,\ldots,r_N;R_1,\ldots,R_P)$$

2. Using your result from question 1, write the nuclear Schrödinger equation for this system, again using $\{R_\alpha\}_{\alpha=1}^{P}$ to describe the positions of the atomic nuclei.

$$\sum_{i=1}^{P}-\frac{\nabla_\alpha^2}{2}+U_k^{BO}(R_1,\ldots,R_P)\chi_{\nu k}(R_1,\ldots,R_P)\equiv E_{\nu k}^{BO}\chi_{\nu k}(R_1,\ldots,R_P)$$

3.* We discussed two approximations for the total energy of a molecule, the Born-Oppenheimer and Born-Huang approximations.
   (a) The Born-Oppenheimer energy is less than the exact energy; the Born-Huang energy is greater.
   (b) The Born-Huang energy is less than the exact energy, the Born-Oppenheimer energy is greater.
   (c) Both the Born-Oppenheimer and Born-Huang energies are less than the true energy.
   (d) Both the Born-Oppenheimer and Born-Huang energies are greater than the true energy.

4. Number the following units in order of *increasing* energy

   __4__ 1 Hartree   __2__ 1 kJ/mol

   __3__ 1 electron volt   __1__ 1 cm^{-1}

5. An Angstrom is 10^{-10} m. One Bohr is

   (a) smaller than an Angstrom. (1 Bohr = .52 Angstroms)
   (b) larger than an Angstrom.

6. Write the radial Schrödinger equation for the Hydrogen atom. Do not use atomic units.

$$\left(-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{\hbar^2 l(l+1)}{2m_e r^2}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right)R_{n,l}(r)=E_n R_{n,l}(r)$$

Name:

7. There has been much recent interest in "exotic" analogues of the hydrogen atom, wherein the electron is replaced by another species. The most popular choice is the muon, which has the same charge as the electron but weighs 207 times more. Assuming the Born-Oppenheimer approximation holds, what are the energy levels of the muon in the presence of an atomic nucleus with charge Z. Express your answer in Hartree units.

$$E_n^\mu \equiv -\frac{207 \cdot Z^2}{2n^2}$$

8. What can we say about the positions of the radial nodes in the 2s, 3s, and 4s orbitals?

The nodes are interleaved. That is, moving away from the origin, we first encounter a node for the 4s orbital, then a node for the 3s orbital. Before the second node of the 3s orbital, there is the node for the 2s orbital and the second node of the 4s orbital. After the second node of the 3s orbital, we have the final node of the 4s orbital.

9. Which of the following statements are true of electronic systems:
   (a) Wave functions must be antisymmetric with respect to exchange of electronic positions.
   (b) Wave functions must respect the equivalence of electrons.
   (c) The Hamiltonian must be symmetric with respect to exchange of electronic positions.
   (d) Wave functions must be antisymmetric with respect to when two electrons' coordinates (both space and spin) are exchanged.
   (e) No two electrons can ever be in the same state at the same time.

10. 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.

We have that

$$\Psi\left(r_1,\sigma_1;\ldots;r_i,\sigma_i;\ldots\ldots;r_j,\sigma_j;\ldots;r_N,\sigma_N\right) = -\Psi\left(r_1,\sigma_1;\ldots;r_j,\sigma_j;\ldots\ldots;r_i,\sigma_i;\ldots;r_N,\sigma_N\right)$$

If the $r_i = r_j$ and $\sigma_i = \sigma_j$, then

$$\Psi\left(r_1,\sigma_1;\ldots;r_i,\sigma_i;\ldots\ldots;r_i,\sigma_i;\ldots;r_N,\sigma_N\right) = -\Psi\left(r_1,\sigma_1;\ldots;r_i,\sigma_i;\ldots\ldots;r_i,\sigma_i;\ldots;r_N,\sigma_N\right)$$

and so

$$\Psi\left(r_1,\sigma_1;\ldots;r_i,\sigma_i;\ldots\ldots;r_i,\sigma_i;\ldots;r_N,\sigma_N\right) = 0$$

$$\left|\Psi\left(r_1,\sigma_1;\ldots;r_i,\sigma_i;\ldots\ldots;r_i,\sigma_i;\ldots;r_N,\sigma_N\right)\right|^2 = 0$$

which establishes what we wish to show.

11. Write a Slater determinantal wave function for the Lithium Atom. Assume the orbitals are orthogonal, and include the appropriate normalization factor.

$$\Psi\left(r_1,\sigma_1;r_2,\sigma_2;r_3,\sigma_3\right) \approx \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_{1s}\left(r_1\right)\alpha\left(1\right) & \psi_{1s}\left(r_2\right)\alpha\left(2\right) & \psi_{1s}\left(r_3\right)\alpha\left(3\right) \\ \psi_{1s}\left(r_1\right)\beta\left(1\right) & \psi_{1s}\left(r_2\right)\beta\left(2\right) & \psi_{1s}\left(r_3\right)\beta\left(3\right) \\ \psi_{2s}\left(r_1\right)\alpha\left(1\right) & \psi_{2s}\left(r_2\right)\alpha\left(2\right) & \psi_{2s}\left(r_3\right)\alpha\left(3\right) \end{vmatrix}$$

Name:

12. Match the following:
   A = Anomalous Zeeman Effect Spectroscopy
   R = Rydberg-State Spectroscopy
   S = Stark Effect Spectroscopy
   Z = Zeeman Effect Spectroscopy (but not Anomalous)

   __A__ Spectroscopy of a non-singlet state in a magnetic field.

   __S__ Spectroscopy of a system in a uniform electric field.

   __R__ Spectroscopy of a highly excited state.

11. Consider a state of the one-electron atom with atomic number Z and principle quantum number n. Assume that l takes on its maximum permissible value for the given value of n. At what distance from the nucleus are you most likely to observe the electron? **(Note that you do not need the normalization constant to work this problem.)**

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

(a) $\hat{L}_z$ **(d)** $\hat{S}^2$ (g) $\hat{L}_x$

(b) $\hat{L}^2$ **(e)** $\hat{J}_x$ (h) $\hat{S}_y$

(c) $\hat{S}_z$

14. *In terms of the Bohr mageton, β_e, the magnetic moment of an electron with spin-quantum number m_s is

(a) $\boldsymbol{\mu}_S \approx -m_s \frac{\beta_e}{\hbar}$ (d) $\boldsymbol{\mu}_S \approx -4\pi m_s \frac{\beta_e}{\hbar}$

(b) $\boldsymbol{\mu}_S \approx -2m_s \frac{\beta_e}{\hbar}$ (e) $\boldsymbol{\mu}_S \approx -\frac{1}{2}m_s \frac{\beta_e}{\hbar}$

(c) $\boldsymbol{\mu}_S \approx +m_s \frac{\beta_e}{\hbar}$

15,16. The ground state term for Cerium is $^3H_4$. If $\Psi_0^{Ce}(\tau)$ is the ground state wave function for Cerium, then 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.

$$\hat{L}^2\Psi_0^{Ce}(\tau) = \hbar^2(5\cdot6)\Psi_0^{Ce}(\tau) = 30\hbar^2\Psi_0^{Ce}(\tau)$$

$$\hat{L}_z\Psi_0^{Ce}(\tau) = \hbar\cdot(5,4,3,2,1,0,-1,-2,-3,-4,-5)\Psi_0^{Ce}(\tau)$$

$$\hat{S}^2\Psi_0^{Ce}(\tau) = \hbar^2(1\cdot2)\Psi_0^{Ce}(\tau) = 2\hbar^2\Psi_0^{Ce}(\tau)$$

$$\hat{S}_z\Psi_0^{Ce}(\tau) = \hbar(1,0,-1)\Psi_0^{Ce}(\tau)$$

$$\hat{J}^2\Psi_0^{Ce}(\tau) = \hbar^2(4\cdot5)\Psi_0^{Ce}(\tau) = 20\hbar^2\Psi_0^{Ce}(\tau)$$

$$\hat{J}_z\Psi_0^{Ce}(\tau) = \hbar\cdot(4,3,2,1,0,-1,-2,-3,-4,-5)\Psi_0^{Ce}(\tau)$$

17. Write an expression for the many-electron operator, $\hat{L}^2(r_1,\dots,r_N)$, in terms of the one-electron operators, $\hat{\boldsymbol{L}}(r_i) = \left[\hat{L}_x(r_i),\ \hat{L}_y(r_i),\ \hat{L}_z(r_i)\right]$.

$$\hat{L}^2 = \sum_{i=1}^N\hat{\boldsymbol{L}}(r_i)\cdot\sum_{j=1}^N\hat{\boldsymbol{L}}(r_j) = \sum_{i=1}^N\hat{L}^2(r_i) + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^N\hat{\boldsymbol{L}}(r_i)\cdot\hat{\boldsymbol{L}}(r_j)$$

18. Back when I pretended to be a physicist, I would often calibrate a spectrometer using the sodium "D" line (where "D" stands for "doublet" in typically confused physics parlance). The sodium "D" line corresponds to the $1s^22s^22p^63s^1 \rightarrow 1s^22s^22p^63p^1$ transition. Use term symbols to label the states on the energy level diagram.
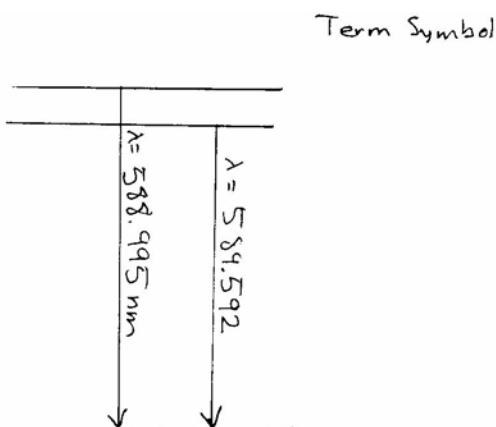
The highest-energy state is $^2P_{3/2}$. The next state is $^2P_{1/2}$. The ground state is $^2S_{1/2}$

19. **We discussed two different methods for approximating the wave functions of molecules, molecular-orbital theory (MO) and valence-bond (VB) theory. Denote the properties of each method with the following letters:**

    D = in its simplest form, does not describe molecular dissociation accurately.

    ECI = exact in the limit where all possible configurations are included in a configuration interaction calculation.

    ER = exact in the limit where all possible "resonance" structures, including ionic terms, are included in the calculation.

    IN = inexact, cannot be improved to achieve full exactness.

    L   = always gives an answer lower than the true answer for an approximate calculation.

    U   = always gives an answer greater than the true answer for an approximate calculation.

VB theory: **ER,U**

MO theory: **D,ECI,U**

20. **We consider a diatomic molecule, with the internuclear axis being the z-axis. (Both nuclei, then, are on the z axis.) Measure the $+/-$ symmetry direction by using the x-z plane as a mirror plane. Then, using the appropriate σ, π, u, g, an $+/-$ designations, what is the symmetry label of the following wave functions.**

21. **Number the states in the order in which they fill as one proceeds through the first-row diatomics.**

Energy Ordering	Orbital Symmetry Label	Molecular Orbital
1	σ_u^+	$\psi_{2s}^{(l)}(\boldsymbol{r}) - \psi_{2s}^{(r)}(\boldsymbol{r})$
2	π_u^+	$\psi_{2p_x}^{(l)}(\boldsymbol{r}) + \psi_{2p_x}^{(r)}(\boldsymbol{r})$
4	π_g^-	$\psi_{2p_y}^{(l)}(\boldsymbol{r}) - \psi_{2p_y}^{(r)}(\boldsymbol{r})$
3	σ_g^+	$\psi_{2p_z}^{(l)}(\boldsymbol{r}) - \psi_{2p_z}^{(r)}(\boldsymbol{r})$

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

  (a) x-direction.   **(b) y-direction**   (c) z-direction

23. **Which first-row homonuclear diatomics have non-singlet ground states?**

   B_2, O_2

24. **Suppose** Ψ_k **is the eigenfunction for a stationary state. We can write the time-dependent eigenfunction as**

$$\Psi_k\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N;t\right) \equiv \Phi_k\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N\right)\cdot\chi(t)$$

where $\Phi_k\left(\boldsymbol{r}_1,\ldots\boldsymbol{r}_N\right)$ **is an eigenfunction of the time-independent Schrödinger equation,**

$$\hat{H}\Phi_k\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N\right) = E_k\Phi_k\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N\right)$$

**What is** $\chi(t)$**?**

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

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

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}$$

26. **You're sitting in the lab trying to figure out why you don't observe any spectral lines corresponding to a transition between the two states your esteemed research advisor is interested in. You run down the hall to your friendly theoretician (that would be me) who provides you with a wave function for the initial state of your system,** Ψ_i **and the final state of your system,** Ψ_f**. If the transition you are seeking is "dipole forbidden", what integral will be zero? (You should not assume that the transition will necessarily be electronic—you can never tell, your advisor might be interested in vibrational transitions. So write the general formula.)**

$$\left\langle \Psi_f\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N;\boldsymbol{R}_1,\ldots,\boldsymbol{R}_P\right)\left|\sum_{i=1}^{N}-e\left(\tfrac{x_i+y_i+z_i}{3}\right)+\sum_{\alpha=1}^{P}Ze\left(\tfrac{X_i+Y_i+Z_i}{3}\right)\right|\Psi_i\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N;\boldsymbol{R}_1,\ldots,\boldsymbol{R}_P\right)\right\rangle$$

27. **The first excited state of** N_2 **is characterized by the excitation of an electron from a bonding to a non-bonding orbital. Sketch the absorption spectrum associated with this transition; label your axes.**
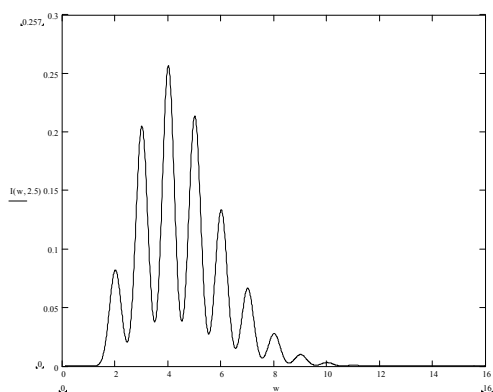
This is a plot of Intensity (= absorptivity) on the vertical axis and frequency on the horizontal axis.

28. **Two of the key approximations underlying Fermi's golden rule were the long wavelength and weak field approximations. Explain (words is OK) the physical meaning of each**

approximation, why it is appropriate, and why it was important to the derivation of Fermi's Golden Rule.

Long wavelength approximation: For small molecules, the wavelength of excitation (typically several hundred Angstroms even in the vacuum UV is much larger than the molecular size. Thence the field due to the light varies little over the extent of the molecule, and so it is reasonable to approximate the "effect" of the light on the molecule as an electric dipole oscillating in time. In particular, we find that quadrupole and magnetic dipole (as well as other higher-order electric and magnetic multipoles) are negligible under most circumstances, and this is a clear consequence of the long-wavelength approximation. The approximation can fail for large molecules or core electrons, but is almost always valid for valence electrons in small molecules.

weak field approximation: The electric and magnetic fields due to a light source are generally MUCH weaker than the fields exerted on electrons and nuclei by each other, with the consequence that we can use perturbation theory to describe the way the light couples to the molecule. In addition, higher order terms in the perturbation series are usually negligible, and so we do not see nonlinear effects (multi-photon processes). This greatly simplifies our expressions for the rate of transitions, since there is really one exceedingly dominant mechanism : absorption of a single quantum of "dipole radiation."

29. **For each type of broadening, there was a characteristic line shape. The width of the line was usually measured using the full-width at half-maximum, Γ, but it is sometimes more convenient to express results in terms of the half-width and half-maximum, $\gamma = \frac{\Gamma}{2}$. Corresponding to each of the following line shapes, write the formula for the lineshape and whether it is associated with inhomogeneous or homogeneous broadening. When you need a proportionality constant, use κ.**

Type of Line Shape	Formula for Line Shape	Type of Broadening
Gaussian	$\frac{\kappa_1}{\gamma} e^{-\kappa_2 \left(\frac{\omega - \omega_0}{\gamma}\right)^2}$	**Inhomogeneous**
Lorentzian	$\dfrac{\kappa \cdot \gamma}{\gamma^2 + (\omega - w_0)^2}$	**Homogeneous**

30. **When a molecule's spectrum is measured in solution, one sees diffusional broadening, which is due to the "jostling" of the solute by the solvent molecules. The model for this process is basically Brownian (random) motion, and we find that if the proportion of the molecules in state i at time zero was p_i, then at time t the number of molecules in this state is just $p_i e^{-2D_{rot}|t|}$,**

where D_{rot} is the rotational diffusion constant. **Which of the following line shapes is most likely to resemble the spectral lines of this system?**
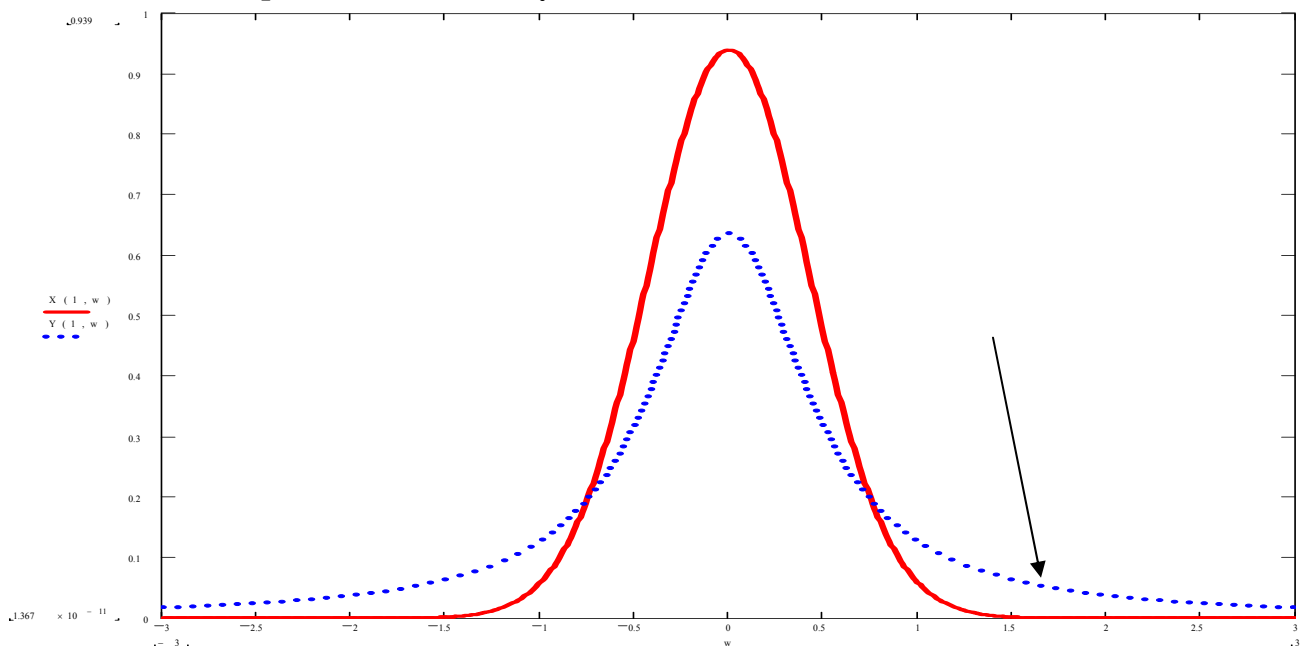
31. **Go back and look at figure 28. You do a "hole burning" experiment, wherein you tune a laser to the peak frequency and then measure the absorbance spectrum again. Draw what you expect to observe. You may assume (even though it is a bad assumption) that the only broadening mechanism that is active is the diffusional broadening discussed in problem 28.**
    Hole burning is an effective method for discerning inhomogeneous broadening—not homogeneous broadening. There is no effect, then, on a Lorentzian curve from "hole burning."

32. **A single Slater determinant is unlikely to be an acceptable wave function when**
    (a) static correlation is important.
    (b) dynamic correlation is important.

33. **Many-Body Perturbation theory is generally an inappropriate method for anions. In words (this can be *very* brief, I'm only looking for the "big idea"), describe why?**
    The perturbation series does not have a large enough "radius of convergence" to address the "real" system for anions. Consequently, many-body-perturbation-theoretic methods are of suspected reliability.

34. **We often call Hartree-Fock theory a "mean-field" or "independent-particle" theory. What do we mean by that?**
    In Hartree-Fock theory the electrons move in the "average" or "mean" field of the other electrons—that is, an electron moves based on where the other electrons USUALLY are, not where they ACTUALLY are. As such, there is no correlation.

35. The Ozone atom has a low-lying excited state that interacts strongly with the ground state Slater determinant. Which computational method(s) are inappropriate for this sort of system?

(a) Use a multi-reference configuration interaction calculation

(b) CCSDTQ

(c) CISD

(d) CISDTQ

(e) Hartree-Fock.

36. We defined one type of Dyson orbital (a.ka. Feynman-Dyson amplitude, generalized overlap amplitude, etc.) as

$$g_k\left(\boldsymbol{z}_{N-1}\right) \equiv \sqrt{N}\int\!\!\int\!\!\int \cdots \int \left(\Psi_k^{(N-1)}\left(\boldsymbol{z}_1,\ldots,\boldsymbol{z}_{N-1}\right)\right)^* \Psi_0^{(N)}\left(\boldsymbol{z}_1,\ldots,\boldsymbol{z}_N\right) d\boldsymbol{z}_1 \ldots d\boldsymbol{z}_{N-1}$$

What is the interpretation of this orbital?

When we take an electron away from the ground state of the N-electron system to form the kth-excited state of the cation, we take it out of $g_k\left(\boldsymbol{z}_N\right)$. That is, the Dyson orbitals are the exact orbitals from which electrons are taken during oxidation and to which they are added during reduction.

In the following problems, you can use the following definitions.

$$h_i \equiv \left\langle \psi_i \left|\hat{h}\right| \psi_i \right\rangle = \left\langle \psi_i \left|-\tfrac{\nabla^2}{2} + v(\boldsymbol{r})\right| \psi_i \right\rangle$$

$$J_{ij} \equiv \left\langle \psi_i\psi_j \left|\tfrac{1}{|r-r'|}\right| \psi_i\psi_j \right\rangle = \int\!\!\int \frac{|\psi_i(\boldsymbol{r})|^2|\psi_j(\boldsymbol{r}')|^2}{|r-r'|} d\boldsymbol{r}d\boldsymbol{r}'$$

37. The energy of the Slater determinant, $\left|\psi_1\psi_2 \ldots \psi_N\right|$ is

$$E = \sum_{i=1}^{N} h_i + \tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(J_{ij} - K_{ij}\right)$$

38. We defined the exchange potential for the system with Slater determinant $\left|\psi_1\psi_2 \ldots \psi_N\right|$ as:

$$\hat{k}(\boldsymbol{r})\,\psi_\alpha(\boldsymbol{r}) \equiv \sum_{i=1}^{N}\left(\delta_{\sigma_i\sigma_\alpha}\int \frac{\psi_i^*(\boldsymbol{r}')\psi_\alpha(\boldsymbol{r}')}{|r-r'|} d\boldsymbol{r}'\psi_i(\boldsymbol{r})\right)$$

39,40. For each of the following "key ideas" or equations, write whether it is associated with

CC = Coupled Cluster Calculations

CI = Configuration Interaction Calculations

DFT = Density-Functional Theory Calculations

GF = Green's Functions

HF = Hartree-Fock Calculations

MP = Moller-Plesset or Many-Body-Perturbation-Theory Calculations.

Name:

__ MP_____ Systematically correct the wave function and energy based on the difference between the true Hamiltonian and the Hartree-Fock Hamiltonian, $\hat{F} \equiv \sum\limits_{i=1}^{N} \hat{f}(\boldsymbol{r}_i)$.

___GF____ Find exact orbitals and energies associated with removing an electron from the system.

___DFT____ Given the ground-state electron density, the wave function can be determined.

___CI____ Write the wave function for the system as a linear combination of the eigenfunctions of the Hartree-Fock Hamiltonian, $\hat{F}$. Optimize the coefficients using the variational principle.

___CC____ Assume that, in any group of k-electrons, no more than $(k-2)$ are moving together in a correlated way.

___GF____ Find the function that, when operated on by , gives back a delta function.

___CI____ $\Psi \approx c_0 \Phi_0 + \sum\limits_{i=1}^{N} \sum\limits_{a=N+1}^{K} c_i^a \Phi_i^a + \sum\limits_{i>j=1}^{N} \sum\limits_{a>b=N+1}^{K} c_{ij}^{ab} \Phi_{ij}^{ab}$

___HF____ Find the Slater determinant with the lowest energy.

Closed Book Problems

1. **Derive the Born-Oppenheimer Approximation:**

(a) **Write the full Schrödinger equation, for both the nuclei and the electrons, for the Hydrogen Molecule Ion, H_2^+ .**

$$\left(-\frac{\nabla_A^2}{2m_p} - \frac{\nabla_B^2}{2m_p} - \frac{\nabla_r^2}{2} - \frac{1}{|r-R_A|} - \frac{1}{|r-R_B|} + \frac{1}{|R_A-R_B|}\right)\Psi_k\left(r,R_A,R_B\right) = E_k^{exact}\Psi_k\left(r,R_A,R_B\right) \quad \text{(C-1-A)}$$

(b) **Derive the electronic and nuclear Schrödinger equations in the Born-Oppenheimer approximation. Indicate each approximation you make. Discuss its validity in a sentence or so.**

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:

$$\Psi_{k\nu}\left(r,R_A,R_B\right) = \psi_k\left(r;R_A,R_B\right)\chi_{k\nu}\left(R_A,R_B\right) \quad \text{(C-1-B)}$$

We substitute into Eq. (C-1-A) and use the identity

$$\nabla_A^2\psi\left(r;R_A,R_B\right)\chi\left(R_A,R_B\right) = \chi\left(R_A,R_B\right)\nabla_A^2\psi\left(r;R_A,R_B\right) + \psi\left(r;R_A,R_B\right)\nabla_A^2\chi\left(R_A,R_B\right)$$
$$+2\nabla_A\psi\left(r;R_A,R_B\right)\cdot\nabla_A\chi\left(R_A,R_B\right) \quad \text{(C-1-C)}$$

to obtain

$$\left(-\frac{\nabla_A^2}{2m_p} - \frac{\nabla_B^2}{2m_p} - \frac{\nabla_r^2}{2} - \frac{1}{|r-R_A|} - \frac{1}{|r-R_B|} + \frac{1}{|R_A-R_B|}\right)\psi_k\left(r;R_A,R_B\right)\chi_{k\nu}\left(R_A,R_B\right)$$
$$= E_{k\nu}^{exact}\psi_k\left(r;R_A,R_B\right)\chi_{k\nu}\left(R_A,R_B\right)$$

$$\left(-\frac{\nabla_A^2}{2m_p} - \frac{\nabla_B^2}{2m_p}\right)\psi_k\left(r;R_A,R_B\right)\chi_{k\nu}\left(R_A,R_B\right)$$
$$+\left(-\frac{\nabla_r^2}{2} - \frac{1}{|r-R_A|} - \frac{1}{|r-R_B|} + \frac{1}{|R_A-R_B|}\right)\psi_k\left(r;R_A,R_B\right)\chi_{k\nu}\left(R_A,R_B\right)$$
$$= E_{k\nu}^{exact}\psi_k\left(r;R_A,R_B\right)\chi_{k\nu}\left(R_A,R_B\right)$$

$$\left(\frac{-1}{2m_p}\right)\begin{vmatrix}\chi_{k\nu}\left(R_A,R_B\right)\nabla_A^2\psi_k\left(r;R_A,R_B\right) + \psi_k\left(r;R_A,R_B\right)\nabla_A^2\chi_{k\nu}\left(R_A,R_B\right) \\ +2\nabla_A\psi_k\left(r;R_A,R_B\right)\cdot\nabla_A\chi_{k\nu}\left(R_A,R_B\right) + \chi_{k\nu}\left(R_A,R_B\right)\nabla_B^2\psi_k\left(r;R_A,R_B\right) \\ +\psi_k\left(r;R_A,R_B\right)\nabla_B^2\chi_{k\nu}\left(R_A,R_B\right) + 2\nabla_B\psi_k\left(r;R_A,R_B\right)\cdot\nabla_B\chi_{k\nu}\left(R_A,R_B\right)\end{vmatrix}$$
$$+\chi_{k\nu}\left(R_A,R_B\right)\left(-\frac{\nabla_r^2}{2} - \frac{1}{|r-R_A|} - \frac{1}{|r-R_B|} + \frac{1}{|R_A-R_B|}\right)\psi_k\left(r;R_A,R_B\right)$$
$$= E_{k\nu}^{exact}\psi_k\left(r;R_A,R_B\right)\chi_{k\nu}\left(R_A,R_B\right)$$

$$\psi_k\left(r;R_A,R_B\right)\left(\frac{-\nabla_A^2}{2m_p} - \frac{-\nabla_A^2}{2m_p}\right)\chi_{k\nu}\left(R_A,R_B\right)$$
$$-\frac{\nabla_A\psi_k(r;R_A,R_B)\cdot\nabla_A\chi_{k\nu}(R_A,R_B)}{m_p} - \frac{\nabla_B\psi_k(r;R_A,R_B)\cdot\nabla_B\chi_{k\nu}(R_A,R_B)}{m_p} + \chi_{k\nu}\left(R_A,R_B\right)\left(\frac{-\nabla_A^2}{2m_p} - \frac{-\nabla_A^2}{2m_p}\right)\psi_k\left(r;R_A,R_B\right)$$
$$+\chi_{k\nu}\left(R_A,R_B\right)\left(-\frac{\nabla_r^2}{2} - \frac{1}{|r-R_A|} - \frac{1}{|r-R_B|} + \frac{1}{|R_A-R_B|}\right)\psi_k\left(r;R_A,R_B\right)$$
$$= E_{k\nu}^{exact}\psi_k\left(r;R_A,R_B\right)\chi_{k\nu}\left(R_A,R_B\right) \quad \text{(C-1-D)}$$

Name:

We note that because the mass of the proton is much larger (almost 2000 times larger!) than the mass of the electron, the terms on the second line in the last equation of derivation (C-1-D) are quite small compared to those on the third line. We set these 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

$$\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right)\left(\frac{-\nabla_A^2}{2m_p}-\frac{-\nabla_A^2}{2m_p}\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)+\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)\left(\begin{array}{c}-\frac{\nabla_r^2}{2}-\frac{1}{|r-\boldsymbol{R}_A|}\\ -\frac{1}{|r-\boldsymbol{R}_B|}+\frac{1}{|\boldsymbol{R}_A-\boldsymbol{R}_B|}\end{array}\right)\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right) \quad \text{(C-1-E)}$$
$$=E_{k\nu}^{BO}\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)$$

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

$$\left(\begin{array}{c}-\frac{\nabla_r^2}{2}-\frac{1}{|r-\boldsymbol{R}_A|}\\ -\frac{1}{|r-\boldsymbol{R}_B|}+\frac{1}{|\boldsymbol{R}_A-\boldsymbol{R}_B|}\end{array}\right)\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right)\equiv U_k^{BO}\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right) \quad \text{(C-1-F)}$$

and substitute this result into Eq. (C-1-E), obtaining the nuclear Schrödinger equation

$$\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right)\left(\frac{-\nabla_A^2}{2m_p}-\frac{-\nabla_A^2}{2m_p}\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)+\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)U_k^{BO}\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right)$$
$$=E_{k\nu}^{BO}\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)$$
$$\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right)\left(\frac{-\nabla_A^2}{2m_p}-\frac{-\nabla_A^2}{2m_p}+U_k^{BO}\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)=E_{k\nu}^{BO}\psi_k\left(\boldsymbol{r};\boldsymbol{R}_A,\boldsymbol{R}_B\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right) \quad \text{(C-1-G)}$$
$$\left(\frac{-\nabla_A^2}{2m_p}-\frac{-\nabla_A^2}{2m_p}+U_k^{BO}\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\right)\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)=E_{k\nu}^{BO}\chi_{k\nu}\left(\boldsymbol{R}_A,\boldsymbol{R}_B\right)$$

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

Name:

2. **Derive the Hellmann-Feynman Theorem.**

Let Ψ_k be a normalized eigenfunction of the Hamiltonian, $\hat{H}$. The Hellmann-Feynman Theorem indicates that we can express the way the energy changes as we change a parameter on which the Hamilotian depends in an especially simple form,

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

This question asks that you derive this form.

We derive (using τ to denote the coordinate dependence of the wave function and the Hamiltonian)

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

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

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

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

$$= \int \left(\begin{array}{c} \frac{\partial \Psi_k^*(\lambda,\tau)}{\partial \lambda} \left(E_k(\lambda) \Psi_k(\lambda,\tau) \right) \\ + \Psi_k^*(\lambda,\tau) \frac{\partial \hat{H}(\lambda,\tau)}{\partial \lambda} \left(\Psi_k(\lambda,\tau) \right) \\ + \left(E_k(\lambda) \Psi_k(\lambda,\tau) \right)^* \frac{\partial \Psi_k(\lambda,\tau)}{\partial \lambda} \end{array} \right) d\tau \qquad \text{(C-2-A)}$$

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

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

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

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

This last form is the Hellmann-Feynman theorem.

Name:

3. **Consider a state of the one-electron atom with atomic number Z and principle quantum number n. Assume that l takes on its maximum permissible value for the given value of n. At what distance from the nucleus are you most likely to observe the electron? (Note that you do not need the normalization constant to work this problem.)**

For the maximum permissible value of the orbital angular momentum quantum number, $l = n - 1$, the wave function of the one-electron atom is

$$\psi_{n,l=n-1,m}(\boldsymbol{r}) \propto r^{n-1} e^{-Zr/n} Y_{n-1}^m(\theta, \phi) \tag{C-3-A}$$

The probability that an electron is R units from the nucleus is then

$$
\begin{aligned}
P(R) &= \int \psi_{n,n-1,m}^*(\boldsymbol{r}) \delta(r - R) \psi_{n,n-1,m}(\boldsymbol{r}) d\boldsymbol{r} \\
&\propto \int_0^\infty \int_0^\pi \int_0^{2\pi} \left| r^{n-1} e^{-Zr/n} Y_{n-1}^m(\theta, \phi) \right|^2 \delta(r - R) r^2 \sin\theta \, dr \, d\theta \, d\phi \\
&\propto \int_0^\infty r^{2n-2} e^{-2Zr/n} r^2 \delta(r - R) \, dr \left(\int_0^\pi \int_0^{2\pi} \left| Y_{n-1}^m(\theta, \phi) \right|^2 \sin\theta \, d\theta \, d\phi \right) \\
&\propto R^{2n} e^{-2ZR/n} \quad (1).
\end{aligned}
\tag{C-3-B}
$$

To find the most probable distance from the nucleus for an electron, we differentiate, so

$$
\begin{aligned}
0 &= \frac{dP}{dR} \\
&= \frac{d\left(R^{2n} e^{-2ZR/n} \right)}{dR} \\
&= 2nR^{2n-1} e^{-2ZR/n} - R^{2n} \left(\frac{-2Z}{n} \right) e^{-2ZR/n} \\
&= 2R^{2n-1} e^{-2ZR} \left(n - \frac{ZR}{n} \right)
\end{aligned}
\tag{C-3-C}
$$

and so

$$R = \frac{n^2}{Z}. \tag{C-3-D}$$

Name:

4.

(a) Write the Simple Linear-Combination of 1s-orbitals wave function for the Hydrogen Molecule.

(b) Write the Simple "Heitler-London" Valence Bond wave function for the Hydrogen Molecule.

(c) Show that the "Valence Bond + Ionic Terms" and the "Molecular Orbital Plus Configuration Interaction" are equivalent.

(a)

$$\Psi_{LCAO}^{MO}\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) \propto \left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\right)\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)\right)\left(\alpha\left(1\right)\beta\left(2\right) - \alpha\left(2\right)\beta\left(1\right)\right) \qquad \text{(C-4-A)}$$

(b)

$$\Psi_{HL}^{VB}\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) = \left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\right)\left(\alpha\left(1\right)\beta\left(2\right) - \alpha\left(2\right)\beta\left(1\right)\right) \qquad \text{(C-4-B)}$$

(c)   Let's start with the configuration-interaction wave function, which we write as:

$$\Psi^{MO+CI}\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) \propto \begin{bmatrix} \left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\right)\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)\right) \\ + \kappa\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right) - \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\right)\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) - \psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)\right) \end{bmatrix}\left(\alpha\left(1\right)\beta\left(2\right) - \alpha\left(2\right)\beta\left(1\right)\right) \text{ (C-4-C)}$$

We note that the "spin" part of the wave function is the same for any two-electron singlet state, so we do not need to keep track of it any longer. Multiplying out the terms, we obtain

$$\Psi^{MO+CI}\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) \propto \begin{bmatrix} \left(1+\kappa\right)\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) + \left(1-\kappa\right)\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right) \\ + \left(1-\kappa\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) + \left(1+\kappa\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right) \end{bmatrix}$$

$$\propto \left(1-\kappa\right)\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right)\right)$$

$$\left(1+\kappa\right)\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)\right) \qquad \text{(C-4-D)}$$

$$\propto \left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right)\right) + \frac{1+\kappa}{1-\kappa}\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)\right)$$

$$\propto \Psi_{HL}^{VB}\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) + \left(\text{ionic term}\right)$$

5.   **Refer to the following *partial* table of microstates for the $3d^2$ configuration:**

M_S/M_L	4	3	2	1	0
1	0	$\left\|\psi_{3d_2}\alpha\ \psi_{3d_1}\alpha\right\|$	$\left\|\psi_{3d_2}\alpha\ \psi_{3d_0}\alpha\right\|$	$\left(\begin{array}{l}\left\|\psi_{3d_1}\alpha\ \psi_{3d_0}\alpha\right\|\\ \left\|\psi_{3d_2}\alpha\ \psi_{3d_{-1}}\alpha\right\|\end{array}\right)$	$\left(\begin{array}{l}\left\|\psi_{3d_1}\alpha\ \psi_{3d_{-1}}\alpha\right\|\\ \left\|\psi_{3d_2}\alpha\ \psi_{3d_{-2}}\alpha\right\|\end{array}\right)$
0	$\left\|\psi_{3d_2}\alpha\ \psi_{3d_2}\beta\right\|$	$\left(\begin{array}{l}\left\|\psi_{3d_2}\alpha\ \psi_{3d_1}\beta\right\|\\ \left\|\psi_{3d_2}\beta\ \psi_{3d_1}\alpha\right\|\end{array}\right)$	$\left(\begin{array}{l}\left\|\psi_{3d_2}\alpha\ \psi_{3d_0}\beta\right\|\\ \left\|\psi_{3d_2}\beta\ \psi_{3d_0}\alpha\right\|\\ \left\|\psi_{3d_1}\beta\ \psi_{3d_1}\alpha\right\|\end{array}\right)$	$\left(\begin{array}{l}\left\|\psi_{3d_1}\alpha\ \psi_{3d_0}\beta\right\|\\ \left\|\psi_{3d_1}\beta\ \psi_{3d_0}\alpha\right\|\\ \left\|\psi_{3d_2}\alpha\ \psi_{3d_{-1}}\beta\right\|\\ \left\|\psi_{3d_2}\beta\ \psi_{3d_{-1}}\alpha\right\|\end{array}\right)$	$\left(\begin{array}{l}\left\|\psi_{3d_1}\alpha\ \psi_{3d_{-1}}\beta\right\|\\ \left\|\psi_{3d_1}\beta\ \psi_{3d_{-1}}\alpha\right\|\\ \left\|\psi_{3d_2}\alpha\ \psi_{3d_{-2}}\beta\right\|\\ \left\|\psi_{3d_2}\beta\ \psi_{3d_{-2}}\alpha\right\|\\ \left\|\psi_{3d_0}\alpha\ \psi_{3d_0}\beta\right\|\end{array}\right)$

(a) What terms are associated with this configuration? (You do not need to list the *J* values.)

$^3F, {}^3P, {}^1G, {}^1D, {}^1S$

(b) What is the ground-state term? (Specify the appropriate *J* value.)

$^3F_2 \qquad J = (3+1) = 4, \ldots, |3-1| = 2$

(c) For what values of M_L and can we find a single Slater determinant that is an eigenfunction of $\hat{L}^2$ and $\hat{S}^2$?

There is only a single Slater determinant for the following values of (M_L, M_S) listed in the table: $(M_L, M_S) = (4,0);(3,1);(2,1)$. However, there are other values not listed in the table, which are related by symmetry. Notably, we have

$$(M_L, M_S) = \begin{cases} (4,0);(-4,0) \\ (3,1);(-3,1);(3,-1);(-3,-1) \\ (2,1);(-2,1);(2,-1);(-2,-1) \end{cases} \qquad\qquad \text{(C-5-A)}$$

Name:

6. **In deriving the exponential decay of the Hydrogen atom we used the general result that the long-range decay of a system's wave function was given by** $\psi(\boldsymbol{r}) \sim e^{-\left(\sqrt{2IP}\right)r}$ **where IP is the ionization potential of the system. Just as we did in class (and in the notes), substitute this wave function into the radial Schrödinger equation,**

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} - \frac{Z}{r}\right)R_{n,l}(r) = ER_{n,l}(r), \tag{2}$$

to derive the ionization potential for the ground state of the hydrogen atom. Remember that for a one-electron system, $-IP$ is equal to the energy of the system.

We substitute the approximate form of the wave function into Eq. (2), remembering that $l = 0$ for the ground state:

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{0(0+1)}{2r^2} - \frac{Z}{r}\right)e^{-\sqrt{2IP}r} = -(IP)e^{-\sqrt{2IP}r}$$

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial e^{-\sqrt{2IP}r}}{\partial r} + 0 \cdot e^{-\sqrt{2IP}r} - \frac{Z}{r}e^{-\sqrt{2IP}r}\right) = -(IP)e^{-\sqrt{2IP}r}$$

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\left(-\sqrt{2IP}\right)e^{-\sqrt{2IP}r}\right) - \frac{Z}{r}e^{-\sqrt{2IP}r}\right) = -(IP)e^{-\sqrt{2IP}r}$$

$$\left(-\frac{1}{2r^2}\left(2r\left(-\sqrt{2IP}\right)e^{-\sqrt{2IP}r} + r^2\left(-\sqrt{2IP}\right)\left(-\sqrt{2IP}\right)e^{-\sqrt{2IP}r}\right) - \frac{Z}{r}e^{-\sqrt{2IP}r}\right) = -(IP)e^{-\sqrt{2IP}r} \tag{C-6-A}$$

$$\left(\frac{\sqrt{2IP}}{r}\right)e^{-\sqrt{2IP}r} - \frac{1}{2}(2IP)e^{-\sqrt{2IP}r} - \frac{Z}{r}e^{-\sqrt{2IP}r} = -(IP)e^{-\sqrt{2IP}r}$$

$$\left(\frac{\sqrt{2IP}}{r}\right)e^{-\sqrt{2IP}r} - \frac{Z}{r}e^{-\sqrt{2IP}r} - (IP)e^{-\sqrt{2IP}r} = -(IP)e^{-\sqrt{2IP}r}$$

$$\left(\frac{\sqrt{2IP}}{r} - \frac{Z}{r}\right)e^{-\sqrt{2IP}r} = 0$$

From this result, we see that

$$\sqrt{2IP} - Z = 0$$
$$\sqrt{2IP} = Z \tag{C-6-B}$$
$$IP = \frac{Z^2}{2}.$$

which is the right result for the Hydrogen atom.

7. Derive Koopmans' theorem for electron removal from a Hartree-Fock determinant.
    For a Slater determinant, $|\psi_1 \dots \psi_N|$, the energy formula is

$$E = \sum_{i=1}^{N} h_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(J_{ij} - K_{ij}\right) \tag{C-7-A}$$

and the orbital energy of the αth orbital is

$$\varepsilon_\alpha = h_\alpha + \sum_{i=1}^{N}\left(J_{i\alpha} - K_{i\alpha}\right)$$

(a) Derive an expression for the change in energy between the neutral system (modeled with the Slater determinant $|\psi_1 \dots \psi_N|$) and the cation modeled by removing the last orbital, ψ_N from the Slater determinant to form the $N-1$ electron state, $|\psi_1 \dots \psi_{N-1}|$. Write the expression you obtain in terms of the orbital energy for the Nth orbital.

The energy of the cation is very similar to the expression for the "neutral" species in Eq. (C-7-A), except now the last orbital is not occupied, so it doesn't enter into the sum. This gives the expression for the energy of $|\psi_1 \dots \psi_{N-1}|$ to be

$$E^+ \equiv \sum_{i=1}^{N-1} h_i + \frac{1}{2}\sum_{i=1}^{N-1}\sum_{j=1}^{N-1}\left(J_{ij} - K_{ij}\right) \tag{C-7-B}$$

and subtracting off Eq. (C-7-A) we get

$$
\begin{aligned}
E^+ - E &\equiv \left(\sum_{i=1}^{N-1} h_i + \frac{1}{2}\sum_{i=1}^{N-1}\sum_{j=1}^{N-1}\left(J_{ij} - K_{ij}\right)\right) - \left(\sum_{i=1}^{N} h_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(J_{ij} - K_{ij}\right)\right) \\
&= \left(\sum_{i=1}^{N-1} h_i + \frac{1}{2}\sum_{i=1}^{N-1}\sum_{j=1}^{N-1}\left(J_{ij} - K_{ij}\right)\right) \\
&\quad - \left(\begin{array}{l}\sum_{i=1}^{N-1} h_i + h_N + \frac{1}{2}\sum_{i=1}^{N-1}\sum_{j=1}^{N-1}\left(J_{ij} - K_{ij}\right) \\ + \frac{1}{2}\sum_{j=1}^{N}\left(J_{Nj} - K_{jN}\right) + \sum_{i=1}^{N}\left(J_{iN} - K_{Ni}\right)\end{array}\right) \\
&= -\left(h_N + \frac{1}{2}\sum_{j=1}^{N}\left(J_{Nj} - K_{jN}\right) + \sum_{i=1}^{N}\left(J_{Ni} - K_{iN}\right)\right) \\
&= -\left(h_N + \sum_{j=1}^{N}\left(J_{Nj} - K_{jN}\right)\right) \\
&= -\varepsilon_N
\end{aligned}
\tag{C-7-C}
$$

Name:

(b)　We said Koopmans' theorem neglects orbital relaxation effects. What does this mean?

The orbitals for the neutral species are solutions of the Hartree-Fock equations,

$$\left[\left(\frac{-\nabla^2}{2}+v(\boldsymbol{r})\right)\psi_\alpha(\boldsymbol{r})+\sum_{i=1}^{N}\left[\begin{array}{c}\int\frac{\psi_i^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\times\psi_\alpha(\boldsymbol{r})\\-\delta_{\sigma_i\sigma_\alpha}\int\frac{\psi_i^*(\boldsymbol{r}')\psi_\alpha(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\times\psi_i(\boldsymbol{r})\end{array}\right]\right]=\varepsilon_\alpha\psi_\alpha(\boldsymbol{r}) \quad\text{(C-7-D)}$$

$$\hat{f}_N(\boldsymbol{r})\psi_\alpha(\boldsymbol{r})=\varepsilon_\alpha\psi_\alpha(\boldsymbol{r})$$

but the orbitals we are using to describe the cation are not solutions to the Hartree-Fock equations for the cation, because we are using the same orbitals as we used to describe the neutral system, yet the summation in the Fock operator for the cation doesn't include the Nth orbital:

$$\left[\left(\frac{-\nabla^2}{2}+v(\boldsymbol{r})\right)\psi_\alpha(\boldsymbol{r})+\sum_{i=1}^{N-1}\left[\begin{array}{c}\int\frac{\psi_i^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\times\psi_\alpha(\boldsymbol{r})\\-\delta_{\sigma_i\sigma_\alpha}\int\frac{\psi_i^*(\boldsymbol{r}')\psi_\alpha(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\times\psi_i(\boldsymbol{r})\end{array}\right]\right.$$
$$\left.+\left(\begin{array}{c}\int\frac{\psi_N^*(\boldsymbol{r}')\psi_N(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\times\psi_\alpha(\boldsymbol{r})\\-\delta_{\sigma_N\sigma_\alpha}\int\frac{\psi_N^*(\boldsymbol{r}')\psi_\alpha(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\times\psi_N(\boldsymbol{r})\end{array}\right)\right]=\varepsilon_\alpha\psi_\alpha(\boldsymbol{r}) \quad\text{(C-7-E)}$$

$$\hat{f}_{N-1}(\boldsymbol{r})\psi_\alpha(\boldsymbol{r})=\varepsilon_\alpha\psi_\alpha(\boldsymbol{r})-\left(\begin{array}{c}\int\frac{\psi_N^*(\boldsymbol{r}')\psi_N(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\times\psi_\alpha(\boldsymbol{r})\\-\delta_{\sigma_N\sigma_\alpha}\int\frac{\psi_N^*(\boldsymbol{r}')\psi_\alpha(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\times\psi_N(\boldsymbol{r})\end{array}\right)$$

That is, the orbitals we are using to describe the cation are not the Hartree-Fock orbitals for the cation. The effect we are neglecting is orbital relaxation: when we remove an electron from the Nth orbital, we "hollow out" the molecule's electron density in the vicinity of this electron, and so there is an "attraction" for the "remaining" electrons to the regions where the ionized electron came from. As a consequence, the orbitals that are occupied in the cation "relax" away from their form in the neutral system.

(c)*　Remember Parr's rule: the correlation energy is approximately 1 electron-volt per valence electron pair. Make an argument that cancellation of errors means Koopmans' theorem

provides a better-than-otherwise-expected description of ionization processes. Would the same argument hold when we add an electron to the system to form an anion?

There are two main approximations in Koopmans' theorem, the neglect of electron correlation (which is inherent in the Hartree-Fock approximation) and the neglect of orbital relaxation. Because the amount of electron correlation increases as the number of electron increases, we have that the correlation energy, $E_c = E_{HF} - E_{exact}$, of the neutral system is greater than that of the cation, so

$$E_{HF}^+ - E_{exact}^+ < E_{HF}^{neutral} - E_{exact}^{neutral} \tag{C-7-F}$$

and so the "Hartree-Fock" ionization potential is less than the true one.

$$IP_{HF} \equiv E_{HF}^+ - E_{HF}^{neutral} < E_{exact}^+ - E_{exact}^{neutral} \equiv IP_{exact} \tag{C-7-G}$$

Now, the Hartree-Fock energy of the cation is less than that obtained by simply removing an orbital from the neutral system (a la Koopmans' theorem), so

$$E_{HF}^+ < E_{Koopmans'}^+ \tag{C-7-H}$$

Consequently, we have that

$$IP_{HF} \equiv E_{HF}^+ - E_{HF}^{neutral} < E_{Koopmans'}^+ - E_{HF}^{neutral} = -\varepsilon_N \tag{C-7-I}$$

and because the orbital relaxtion error and the correlation error have opposite sign, we expect that the Koopmans' theorem approximation will be "better than expected"—the errors in these two approximations tend to cancel out.

This cannot be said for anions, because for an anion, the correlation energy is larger than it is for the neutral,

$$E_{HF}^- - E_{exact}^- > E_{HF}^{neutral} - E_{exact}^{neutral}, \tag{C-7-J}$$

so that the correlation energy error and orbital relaxation tend to add. As a consequence, we find Koopmans' theorem is especially bad for anions.

Name:

"Thinking" Problems

1. Hypervirial Theorem. (Twenty points)

(a) Let $\hat{A}$ be a Hermitian operator that does not change with respect to time. $H(\boldsymbol{\tau},t)$ is the Hamiltonian for the system and $\Psi(\boldsymbol{\tau},t)$ is the wave function for the system.

Show that the rate of change in the expectation value of $\hat{A}$ is then given by the formula

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

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

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

Note that the form $\Psi(\boldsymbol{\tau},t)=\psi(\boldsymbol{\tau})e^{-iEt/\hbar}$ is **only** true for time-dependent Hamiltonians, as will be obvious from the derivation (see the notes on spectroscopy or any good quantum book). If you write $\Psi(\boldsymbol{\tau},t)=\psi(\boldsymbol{\tau})e^{-i\hat{H}(\boldsymbol{\tau},t)t/\hbar}$ 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.

On partial credit: I gave partial credit to those who knew that the time-dependent Schrödinger equation was the key and could not figure out how to use it and also to those who used the ansatz $\Psi(\boldsymbol{\tau},t)=\psi(\boldsymbol{\tau})e^{-iEt/\hbar}$, because they did get the right result and the analysis is, after all, very similar to that for the Heisenberg form.

To the derivation:

$$\frac{d\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle}{dt} = \left\langle \frac{\partial\Psi(\boldsymbol{\tau};t)}{\partial t}\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle + \left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\frac{\partial\Psi(\boldsymbol{\tau};t)}{\partial t}\right\rangle$$
$$+ \left\langle \Psi(\boldsymbol{\tau};t)\left|\frac{\partial\hat{A}(\boldsymbol{\tau})}{\partial t}\right|\Psi(\boldsymbol{\tau};t)\right\rangle \tag{T-1-B}$$

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

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

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

and take the complex conjugate, which shows that

Name:

$$\frac{\partial \Psi^*(\boldsymbol{\tau},t)}{\partial t} = \left(\frac{-i}{\hbar}\hat{H}(\boldsymbol{\tau},t)\Psi(\boldsymbol{\tau},t)\right)^*$$
$$= \left(\frac{-i}{\hbar}\right)^*\left(\hat{H}(\boldsymbol{\tau},t)\Psi(\boldsymbol{\tau},t)\right)^* \qquad \text{(T-1-D)}$$
$$= \frac{i}{\hbar}\left(\hat{H}(\boldsymbol{\tau},t)\Psi(\boldsymbol{\tau},t)\right)^*$$

and substitute Eq. (T-1-D) for the first term and Eq. (T-1-C) for the second term in Eq. (T-1-B). so that

$$\frac{d\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle}{dt} = \left\langle \frac{\partial \Psi(\boldsymbol{\tau};t)}{\partial t}\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle + \left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\frac{\partial \Psi(\boldsymbol{\tau};t)}{\partial t}\right\rangle$$
$$= \frac{i}{\hbar}\left\langle \hat{H}(\boldsymbol{\tau};t)\Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle \qquad \text{(T-1-E)}$$
$$- \frac{i}{\hbar}\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\hat{H}(\boldsymbol{\tau};t)\Psi(\boldsymbol{\tau};t)\right\rangle.$$

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

$$\frac{d\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle}{dt} = \frac{i}{\hbar}\left\langle \hat{H}(\boldsymbol{\tau};t)\Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle$$
$$- \frac{i}{\hbar}\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\right|\hat{H}(\boldsymbol{\tau};t)\Psi(\boldsymbol{\tau};t)\right\rangle$$
$$= \frac{i}{\hbar}\left[\begin{array}{c}\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{H}(\boldsymbol{\tau};t)\hat{A}(\boldsymbol{\tau})\right|\Psi(\boldsymbol{\tau};t)\right\rangle \\ -\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{A}(\boldsymbol{\tau})\hat{H}(\boldsymbol{\tau};t)\right|\Psi(\boldsymbol{\tau};t)\right\rangle\end{array}\right] \qquad \text{(T-1-F)}$$
$$= \frac{i}{\hbar}\left\langle \Psi(\boldsymbol{\tau};t)\left|\hat{H}(\boldsymbol{\tau};t)\hat{A}(\boldsymbol{\tau}) - \hat{A}(\boldsymbol{\tau})\hat{H}(\boldsymbol{\tau};t)\right|\Psi(\boldsymbol{\tau};t)\right\rangle$$
$$= \frac{i}{\hbar}\left\langle \Psi(\boldsymbol{\tau};t)\left|\left[\hat{H}(\boldsymbol{\tau};t),\hat{A}(\boldsymbol{\tau})\right]\right|\Psi(\boldsymbol{\tau};t)\right\rangle$$

Name:

(b) **Suppose the Hamiltonian of the system does not depend on the time. Show that then**

$$\left\langle \Psi\left(\boldsymbol{\tau};t\right)\left|\left[\hat{H},\hat{A}\right]\right|\Psi\left(\boldsymbol{\tau};t\right)\right\rangle = 0\,.$$

This is called Hirshfelder's hypervirial theorem. What does this say about the properties of "stationary" states?

This is "yet another" exercise in the properties of Hermitian operators and using the fact that, for a Hamiltonian that does not depend on time, the time-independent Schrödinger equation can be used, namely

$$\hat{H}\left(\boldsymbol{\tau}\right)\Psi\left(\boldsymbol{\tau},t\right) = E\Psi\left(\boldsymbol{\tau},t\right).\tag{T-1-G}$$

So

$$
\begin{aligned}
\left\langle \Psi\left(\boldsymbol{\tau};t\right)\left|\left[\hat{H},\hat{A}\right]\right|\Psi\left(\boldsymbol{\tau};t\right)\right\rangle &= \left\langle \Psi\left(\boldsymbol{\tau};t\right)\left|\hat{H}\hat{A}-\hat{A}\hat{H}\right|\Psi\left(\boldsymbol{\tau};t\right)\right\rangle \\
&= \left\langle \Psi\left(\boldsymbol{\tau};t\right)\left|\hat{H}\hat{A}\right|\Psi\left(\boldsymbol{\tau};t\right)\right\rangle - \left\langle \Psi\left(\boldsymbol{\tau};t\right)\left|\hat{A}\hat{H}\right|\Psi\left(\boldsymbol{\tau};t\right)\right\rangle \\
&= \left\langle \hat{H}\Psi\left(\boldsymbol{\tau};t\right)\left|\hat{A}\right|\Psi\left(\boldsymbol{\tau};t\right)\right\rangle - \left\langle \Psi\left(\boldsymbol{\tau};t\right)\left|\hat{A}\right|\hat{H}\Psi\left(\boldsymbol{\tau};t\right)\right\rangle \\
&= \left\langle E\Psi\left(\boldsymbol{\tau};t\right)\left|\hat{A}\right|\Psi\left(\boldsymbol{\tau};t\right)\right\rangle - \left\langle \Psi\left(\boldsymbol{\tau};t\right)\left|\hat{A}\right|E\Psi\left(\boldsymbol{\tau};t\right)\right\rangle \qquad \text{(T-1-H)} \\
&= E\left(\left\langle \Psi\left(\boldsymbol{\tau};t\right)\left|\hat{A}\right|\Psi\left(\boldsymbol{\tau};t\right)\right\rangle - \left\langle \Psi\left(\boldsymbol{\tau};t\right)\left|\hat{A}\right|\Psi\left(\boldsymbol{\tau};t\right)\right\rangle\right) \\
&= E\cdot 0 \\
&= 0.
\end{aligned}
$$

This indicates that if $\Psi\left(\boldsymbol{\tau},t\right)$ is an eigenfunction of a time-dependent Hamiltonian, then the values of properties do not change. Simply stated: the properties of "stationary states" of time-independent systems do not change—that's why they're called stationary states!!

Name:

(c) Let $\hat{A} \equiv \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \hat{\boldsymbol{p}}_i = \sum_{i=1}^{N} \boldsymbol{r}_i \cdot (-i\hbar) \nabla_i$. **Using the fact that** $\left[\hat{H}, \boldsymbol{r}_i\right] \equiv \dfrac{-i\hbar}{m_e} \hat{\boldsymbol{p}}_i$ **and** $\left[\hat{H}, \hat{\boldsymbol{p}}_i\right] = i\hbar \nabla_i V(\boldsymbol{\tau})$ **to derive**

$$\left\langle \Psi \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i V \right| \Psi \right\rangle = 2 \left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle$$

The Hamiltonian is given by $\hat{H} = \hat{T} + \hat{V}$

This problem uses the identity $\left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right]$. In particular, substituting $\hat{A} \equiv \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \hat{\boldsymbol{p}}_i$ into the hypervirial theorem, we have

$$
\begin{aligned}
0 &= \left\langle \Psi(\boldsymbol{\tau};t) \left| \left[\hat{H}, \hat{A}\right] \right| \Psi(\boldsymbol{\tau};t) \right\rangle \\
&= \left\langle \Psi(\boldsymbol{\tau};t) \left| \left[\hat{H}, \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \hat{\boldsymbol{p}}_i \right] \right| \Psi(\boldsymbol{\tau};t) \right\rangle \\
&= \sum_{i=1}^{N} \left\langle \Psi(\boldsymbol{\tau};t) \left| \left[\hat{H}, \boldsymbol{r}_i \cdot \hat{\boldsymbol{p}}_i \right] \right| \Psi(\boldsymbol{\tau};t) \right\rangle \\
&= \sum_{i=1}^{N} \left\langle \Psi(\boldsymbol{\tau};t) \left| \boldsymbol{r}_i \cdot \left[\hat{H}, \hat{\boldsymbol{p}}_i\right] + \left[\hat{H}, \boldsymbol{r}_i\right] \cdot \hat{\boldsymbol{p}}_i \right| \Psi(\boldsymbol{\tau};t) \right\rangle \\
&= \sum_{i=1}^{N} \left\langle \Psi(\boldsymbol{\tau};t) \left| \boldsymbol{r}_i \cdot i\hbar \nabla_i V(\boldsymbol{\tau}) + \dfrac{-i\hbar}{m_e} \hat{\boldsymbol{p}}_i \cdot \hat{\boldsymbol{p}}_i \right| \Psi(\boldsymbol{\tau};t) \right\rangle
\end{aligned}
\tag{T-1-I}
$$

$$\sum_{i=1}^{N} \left\langle \Psi(\boldsymbol{\tau};t) \left| \dfrac{\hat{\boldsymbol{p}}_i \cdot \hat{\boldsymbol{p}}_i}{m_e} \right| \Psi(\boldsymbol{\tau};t) \right\rangle = \sum_{i=1}^{N} \left\langle \Psi(\boldsymbol{\tau};t) \left| \boldsymbol{r}_i \cdot \nabla_i V(\boldsymbol{\tau}) \right| \Psi(\boldsymbol{\tau};t) \right\rangle$$

Now, from classical physics we know that the kinetic energy is given by $T = \dfrac{\boldsymbol{p} \cdot \boldsymbol{p}}{2m} = \dfrac{1}{2} mv^2$, and you *should* remember the same thing from discussions of the importance and significance of each term in the Schrödinger equation. So

$$\sum_{i=1}^{N} \left\langle \Psi(\boldsymbol{\tau};t) \left| \dfrac{2\hat{\boldsymbol{p}}_i \cdot \hat{\boldsymbol{p}}_i}{2m_e} \right| \Psi(\boldsymbol{\tau};t) \right\rangle = \sum_{i=1}^{N} \left\langle \Psi(\boldsymbol{\tau};t) \left| \boldsymbol{r}_i \cdot \nabla_i V(\boldsymbol{\tau}) \right| \Psi(\boldsymbol{\tau};t) \right\rangle$$

$$2 \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \dfrac{\hat{\boldsymbol{p}}_i \cdot \hat{\boldsymbol{p}}_i}{2m_e} \right| \Psi(\boldsymbol{\tau};t) \right\rangle = \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i V(\boldsymbol{\tau}) \right| \Psi(\boldsymbol{\tau};t) \right\rangle \tag{T-1-J}$$

$$2 \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \hat{T} \right| \Psi(\boldsymbol{\tau};t) \right\rangle = \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i V(\boldsymbol{\tau}) \right| \Psi(\boldsymbol{\tau};t) \right\rangle$$

There is a reason why I wrote out the form of the momentum operator in the statement of the problem. Figuring that you might forget the elementary $T = \frac{p^2}{2m}$, you

Name:

could still derive this result by substituting the form of the momentum operator because ALL of you know that $\hat{T} = \sum_{i=1}^{N} -\frac{\hbar^2 \nabla_i^2}{2m_e} = \sum_{i=1}^{N} \frac{-i\hbar \nabla_i \cdot (-i\hbar \nabla_i)}{2m_e}$.

(d) Show that, for an atom, this implies:

$$\left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle = -\left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle$$
$$= \tfrac{1}{2} \left\langle \Psi \left| \hat{V} \right| \Psi \right\rangle$$

This is called the virial theorem. (Remember that $r_i \cdot \nabla_i f(r_i) = r_i \frac{\partial f(r_i)}{\partial r_i}$ if $f(r)$ does not depend on the angular coordinates, θ and ϕ .)

We use our result from the previous problem, and substitute in the form of the potential operator for an atom, so that

$$
\begin{aligned}
\left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \hat{V} \right| \Psi(\boldsymbol{\tau};t) \right\rangle &= \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \left(\hat{V}_{ne} + \hat{V}_{ee} \right) \right| \Psi(\boldsymbol{\tau};t) \right\rangle \\
&= \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i V_{ne} \right| \Psi(\boldsymbol{\tau};t) \right\rangle + \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i V_{ee} \right| \Psi(\boldsymbol{\tau};t) \right\rangle \\
&= \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \left(\sum_{j=1}^{N} \frac{-Z}{r_j} \right) \right| \Psi(\boldsymbol{\tau};t) \right\rangle \\
&\quad + \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \sum_{j=1}^{N} \sum_{k=j+1}^{N} \frac{1}{|r_j - r_k|} \right| \Psi(\boldsymbol{\tau};t) \right\rangle \\
&= \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \left(\frac{-Z(-\boldsymbol{r}_i)}{r_i^3} \right) \right| \Psi(\boldsymbol{\tau};t) \right\rangle \\
&\quad + \left\langle \Psi(\boldsymbol{\tau};t) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \sum_{j=1}^{N} \sum_{k=j+1}^{N} \nabla_i \frac{1}{|r_j - r_k|} \right| \Psi(\boldsymbol{\tau};t) \right\rangle
\end{aligned}
$$

(T-1-K)

The last line follows from the fact that the derivative with respect to $\boldsymbol{r}_i$ of the terms in the potential that do not depend on $\boldsymbol{r}_i$ must be zero. The electron-electron form is a bit tricky, but very similar to analysis we have done elsewhere in the course (evaluating the commuator of $\hat{L}_z$ and $\hat{H}$ and, once again, I reiterate: if you don't see how to work a problem "in general", try it first for a simple (three electron, or even two electron) case!!

Since you can "yank" one method of derivation directly from the notes, let's try a different method (the one I would use if I had been testee rather than tester). Use the chain rule for derivatives to obtain:

$$\frac{\partial}{\partial x_i} = \frac{\partial}{\partial (x_i - x_k)} \frac{d(x_i - x_k)}{dx_i} = \frac{\partial}{\partial (x_i - x_k)} \tag{T-1-L}$$

Name:

and so $\nabla_{r_i} = \nabla_{r_i - r_k}$ and

$$\nabla_{r_i} \tfrac{1}{|r_i - r_k|} = \nabla_{r_i - r_k} \tfrac{1}{|r_i - r_k|} = -\frac{(\boldsymbol{r}_i - \boldsymbol{r}_k)}{\left|\boldsymbol{r}_i - \boldsymbol{r}_k\right|^3} \tag{T-1-M}$$

and

$$\nabla_{r_i} \tfrac{1}{|r_j - r_i|} = \nabla_{r_j - r_i} \tfrac{1}{|r_j - r_i|} = \frac{(\boldsymbol{r}_i - \boldsymbol{r}_k)}{\left|\boldsymbol{r}_i - \boldsymbol{r}_k\right|^3} \tag{T-1-N}$$

Then we have

$$\left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \hat{V} \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle = \left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N} Z\left(\frac{\boldsymbol{r}_i \cdot \boldsymbol{r}_i}{r_i^3}\right) \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle$$

$$+ \left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \sum_{j=1}^{N}\sum_{k=j+1}^{N} \left[\begin{matrix} \delta_{ji}\left(\nabla_{r_i-r_k}\tfrac{1}{|r_j-r_k|}\right) \\ + \delta_{ki}\left(\nabla_{r_i-r_j}\tfrac{1}{|r_j-r_i|}\right)\end{matrix}\right] \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle \tag{T-1-O}$$

where the form of the $\hat{V}_{ee}$ term reflect the fact that the derivative with respect to $\boldsymbol{r}_i$ of $\tfrac{1}{|r_j-r_k|}$ is zero unless j or k is equal to i. Then we have

$$\left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \hat{V} \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle$$

$$= \left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N} Z\left(\frac{r_i^2}{r_i^3}\right) \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle + \left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=j+1}^{N} \boldsymbol{r}_i \cdot \left[\begin{matrix} -\delta_{ji}\left(\frac{r_i-r_k}{|r_j-r_k|^3}\right) \\ + \delta_{ki}\left(\frac{r_j-r_i}{|r_j-r_i|^2}\right)\end{matrix}\right] \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle$$

$$= \left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N} \frac{Z}{r_i} \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle + \left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{j=1}^{N}\sum_{k=j+1}^{N}\sum_{i=1}^{N} \boldsymbol{r}_i \cdot \left[\begin{matrix} -\delta_{ji}\left(\frac{r_i-r_k}{|r_j-r_k|^3}\right) \\ + \delta_{ki}\left(\frac{r_j-r_i}{|r_j-r_i|^2}\right)\end{matrix}\right] \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle$$

$$= -\left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N} \frac{-Z}{r_i} \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle + \left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{j=1}^{N}\sum_{k=j+1}^{N} \left(\boldsymbol{r}_k - \boldsymbol{r}_j\right)\cdot\left(\frac{r_j-r_k}{|r_j-r_k|^3}\right) \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle \tag{T-1-P}$$

$$= -\left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N} \frac{-Z}{r_i} \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle - \left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{j=1}^{N}\sum_{k=j+1}^{N} \frac{(r_j-r_k)\cdot(r_j-r_k)}{|r_j-r_k|^3} \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle$$

$$= -\left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \sum_{i=1}^{N} \frac{-Z}{r_i} + \sum_{j=1}^{N}\sum_{k=j+1}^{N} \frac{1}{|r_j-r_k|} \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle$$

$$= -\left\langle \Psi\left(\boldsymbol{\tau};t\right) \left| \hat{V} \right| \Psi\left(\boldsymbol{\tau};t\right) \right\rangle$$

This gives the desired relationship between the kinetic and potential energy of an atom, namely,

$$2T = -V \tag{T-1-Q}$$

26

At this stage, completing the derivation relies on the fact that $E = T + V$, so that

$$E = T + V$$
$$= \frac{-V}{2} + V \qquad \text{(T-1-R)}$$
$$= \frac{V}{2}$$

and

$$E = T + V$$
$$= T - 2T \qquad \text{(T-1-S)}$$
$$= -T.$$

Name:

2. Perturbation Theory (first final)

Another one of Hirshfelder's leading contributions to chemistry was the development of perturbation series about the separated atom limit. This, however, is a bit complicated. A less useful, but still relevant, expansion is based on perturbation series about the united atom limit.

(a) Write the Schrödinger Equation for a one-electron diatomic molecule with nuclei at $\left(0,0,\pm\frac{R}{2}\right)$ and atomic charges Z_1 and Z_2. What is the form of the "perturbation" when we go from $R = 0$ to some small value of R.

The Schrödinger equation is pretty simple, just

$$\left(-\frac{\nabla^2}{2} - \frac{Z_1}{\left|r-[0,0,-\frac{R}{2}]\right|} - \frac{Z_2}{\left|r-[0,0,-\frac{R}{2}]\right|}\right)\Psi_k(r,R) = E_k(R)\Psi_k(r,R) \tag{T-2-A}$$

The form of the perturbation when we go from $R = 0$ to some small value of R can be written explicitly (which all of the testers did), as

$$\Delta\hat{H} = -\frac{Z_1}{\left|r-[0,0,-\frac{R}{2}]\right|} - \frac{Z_2}{\left|r-[0,0,-\frac{R}{2}]\right|} - \frac{Z_1+Z_2}{r} \tag{T-2-B}$$

But if you examine the form and compare to the definition of the derivative, you see that

$$\lim_{R\to 0}\left(-\frac{Z_1}{\left|r-[0,0,-\frac{R}{2}]\right|} - \frac{Z_2}{\left|r-[0,0,-\frac{R}{2}]\right|} - \frac{Z_1+Z_2}{r}\right) = R\frac{d\hat{H}}{dR}\bigg|_{R=0} \tag{T-2-C}$$

in the limit of small R. The most useful form of the perturbation is simply

$$\Delta H \equiv R\frac{d\hat{H}}{dR}\bigg|_{R=0} + \frac{R^2}{2}\frac{d^2\hat{H}}{dR^2}\bigg|_{R=0} + \frac{R^3}{3!}\frac{d^3\hat{H}}{dR^3}\bigg|_{R=0} + \cdots \tag{T-2-D}$$

(b) Using the appropriate equations, describe how you will find the first-order corrections to the energy and the wave functions using the appropriate "united atom" wave functions for the $1s, 2s,$ and $2p_{x,y,z}$ states.

Many of you described how the perturbation theory equations were derived here. That is fine, and you got some partial credit since I figured that in the limit as "testing time" went to infinity and "stress" went to zero (if this limit can be accessed at all), you'd probably be able to figure it out. I was mostly looking for the fact that you knew that the first-order change in energy would be given by

$$\Delta E^{(1)} = \left\langle\Psi(r,R=0)\left|\Delta H\right|\Psi(r,R=0)\right\rangle \tag{T-2-E}$$

for a non-degenerate state and for a degenerate state (like the 2s and 2p states), that the eigenvalues of the perturbation matrix

$$V_{ij} = \left\langle\Psi_{2s;2p_{x,y,z}}(r,R=0)\left|\Delta H\right|\Psi_{2s;2p_{x,y,z}}(r,R=0)\right\rangle \tag{T-2-F}$$

gave the first order change in energy. Here ΔH can be given by Eq. (T-2-B) or by $\frac{d\hat{H}}{dR}$, according to the preference of the user.

Name:

The first order correction to the wave function is then

$$\Psi_k(\boldsymbol{r}) = \sum_{\substack{i=0 \\ E_i \neq E_k}}^{\infty} \frac{\langle \Psi_k | \Delta H | \Psi_i \rangle}{E_i - E_k} \Psi_i(\boldsymbol{r}) \tag{T-2-G}$$

where the sum proceeds only over states whose zeroth order energy is different from the state being corrected.

2. Perturbation Theory (Second Examination)
Another one of Hirshfelder's leading contributions to chemistry was the development of perturbation series about the separated atom limit.

(a) Write the Schrödinger Equation for a one-electron diatomic molecule with nuclei at $\left(0,0,\pm\frac{R}{2}\right)$ and atomic charges Z_1 and Z_2. Write a form of the "perturbation" when we go from $R = \infty$ to some smaller value of R. (Hint: it is difficult to write a perturbation in terms of the change of a variable away from infinity. So you may want to use the fact $\frac{1}{R} \to 0$ as $R \to \infty$, or another similar functional relation.)

The Hamiltonian is the same as Eq. (T-2-A). However, this time the perturbation (which can only really be written using the "derivative" form), is

$$\frac{d\hat{H}}{d\left(\frac{1}{R}\right)}\left(\frac{1}{R}\right) + \frac{1}{2}\frac{d^2\hat{H}}{d\left(\frac{1}{R}\right)^2}\left(\frac{1}{R}\right)^2 + \frac{1}{3!}\frac{d^3\hat{H}}{d\left(\frac{1}{R}\right)^3}\left(\frac{1}{R}\right)^3 + \dots \tag{T-2-H}$$

(b) Using the appropriate equations, describe how you will find the first-order corrections to the energy and the wave functions using the appropriate "separated atom" wave functions for the $1s, 2s,$ and $2p_{x,y,z}$ states.

This is the same as before; only the perturbation changes.

(c) What do you expect to be the first non-vanishing order in the perturbation expansion for the energy?

Looking at the perturbation series,

$$E\left(\frac{1}{R}\right) = E(R \to \infty) + \frac{dE(R)}{d\left(\frac{1}{R}\right)}\bigg|_{\frac{1}{R}=0}\left(\frac{1}{R}\right) + \frac{d^2E(R)}{d\left(\frac{1}{R}\right)^2}\bigg|_{\frac{1}{R}=0}\left(\frac{1}{R^2}\right) + \frac{d^3E(R)}{d\left(\frac{1}{R}\right)^3}\bigg|_{\frac{1}{R}=0}\left(\frac{1}{R^3}\right) + \dots$$

and recalling that interaction between an atom and an ion is a $\frac{1}{R^3}$ interaction, it is clear that the first non-vanishing order of perturbation theory is the third.

Name:

Name:

3. The Fermi-Amaldi Model (20 points).

A popular early model for the atomic Hamiltonian was the Fermi-Amaldi model, where

$$\hat{H} \approx \sum_{i=1}^{N} \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + \left(\frac{N-1}{2N} \right) \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' \right) \tag{T-3-A}$$

where $\rho(\boldsymbol{r})$ is the electron density,

$$\rho(\boldsymbol{r}) \equiv \left\langle \Psi \left| \sum_{i=1}^{N} \delta(\boldsymbol{r}_i - \boldsymbol{r}) \right| \Psi \right\rangle \tag{T-3-B}$$

(a)* Show that the energy in the Fermi-Amaldi Model is given by

$$E^{FA}[\Psi] \equiv \left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \left\langle \Psi \left| V_{ne} \right| \Psi \right\rangle + \tfrac{1}{2} \left(\tfrac{N-1}{N} \right) \iint \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}d\boldsymbol{r}' \tag{T-3-C}$$

Substituting, we have that

$$E^{FA} = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle$$

$$= \left\langle \Psi \left| \sum_{i=1}^{N} \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + \left(\frac{N-1}{2N} \right) \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}_i-\boldsymbol{r}'|} d\boldsymbol{r}' \right) \right| \Psi \right\rangle$$

$$= \left\langle \Psi \left| \hat{T} + \hat{V}_{ne} + \frac{N-1}{2N} \sum_{i=1}^{N} \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}_i-\boldsymbol{r}'|} d\boldsymbol{r}' \right| \Psi \right\rangle$$

$$= \left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{V}_{ne} \right| \Psi \right\rangle + \frac{N-1}{2N} \int \rho(\boldsymbol{r}') \left\langle \Psi \left| \sum_{i=1}^{N} \frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}'|} \right| \Psi \right\rangle d\boldsymbol{r}'$$

$$= \left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{V}_{ne} \right| \Psi \right\rangle + \frac{N-1}{2N} \int \rho(\boldsymbol{r}') \left\langle \Psi \left| \sum_{i=1}^{N} \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \delta(\boldsymbol{r}-\boldsymbol{r}_i) d\boldsymbol{r} \right| \Psi \right\rangle d\boldsymbol{r}'$$

$$= \left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{V}_{ne} \right| \Psi \right\rangle + \frac{N-1}{2N} \iint \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \left\langle \Psi \left| \sum_{i=1}^{N} \delta(\boldsymbol{r}-\boldsymbol{r}_i) \right| \Psi \right\rangle d\boldsymbol{r}d\boldsymbol{r}'$$

$$= \left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{V}_{ne} \right| \Psi \right\rangle + \frac{N-1}{2N} \iint \frac{\rho(\boldsymbol{r}')\rho(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}d\boldsymbol{r}' \tag{T-3-D}$$

This analysis is very similar to that used in deriving the Hohenberg-Kohn theorem in density functional theory, though I did it a little bit differently here than I did on the board (and in my dissertation), just for the sake of showing a different way of doing this.

(b) What is the purpose of the $\frac{N-1}{N}$ factor?

Because electrons do not interact with themselves, an electron interacts only with *N-1* other electrons. Remembering that the "self energy" of a charge distribution interacting with itself is just $\frac{1}{2} \iint \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}d\boldsymbol{r}'$, we see that the $\frac{N-1}{N}$ factor is just a "correction" for the "self-interaction" error of an electron with itself; the role of this factor, then, is to remove the term in the electron-electron repulsion energy that pertains to an electron interacting with itself.

The "picture" behind the derivation of the Fermi-Amaldi model is that the probability of observing an electron at $\boldsymbol{r}$ is $\rho(\boldsymbol{r})$, and that if there is an electron at $\boldsymbol{r}$, the probability of observing

another electron at r' must be given by a conditional distribution, $\rho_{cond.}(r';r)$ (which will generally depend on where the first electron is), that integrates to $N-1$ electrons. The simplest possible choice for $\rho_{cond}(r';r)$ is $\frac{N-1}{N}\rho(r')$, which assumes that probability of observing an electron at r' given that there is an electron at r does not depend on r *at all*, which is clearly wrong—when r' and r are very close together, we expect $\rho_{cond}(r,r') \approx 0$. Making this assumption gives the Fermi-Amaldi model. So the Fermi-Amaldi model is not very good (it is even worse than the (usual) Hartree Approximation!!), but it is sometimes useful because it is SO simple. It is remarkable, for instance, that the Fermi-Amaldi model already gives "shell structure", effective nuclear charges, and reasonable (not perfect, but quite good) excitation energies, along with a Rydberg spectrum with **stunning** accuracy. (For a challenge, try explaining THAT over your summer break! (It's not that hard.))

(c)* **A model is said to be size consistent if, in the separated atom limit, the molecular energy is the sum of the atomic energies. In the limit of infinite internuclear distance, we can approximate the ground-state wave function of the Hydrogen molecule as**

$$\Psi(r_1, r_2) = \psi_{1s}(r_1 - R_A)\psi_{1s}(r_2 - R_B) \tag{T-3-E}$$

where R_A and R_B are the positions of the protons. (When they are infinitely far apart, electrons are clearly distinguishable from one another.) Using this wave function in the Fermi-Amaldi energy formula, show that the Fermi-Amaldi model is *not size-consistent*: the energy of the "separated atom limit" is actually greater than the energy of two isolated hydrogen atoms.

The kinetic energy and electron-nuclear attraction energies are size consistent, which is easy to see from the definition. What you need to do is study the electron-electron repulsion term:

$$\underbrace{\left(\frac{N_{H_2}-1}{2N_{H_2}}\right)\int\int\frac{\rho_{H_2}(r)\rho_{H_2}(r')}{|r-r'|}dr'dr}_{\text{The Fermi-Amaldi Form}} \quad \overset{?}{>} \quad \underbrace{\begin{aligned}&\left(\frac{N_H-1}{2N_H}\right)\int\int\frac{\rho_H(r)\rho_H(r')}{|r-r'|}drdr'\\ +&\left(\frac{N_H-1}{2N_H}\right)\int\int\frac{\rho_H(r)\rho_H(r')}{|r-r'|}drdr'\end{aligned}}_{\text{when R}\to\infty\text{ the system becomes two isolated hydrogen atoms}} \tag{T-3-F}$$

where we have listed the two Hydrogen atoms separately for simplicity. Since a hydrogen atom has one electron ($N_H = 1$) and the Hydrogen molecule has 2 electrons, we have that

$$\left(\frac{2-1}{2\cdot 2}\right)\int\int\frac{\rho_{H_2}(r)\rho_{H_2}(r')}{|r-r'|}dr'dr > 0$$

$$\tfrac{1}{4}\int\int\frac{\rho_{H_2}(r)\rho_{H_2}(r')}{|r-r'|}dr'dr > 0 \tag{T-3-G}$$

The integral is always positive: since the electron density is nonnegative as is $\frac{1}{|r-r'|}$, the integrand is nonnegative, and the integral of a nonnegative integrand (that is not zero everywhere) is always positive. It follows that the Fermi-Amaldi approximation is not size-consistent because, even when two hydrogen atoms are infinitely separated, the electron-electron repulsion does not vanish. In fact, quite generally, the Fermi-Amaldi model overestimates the energy (but this is not so easy to show).

Name:

The solution to the Fermi-Amaldel model can be found by solving a set of equations for the Fermi-Amaldi (FA) orbitals,

$$\left[-\frac{\nabla^2}{2} - \frac{Z}{r} + \left(\frac{N-1}{N}\right) \int \frac{\rho(r')}{|r - r'|} dr' \right] \psi_i^{FA}(r) = \varepsilon_i^{FA} \psi_i^{FA}(r) \qquad \textbf{(T-3-H)}$$

where

$$\rho(r') \equiv \sum_{i=1}^{N} \left| \psi_i^{FA}(r') \right|^2 \qquad \textbf{(T-3-I)}$$

(d)   Explain how you would derive these equations (i.e., what are the "key steps"). You do not need to actually derive them.

Just like the Hartree-Fock case, there is no electron-electron repulsion term in the Fermi-Amaldi Hamiltonian. Each electron moves in an "average" potential due to the other electrons, as determined by the orbitals in which those electrons reside by Eq. (T-3-I). Since there is no electron-electron repulsion term we have that, just as for the Hartree-Fock equations, the ground state energy is a Slater determinant of the Fermi-Amaldi orbitals. To find the orbitals, we can minimize the energy as a functional of those orbitals, and we obtain the Fermi-Amaldi equations, (T-3-H), by setting the functional derivative of the Fermi-Amaldi energy, Eq. (T-3-C) with respect to the orbitals equal to zero. That is,

$$\frac{\delta E_{FA}\left[\{\psi_i^{FA}\}_{i=1}^N\right]}{\delta \psi_\alpha^{FA}(r)} = 0 \qquad \textbf{(T-3-J)}$$

gives the Fermi-Amaldi equations. This is exactly analogous to the derivation of the Hartree-Fock equations!

(e)   One says that the Fermi-Amaldi Equations have to be solved "self-consistently. What does this mean?

Because the electron density depends on the Fermi-Amaldi orbitals, but solving the Fermi-Amaldi equations to determine the orbitals requires knowledge of the electron density, we must solve Eqs. (T-3-H) and (T-3-I) to self consistency: that is, the electron density put into the Fermi-Amaldi equations must be the same as the density of the orbitals obtained by solving the Fermi-Amaldi equations.

To actually find the "self-consistent" orbitals, one can **(1)** "guess" a density, **(2)** solve the Fermi-Amaldi equations, (T-3-H), for the Fermi-Amaldi orbitals, $\left\{\psi_i^{FA}\right\}_{i=1}^N$, **(3)** compute the density from Eq. (T-3-I), **(4)** substitute the improved density into the Fermi-Amaldi equations, **(5)** solve for the new orbitals, and **(6)** continue doing steps **(4)** and **(5)** until the density (or orbitals) "in" and the density (or orbitals) "out" are the same.