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Quiz 11

Chemistry 3BB3; Winter 2004

- In “words”, the essence of the Hartree-Fock method is to**
 - find the Slater determinant, Φ , that is “closest” to the exact wave function, Ψ .
 - find the Slater determinant, Φ , that has the lowest energy $\langle \Phi | \hat{H} | \Phi \rangle$.
 - find the Slater determinant, Φ , that gives the best approximation to the system’s ground state energy, E .
 - find the Slater determinant, Φ , that has the exact ground state density, $\rho(\mathbf{r})$.
 - both (b) and (c)
 - both (c) and (d)
- Koopmans’ Theorem gives us an interpretation for the energy of the occupied and unoccupied orbitals in Hartree-Fock theory. In particular,**

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

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

- We wrote the Hartree-Fock energy formula in terms of the following quantities**

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

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

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

What is the appropriate formula for E_{HF}

- | | |
|---|---|
| (a) $E_{HF} = \sum_{i=1}^N h_i + \sum_{i=1}^N \sum_{j=1}^N J_{ij} - K_{ij}$ | (e) $E_{HF} = \sum_{i=1}^N h_i + 2 \sum_{i=1}^N \sum_{j=1}^N J_{ij} - K_{ij}$ |
| (b) $E_{HF} = \sum_{i=1}^N h_i - \sum_{i=1}^N \sum_{j=1}^N J_{ij} - K_{ij}$ | (f) $E_{HF} = \sum_{i=1}^N h_i - 2 \sum_{i=1}^N \sum_{j=1}^N J_{ij} - K_{ij}$ |
| (c) $E_{HF} = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N J_{ij} - K_{ij}$ | (g) $E_{HF} = \sum_{i=1}^N h_i + \sum_{i=1}^N \sum_{j=1}^N J_{ij} + K_{ij}$ |
| (d) $E_{HF} = \sum_{i=1}^N h_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N J_{ij} - K_{ij}$ | (h) $E_{HF} = \sum_{i=1}^N h_i + \sum_{i=1}^N \sum_{j=1}^N J_{ij} + \frac{1}{2} K_{ij}$ |

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

$$-\frac{\nabla^2}{2} \psi_\alpha(\mathbf{r}) + v(\mathbf{r}) \psi_\alpha(\mathbf{r}) - \sum_{\sigma} \int \frac{\psi_\alpha^*(\mathbf{r}') \psi_\alpha(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \psi_\alpha(\mathbf{r}, \sigma) = \varepsilon_\alpha \psi_\alpha(\mathbf{r}, \sigma)$$

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

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

What is the formula for:

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

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5. Which of the following terms are associated with the Hartree-Fock method:

- (a) Independent particle method/model. (c) Self-Consistent Field method.
(b) Mean-field method. (d) density-functional theory.

6. We are interested in where an base (nucleophile) undergoes electrophilic attack by an acid. According to frontier molecular orbital theory, this occurs where there is a high probability of observing electrons that are easily removed from the molecule. These locations of the molecule are located by finding places where

- (a) $\psi_{HOMO}(\mathbf{r})$ is large. (e) $|\psi_{HOMO}(\mathbf{r})|^2$ is large. (i) The electron density is
(b) $\psi_{HOMO}(\mathbf{r})$ is small. (f) $|\psi_{HOMO}(\mathbf{r})|^2$ is small. large.
(c) $\psi_{LUMO}(\mathbf{r})$ is large. (g) $|\psi_{LUMO}(\mathbf{r})|^2$ is large.
(d) $\psi_{LUMO}(\mathbf{r})$ is small. (h) $|\psi_{LUMO}(\mathbf{r})|^2$ is small.

7. Which of the following statements are implied by the Hohenberg-Kohn Theorem.

- (a) The electron density determines the electronic energy of the ground state.
(b) The electron density determines the dipole moment of the ground state.
(c) The electron density determines the electron-electron repulsion energy in the ground state.

8. We choose an effective external potential, $v(\mathbf{r}) + v_J(\rho; \mathbf{r}) + v_{xc}(\rho; \mathbf{r})$, such that the ground state density of the system with this external potential and no electron-electron repulsion has the same density as the system with external potential $v(\mathbf{r})$ and electron-electron repulsion. This is the idea behind the

- (a) Hartree-Fock method. (c) Slater-Kohn method. (e) Becke-Parr method.
(b) Hartree-Slater method. (d) Hohenberg-Kohn method. (f) Kohn-Sham method.

9. $E_{xc}(\rho)$ is called the

- (a) Exchange energy. (c) Exchange correction. (e) Hohenberg-Kohn
(b) Exchange-correlation energy (d) Correlation correction. functional.
(f) Slater-Kohn energy

10. We wrote several expressions for the energy in Kohn-Sham density-functional theory. Write one of them.

10-point Bonus: We wrote an equation for the Hartree-Fock energy in terms of the Hartree-Fock orbital energies. What was it? (This can be derived from your answer in problems 3 and 4.)

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Key for 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, $\rho(\mathbf{r})$.

(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 particular

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:

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

with

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

and

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

What is the formula for K_{ij} ?

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

4. We said that the Hartree-Fock Equations were

$$-\frac{\nabla^2}{2} \psi_\alpha(\mathbf{r}) + v(\mathbf{r}) \psi_\alpha(\mathbf{r}) + \sum_{j=1}^N \int \frac{\psi_j^*(\mathbf{r}') \psi_\alpha(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \psi_j(\mathbf{r}) = \epsilon_\alpha \psi_\alpha(\mathbf{r})$$

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

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

What is the formula for:

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

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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, $\tau \equiv \mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N$. This differential equation was:

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

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

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

We derived the following expression for the wave function,

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

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?

Moller-Plesset Perturbation theory or Many-Body Perturbation Theory

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

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

where Φ_0 is the Hartree-Fock wave function and $\Phi_{ij\dots}^{ab\dots}$ means "excite electrons from the occupied orbitals

ψ_i, ψ_j, \dots of the Hartree-Fock wave function into the unoccupied orbitals, ψ_a, ψ_b, \dots of the Hartree Fock wave

function. The coefficients, $c_0, c_i^a, c_{ij}^{ab}, \dots$, 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

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?

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Coupled Cluster Singles and Doubles, CCSD

9. We said that the ground state electron density, $\rho(\mathbf{r})$, 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) dynamic correlation.

(b) static correlation.