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Test 2

Chemistry 3BB3; Winter 2003

Part 1. Multiple-Choice/Short Answer (2 points each) (50 points)

1. Using the following definitions,

$$\hat{T}_e \equiv -\frac{\nabla_{r_1}^2}{2} - \frac{\nabla_{r_2}^2}{2} \qquad\qquad \hat{T}_n \equiv -\frac{\nabla_{R_1}^2}{2M_1} - \frac{\nabla_{R_2}^2}{2M_2}$$

$$\hat{V}_{ee} \equiv \frac{1}{|r_1 - r_2|} \qquad\qquad \hat{V}_{nn} \equiv \frac{Z_1 Z_2}{|R_1 - R_2|}$$

$$\hat{V}_{ne} \equiv -\frac{Z_1}{|r_1 - R_1|} - \frac{Z_2}{|r_1 - R_2|} - \frac{Z_1}{|r_2 - R_1|} - \frac{Z_2}{|r_2 - R_2|}$$

the Schrödinger equation for the electrons, in the Born-Oppenheimer approximation, can be written as

$$\left(\hat{T}_e + V_{ne} + V_{ee} + V_{nn}\right)\Psi\left(r_1, r_2; R_1, R_2\right) = U\left(R_1, R_2\right)\Psi\left(r_1, r_2; R_1, R_2\right)$$

What is the Schrödinger equation for the nuclei in the Born-Oppenheimer approximation?

$$\left(\hat{T}_N + U\left(R_1, R_2\right)\right)\chi_n\left(R_1, R_2\right) = E \cdot \chi_n\left(R_1, R_2\right)$$

2. Write the energy formula for the ground and excited states of a one-electron atom with atomic number Z. You can use atomic units.

$$E \equiv -\frac{Z^2}{2n^2}$$

Cerium has an electron configuration of $[\mathrm{Xe}]6s^2 4f^1 5d^1$.

3. List the term symbols associated with Cerium's ground state in order of increasing energy (ground state first). You do not have to specify the "J" values.

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

4a. Is the following wave function an acceptable approximate wave function for the Helium atom?

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

YES

4b. Is $\Psi\left(r_1, \sigma(1), r_2, \sigma(2)\right) = \psi_{2s}\left(r_1\right)\psi_{2s}\left(r_2\right)\dfrac{\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)}{\sqrt{2}}$ an acceptable wave function for first doubly-excited singlet state of the Helium atom?

YES

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

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

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

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

7. **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 $\chi(t)$?

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

8. **The sinc function is defined as**
$$\operatorname{sinc}(x) = \frac{\sin(x)}{x}$$

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

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}$$
$$\text{OR}$$
$$\nu_{fi} = \frac{E_f - E_i}{h}$$

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We mentioned several different approximations that underlie Fermi's Golden Rule. We have:

L = "long wavelength" approximation.
T = "long time" approximation.
W = "weak field" approximation

In addition, in discussing the vibrational structure of spectral lines in molecules, we spoke about the

F = Condon approximation (often called the Franck-Condon approximation)

When these approximations are not valid, we can observe spectral lines we would not otherwise observe. For example, we observe

m = Magnetic Dipole Transitions
n = Non-linear optical effects
q = Electric Quadrupole Transitions
s = spin-orbital coupling effects
v = vibronic coupling effects

10-14. Below, I have written several different "corrections" to Fermi's Golden Rule. For each case, write which approximation has been "revised" (F,L,T,W) and if applicable, what sorts of effects you expect to see (m,n,q,s,v)

Approximation (F,L,T,W)	Effect Observed (m,n,q,s,v)	The appropriate "correction" to Fermi's Golden Rule
T time dependence only vanishes in "long time" limit		$$W_{fi} = \frac{V^2 t}{\hbar^2} \int\limits_0^\infty \left|\left\langle \Phi_f \left|\hat{\mu}_x\right| \Phi_i \right\rangle\right|^2 g\left(\hbar\omega\right) \left[\begin{array}{c} \left(\mathrm{sinc}\left(\left(\omega_{fi} - \omega\right)\frac{t}{2}\right)\right)^2 \\ + \left(\mathrm{sinc}\left(\left(\omega_{fi} + \omega\right)\frac{t}{2}\right)\right)^2 \\ -\frac{2\pi}{t}\delta\left(\omega_{fi} - \omega\right) \end{array} \right] d\left(\hbar\omega\right)$$
W In a "strong" field, a system can absorb two "weak" photons at once, so $E_f - E_i = 2h\nu = \omega_{fi}$	**n** nonlinear since it depends on the fields magnitude (V^2) squared.	$$W_{fi} = \frac{2\pi V^4 g\left(\frac{\hbar\omega_{fi}}{2}\right)\left|\left\langle \Phi_f \left|\hat{\mu}_x\right| \Phi_i \right\rangle\right|^2}{\hbar}$$
L The magnetic dipole transition rate is proportional to the wave vector, k^2, which is zero for "long wave length"	**m**	$$W_{fi} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right) k^2 \left|\left\langle \Phi_f \left|\sum_{i=1}^N \beta_e \hat{L}_y\left(\boldsymbol{r}_i\right) + \sum_{\alpha=1}^P \frac{\beta_e}{M_\alpha}\hat{L}_y\left(\boldsymbol{R}_\alpha\right)\right| \Phi_i \right\rangle\right|^2}{\hbar}$$
F If we cannot assume the nuclei are still—a vibronic coupling process—then the Condon approximation is not valid	**v**	$$W_{\mu f,\nu i} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)}{\hbar}\left|\left\langle \chi_{\mu f}\left|\sum_{\alpha=1}^P \boldsymbol{R}_\alpha \cdot \nabla_\alpha \mu_{fi}\left(\boldsymbol{R}_1,\ldots\boldsymbol{R}_P\right)\right|\chi_{\nu i}\right\rangle\right|^2$$
L The electric quadrupole transition rate is proportional to the wave vector, k^2, which is zero for "long wave length"	**q**	$$W_{fi} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right) k^2 \left|\left\langle \Phi_f \left|\sum_{i=1}^N ex_i z_i + \sum_{\alpha=1}^P -Z_\alpha e\left(x_\alpha z_\alpha\right)\right| \Phi_i \right\rangle\right|^2}{\hbar}$$

The following potential energy surfaces pertain to a "predissociation" process:
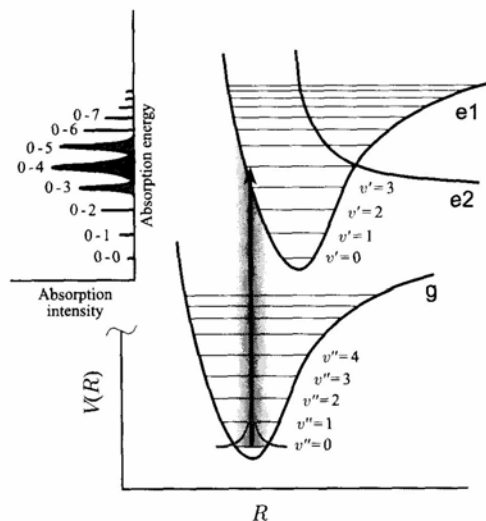

15a. Observe the broadening of the spectral lines near the dissociation threshold. This is a case of

    (a) inhomogeneous broadening.

(b) homogeneous broadening. (every molecule is affected equally—it depends on the "system" (the way the potential energy surfaces look), not the individual molecular state.

15b. Which of the following curves will most strongly resemble the line shape?
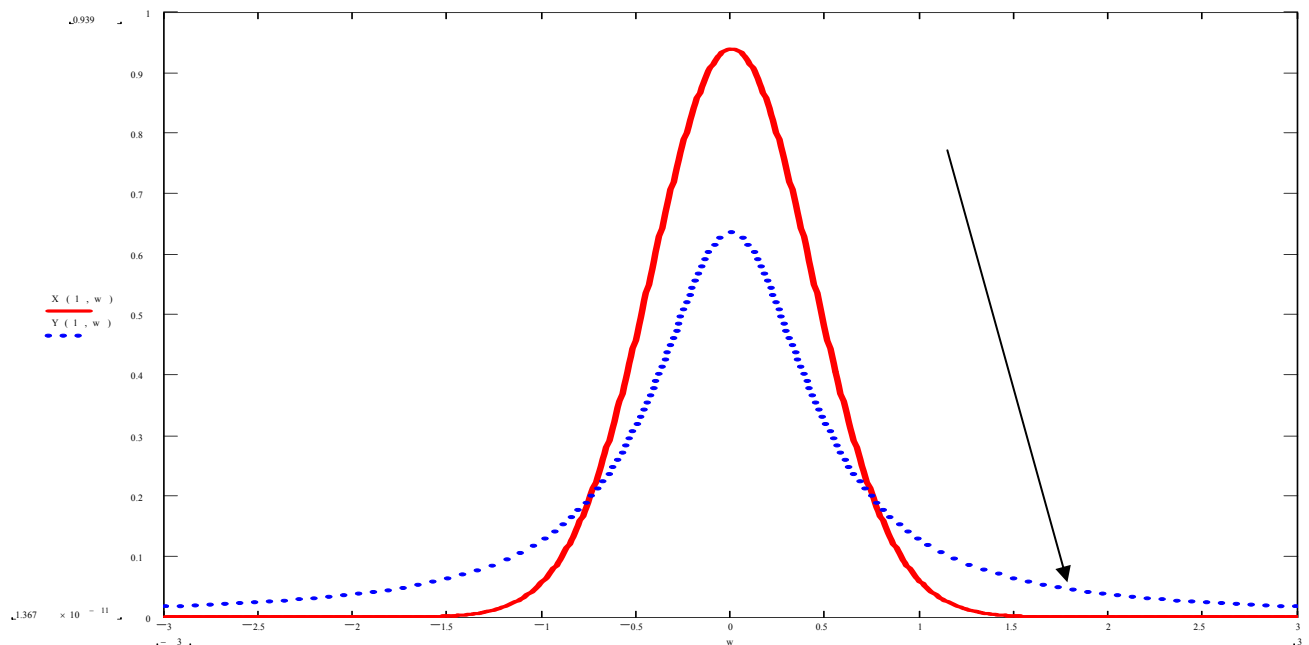
NOTE: If you missed part "a" but answered part "b" right for your wrong answer, then you got 1 point.

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3 pt. Bonus

- Using a formula for the lineshape (if you leave out constants of proportionality that will be OK), discuss why this broadening occurs. Even if you can't write down the formula, you can get some credit if you can describe, in words, why this occurs.

The lineshape formula is

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

In predissociation, once the state is excited to some level with an energy greater-than or equal to the "crossing energy", then there is a "decay process" whereby the state can "jump" to the dissociative potential energy surface. Means that the probability of the state being in the state i actually decays with time with some constant, $e^{-\zeta t}$. We call this "lifetime" broadening, since it is the "reduced lifetime" of the state that causes the lines to broaden.

Now, there are a lot of models for the "lifetime" of this state, but some salient principle are helpful. For instance, if the energy of the state very nearly matches the "crossing point", then the turning point of the molecular vibration will be in the vicinity of the crossing point, and so the molecule will spend a lot of time in states that resemble the states at the "crossing point". On the other hand, if the energy is much greater than that at the crossing point, then the molecule will be moving very fast when it gets to the conformation where it can "cross", and it is effectively trapped on its "home surface." (This of this analogy. You are trying to turn into a driveway. You likelihood of making it is much greater if there is a "stoplight" at the driveway that makes you slow down. But if you are gunning the engine at 100 km/h, then you aren't likely to make the turn.)

When we put the "decay" into the lineshape formula, we get

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

which is what the "final answer" is, since the integral (to get the Gaussian) has already been done by us in several contexts.

16. 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, $\gamma = \frac{\Gamma}{2}$. Write the appropriate "name" an "formula" for the spectral lineshape associated with inhomogeneous and homogeneous broadening. If you need to use a constant of proportionality because you do not know a normalization-type factor, use the number κ. (What I want to see is that you understand how the "line width" enters into the formula in a *qualitative* sense.)

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

17. In the Hydrogen molecule, which of the following transitions would be electric dipole allowed.

(a) $\sigma_g \to \sigma_u$ (b) $\sigma_u \to \pi_u$ (c) $\sigma_g \to \pi_g$ **(d)** $\sigma_u \to \pi_g$

Note: The fact only $u \to g$ and $g \to u$ is allowed is called the Laporte Rule.

18,19. 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.

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

Bonus: 4 points. Write an approximate linear-combination-of-atomic-orbitals wave function for each of the following symmetry labels. The orientation of the molecule is the same as above

Symmetry Label	LCAO Molecular Orbital
δ_u^+	$\psi_{3d_{x^2-y^2}}^{(l)}(\boldsymbol{r}) - \psi_{3d_{x^2-y^2}}^{(r)}(\boldsymbol{r})$
δ_g^+	$\psi_{3d_{x^2-y^2}}^{(l)}(\boldsymbol{r}) + \psi_{3d_{x^2-y^2}}^{(r)}(\boldsymbol{r})$
δ_u^-	$\psi_{3d_{xy}}^{(l)}(\boldsymbol{r}) - \psi_{3d_{xy}}^{(r)}(\boldsymbol{r})$
δ_g^-	$\psi_{3d_{xy}}^{(l)}(\boldsymbol{r}) + \psi_{3d_{xy}}^{(r)}(\boldsymbol{r})$

20. **Write a "Valence Bond plus Ionic" wave function for the ground state of the Hydrogen atom. Do not forget the "spin part" of the wave function. Weight the ionic terms with the number, κ. You do not need to worry about the normalization constant.**

$$\Psi_{VB+\kappa(Ionic)}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right) \propto \begin{pmatrix} \psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right) \\ +\kappa\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)\right) \end{pmatrix}\left(\alpha\left(1\right)\beta\left(2\right) - \alpha\left(2\right)\beta\left(1\right)\right)$$

21. **Write a "Molecular Orbital plus Configuration Interaction" wave function for the Hydrogen atom. Do not forget the "spin part" of the wave function. Weight the ionic terms with the number, δ. You do not need to worry about the normalization constant.**

$$\Psi_{MO+\delta(CI)}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right) \propto \begin{pmatrix} \left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\right)\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)\right) \\ +\delta\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_1\right) - \psi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\right)\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}_2\right) - \psi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)\right) \end{pmatrix}\left(\alpha\left(1\right)\beta\left(2\right) - \alpha\left(2\right)\beta\left(1\right)\right)$$

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

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

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

$$K_{ij} = \left\langle \psi_i\psi_j \left| \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \right| \psi_j\psi_i \right\rangle = \delta_{\sigma_i\sigma_j}\iint \frac{\left(\psi_i^*\left(\boldsymbol{r}'\right)\psi_j\left(\boldsymbol{r}'\right)\right)\left(\psi_j^*\left(\boldsymbol{r}\right)\psi_i\left(\boldsymbol{r}\right)\psi_j^*\left(\boldsymbol{r}\right)\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}d\boldsymbol{r}'$$

$$\hat{h}\left(\boldsymbol{r}\right) \equiv \frac{-\nabla^2}{2} + v\left(\boldsymbol{r}\right)$$

$$j\left(\boldsymbol{r}\right) = \left(\sum_{i=1}^{N}\int \frac{|\psi_i(\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\right)$$

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

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

23. **The orbital energy of the αth orbital, $\psi_\alpha\left(\boldsymbol{z}\right)$, is:**

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

24. **The exchange integral, K_{ij} when $i \neq j$, is**

   (a) positive and greater than J_{ij} **(b)positive and less than J_{ij}**

   (c) negative and $-K_{ij} > J_{ij}$.   (d) negative and $-K_{ij} < J_{ij}$

   (e) equal to J_{ij}

25. **Define the exchange operator with**

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

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5 point Bonus: Write the Hartree-Fock equations. Describe how they are solved, taking care to explain why Hartree-Fock is sometimes called a "self-consistent field" method.

$$\hat{f}(\boldsymbol{r})\,\psi_\alpha(\boldsymbol{r}) = \left(\hat{h}(\boldsymbol{r}) + j(\boldsymbol{r}) + \hat{k}(\boldsymbol{z})\right)\psi_\alpha(\boldsymbol{r})$$

$$= \left(\frac{-\nabla^2}{2} + v(\boldsymbol{r}) + j(\boldsymbol{r}) + \hat{k}(\boldsymbol{z})\right)\psi_\alpha(\boldsymbol{r})$$

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

This explanation is lifted straight from the notes:

1. "Guess" an initial Slater determinant of orbitals, $\Phi^{(in)} \equiv \left|\psi_1^{(in)} \ldots \psi_N^{(in)}\right|$.

2. Construct the Coulomb, $j\left[\left\{\psi^{(in)}\right\};\boldsymbol{r}\right]$, and exchange, $\hat{k}\left[\left\{\psi^{(in)}\right\};\boldsymbol{z}\right]$, potentials using the orbitals from this Slater determinant.

3. Construct the Fock operator. Now the Hartree-Fock equations are just a series of one-electron eigenvalue problems, which can be solved (just like the Hydrogen atom, only they are more difficult). One obtains a new set of orbitals, $\left\{\psi_i^{(out)}\right\}$, since

$$\hat{f}\left[\left\{\psi^{(in)}\right\};\boldsymbol{r}\right]\psi_\alpha^{(out)}(\boldsymbol{z}) = \varepsilon_\alpha^{(out)}\psi_\alpha^{(out)}(\boldsymbol{z})$$

4. There are two possibilities.

   It could be that the "new" orbitals and the "old" orbitals are the same—or at least similar enough that we can consider the problem to be "solved."

   - The second possibility is that the difference between the "output" orbitals, $\left\{\psi_i^{(out)}\right\}$, and the "input" orbitals, $\left\{\psi_i^{(in)}\right\}$, is unacceptably large. In this case, we know that the Hartree-Fock equations are not solved by the "input" orbitals, and we should try to improve the orbitals in some way. One possibility is to take the "output" orbitals and use them the revised "guess" for the "input" orbitals,

   $$\psi_i^{(in)}(\boldsymbol{z}) \leftarrow \psi_i^{(out)}(\boldsymbol{z}).$$

   then one goes back to step 2, and repeats the process until eventually the "input" and "output" orbitals are "close enough" for our purposes.

   Recalling that the electric field is simply the negative gradient of the potential, Hartree-Fock is thus said to be a *self-consistent field* (SCF) method: *at convergence, the field induced by the orbitals,* $-\nabla\left(v(\boldsymbol{r}) + j\left[\left\{\psi^{(in)}\right\};\boldsymbol{r}\right] + \hat{k}\left[\left\{\psi^{(in)}\right\};\boldsymbol{z}\right]\right)$ *and the orbitals induced by the are one and the same or, to use the technical term, consistent.*

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5 point Bonus: Derive:
$$\Psi\left(\boldsymbol{\tau}\right)=\sum_{n=0}^{\infty}\left[\left[\left(\hat{I}-\hat{P}\right)\left(E-\hat{F}\right)^{-1}\left(\hat{H}-\hat{F}\right)\right]^{n}\Phi_{HF}\left(\boldsymbol{\tau}\right)\right]$$

where
$$\hat{P}\Psi\left(\boldsymbol{\tau}\right)=\left\langle\Phi_{HF}\left|\Psi\left(\boldsymbol{\tau}\right)\right\rangle\Phi_{HF}\left(\boldsymbol{\tau}\right)\right.$$

and
$$\hat{F}\equiv\sum_{i=1}^{N}\hat{f}\left(\boldsymbol{r}_{i}\right)$$

You can use the intermediate normalization,
$$\left\langle\Phi_{HF}\left|\Psi\left(\boldsymbol{\tau}\right)\right\rangle=1\right.,$$

Start with the Schrödinger Equation:
$$\hat{H}\ \Psi\ \left(\boldsymbol{\tau}\right)=E\ \Psi\ \left(\boldsymbol{\tau}\right)$$
$$\left(\hat{F}+\hat{V}\right)\Psi\ \left(\boldsymbol{\tau}\right)=E\Psi\ \left(\boldsymbol{\tau}\right)$$
$$\left(\mathbb{E}-\hat{F}-\hat{V}\right)\Psi\ \left(\boldsymbol{\tau}\right)=\left(\mathbb{E}-E\right)\Psi\ \left(\boldsymbol{\tau}\right)$$
$$\left(\mathbb{E}-\hat{F}\right)\Psi\ \left(\boldsymbol{\tau}\right)=\left(\mathbb{E}-E+\hat{V}\right)\Psi\ \left(\boldsymbol{\tau}\right)$$
$$\Psi\left(\boldsymbol{\tau}\right)=\left(\mathbb{E}-\hat{F}\right)^{-1}\left(\mathbb{E}-E+\hat{V}\right)\Psi\left(\boldsymbol{\tau}\right),$$

Now, choose
$$\mathbb{E}=E\qquad\text{Brillouin-Wigner form}$$

So
$$\left(\hat{I}-\hat{P}\right)\Psi\left(\boldsymbol{\tau}\right)=\left(\hat{I}-\hat{P}\right)\left(E-\hat{F}\right)^{-1}\left(\hat{V}\right)\Psi\left(\boldsymbol{\tau}\right)$$
$$\Psi\left(\boldsymbol{\tau}\right)-\left\langle\Phi_{HF}\left|\Psi\right\rangle\Phi_{HF}\left(\boldsymbol{\tau}\right)=\left(\hat{I}-\hat{P}\right)\left(E-\hat{F}\right)^{-1}\left(\hat{V}\right)\Psi\left(\boldsymbol{\tau}\right)\right.$$
$$\Psi\left(\boldsymbol{\tau}\right)=\Phi_{HF}\left(\boldsymbol{\tau}\right)+\left(\hat{I}-\hat{P}\right)\left(E-\hat{F}\right)^{-1}\left(\hat{V}\right)\Psi\left(\boldsymbol{\tau}\right)$$
$$\Psi\left(\boldsymbol{\tau}\right)=\Phi_{HF}\left(\boldsymbol{\tau}\right)+\left(\hat{I}-\hat{P}\right)\left(E-\hat{F}\right)^{-1}\left(\hat{V}\right)\left(\Phi_{HF}\left(\boldsymbol{\tau}\right)+\left(\hat{I}-\hat{P}\right)\left(E-\hat{F}\right)^{-1}\left(\hat{V}\right)\Psi\left(\boldsymbol{\tau}\right)\right)$$
$$=\sum_{m=0}^{\infty}\left(\left(\hat{I}-\hat{P}\right)\left(E-\hat{F}\right)^{-1}\left(\hat{V}\right)\right)^{m}\Phi_{HF}\left(\boldsymbol{\tau}\right)$$

Finally, using the definition $\hat{H}=\hat{F}+\hat{V}$, we have
$$\Psi\left(\boldsymbol{\tau}\right)=\left(\left(\hat{I}-\hat{P}\right)\left(E-\hat{F}\right)^{-1}\left(\hat{H}-\hat{F}\right)\right)^{m}\Phi_{HF}\left(\boldsymbol{\tau}\right)$$

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26-31. **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.

_MP_____ Systematically correct the wave function and energy based on the difference between the true Hamiltonian and the Hartree-Fock Hamiltonian, $\hat{F} \equiv \sum_{i=1}^{N} \hat{f}(r_i)$.

___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_____ Assuming 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 $\left(E - \hat{H}\right)$, gives back a delta function.

___DFT_____ $E_{xc}[\rho] = T[\rho] - \sum_{i=1}^{N} \left\langle \psi_i \left| -\frac{\nabla^2}{2} \right| \psi_i \right\rangle + V_{ee}[\rho] - \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r - r'|} dr dr'$

___GF_____ $\sum_{k=1}^{\infty} \frac{\psi_k(z)\psi_k^*(z')}{\varepsilon - \varepsilon_k}$ **(This is the Hartree-Fock Green's function, so I took HF here too.)**

__CC_____
$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + v(r_1) + v(r_2) + \frac{1}{|r_1 - r_2|}\right)\Gamma_2^{\Phi}(z_1, z_2; z_1', z_2')$$
$$+ \iint \delta(z_3 - z_3')\left(-\frac{\nabla_3^2}{2} + v(r_3) + \frac{1}{|r_1 - r_3|} + \frac{1}{|r_2 - r_3|}\right)\Gamma_3^{\Phi}(z_1, z_2, z_3; z_1, z_2, z_3')dz_3 dz_3'$$
$$+ \frac{1}{2}\iint \frac{1}{|r_3 - r_4|}\Gamma_4^{\Phi}(z_1, z_2, z_3; z_4; z_1, z_2, z_3, z_4)dz_3 dz_4$$
$$= E\Gamma_2^{\Phi}(z_1, z_2; z_1', z_2')$$

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

___DFT_____ The Kohn-Sham method.

Name:

Thinking Problems

Hints are available. Each problem is with 20 points.

1. Photoelectron Spectroscopy

In our discussion of the one-electron Green's function, we said that the Dyson orbitals (or Feynman-Dyson Amplitudes, or Generalized Overlap Amplitudes) were the "right" orbitals for describing chemical processes. The question arises: do these orbitals have any direct spectroscopy relevance.

When measuring ionization potentials, the most frequently used technique is photoelectron spectroscopy. A common set-up is as follows. One places ones sample in a large container (often an oven, which is used to vaporize liquid and solid samples). Then one irradiates the sample with UV light. A common source (probably the most common) is the so-called Helium I (HeI) line, which arises from the $^1P \to {}^1S$ transition and has a wavelength of 585 Å.

(a) Write the formula for the energy of a 585 Å photon.

$$E_{photon} = h\nu = \frac{hc}{\lambda} = \frac{hc}{585 \text{ Å}}$$

Using your result from part (a) we find that the photon energy is .7797 Hartree. For some systems, this energy can induce an excitation from an initial state to a final state. However, for many systems—especially molecular systems—the ionization potential of the system is less than .7797 Hartree. (A typical ionization potential is about .5 Hartree.) What occurs, then, is that the molecule is ionized, and the process is

$$M + h\nu \to M_k^+ + e^-$$
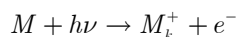
where M_k^+ is the kth excited state of the cation. Experimentally, we measure the kinetic energy of the ionized electron (typically by measuring how strong a field has to be in order to "stop" the electron).

(b) The ionization potential (from ground state to ground state) of the Beryllium atom is .3426 Hartree. If the HeI line is used in the spectrometer, what do you predict the kinetic energy of the "fastest" electrons we observe will be?

$$
\begin{aligned}
T &= E_{total} - I \\
&= h\nu - I \\
&= .7797 - .3426 \text{ Hartree} \\
&= .4371 \text{ Hartree}
\end{aligned}
$$

The final state of the system is clearly a "free electron" and a state of the cation. Recall, in particular, that while we have concentrated on the "bound states" of atoms, there were also "continuum" states—states with positive energy. Let's denote the wave function for a continuum state describing an electron with kinetic energy T as

$$\xi_T(z) \equiv \left| \begin{array}{l} \text{"scattering" or "continuum" eigenfunction} \\ \text{corresponding to an electron with kinetic} \\ \text{energy equal to T.} \end{array} \right. \tag{1}$$

Even though the electron is "free", the mere existence of the nucleus affects the detailed form of $\xi_T(z)$, and so $\xi_T(z)$ is system independent. In addition, there are an infinite number of different functions that satisfy the definition in Eq. (1).

Suppose the long-wavelength approximation is good. Then the dipole moment acting on the ith electron in the system can cause the electron to ionize, so that the system changes from the ground state of the neutral system, $\Psi(z_1, ..., z_N)$, with energy E to a state of the ion, $\xi_T(z_i)\Psi_k^+(z_1, ..., z_{i-1}, z_{i+1}, ..., z_N)$. The total ionization "cross section" is just the sum of this process, the corresponding process for the other $N-1$ electrons in the system.

(c) Based on the preceding model, write a formula for the rate at which the ith electron in the system is removed to form an excited state of the cation where the ionized electron is described by $\xi_T(z_i)$.

We need to write a formula for the spectroscopic transition rate from the "initial" to the "final" state. This is the content of Fermi's Golden Rule:

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

Now, from the above text, the "initial" state is the ground state of the neutral system, and its wave function is $\Psi(z_1, ..., z_N)$. The final state is the wave function of the cation with electron i removed, an in a "free-electron" orbital. The wave function of the final state is then $\xi_T(z_i)\Psi_k^+(z_1, ..., z_{i-1}, z_{i+1}, ..., z_N)$. The dipole operator "induced" the transition, so it was acting on the electron that was ionized—write the dipole operator as $\hat{\mu}(z_i)$.

This much of the problem is "given"—I'm just repeating it here so you can see how it "fits together." Now, we just substitute into Fermi's Golden Rule, which gives

$$W_{fi} = \frac{2\pi V^2}{\hbar} g(\hbar\omega_{fi}) \left| \left\langle \xi_T(z_i)\Psi_k^+(z_1, ..., z_{i-1}, z_{i+1} ... z_N) \left| \hat{\mu}(z_i) \right| \Psi(z_1, ... z_N) \right\rangle \right|^2$$

Next, we need to recognize that when we take a wave function for a cation times a wave function for a neutral molecule and integrate over all but one coordinate, z_i, we get the Dyson orbital, $g_k(z_i)$. This fundamental recognition is very important, but there are a lot of "hints"—note that the *very first sentence* of the problem hinted that the Dyson orbitals/Feynman-Dyson

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Amplitudes/Generalized Overlap Amplitudes would be important here. Parts "D" and "E" also mention these orbitals.

The definition of the "ionization" Dyson orbitals is:

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

This is Eq. (217) in the notes, with electron "i" replacing electron "N" as the variable of integration. Directly from this equation, we see that:

$$\left\langle \Psi_k^+ \left(\boldsymbol{z}_1, \ldots, \boldsymbol{z}_{i-1}, \boldsymbol{z}_{i+1} \ldots \boldsymbol{z}_N \right) \middle| \Psi \left(\boldsymbol{z}_1, \ldots \boldsymbol{z}_N \right) \right\rangle_{1,2\ldots i-1, i+1, \ldots N} = \frac{g_k(\boldsymbol{z}_i)}{\sqrt{N}}$$

where the notation indicates that we do not intergrate over the ith-electron.

Look at the Fermi's Golden Rule expression—if we do the "integration" in the bra-ket over electrons 1,2,...i-1,i+1,...N first, and then the integration over electron i second, then we obtain

$$W_{fi} = \frac{2\pi V^2}{\hbar} g\left(\hbar \omega_{fi} \right) \left| \left\langle \xi_T(\boldsymbol{z}_i) \middle| \hat{\mu}(\boldsymbol{z}_i) \middle| \left\langle \Psi_k^+ \left(\boldsymbol{z}_1, \ldots, \boldsymbol{z}_{i-1}, \boldsymbol{z}_{i+1} \ldots \boldsymbol{z}_N \right) \middle| \Psi \left(\boldsymbol{z}_1, \ldots \boldsymbol{z}_N \right) \right\rangle_{1,2\ldots i-1, i+1, \ldots N} \right\rangle_i \right|^2$$

Substituting the definition for the Dyson orbital into this expression, we have

$$W_{fi} = \frac{2\pi V^2}{\hbar} g\left(\hbar \omega_{fi} \right) \left| \left\langle \xi_T(\boldsymbol{z}_i) \middle| \hat{\mu}(\boldsymbol{z}_i) \middle| \frac{g_k(\boldsymbol{z}_i)}{\sqrt{N}} \right\rangle_i \right|^2$$

$$W_{fi} = \frac{2\pi V^2}{N\hbar} g\left(\hbar \omega_{fi} \right) \left| \left\langle \xi_T \middle| \hat{\mu} \middle| g_k \right\rangle \right|^2$$

Note that I put in A LOT of steps here that would not be required—or even expected—in your solution.

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(d) We cannot assume that the ith electron is ionized—all the electrons are equivalent. To form the total transition rate, we must multiply the preceding result by the number of electrons, N, since the total rate is the sum of the ionization rate for electron 1, electron 2, electron 3 .... electron N. In addition, since there are many states for the free electron with the same kinetic energy, we should sum over these states, so the total rate of ionization to form electrons with a given kinetic energy is $N\sum_{\xi_T}\left(\text{rate from part (c)}\right).$

Show that this gives a simple formula for the transition rate (in particular, the dependence on the number of electrons should drop out) in terms of the Dyson orbitals.

Chug and Plug on the result from the last section. The "N" cancels out the "N" in the denominator. Summing over the continuum eigenstates gives:

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

Attached is a table including Ionization potentials computed from an accurate Configuration Interaction calculation for Beryllium, as well as experimental data.

Be$^+$	EKT				CI			Expt.
	GOA	IP	m	Overlap	GOA	IP	m	IP
$1s^2 2s$	$s1$	0.3420	0.8884	1.000 000	$s1$	0.3420	0.8883	0.3426[a]
$1s^2 3s$	$s2$	0.7478	0.2039×10^{-1}	0.999 994	$s2$	0.7436	0.1919×10^{-2}	0.7446[a]
$1s^2 4s$					$s3$	0.8681	0.1509×10^{-2}	0.8687[a]
$1s^2 5s$	$s3$	1.0318	0.2162×10^{-2}	0.9987	$s4$	0.9387	0.1162×10^{-2}	0.9228[a]
$1s^2 6s$					$s5$	1.1797	0.7607×10^{-3}	0.9511[a]
$1s^2 7s$	$s4$	1.7615	0.3652×10^{-3}	0.8960	$s6$	1.7430	0.1387×10^{-3}	0.9678[a]
$1s^2 8s$	$s5$	3.2129	0.3274×10^{-2}	0.9401	$s7$	2.8528	0.7930×10^{-4}	
$1s 2s^2$	$s6$	4.6936	0.9851	0.999 997	$s8$	4.5353	0.760852	4.5408[b]
$1s^2 2p$	$p1$	0.4888	0.2922×10^{-1}	1.0000	$p1$	0.4881	0.2917×10^{-1}	0.4881[a]
$1s^2 3p$	$p2$	1.0388	0.5559×10^{-4}	0.9948	$p2$	0.7819	0.4324×10^{-4}	0.7823[a]
$1s^2 4p$					$p3$	0.8835	0.1650×10^{-4}	0.8837[a]
$1s^2 5p$					$p4$	0.9342	0.1571×10^{-4}	0.9302[a]
$1s^2 3d$	$d1$	0.8516		0.9995	$d1$	0.7973		0.7894

Note that ionization potentials are observed not only for the $1s^2 2s^2 \rightarrow 1s^2 2s^1$ transition, but also for other states, e.g., $1s^2 2s^2 \rightarrow 1s^2 2p^1$. These states are said to represent "shake-up" transitions because the electrons that were "left behind" were "shaken up" by the excitation process. I use a crude billiard ball analogy: when you fire the cue ball at one of the billiards, there is some chance you will accidentally hit another one of the billiards along the way, thereby "exciting" that ball even as you "remove" the targeted ball from the table (that is, presuming you are better than me at pool.)

For the CI calculation, the value of "m" is exactly the normalization constant for the Dyson orbital,

$$\left\langle g_k\,\middle|\,g_k\right\rangle = m_k \tag{2}$$

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(e) In general, observing shake-up transitions is difficult because the number of photoelectrons—which measures the intensity of the transition—is much smaller. Based on your rate formula and Eq. (2), why do you think this is so.

Look back at Fermi's golden rule. We always used "normalized" wave functions in the rule, yet Eq. (2) leads us to conclude that the Dyson orbitals are not normalized. Let's define the normalized Dyson orbitals:

$$\gamma_k(\boldsymbol{z}) = \frac{g_k(\boldsymbol{z})}{\sqrt{m_k}}.$$

Substituting this expression the "Fermi's Golden Rule" expression for the transition rate gives

$$W_{fi} = \sum_{\xi_T} \left[\frac{2\pi V^2}{\hbar} g\left(\hbar\omega_{fi}\right) \right] \left| \left\langle \xi_T \left| \hat{\mu} \right| \sqrt{m}\gamma_k \right\rangle \right|^2$$

$$W_{fi} = \sum_{\xi_T} \left[\frac{2\pi V^2}{\hbar} g\left(\hbar\omega_{fi}\right) \right] \cdot m_k \cdot \left| \left\langle \xi_T \left| \hat{\mu} \right| \gamma_k \right\rangle \right|^2$$

This last formula now has a form that is more conventional—the "wave functions" for the "orbital of the initial electronic state", $\gamma_k(\boldsymbol{z})$, and the "final electronic state", $\xi_T(\boldsymbol{z})$ are both normalized. (Actually, the normalization of a continuum eigenstate is a bit tricky, but it is normalized "in a sense.") Some of you may have found it helpful to refer to the discussion of "orbital transitions" in the spectroscopy notes—pages 26 and following.

Anyway, from our revised form with "normalized" initial and final orbitals for the electron, it is clear that the rate is roughly proportional to m as long as the "other effects" (based on changing γ_k are not "too important). In particular, small m" gives a small rate, so the more "highly excited" final states of the cation are produced at a lower rate than the "simple" ionization process to the ground state of the cation.

As a piece of minutiae, one reason this treatment is justified is because there are so many states in the "sum" over continuum states, ξ_T, that the rate is not that sensitive to the "details" of $\gamma_k(\boldsymbol{z})$. The number of photoelectrons with the kinetic energy appropriate to a given process, then, is readily (if crudely) approximated approximated by m. You'll note, for example, that the one state

that was *not* observed experimentally was the $1s^2 8s$ state of the cation, which is not observed both because it is weak and because there are so many states "nearby" in energy that it becomes difficult to resolve (much less assign) the spectrum at this point.

(f) Show that if you approximate $g_k(r)$ using Koopmans' theorem (that is, using the Hartree-Fock wave function and the appropriate state of its cation), that $m = 0$. Why do you think $m > 0$ for more accurate treatments? (I'll give "bonus points" if your penetrating intellect can argue (no equations necessary) why m_k decreases as the "shake up level" increases. That is, why is the "occupation number" for the Dyson orbital associated with the $1s^2 3s^1$ state of the cation greater than that correspond to the $1s^2 8s^1$ state.)

In this approximation, the initial state is:

$$\Psi \approx \left| \psi_1 \psi_2 \ldots \psi_N \right|$$

and the final state is

$$\Psi_k^+ \approx \left| \psi_1 \ldots \psi_{N-2} \psi_k \right|$$

That is, we both took away an electron from orbital N *and excited an electron from orbital $N-2$ to an orbital that is not occupied in the ground state.* Here $k = 3s$ or $k = 8s$, say, while $N = 4$. Substituting these approximate wave functions into the definition of the Dyson orbital (cf. part **(c)**),

Now, we can immediately see, when we write out the "integral" we need to do,

$$\frac{1}{\sqrt{N}} g_k(z) \equiv \left\langle \Psi_k^+ \middle| \Psi \right\rangle_{1 \ldots N-1}$$
$$\approx \left\langle \left| \psi_1 \ldots \psi_{N-2} \psi_k \right| \middle\| \psi_1 \ldots \psi_N \right| \right\rangle_{1 \ldots N-1}$$
$$\approx \left\langle \left| \psi_1(z_1) \ldots \psi_{N-2}(z_{N-2}) \psi_k(z_{N-1}) \right| \middle\| \psi_1(z_1) \ldots \psi_N(z_N) \right| \right\rangle + permutations$$

The subsequent analysis is very similar to that on page 63 in the notes on computation. I would argue, by inspection, that:

- when we write out the terms in the Slater determinant and integrate, we have a sum of terms, and each term takes the form of a product of integrals like

$$\left\langle \psi_i \middle| \psi_j \right\rangle$$

and integrals like

$$\langle \psi_k | \psi_j \rangle$$

where i is a "core orbital" of the cation $(1 \leq i \leq N-2)$ and j is an "occupied orbital" in the neutral $(1 \leq j \leq N)$. The first form of the integral, $\langle \psi_{i \neq k} | \psi_j \rangle$ can be zero or one, but the latter factor, $\langle \psi_k | \psi_j \rangle$, is **_always_** zero. Thus, a product of terms of both types will be zero, a sum of a product such terms will still be zero, and so $g_k(\boldsymbol{z}) = 0$ for a shake-up transition in this model.

- If you did not recognize the above—again, I reiterate—if you "don't' get it" do it for a simple case (just 2 or 3 electrons will be enough to see the basic trends), you could do thus using the "Hartree product rule" (see the theorems on page 24). First, to get the desired form, we need to rewrite the integral using

$$
\begin{aligned}
g_k(\boldsymbol{x}) &= \int g_k(\boldsymbol{z}_N) \delta(\boldsymbol{z}_N - \boldsymbol{x}) d\boldsymbol{z}_N \\
&\approx \int \langle |\psi_1 \ldots \psi_{N-2} \psi_k| | |\psi_1 \ldots \psi_N| \rangle_{1 \ldots N-1} \delta(\boldsymbol{z}_N - \boldsymbol{x}) d\boldsymbol{z}_N \\
&\approx \langle |\psi_1 \ldots \psi_{N-2} \psi_k| |\delta(\boldsymbol{z}_N - \boldsymbol{x})| |\psi_1 \ldots \psi_N| \rangle_{1 \ldots N}
\end{aligned}
$$

which is the "conventional form" for a one-electron integral. This is a one-electron integral, and using the "generalized Hartree-product rule" (theorem 2 on page 24), we have

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$$g_k\left(\boldsymbol{x}\right) \approx \sqrt{N!}\left\langle\left(\psi_1\ldots\psi_{N-2}\psi_k\left|\left|\delta\left(\boldsymbol{z}_N-\boldsymbol{x}\right)\right|\right|\psi_1\ldots\psi_N\right|\right\rangle_{1\ldots N}$$

$$\approx \int\sqrt{N!}\left\langle\left(\psi_1\ldots\psi_{N-2}\psi_k\left|\left|\psi_1\ldots\psi_N\right)+\sum_{permutations}\left|\psi_1\ldots\psi_N\right)\right|\right\rangle_{1\ldots N-1}\delta\left(\boldsymbol{z}_N-\boldsymbol{x}\right)d\boldsymbol{z}_N$$

$$\approx \sqrt{N!}\int\left\langle\left(\psi_1\ldots\psi_{N-2}\psi_k\left|\left|\psi_1\ldots\psi_N\right)\right)\right\rangle_{1\ldots N-1}\delta\left(\boldsymbol{z}_N-\boldsymbol{x}\right)d\boldsymbol{z}_N$$

$$+\sqrt{N!}\int\left\langle\left(\psi_1\ldots\psi_{N-2}\psi_k\left|\sum_{permutations}\left|\psi_1\ldots\psi_N\right)\right)\right\rangle_{1\ldots N-1}\delta\left(\boldsymbol{z}_N-\boldsymbol{x}\right)d\boldsymbol{z}_N$$

$$=\sqrt{N!}\left\langle\psi_k\left|\psi_{N-1}\right\rangle\prod_{i=1}^{N-2}\left\langle\psi_i\left|\psi_i\right\rangle+\sqrt{N!}\left(\text{permutation term}\right)\right.$$

$$(3)$$

and we note that no matter how we "change the order" of the orbitals, there will always be an orbital assigned to electron $\boldsymbol{z}_{N-1}$, this orbital will never be ψ_k, and so the integrals will always be zero.

The "second part" of this problem tests whether you remember why Koopmans' theorem (which is what we just did, more or less) is approximate. There are two effects. One is the neglect of electron correlation. The second, often more important, effect is the neglect of orbital relaxation: after you remove an electron from an orbital or excite an electron from one orbital to another (or both), the orbitals "rearrange" or "relax" to ease the stress to which they have been applied. When this "relaxation" is taken into account, you find $m_k > 0$.

As for the "bonus", "orbital relaxation" occurs because the orbitals mix together. This can be explained because, when the occupied orbitals change, the Hartree-Fock potential changes. But, by the "self-consistent" argument, when the potential changes, the orbital must change also, and this is the essence of "orbital relaxation." Think about treating the "change in Hartree-Fock potential" due to "ionization + shake-up" as a perturbation, $\Delta v_{HF}\left(\boldsymbol{r}\right)$. Then we can, from perturbation theory, approximate the new (perturbed) orbitals as

$$\Delta\psi_\alpha^{ion}\left(\boldsymbol{r}\right)\equiv\sum_{\substack{i=1\\i\neq\alpha}}^{\infty}\frac{\left\langle\psi_\alpha\left|\Delta v_{HF}\left(\boldsymbol{r}\right)\right|\psi_i\left(\boldsymbol{r}\right)\right\rangle}{\varepsilon_\alpha-\varepsilon_i}\psi_i\left(\boldsymbol{r}\right)$$

where we have just taken the "standard" perturbation theory expression for the change for a wave function due to a change in potential. Note that

- orbitals that are close together in energy have a small denominator, and so the "mixing" is large. That is, in orbital relaxation, we expect that $\psi_\alpha(\boldsymbol{r}) \to \sum_{i=1}^{\infty} c_i \psi_i(\boldsymbol{r})$ but that, because the perturbation is "small", the components of the "close-by orbitals", $\psi_{\alpha+1}(\boldsymbol{r}), \psi_{\alpha-1}(\boldsymbol{r})$, etc., are expected to be largest.

- orbitals that are "well separated" in energy are not expected to mix very much.

Now, referring back to the "old work", we recall that the reason $m_k = 0$ in Hartree-Fock theory for a "shake-up" transition was because we had integrals like $\langle \psi_k | \psi_i \rangle$, which were zero because $1 \le i \le N$. But this is no longer the case now, because the "relaxed orbital" ψ_k has a small component in the direction ψ_i. In fact, we have that

$$m_k \propto \sum_{i=1}^{N} \left| \frac{\langle \psi_k | \Delta v_{HF}(\boldsymbol{r}) | \psi_i(\boldsymbol{r}) \rangle}{\varepsilon_k - \varepsilon_i} \right|^2 + (corrections)$$

but, owing to the size of the denominator, this "occupation number" will be smaller for more highly excited states, because the denominators are larger. By far the most important terms are the last two terms in the above sum.

What I was looking for here, though, was not anything as detailed as the above. I wanted you to be able to say—make some sort of "hand-waving" argument for—that "highly excited orbitals" are "more orthogonal" to the core orbitals than the lower-lying orbitals. One possible argument would be based on the number of nodes.

(g) On the next page, I have plotted the lowest states of the Hydrogen molecule and hydrogen molecule ion. Plot the number of electrons in a photoelectron spectroscopy experiment using the He(I) line versus vs. kinetic energy.

This is a Franck-Condon problem. Look back at the "vibrational structure in electronic transitions" section of your notes—did we ever make any approximations that would make these considerations not true in photoionization? No. On intuitive grounds, we have that there are a number of states—electronic states given by the curves (as drawn) and vibrational states, given by the "sketches" I've placed in the "revised" curves. When we ionize the system, we can also change the vibrational state of the system, so we observe a "Franck-Condon progression" of more-or-less equispaced lines.

What am I looking for? Well, I want to see the "tell-tale bumps" due to the vibrational transitions. I want to see that since the energy gap between the curves looks like about .55 Hartree, and the energy of the HeI line is .78 Hartree, then there are no electrons with kinetic energy greater than $.78 - .55 = .23$ Hartree. I want you to recognize that the energy of the process

$$H_2 \rightarrow H^+ + H$$

is, from the figure, greater than 1 Hartree (it is actually 1.174 Hartree), so that we cannot observe dissociation with the He(I) line. Therefore, we see a "Franck-Condon progression" that starts at .23 Hartree and moves along for a while, ending (somewhat abruptly, perhaps, or dying off gradually—I don't care). (In actuality, it will tend to die off gradually since very highly excited vibrational states of the cation will be almost orthogonal to the ground vibrational state, but non-Franck-Condon effects are also important here (and this tends to lengthen the progression. So I'm not planning to be "picky" about this).

The "lines" should be spaced by something between .01 and .001 Hartree— that is the "average spacing" of vibrational energy levels. So we get something like the plot on the next page.
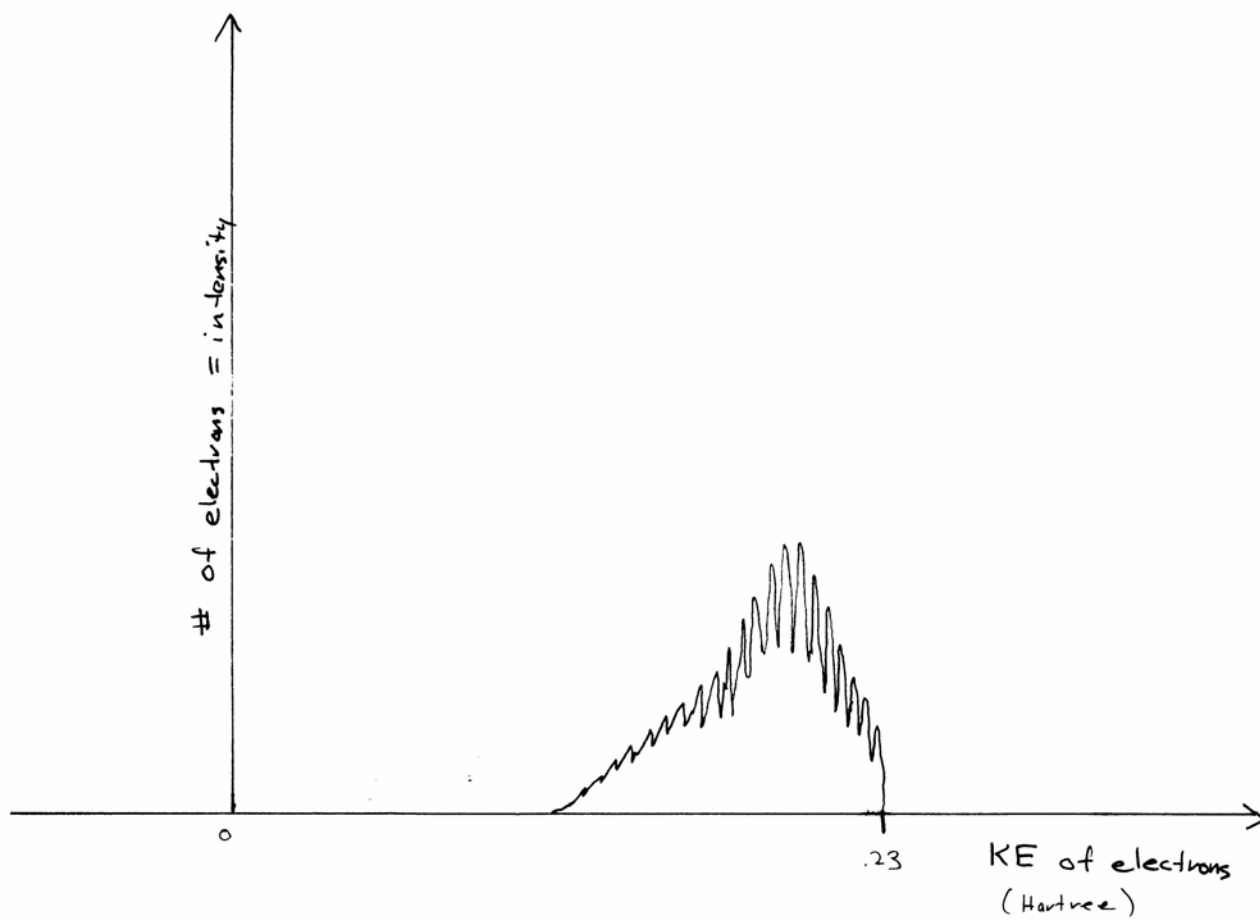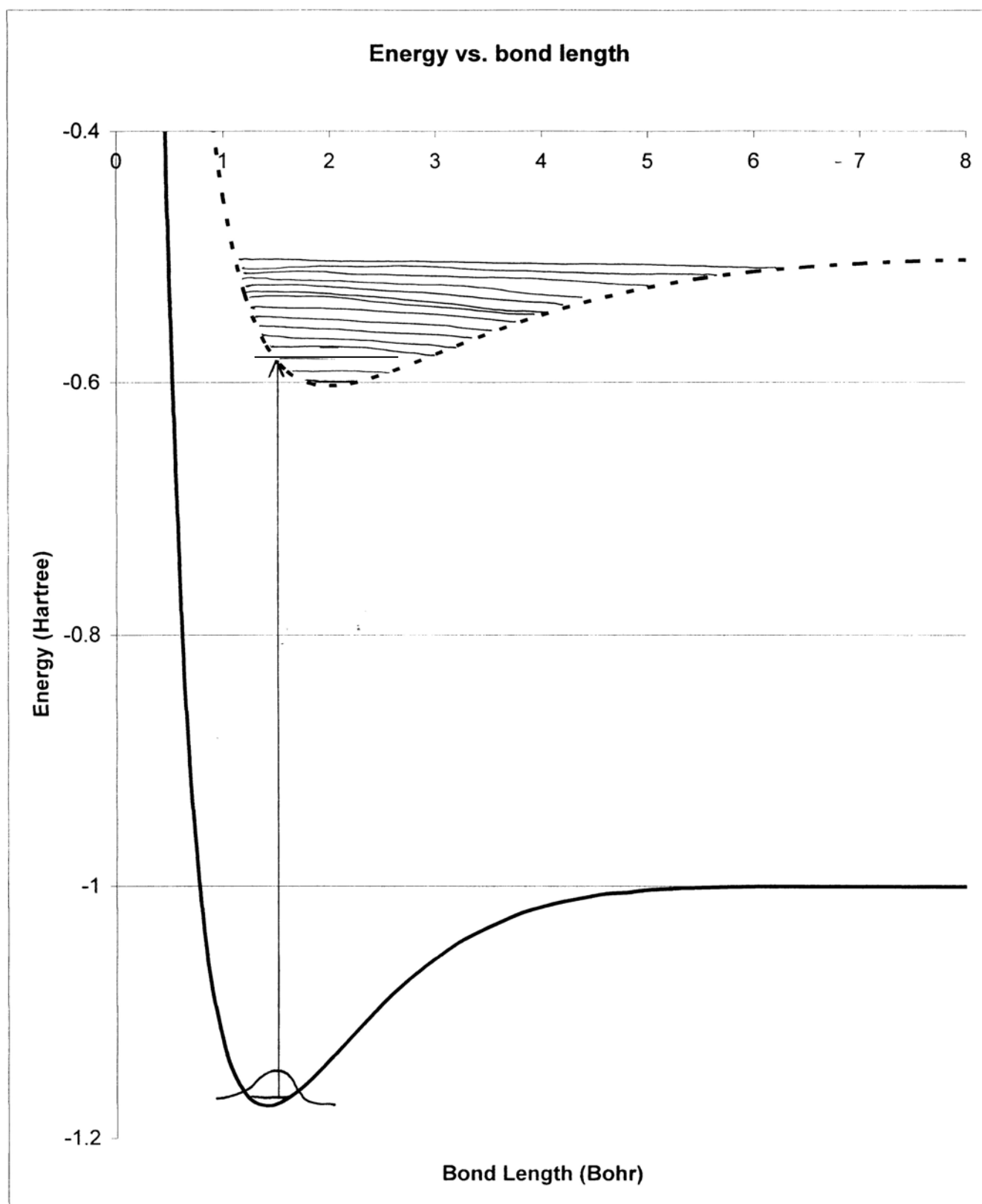
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Figure: Potential energy curves for the Hydrogen molecule (solid) and Hydrogen molecule ion, (dotted). The bond length of H_2 is about 1.4 Bohr. For H_2^+ it is about 2.0 Bohr.

2. **Static versus Dynamic Correlation.**

Consider a three-electron system, with Slater determinant $|\psi_1\psi_2\psi_3|$. To refine our treatment, let us suppose that the excited state, $|\psi_1\psi_4\psi_5|$, is the most important "correction" to this Slater determinant. If so, then the normalized wave function

$$\Psi(z_1, z_2, z_3) \equiv D|\psi_1\psi_2\psi_3| + \sqrt{1 - D^2}\,|\psi_1\psi_4\psi_5| \qquad (4)$$

can be considered an improved model for the ground state. Here $0 \leq D \leq 1$, and you can assume all wave functions and orbitals are real and orthonormal.

(a) **When static correlation is important, do you expect $\sqrt{1 - D^2}$ to be large or small?**

Large. but still less than D. A typical value might be $\sqrt{1 - D^2} \approx .3$ (which gives $D \approx .8$). For "dynamic" correlation, taking $\sqrt{1 - D^2} \lesssim .1$ would be reasonable.

(b) **Compute the probability of observing one electron with space/spin z and another electron with space-spin z'. How does this expression depend on the size of D? When the primary role of the additional determinant is to help provide "dynamic correlation terms" in the Hartree-Fock determinant, does the way electrons are arranged relative to each other?**

I'll confess this problem is a bit tedious. But it isn't really hard. There is a key idea here: if you have a "two-electron" quantity, make it "look like" the two-electron integrals you've already done (or that I've already done in the notes). Moreover, it is "just" a three-electron integral, so you can do it directly—by hand. Finally, there are Eqs. (245) and (246) in the notes—they do EXACTLY what you want (though I chose a different convention there from what I'll choose in the key.

I'm going to resist the temptation to just copy from the notes, though, since most of you seemed to struggle with this problem. The probability there is an electron at z is given by

$$\rho(z) \equiv \left\langle \Psi \left| \sum_{i=1}^{N} \delta(z_i - z) \right| \Psi \right\rangle$$

while the probability there is both this electron at z and another electron at z' is

$$\rho_2(z, z') \equiv \left\langle \Psi \left| \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \delta(z_i - z)\delta(z_j - z') \right| \Psi \right\rangle$$

Name:

I could have chosen a different "convention" for the normalization (many people would choose $j > i$, so they were counting 'unique pairs' of electrons. Still, that's a fine point.

The equation for the electron density looks a lot like the one-electron integrals in the notes. The equation for the pair-electron density (or 2-density) resembles the two electron integrals with one key difference: each individual operator is not invariant to changes between z_i and z_j (unlike $\hat{v}_{ee}(z_i, z_j) = \frac{1}{|r_i - r_j|}$)— changing i and j in $\delta(z_i - z)\delta(z_j - z')$ changes the roles of z and z'. We can regain the symmetry, however, by writing the pair density as

$$\rho_2(z, z') \equiv \left\langle \Psi \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left[\delta(z_i - z)\delta(z_j - z') + \delta(z_i - z')\delta(z_j - z) \right] \right| \Psi \right\rangle$$

Let's just call this operator

$$\rho_2(z, z') \equiv \left\langle \Psi \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \hat{\rho}_2(z_i, z_j) \right| \Psi \right\rangle.$$

Now, substitute in the form of the wave function we are interested in, Eq. (4), and multiply out the terms.

$$\rho_2(z, z') \equiv \left\langle \Psi \left| \sum_{i=1}^{N} \sum_{j \neq i}^{N} \delta(z_i - z)\delta(z_j - z') \right| \Psi \right\rangle$$

$$= \left\langle \begin{pmatrix} D |\psi_1 \psi_2 \psi_3| \\ +\sqrt{1 - D^2} |\psi_1 \psi_4 \psi_5| \end{pmatrix} \left| \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{\rho}_2(z_i, z_j) \right| \begin{pmatrix} D |\psi_1 \psi_2 \psi_3| \\ +\sqrt{1 - D^2} |\psi_1 \psi_4 \psi_5| \end{pmatrix} \right\rangle$$

$$= D^2 \left\langle |\psi_1 \psi_2 \psi_3| \left| \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{\rho}_2(z_i, z_j) \right| |\psi_1 \psi_2 \psi_3| \right\rangle$$

$$+ D\sqrt{1 - D^2} \left[\begin{array}{l} \left\langle |\psi_1 \psi_2 \psi_3| \left| \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{\rho}_2(z_i, z_j) \right| |\psi_1 \psi_4 \psi_5| \right\rangle \\ + \left\langle |\psi_1 \psi_4 \psi_5| \left| \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{\rho}_2(z_i, z_j) \right| |\psi_1 \psi_2 \psi_3| \right\rangle \end{array} \right]$$

$$+ (1 - D^2) \left\langle |\psi_1 \psi_4 \psi_5| \left| \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{\rho}_2(z_i, z_j) \right| |\psi_1 \psi_4 \psi_5| \right\rangle$$

Since we were told the orbitals were real, we can simplify this form to

$$\rho_2(z, z') \equiv D^2 \left\langle |\psi_1 \psi_2 \psi_3| \left| \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{\rho}_2(z_i, z_j) \right| |\psi_1 \psi_2 \psi_3| \right\rangle$$

$$+ 2D\sqrt{1 - D^2} \left(\left\langle |\psi_1 \psi_2 \psi_3| \left| \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{\rho}_2(z_i, z_j) \right| |\psi_1 \psi_4 \psi_5| \right\rangle \right)$$

$$+ (1 - D^2) \left\langle |\psi_1 \psi_4 \psi_5| \left| \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{\rho}_2(z_i, z_j) \right| |\psi_1 \psi_4 \psi_5| \right\rangle$$

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You should be able to answer the question at this point, without needing to go any further. So let me answer the question here, and then I'll multiply it out just to show you how it's done.

The first term is equal to the pair-electron-density of the Hartree-Fock wave function, and is weighted by D^2. The last term is similar, but for the "excited state." It depends on $1 - D^2$. The "hard part" is the cross term. First of all, it is not zero—it has the same form as the term in the CI matrix expansion for a double excitation (cf. Eq. (246) or (276) for how to get this formula—it is not very hard, it is just a simple application of the "Hartree-Product rule" with two different orbitals.) In particular, the "cross term" has the form:

$$\left\langle \Phi \left| \hat{H} \right| \Phi_{ij}^{ab} \right\rangle = \left\langle \Phi \left| \hat{V}_{ee} \right| \Phi_{ij}^{ab} \right\rangle$$
$$= \left\langle \Phi \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \hat{v}_{ee}\left(r_i, r_j\right) \right| \Phi_{ij}^{ab} \right\rangle$$
$$= \left\langle \psi_i \psi_j \left| \hat{v}_{ee} \right| \psi_a \psi_b \right\rangle - \left\langle \psi_i \psi_j \left| \hat{v}_{ee} \right| \psi_b \psi_a \right\rangle$$

So we have:

$$\rho_2\left(z, z'\right) \equiv D^2 \rho_2^{HF}\left(z, z'\right) + (1 - D^2)\rho_2^{excited}\left(z, z'\right)$$
$$+ 2D\sqrt{1 - D^2}\left(\left\langle \psi_i \psi_j \left| \hat{\rho}_2 \right| \psi_a \psi_b \right\rangle - \left\langle \psi_i \psi_j \left| \hat{\rho}_2 \right| \psi_b \psi_a \right\rangle\right)$$

We are supposed to discuss the *change* in the way electrons are arranged relative to each other in the Hartree-Fock (uncorrelated) case. So we subtract off $\rho_2^{HF}\left(z, z'\right)$ to obtain

$$\Delta\rho_2\left(z, z'\right) \equiv D^2 \rho_2^{HF}\left(z, z'\right) + (1 - D^2)\rho_2^{excited}\left(z, z'\right)$$
$$+ 2D\sqrt{1 - D^2}\left(\left\langle \psi_i \psi_j \left| \hat{\rho}_2 \right| \psi_a \psi_b \right\rangle - \left\langle \psi_i \psi_j \left| \hat{\rho}_2 \right| \psi_b \psi_a \right\rangle\right)$$
$$- \rho_2^{HF}\left(z, z'\right)$$
$$= \left(1 - D^2\right)\left(\rho_2^{excited}\left(z, z'\right) - \rho_2^{HF}\left(z, z'\right)\right)$$
$$+ 2D\sqrt{1 - D^2}\left(\left\langle \psi_i \psi_j \left| \hat{\rho}_2 \right| \psi_a \psi_b \right\rangle - \left\langle \psi_i \psi_j \left| \hat{\rho}_2 \right| \psi_b \psi_a \right\rangle\right)$$

If dynamic correlation is important, then D is close to 1. So $1 - D^2$ will be small and $D\sqrt{1 - D^2} \approx \sqrt{1 - D^2}$ will be small, but the square root of a small number is comparatively large ($\sqrt{\frac{1}{100}} = \frac{1}{10}$, etc.). So we conclude that the "important term" is the second term, and that it's size is proportional to $D\sqrt{1 - D^2}$ (which is small) but that the first term is much smaller yet.

To see this more explicitly, let $D = 1 - \varepsilon$. Then

$$\Delta\rho_2\left(z,z'\right) = \left(1-(1-\varepsilon)^2\right)\left(\rho_2^{excited}\left(z,z'\right)-\rho_2^{HF}\left(z,z'\right)\right)$$
$$+2\left(1-\varepsilon\right)\sqrt{1-(1-\varepsilon)^2}\left(\left\langle\psi_i\psi_j\left|\hat{\rho}_2\right|\psi_a\psi_b\right\rangle-\left\langle\psi_i\psi_j\left|\hat{\rho}_2\right|\psi_b\psi_a\right\rangle\right)$$
$$=\left(1-1+2\varepsilon-\varepsilon^2\right)\left(\rho_2^{excited}\left(z,z'\right)-\rho_2^{HF}\left(z,z'\right)\right)$$
$$+2\left(1-\varepsilon\right)\sqrt{1-1+2\varepsilon-\varepsilon^2}\left(\left\langle\psi_i\psi_j\left|\hat{\rho}_2\right|\psi_a\psi_b\right\rangle-\left\langle\psi_i\psi_j\left|\hat{\rho}_2\right|\psi_b\psi_a\right\rangle\right)$$
$$\approx 2\varepsilon\left(\rho_2^{excited}\left(z,z'\right)-\rho_2^{HF}\left(z,z'\right)\right)$$
$$+2\sqrt{2}\cdot\sqrt{\varepsilon}\left(\left\langle\psi_i\psi_j\left|\hat{\rho}_2\right|\psi_a\psi_b\right\rangle-\left\langle\psi_i\psi_j\left|\hat{\rho}_2\right|\psi_b\psi_a\right\rangle\right)$$

(we neglect terms that are proportional to $\varepsilon^{3/2}$ (or higher powers of ε) as small). Again, we notice that the "second term" is a lot more important.

If you really want an explicit expression for $\Delta\rho_2(z,z')$ (and I did not ask for this, but I put it in my "test-day" solution since people seemed to be trying to find it), then you just note that, for instance,

$$\rho_2^{HF}\left(z,z'\right)=\left\langle\left|\psi_1\psi_2\psi_3\right|\left|\sum_{i=1}^{2}\sum_{j=i+1}^{3}\hat{\rho}_2\left(z_i,z_j\right)\right|\left|\psi_1\psi_2\psi_3\right|\right\rangle$$

and use the result on two-electron integrals between Slater determinants, for example, Eq. (83). Replacing ψ_2 with ψ_4 and ψ_3 with ψ_5 in the above formula gives $\rho_2^{excited}(z,z')$.

(c) Compute the probability of observing an electron with space/spin z for the wave function, Eq. (4). How does this expression depend on the size of D? When the primary role of the additional determinant is to help provide "dynamic correlation terms" in the Hartree-Fock determinant, does the way electrons are arranged in space change significantly?

There is an "easy way" and a "hard way" to do this problem.

The masochist's method:

The "hard way" is not that hard—go back to the expression for the electron density at the start of part (b). We have

Name:

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

$$= \left\langle \left(\begin{array}{l} D\left|\psi_1\psi_2\psi_3\right| \\ +\sqrt{1-D^2}\left|\psi_1\psi_4\psi_5\right| \end{array} \right) \left| \sum_{i=1}^{N} \delta\left(\boldsymbol{z}_i - \boldsymbol{z}\right) \right| \left(\begin{array}{l} D\left|\psi_1\psi_2\psi_3\right| \\ +\sqrt{1-D^2}\left|\psi_1\psi_4\psi_5\right| \end{array} \right) \right\rangle$$

$$= D^2 \left\langle \left|\psi_1\psi_2\psi_3\right| \left| \sum_{i=1}^{N} \delta\left(\boldsymbol{z}_i - \boldsymbol{z}\right) \right| \left|\psi_1\psi_2\psi_3\right| \right\rangle$$

$$+ D\sqrt{1-D^2} \left(\begin{array}{l} \left\langle \left|\psi_1\psi_2\psi_3\right| \left| \sum_{i=1}^{N} \delta\left(\boldsymbol{z}_i - \boldsymbol{z}\right) \right| \left|\psi_1\psi_4\psi_5\right| \right\rangle \\ + \left\langle \left|\psi_1\psi_4\psi_5\right| \left| \sum_{i=1}^{N} \delta\left(\boldsymbol{z}_i - \boldsymbol{z}\right) \right| \left|\psi_1\psi_2\psi_3\right| \right\rangle \end{array} \right)$$

$$+ (1-D^2) \left\langle \left|\psi_1\psi_4\psi_5\right| \left| \sum_{i=1}^{N} \delta\left(\boldsymbol{z}_i - \boldsymbol{z}\right) \right| \left|\psi_1\psi_4\psi_5\right| \right\rangle$$

$$= D^2 \left\langle \left|\psi_1\psi_2\psi_3\right| \left| \sum_{i=1}^{N} \delta\left(\boldsymbol{z}_i - \boldsymbol{z}\right) \right| \left|\psi_1\psi_2\psi_3\right| \right\rangle$$

$$+ 2D\sqrt{1-D^2} \left(\left\langle \left|\psi_1\psi_2\psi_3\right| \left| \sum_{i=1}^{N} \delta\left(\boldsymbol{z}_i - \boldsymbol{z}\right) \right| \left|\psi_1\psi_4\psi_5\right| \right\rangle \right)$$

$$+ (1-D^2) \left\langle \left|\psi_1\psi_4\psi_5\right| \left| \sum_{i=1}^{N} \delta\left(\boldsymbol{z}_i - \boldsymbol{z}\right) \right| \left|\psi_1\psi_4\psi_5\right| \right\rangle$$

The term on the first line is just the Hartree-Fock density (times D^2) The integral on the last line is just the density of the excited state, $\rho^{exc.}(\boldsymbol{z})$. What about the cross term? The cross term is between two Slater determinants that differ by two orbitals, but the operator is only a one-electron operator. It's zero! (This follows directly from the table on page 18—integrals of "one-electron" operators between determinants (or Hartree products—remember Slater determinants are just sums of Hartree-product terms) that differ by more than one orbital are always zero. Again, this is only three-electrons—you can "write it out.")

So we have

$$\rho\left(\boldsymbol{z}\right) = D^2 \rho^{HF}\left(\boldsymbol{z}\right) + \left(1 - D^2\right) \rho^{exc.}\left(\boldsymbol{z}\right) + 2D\sqrt{1-D^2}\left(0\right)$$

and so the "change in density" is

$$\Delta\rho\left(\boldsymbol{z}\right) = \left(1 - D^2\right)\left(\rho^{exc.}\left(\boldsymbol{z}\right) - \rho^{HF}\left(\boldsymbol{z}\right)\right)$$
$$\text{OR}$$
$$\Delta\rho\left(\boldsymbol{r}\right) = \left(2\varepsilon - \varepsilon^2\right)\left(\rho^{exc.}\left(\boldsymbol{z}\right) - \rho^{HF}\left(\boldsymbol{z}\right)\right)$$

(5)

which much, much smaller than the size of the change in the pair distribution.

When we have static correlation, then $\sqrt{1-D^2} \lesssim .1$ and so the change in density is very small—on the order of 1% of the difference in density between the

ground and excited states. This is more-or-less insignificant. (By contrast, the change in the "pair density" is of the order of 10% of the "cross term" from problem (b), which is substantial.)

The Easy Way:

I said there was a hard and an easy way to work the problem. The easy way is to simply integrate the result from part (b): the probability of observing an electron at z is just

$$\rho(z) \propto \int \rho_2\left(z, z'\right) dz'.$$

We immediately obtain

$$
\begin{aligned}
\rho(z) &\propto D^2 \rho^{HF}(z) + \left(1 - D^2\right) \rho^{exc.}(z) \\
&\quad + 2D\sqrt{1 - D^2} \int \left(\left\langle \psi_i \psi_j \left| \hat{\rho}_2 \right| \psi_a \psi_b \right\rangle - \left\langle \psi_i \psi_j \left| \hat{\rho}_2 \right| \psi_b \psi_a \right\rangle\right) dz' \\
&\propto D^2 \rho^{HF}(z) + \left(1 - D^2\right) \rho^{exc.}(z) \\
&\quad + 2D\sqrt{1 - D^2} \int \left(\psi_i(z) \psi_a(z) \psi_j\left(z'\right) \psi_b\left(z'\right) - \psi_i(z) \psi_a(z) \psi_b\left(z'\right) \psi_j\left(z'\right)\right) dz' \\
&\propto D^2 \rho^{HF}(z) + \left(1 - D^2\right) \rho^{exc.}(z) \\
&\quad + 2D\sqrt{1 - D^2} \left(\psi_i(z) \psi_a(z) \left\langle \psi_b \middle| \psi_j \right\rangle - \psi_j(z) \psi_a(z) \left\langle \psi_b \middle| \psi_i \right\rangle\right) \\
&\propto D^2 \rho^{HF}(z) + \left(1 - D^2\right) \rho^{exc.}(z)
\end{aligned}
\tag{6}
$$

This is enough to do the preceding analysis.

(d) Derive an expression for the difference in energy between the two Slater determinants in Eq. (4).

Just subtract the energy formulae for the Slater determinants. Then we use group terms so we can use the definition of the orbital energy. You could use the "summation" notation, but for three electrons it is probably simpler to just write everything out explicitly.

Name:

$$
\begin{aligned}
E_{exc}^{i \to a} &\approx E_{23}^{45} - E_{HF} \\
&\approx \left(h_1 + h_4 + h_5 + J_{14} + J_{15} + J_{45} - J_{14} - K_{15} - K_{45} \right) \\
&\quad - \left(h_1 + h_2 + h_3 + J_{13} + J_{12} + J_{23} - K_{12} - K_{13} - K_{23} \right) \\
&\approx \left[\begin{array}{l} h_4 + \left(J_{14} - K_{14} \right) + \left(J_{24} - K_{24} \right) + \left(J_{34} - K_{34} \right) - \left(\left(J_{24} - K_{24} \right) + \left(J_{34} - K_{34} \right) \right) \\ + h_5 + \left(J_{15} - K_{15} \right) + \left(J_{25} - K_{25} \right) + \left(J_{35} - K_{35} \right) - \left(\left(J_{25} - K_{25} \right) + \left(J_{35} - K_{35} \right) \right) \\ + \left(J_{45} - K_{45} \right) \end{array} \right] \\
&\quad - \left[\begin{array}{l} h_2 + \left(J_{12} - K_{12} \right) + \left(J_{23} - K_{23} \right) \\ h_3 + \left(J_{13} - K_{13} \right) + \left(J_{23} - K_{23} \right) - \left(J_{23} - K_{23} \right) \end{array} \right] \\
&= \left(\varepsilon_4 + \varepsilon_5 - \varepsilon_2 - \varepsilon_3 \right) - \left[\begin{array}{l} \left(J_{24} - K_{24} \right) + \left(J_{34} - K_{34} \right) \\ + \left(J_{25} - K_{25} \right) + \left(J_{35} - K_{35} \right) \end{array} \right] + \left[\begin{array}{l} \left(J_{23} - K_{23} \right) \\ + \left(J_{45} - K_{45} \right) \end{array} \right]
\end{aligned}
\tag{7}
$$

(e) Do you expect this expression to overestimate or underestimate the true excitation energy? (You DO NOT need to do any computations to answer this question!!)

It will underestimate the excitation energy: the "repulsion between states" due to the "non-crossing" rule tends to broaden the gap, and so the "correlated" excitation energy will be large (presuming our very simple CI expansion is any good.