Name:

Quiz 6

Chemistry 3BB3; Winter 2003

This quiz is on "computation."

1. **In "words", the essence of the Hartree-Fock method is to**
   (a) find the Slater determinant, Φ, that is "closest" to the exact wave function, Ψ.
   (b) find the Slater determinant, Φ, that has the lowest energy $\langle \Phi | \hat{H} | \Phi \rangle$.
   (c) find the Slater determinant, Φ, that gives the best approximation to the system's ground state energy, E.
   (d) find the Slater determinant, Φ, that has the exact ground state density, $\rho(\boldsymbol{r})$.
   (e) both (b) and (c)
   (f) both (c) and (d)

2. **Koopmans' Theorem gives us an interpretation for the energy of the occupied and unoccupied orbitals in Hartree-Fock theory. In particularly**

   The highest occupied orbital's energy is approximately equal to _____

   The lowest unoccupied orbital's energy is approximately equal to _____

3. **We wrote the Hartree-Fock energy formula in the form:**
$$E_{HF} = \sum_{i=1}^{N} h_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(J_{ij} - K_{ij} \right)$$
   with
$$h_i \equiv \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle = \left\langle \psi_i \left| -\frac{\nabla^2}{2} + v(\boldsymbol{r}) \right| \psi_i \right\rangle$$
   and
$$J_{ij} \equiv \left\langle \psi_i \psi_j \left| \frac{1}{|r-r'|} \right| \psi_i \psi_j \right\rangle = \iint \frac{|\psi_i(\boldsymbol{r})|^2 |\psi_j(\boldsymbol{r}')|^2}{|r-r'|} d\boldsymbol{r} d\boldsymbol{r}'$$
   What is the formula for K_{ij}?

   $$K_{ij} =$$

4. **We said that the Hartree-Fock Equations were**
$$\left(\frac{-\nabla^2}{2} + v(\boldsymbol{r}) + j(\boldsymbol{r}) - \hat{k}(\boldsymbol{r}, \sigma) \right) \psi_\alpha(\boldsymbol{r}, \sigma) = \varepsilon_\alpha \psi_\alpha(\boldsymbol{r}, \sigma)$$
   where σ denotes the spin of the electron. We had, for instance,
$$\hat{k}(\boldsymbol{z}) \psi_\alpha(\boldsymbol{z}) \equiv \sum_{i=1}^{N} \delta_{\sigma_i \sigma_\alpha} \iint \frac{\psi_i^*(\boldsymbol{r}') \psi_\alpha(\boldsymbol{r}')}{|r-r'|} d\boldsymbol{r}' \psi_i(\boldsymbol{r})$$
   What is the formula for:

   $$j(\boldsymbol{r}) =$$

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5. We said that the many-electron Green's function, $G(\tau, \tau'; E)$ satisfied an inhomogeneous differential equation similar to the Schrödinger equation. (Here τ denotes the spatial and spin coordinates of the electrons, $\tau \equiv (r_1, \sigma_1; r_2, \sigma_2; \ldots r_N, \sigma_N)$. This differential equation was:

$$\left(E - \hat{H}(\tau)\right) G(\tau, \tau'; E) =$$

6. Define $\hat{V}$ to be the difference between the system's Hamiltonian and the Hartree-Fock Hamiltonian, namely,

$$\hat{V} \equiv \hat{H} - \hat{F}$$

where

$$\hat{F} \equiv \sum_{i=1}^{N} \hat{f}(r_i, \sigma_i) \equiv \sum_{i=1}^{N} \left(\hat{h}(r_i) + j(r_i) - \hat{k}(r_i, \sigma_i)\right).$$

We derived the following expression for the wave function,

$$\Psi(\tau) = \sum_{n=0}^{\infty} \left[\left[\left(\hat{I} - \hat{P}\right)\left(E - \hat{F}\right)^{-1} \hat{V}\right]^n \Phi_{HF}(\tau)\right]$$

where

$$\hat{P}\Psi \propto \Phi_{HF},$$

Φ_{HF} is the Hartree-Fock Wave function, E is the exact energy, and $\hat{I}$ is the identity operator. This is the key expression for the wave function in what sort of calculation?

7. We said that we could write the exact wave function as

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

$$+ \sum_{i>j>k=1}^{N} \sum_{a>b>c=N+1}^{K} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \sum_{i>j>k>l=1}^{N} \sum_{a>b>c>d=N+1}^{K} c_{ijkl}^{abcd} \Phi_{ijkl}^{abcd} + \ldots$$

where Φ_0 is the Hartree-Fock wave function and $\Phi_{ij\ldots}^{ab\ldots}$ means "excite electrons from the occupied orbitals $\psi_i, \psi_j, \ldots$ of the Hartree-Fock wave function into the unoccupied orbitals, $\psi_a, \psi_b, \ldots$ of the Hartree Fock wave function. The coefficients, $c_0, c_i^a, c_{ij}^{ab}, \ldots$, are then chosen to minimize the energy, $E \equiv \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$.

This expression for the wave function is the key expression in what sort of calculation?

If we stop after the third term (the last term on the first line), we say that we are doing what sort of calculation?

8. **We considered a method where we made critical use of the electron cumulants. In particular, we considered the "second" cumulant, which described the "non-independence" of electrons. We then decided, somewhat arbitrarily, to decide that given three electrons, at least one of them would always be acting independently of the others. This is the "big idea" behind what sort of method?**

9. **We said that the ground state electron density, $\rho(r)$, could be used to determine any desired property of a chemical system and, in particular, its wave function. This is called the:**
   (a) Pauling-Wilson Theorem
   (b) Brillouin Theorem
   (c) Hartree-Slater Theorem
   (d) Hohenberg-Kohn Theorem
   (e) Kohn-Slater Theorem
   (f) Parriser-Parr Theorem
   (g) Ayers Theorem (don't I wish).

10. **We said that sometimes Hartree-Fock theory is an extremely poor model because there it is very difficult to describe the wave function of the system as being "dominated" by a single Slater determinant. We cited the Ozone molecule as an example. The "correlation energy" gained by considering a "few" very important Slater determinants, typically representing states that are very close together in energy, is called:**
   (a) static correlation.
   (b) dynamic correlation.

Key for Quiz 6

Chemistry 3BB3; Winter 2003

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   (d) find the Slater determinant, Φ, that has the exact ground state density, $\rho(\mathbf{r})$.
   (e) both (b) and (c)
   (f) both (c) and (d)

2. **Koopmans' Theorem gives us an interpretation for the energy of the occupied and unoccupied orbitals in Hartree-Fock theory. In particularly**

   The highest occupied orbital's energy is approximately equal to ___ $-I$; I = ionization potential__

   The lowest unoccupied orbital's energy is approximately equal to ___ $-A$, A = electron affinity____

3. **We wrote the Hartree-Fock energy formula in the form:**

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

   with

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

   and

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

   What is the formula for K_{ij}?

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

4. **We said that the Hartree-Fock Equations were**

$$\left(\tfrac{-\nabla^2}{2} + v(\mathbf{r}) + j(\mathbf{r}) - \hat{k}(\mathbf{r},\sigma)\right)\psi_\alpha(\mathbf{r},\sigma) = \varepsilon_\alpha \psi_\alpha(\mathbf{r},\sigma)$$

   where σ denotes the spin of the electron. We had, for instance,

$$\hat{k}(\mathbf{z})\psi_\alpha(\mathbf{z}) \equiv \sum_{i=1}^{N} \delta_{\sigma_i \sigma_\alpha} \iint \frac{\psi_i^*(r')\psi_\alpha(r')}{|r-r'|} d\mathbf{r}' \psi_i(\mathbf{r})$$

   What is the formula for:

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

Name:

5. We said that the many-electron Green's function, $G\left(\boldsymbol{\tau}, \boldsymbol{\tau}'; E\right)$ satisfied an inhomogeneous differential equation similar to the Schrödinger equation. (Here $\boldsymbol{\tau}$ denotes the spatial and spin coordinates of the electrons, $\boldsymbol{\tau} \equiv \left(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_2, \sigma_2; \ldots \boldsymbol{r}_N, \sigma_N\right)$. This differential equation was:

$$\left(E - \hat{H}\left(\boldsymbol{\tau}\right)\right) G\left(\boldsymbol{\tau}, \boldsymbol{\tau}'; E\right) = \delta\left(\boldsymbol{\tau} - \boldsymbol{\tau}'\right)$$

6. Define $\hat{V}$ to be the difference between the system's Hamiltonian and the Hartree-Fock Hamiltonian, namely,

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where

$$\hat{F} \equiv \sum_{i=1}^{N} \hat{f}\left(\boldsymbol{r}_i, \sigma_i\right) \equiv \sum_{i=1}^{N}\left(\hat{h}\left(\boldsymbol{r}_i\right) + j\left(\boldsymbol{r}_i\right) - \hat{k}\left(\boldsymbol{r}_i, \sigma_i\right)\right).$$

We derived the following expression for the wave function,

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

where

$$\hat{P}\Psi \propto \Phi_{HF},$$

Φ_{HF} is the Hartree-Fock Wave function, E is the exact energy, and $\hat{I}$ is the identity operator. This is the key expression for the wave function in what sort of calculation?

Moller-Plesset Perturbation theory or Many-Body Perturbation Theory

7. We said that we could write the exact wave function as

$$\Psi = c_0\Phi_0 + \sum_{i=1}^{N}\sum_{a=N+1}^{K} c_i^a\Phi_i^a + \sum_{i>j=1}^{N}\sum_{a>b=N+1}^{K} c_{ij}^{ab}\Phi_{ij}^{ab}$$
$$+ \sum_{i>j>k=1}^{N}\sum_{a>b>c=N+1}^{K} c_{ijk}^{abc}\Phi_{ijk}^{abc} + \sum_{i>j>k>l=1}^{N}\sum_{a>b>c>d=N+1}^{K} c_{ijkl}^{abcd}\Phi_{ijkl}^{abcd} + \ldots$$

where Φ_0 is the Hartree-Fock wave function and $\Phi_{ij\ldots}^{ab\ldots}$ means "excite electrons from the occupied orbitals $\psi_i, \psi_j, \ldots$ of the Hartree-Fock wave function into the unoccupied orbitals, $\psi_a, \psi_b, \ldots$ of the Hartree Fock wave function. The coefficients, $c_0, c_i^a, c_{ij}^{ab}, \ldots$, are then chosen to minimize the energy, $E \equiv \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$.

This expression for the wave function is the key expression in what sort of calculation?

Configuration Interaction; CI

If we stop after the third term (the last term on the first line), we say that we are doing what sort of calculation?

Configuration Interaction Singles and Doubles Excitations; CISD

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Name:

Coupled Cluster Singles and Doubles, CCSD

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