Question 1. Write down the electronic Hamiltonian in the coordinate representation. You may use atomic units. If you use one-electron and two-electron operators in your answer, please define what they are. (3 points)

$$\hat{H}_e = -\sum_{i}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i}^{N}\sum_{A}^{M} \frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|} + \sum_{i}^{N}\sum_{j>i}^{N} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}$$

Question 2. Explain the difference between the quantum mechanical operator $\hat{H}$ and the algebraic operator $\hat{\mathscr{H}}$ in one sentence. (2 points)

The quantum-mechanical $\hat{H}$ is a operator that operates on a state vector to give a new state vector, while an algebraic $\hat{\mathscr{H}}$ is $\hat{H}$ in a specific representation. For example, in the x-representation, the algebraic operator $\mathscr{H}(x)$ operates on a function of position $\psi(x) = \langle x|\psi\rangle$ to give a new function of position.

Question 3. Qualitatively explain what is meant by the equation:

$$|\phi\rangle = \sum_{all\ i} |i\rangle \langle i|\phi\rangle$$

In your explanation, be sure to include the qualitative interpretations of $\langle i|\phi\rangle$, state vector $|\phi\rangle$, state vectors $|i\rangle$, and what we mean by the term "resolution of the identity". (5 points)

$|\phi\rangle$ is an abstract entity which represents a quantum mechanical state. Base states $|i\rangle$ are used to describe the "space" of what we want to represent. $\langle i|\phi\rangle$ is the amplitude to go from state ϕ into one of the base states i, and is just a complex number. Any state vector $|\phi\rangle$ can be represented as a linear combination of base vectors $|i\rangle$, with the coefficients being the the amplitude to go from state $|\phi\rangle$ into the base states. To put it another way, we can represent $|\phi\rangle$ as a superposition of base states. The resolution of the identity $\sum_{all\ i} |i\rangle \langle i|$ acts like an identity operator, and is used to expand a state vector in some basis.

Question 4. Qualitatively (i.e., without equations, unless you really prefer it) explain the major steps required to get from the time-independent Schrödinger equation to the Roothaan-Hall equations. Make sure to touch on the following details:

- the Hamiltonian

- the form and composition of the wavefunction

- how the expectation value of the Hamiltonian for this wavefunction $E = \langle \Phi \mid \hat{H} \mid \Phi \rangle$ relates to the Hartree-Fock equations

- how the Hartree-Fock equations relate to the Roothaan-Hall equations

(8 points)

In the time-independent Schrödinger equation, a Hamiltonian operator acts on a wavefunction, which contains all knowable information about a system The Hamiltonian operator is constructed from all relevant interactions between the particles in a chemical system. The full Hamiltonian contains potential (electron–repulsion, electron–nuclear attraction, nuclear–repulsion) and kinetic (electron and nuclear) terms. Under the Born-Oppenheimer approximation, we solve for electron motion assuming a fixed nuclei. The nuclear-repulsion term becomes a constant and the nuclear kinetic energy term becomes zero, leaving us with an electronic Hamiltonian expressed as a sum of one-electron and two-electron operators. Electronic wavefunctions are approximated from a set of one-electron wavefunctions, and specifically, spin-orbitals. To build in the antisymmetric properties of the wavefunction, we write the total N-electron wavefunction as a Slater determinant $|\Phi\rangle$. The expectation value of the energy of the Slater determinant is just $E = \langle\Phi|\hat{H}|\Phi\rangle$. Of course, we do not know the functional form of the spin-orbitals. Any random choice of orbitals will give

us some energy. The Hartree-Fock (HF) equations are obtained by minimizing $E = \langle \Phi | \hat{H} | \Phi \rangle$ under the constraint that the orbitals are orthonormal. In short, they describe the conditions for the best possible set of spin orbitals which minimize the energy $E = \langle \Phi | \hat{H} | \Phi \rangle$. In practice, this is hard to do. Instead of finding the exact Hartree–Fock molecular orbitals, the Roothaan–Hall method approximates the "exact" HF MOs by a linear combination of atomic orbital basis functions.

Question 5. Beginning from the restricted-determinant form for the 1st Slater-Condon rule:

$$E = 2 \sum_{i}^{N/2} \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{i}^{N/2} \sum_{j}^{N/2} 2 \langle \phi_i \phi_j | \hat{g} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g} | \phi_j \phi_i \rangle$$

expand each spatial orbital as a linear combination of atomic orbitals:

$$\langle \phi_i | = \sum_{p} \langle \chi_p | C_{pi}^* \quad | \phi_i \rangle = \sum_{q} | \chi_q \rangle C_{qi} \quad \langle \phi_j | = \sum_{r} \langle \chi_r | C_{rj}^* \quad | \phi_j \rangle = \sum_{s} | \chi_s \rangle C_{sj}$$

and derive the RHF energy expression for molecular orbitals (MOs) approximated by a linear combination of atomic orbital basis functions. (3 points)

One-electron term: $2 \sum_{i}^{N/2} \langle \phi_i | \hat{h} | \phi_i \rangle$

Expand ϕ_i using given definitions:

$$2 \sum_{i}^{N/2} \langle \phi_i | \hat{h} | \phi_i \rangle = 2 \sum_{i}^{N/2} \sum_{p} \langle \chi_p | C_{pi}^* \hat{h} | \phi_i \rangle$$

$$= 2 \sum_{i}^{N/2} \sum_{p} \sum_{q} \langle \chi_p | C_{pi}^* \hat{h} | \chi_q \rangle C_{qi}$$

We can take out the coefficients since they are just numbers, and just represent the sums over p and q under one summation symbol:

$$2 \sum_{i}^{N/2} \langle \phi_i | \hat{h} | \phi_i \rangle = 2 \sum_{i}^{N/2} \sum_{pq} C_{pi}^* C_{qi} \langle \chi_p | \hat{h} | \chi_q \rangle$$

$\sum_{i}^{N/2} C_{pi}^* C_{qi}$ is just the density matrix written as D_{pq}:

$$2 \sum_{i}^{N/2} \langle \phi_i | \hat{h} | \phi_i \rangle = 2 \sum_{pq} D_{pq} \langle \chi_p | \hat{h} | \chi_q \rangle$$

Two-electron terms: $\sum_{i}^{N/2} \sum_{j}^{N/2} 2 \langle \phi_i \phi_j | \hat{g} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g} | \phi_j \phi_i \rangle$

$$\sum_{i}^{N/2} \sum_{j}^{N/2} 2 \langle \phi_i \phi_j | \hat{g} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g} | \phi_j \phi_i \rangle = \sum_{i}^{N/2} \sum_{j}^{N/2} \sum_{pqrs} 2 \langle \chi_p \chi_r | C_{pi}^* C_{rj}^* \hat{g} | \chi_q \chi_s \rangle C_{qi} C_{sj} - \langle \chi_p \chi_r | C_{pi}^* C_{rj}^* \hat{g} | \chi_s \chi_q \rangle C_{sj} C_{qi}$$

$$= \sum_{i}^{N/2} \sum_{j}^{N/2} \sum_{pqrs} C_{pi}^* C_{rj}^* C_{qi} C_{sj} \left(2 \langle \chi_p \chi_r | \hat{g} | \chi_q \chi_s \rangle - \langle \chi_p \chi_r | \hat{g} | \chi_s \chi_q \rangle \right)$$

$$= \sum_{pqrs} \sum_{i}^{N/2} C_{pi}^* C_{qi} \sum_{j}^{N/2} C_{rj}^* C_{sj} \left(2 \langle \chi_p \chi_r | \hat{g} | \chi_q \chi_s \rangle - \langle \chi_p \chi_r | \hat{g} | \chi_s \chi_q \rangle \right)$$

$\sum\limits_{i}^{N/2} C_{pi}^* C_{qi}$ is just the density matrix D_{pq} and $\sum\limits_{j}^{N/2} C_{rj}^* C_{sj}$ is just the density matrix D_{rs}:

$$\sum_{i}^{N/2}\sum_{j}^{N/2} 2\langle\phi_i\phi_j|\hat{g}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|\hat{g}|\phi_j\phi_i\rangle = \sum_{pqrs} D_{pq}D_{rs}\left(2\langle\chi_p\chi_r|\hat{g}|\chi_q\chi_s\rangle - \langle\chi_p\chi_r|\hat{g}|\chi_s\chi_q\rangle\right)$$

Final answer:
$$2\sum_{pq} D_{pq}\langle\chi_p\mid\hat{h}\mid\chi_q\rangle + \sum_{pqrs} D_{pq}D_{rs}\left(2\langle\chi_p\chi_r|\hat{g}|\chi_q\chi_s\rangle - \langle\chi_p\chi_r|\hat{g}|\chi_s\chi_q\rangle\right)$$

Question 6. Suppose you have a basis-set composed of 4 Gaussian basis functions

$$\chi_1(r)\quad \chi_2(r)\quad \chi_3(r)\quad \chi_4(r)$$

Suppose further you perform a *restricted* Hartree-Fock computation (i.e., using the Roothaan-Hall equations) using this basis on a system with 4 electrons and obtain the following molecular orbital coefficients:

$$\mathbf{C} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} \\ C_{21} & C_{22} & C_{23} & C_{24} \\ C_{31} & C_{32} & C_{33} & C_{34} \\ C_{41} & C_{42} & C_{43} & C_{44} \end{bmatrix}$$

where each column above corresponds to the coefficients for one molecular orbital, and the relative energies of each molecular orbital are in increasing order from left to right.
Write down a valid form for the ground-state Slater Determinant wavefunction in terms of the above basis functions χ and coefficients C_{ij}. Make sure to distinguish between different electron's coordinates and include spin functions α and β in your answer. You do not need to explicitly expand all permutations of molecular orbital products; you may use the antisymmetrizer operator $\hat{A}$ or use the matrix-like representation for a determinant. (3 points)

First, we know that the Slater determinant for an 4 electron system is defined as:

$$\Phi = \sqrt{4!}\hat{A}(\psi_1^1\psi_2^2\psi_3^3\psi_4^4)$$

where ψ is our spin-orbital, containing a spatial function ϕ and a spin function α or β. We can explicitly write the spatial and spin parts in the Slater determinant:

$$\Phi = \sqrt{4!}\hat{A}[\phi_1(1)\alpha(1)\phi_1(2)\beta(2)\phi_2(3)\alpha(3)\phi_2(4)\beta(4)]$$

Note that in the restricted framework, each spatial orbital ϕ_i holds 2 electrons. In this question, the 4 bare Guassian basis functions *are* the basis of atomic orbitals. In the Roothaan-Hall method, spatial part of spin-orbitals are represented as a linear combination of the atomic orbitals. The coefficients for this expansion is given in the matrix $\mathbf{C}$. The problem states that each column of $\mathbf{C}$ correspond to the coefficients for one molecular orbital, and the relative energies of each molecular orbital are in increasing order from left to right. Thus, we can expand the first two spatial orbitals as:

$$\phi_1(r) = \sum_{i=1}^{4} C_{i1}\chi_i(r) \tag{1}$$

$$\phi_2(r) = \sum_{i=1}^{4} C_{i2}\chi_i(r) \tag{2}$$

We can plug this expansion into the Slater determinant:

$$\Phi = \sqrt{4!}\hat{A}\left[\sum_{i=1}^{4}C_{i1}\chi_i(1)\alpha(1)\cdot\sum_{i=1}^{4}C_{i1}\chi_i(2)\beta(2)\cdot\sum_{i=1}^{4}C_{i2}\chi_i(3)\alpha(3)\cdot\sum_{i=1}^{4}C_{i2}\chi_i(4)\,beta(4)\right]$$

You can also represent the Slater determinant with spin-orbitals as:

$$\Phi = \frac{1}{\sqrt{4!}}\begin{vmatrix} \psi_1^1 & \psi_2^1 & \psi_3^1 & \psi_4^1 \\ \psi_1^2 & \psi_2^2 & \psi_3^2 & \psi_4^2 \\ \psi_1^3 & \psi_2^3 & \psi_3^3 & \psi_4^3 \\ \psi_1^4 & \psi_2^4 & \psi_3^4 & \psi_4^4 \end{vmatrix}$$

Written explicitly with spatial and spin parts:

$$\Phi = \frac{1}{\sqrt{4!}}\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) & \phi_2(1)\alpha(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) & \phi_2(2)\alpha(2) \\ \phi_1(3)\alpha(3) & \phi_1(3)\beta(3) & \phi_2(3)\alpha(3) & \phi_2(3)\alpha(3) \\ \phi_1(4)\alpha(4) & \phi_1(4)\beta(4) & \phi_2(4)\alpha(4) & \phi_2(4)\alpha(4) \end{vmatrix}$$

You could in theory write out the full expansion of $\phi_1(r)$ and $\phi_2(r)$ for every term explicitly in the expression above, but it would be sufficient to just define them using Equations 1 and 2.