

Answer Key

1. (5 points) Write down the Hamiltonian Operator for a system on N electrons and M nuclei.

The Hamiltonian is

$$\hat{H} = \sum_{i=1}^N \hat{f}(i) + \sum_{i<j}^N g(i, j) + \sum_{k<l}^{nuclei} \frac{Z_k Z_l}{|\vec{R}_k - \vec{R}_l|}$$

The one electron operator is

$$\hat{f}(i) = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^{nuclei} \frac{Z_k}{|\vec{r}_i - \vec{R}_k|}$$

where $-\frac{1}{2} \nabla_i^2$ is the kinetic energy operator for the *i*th electron

and $-\sum_{k=1}^{nuclei} \frac{Z_k}{|\vec{r}_i - \vec{R}_k|}$ is the nuclear attraction operator for the *i*th electron.

The two-electron operator is

$$g(i, j) = \frac{1}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{r_{ij}}$$
 and is the electron-electron repulsion operator for electrons *i* and *j*,

and finally $\sum_{k<l}^{nuclei} \frac{Z_k Z_l}{|\vec{R}_k - \vec{R}_l|}$ is the nuclear-nuclear repulsion term.

2. (5 points) State the variation principle.

Given a function ϕ that satisfies the boundary conditions on the exact wave function ψ the energy

$$E = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

is greater than or equal to the lowest energy exact eigenvalue of \hat{H} .

3. (5 points) Define the Hartree-Fock wave function for a system of N electrons.

The Hartree-Fock wave function is the best single determinant wave function one can obtain in the sense that it gives the lowest energy.

4. (15 points) Distinguish between the following:

a. Restricted Hartree-Fock

In the Restricted Hartree-Fock (RHF) wavefunction each spatial molecular orbital is doubly occupied and hosts both an α & β electron spin.

b. Restricted Open-Shell Hartree-Fock

In the Restricted Open-Shell Hartree-Fock (ROHF) wavefunction each doubly occupied spatial molecular orbital hosts both an α & β electron spin while the open shell orbitals have either an α or β spin.

c. Unrestricted Hartree-Fock

In the Unrestricted Hartree-Fock (UHF) wavefunction the spatial molecular orbitals associated with α spins are optimized independently from those associated with β spins. Consequently and UHF wavefunction is not an eigenfunction of \hat{S}^2 .

5. (5 points) Define correlation energy.

Correlation energy is the difference between the exact eigenvalue of the Schrodinger equation and the restricted (open or closed) Hartree-Fock energy of the system.

6. (5 points) How are the Hartree-Fock equations derived?

If ψ is the Hartree-Fock wavefunction

$$\psi(1, 2, 3, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \dots & \phi_2(N) \\ \vdots & \vdots & \dots & \vdots \\ \phi_N(1) & \phi_N(2) & \dots & \phi_N(N) \end{vmatrix}$$

the spin-orbitals are obtained by solving the equations that result from minimizing the electronic energy with respect to each orbitals. One forms the functional derivatives

$\frac{\delta E}{\delta \phi_i} = 0$ for $i = 1, 2, 3, \dots, N$ subject to the constraints $\langle \phi_i | \phi_j \rangle = \delta_{ij}$. The resulting equations

determine $\{\phi_i\}_{i=1}^N$ and thus the Hartree-Fock wavefunction ψ .

7. (10 points) Write down the Hartree-Fock equations for a system on N electrons

The Hartree-Fock equations are

$$\hat{F}\phi_i = \varepsilon_i\phi_i$$

where the Fock operator \hat{F} is given by

$$\hat{F} = \hat{f}(1) + \sum_{j=1}^N \int d\tau(2) \phi_j^*(2) g(1,2) (1 - \hat{P}_{12}) \phi_j(2)$$

with the symbols defined above. \hat{P}_{12} is the transposition operator.

8. (5 points) What is meant by "basis set"?

The most common method of solving the Hartree-Fock equations for the molecular orbitals, ϕ_i is to expand these orbitals in terms of a set of functions $\{\chi_\mu\}_{\mu=1}^M$ which are usually obtained from atomic calculations. The group of functions $\{\chi_\mu\}_{\mu=1}^M$ is called a basis set.

9. (5 points) Write down the matrix form of the Hartree-Fock equations.

The matrix form of the Hartree-Fock equations is

$$F\vec{C}_i = \varepsilon_i\Delta\vec{C}_i$$

where the Fock matrix F and the overlap matrix Δ are given by

$(F)_{\mu\nu} = \langle \chi_\mu | \hat{F} | \chi_\nu \rangle$ and $(\Delta)_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ and the eigenvectors \vec{C}_i determine the molecular orbitals via

$$\phi_i = \sum_{\mu=1}^M \chi_\mu C_{\mu i}$$

10. (5 points) What bottlenecks, if any, are there to the solution of the Hartree-Fock equations?

For small systems, say fewer than 25 atoms, there are essentially none. For larger systems the increased number of basis functions requires enormous numbers of integrals to be calculated. If the basis set consists of M functions one must calculate $\sim \frac{M^4}{8}$ integrals.

For $M=1000$ this is a big number. Secondly one must extract several eigenvalues and eigenvectors from large matrices. For $M=1000$ the matrix could be 1000×1000 .

11. (5 points) Name a molecular property that is predicted fairly well in the Hartree-Fock approximation.

Most often the geometry (bond lengths and bond angles) is well predicted.

12. (5 points) Name a molecular property that is poorly predicted by the Hartree-Fock approximation.

Almost always the energy of a system is poorly predicted.

13. (5 points) How may one improve on the Hartree-Fock approximation?

One improves upon the Hartree-Fock approximation by increasing the variational degrees of freedom in the approximate wavefunction. This usually means adding additional determinants in the expansion of the molecular wavefunction. How one determines the relative weights of these determinants defines the approximation being used. If one uses the variation principle one is using the configuration interaction method; if one uses perturbation theory one is using one of the Moller-Plesset (MP) methods; if one uses an exponential ansatz to introduce the additional determinants one usually obtains the relative weights by solving coupled algebraic equations; etc. Additionally one could use a variant of Density-Functional Theory.

14. (20 points) Identify the contributions of the following to the Hartree-Fock method.

a. Douglas Hartree

Suggested that the approximate wavefunction be a (Hartree) product of atomic or molecular orbitals. Determined these orbitals for many atoms by solving the Hartree equations numerically.

b. Vladimir Fock

Pointed out that the Hartree product ansatz for the wavefunction did not satisfy the antisymmetrization principle that requires the exact wavefunction be antisymmetric to the interchange of the coordinates of any two electrons. Derived the equations that determined the orbitals with this constraint. These are the Hartree-Fock equations in use today.

c. Robert Mulliken

Introduced, in the early 1930's, the concept of a molecular orbital as a means of interpreting molecular spectra. Hartree and Fock derived the equations that determine these molecular orbitals.

d. Clemens Roothaan

A Ph.D student of Mulliken's at the University of Chicago who in the early 1950's introduced the idea of a basis set expansion of the Hartree-Fock or molecular orbitals and ushered in the era of *ab-initio* calculations on polyatomic molecules.

e. John Pople

Principal architect of the Gaussian system of programs that allowed non-specialists in computational chemistry to use *ab-initio* calculations, especially molecular orbital calculations, in their research.