Advanced Quantum Mechanics & Spectroscopy
(CHEM 7520)

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Week 7-9: Advanced electronic structure theory

VIII. FORM OF THE EXACT WAVEFUNCTION: FULL CONFIGURATION INTERACTION

1) Previously, we have discussed how atom-centered basis sets can be used to represent the molecular orbitals using the linear combination:

$$|\phi_i\rangle \;=\; \sum_{\mu}^{n} C_{\mu}^{i}\, |\chi_\mu\rangle \tag{1}$$

As we increase the size of the basis set ($n \to \infty$), the energy obtained at the end of the SCF optimization will approach the lowest possible Hartree-Fock energy (so-called Hartree-Fock basis set limit), which corresponds to the best (in the variational sense) molecular orbitals and the Hartree-Fock wavefunction

$$|\Psi(1,\ldots,N)\rangle = \mathscr{A}(1,\ldots,N)\prod_{i}^{N}\psi_i(i) \tag{2}$$

However, except in rare situations (such as when the number of electrons $N = 1$), the Hartree-Fock energy is not equal to the exact electronic energy, even if the basis set $|\chi_\mu\rangle$ is complete. This is because in Hartree-Fock theory the many-electron wavefunction is approximated as an antisymmetrized product of spin-orbitals, which is not true for the exact wavefunction in general.

2) How can we construct the exact wavefunction? Let's assume that the spin-orbitals $|\psi_i(1)\rangle$ form a complete one-electron basis set. Thus, any one-electron wavefunction $|\Psi(1)\rangle$ can be represented as a linear combination:

$$|\Psi(1)\rangle = \sum_i a_i\, |\psi_i(1)\rangle \tag{3}$$

where a_i is expansion coefficient. Now, let's consider a two-electron wavefunction $|\Psi(1,2)\rangle$. We can represent it in a similar way if we keep the coordinate 2 constant:

$$|\Psi(1,2)\rangle = \sum_i a_i(2)\,|\psi_i(1)\rangle \tag{4}$$

where the expansion coefficients $a_i(2)$ are now functions of the coordinate 2. Since $a_i(2)$ is a one-electron function, it can be expanded in the complete set $|\psi_i\rangle$ as:

$$a_i(2) = \sum_j b_{ij}\,|\psi_j(2)\rangle \tag{5}$$

Thus, the two-electron wavefunction can be expanded as:

$$|\Psi(1,2)\rangle = \sum_{ij} b_{ij}\,|\psi_i(1)\rangle\,|\psi_j(2)\rangle \tag{6}$$

We require $|\Psi(1,2)\rangle$ to be antisymmetric: $|\Psi(1,2)\rangle = -\,|\Psi(2,1)\rangle$. This holds if $b_{ij} = -b_{ji}$, $b_{ii} = 0$. We can rewrite the expansion as:

$$\begin{aligned}
|\Psi(1,2)\rangle &= \sum_i \sum_{j>i} b_{ij}\,|\psi_i(1)\rangle\,|\psi_j(2)\rangle + \sum_i \sum_{j<i} b_{ij}\,|\psi_i(1)\rangle\,|\psi_j(2)\rangle \\
&= \sum_i \sum_{j>i} b_{ij}\,|\psi_i(1)\rangle\,|\psi_j(2)\rangle - \sum_i \sum_{j<i} b_{ji}\,|\psi_i(1)\rangle\,|\psi_j(2)\rangle \\
&= \sum_i \sum_{j>i} b_{ij}\,|\psi_i(1)\rangle\,|\psi_j(2)\rangle - \sum_i \sum_{i<j} b_{ij}\,|\psi_j(1)\rangle\,|\psi_i(2)\rangle \\
&= \sum_i \sum_{j>i} b_{ij}\left[|\psi_i(1)\rangle\,|\psi_j(2)\rangle - |\psi_j(1)\rangle\,|\psi_i(2)\rangle\right] \\
&= \sum_{i<j} \sqrt{2} b_{ij}\,|\psi_i \psi_j\rangle
\end{aligned} \tag{7}$$

We obtain that an arbitrary antisymmetric two-electron wavefunction can be exactly expanded in terms of all unique determinants formed from a complete set of the one-electron spin-orbitals. This argument is readily expanded to more than two variables, so that *the exact wavefunction for the ground and excited states of the N-electron system can be written as a linear combination of all possible N-electron Slater determinants formed from a complete set of spin-orbitals* $|\psi_i\rangle$.

3) We can construct all possible determinants by starting with the Hartree-Fock Slater determinant. Recall that for a basis set of n atomic orbitals, there are n spatial and $2n$ spin-orbitals. Out of these $2n$ spin-orbitals, only N spin-orbitals with lowest orbital energies are occupied in the Hartree-Fock determinant (where

N is the number of electrons). The remaining $2n - N$ spin-orbitals are usually called **unoccupied** or **virtual**. To distinguish between the two types of orbitals, we will use indices i, j, k, l, m, n to denote the spin-orbitals occupied in the Hartree-Fock determinant and a, b, c, d, e, f to label the unoccupied spin-orbitals.

4) Starting with the Hartree-Fock determinant $|\Phi_0\rangle$, we can construct new determinants by exciting electrons from occupied to unoccupied spin-orbitals. First, we construct *singly excited determinants* $|\Phi_i^a\rangle$, which are formed by substituting a single spin-orbital $|\psi_i\rangle$ occupied in $|\Phi_0\rangle$ by an unoccupied spin-orbital $|\psi_a\rangle$. A collection of all determinants $|\Phi_i^a\rangle$ for all combinations of i and a will include all possible singly excited determinants. In a similar way, we can construct *doubly excited determinants* $|\Phi_{ij}^{ab}\rangle$ by substituting a pair of spin-orbitals $|\psi_i\rangle$ and $|\psi_j\rangle$ by $|\psi_a\rangle$ and $|\psi_b\rangle$, respectively, for all unique combinations of i and j, a and b. If we construct up to all possible N-electron excitations, the exact wavefunction can be written as a linear combination:

$$|\Psi\rangle = c_0 |\Phi_0\rangle + \sum_{ia} c_i^a |\Phi_i^a\rangle + \sum_{\substack{i<j \\ a<b}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{\substack{i<j<k \\ a<b<c}} c_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \ldots \tag{8}$$

Here, the summation is performed over the unique Slater determinants, thus the summation indices are restricted (e.g., $i < j$). Since every determinant in the expansion (8) can be defined by specifying an electronic configuration (or molecular orbital diagram), a procedure of expanding the wavefunction in terms of the determinants with different number of excitations is called **configuration interaction**.

5) In Eq. (8), determinants $|\Phi_I\rangle = \{|\Phi_0\rangle, |\Phi_i^a\rangle, |\Phi_{ij}^{ab}\rangle, \ldots\}$ form a complete set of N-electron basis functions. Thus, any exact wavefunction can be expanded in the form of Eq. (8). Therefore, to solve the electronic Schrödinger equation exactly, we must work with (i) a complete (infinite) one-electron basis set of spin-orbitals $|\psi_p\rangle$ and (ii) a complete (infinite) N-electron basis set of Slater determinants. Unfortunately, this procedure is not practical, because we cannot work with infinite basis sets.

6) If we work with a finite set of spin-orbitals $\{|\psi_p\rangle\}_{p=1}^{2n}$, all possible determinants formed from these spin-orbitals will not form a complete N-electron basis set. Solving the electronic Schrödinger equation in this basis would correspond to the exact solution within the finite one-electron basis set represented by $2n$ spin-orbitals. This procedure is called **full configuration interaction** (full CI). Even for small systems and minimal basis sets the number of determinants that must be

included in the full CI computation is extremely large:

$$\mathrm{N_{FCI}} = \binom{2n}{N} = \frac{2n!}{(2n-N)!N!} \tag{9}$$

For a closed-shell molecule in the singlet ground state ($S = 0$), it is not necessary to consider excitations of electrons that change the number of α and β electrons. In this case, the number of determinants necessary to include in the full CI procedure is smaller:

$$\mathrm{N_{FCI}^{M_S=0}} = \binom{n}{N/2}^2 \tag{10}$$

Here, the superscript indicates that only determinants with a total spin projection $\mathrm{M_S} = 0$ are included.

7) We can make several important conclusions by analyzing the form of the exact wavefunction in Eq. (8). First, the *true (exact) wavefunction is multiconfigurational*. Although chemists are used to think that the electrons occupy a well-defined set of molecular orbitals (a single electronic configuration), this view of chemistry is only valid when a single electronic configuration (usually, $|\Phi_0\rangle$) dominates the expansion (8). In other words, this view is valid only when the Hartree-Fock wavefunction provides a good approximation to the exact wavefunction. If more than one Slater determinant has a large contribution in Eq. (8), the Hartree-Fock approximation breaks down and the electronic structure of a molecule cannot be represented using a single electronic configuration. We will discuss these situations in more detail later in the course.

8) Second, Eq. (8) suggests a systematic approach to go beyond the single-determinant (Hartree-Fock) description of the electronic wavefunction. Rather than including all possible determinants in the expansion (8), we can include determinants only up to a certain excitation level. This approach is usually called **truncated configuration interaction**. If we include up to all possible double excitations, this approach is called *configuration interaction with single and double excitations* (CISD). If the Hartree-Fock determinant $|\Phi_0\rangle$ dominates the expansion (8) with a large coefficient ($|c_0| > 0.9$), CISD usually provides an accurate approximation to the electronic wavefunction. If we include up to triple excitations, we call the approach as *configuration interaction with single, double, and triple excitations* (CISDT). We can continue by including the higher-order excitations (e.g., CISDTQ, CISDTQ5, etc) up to all N-electron excitations, which

is equivalent to full CI. One of the disadvantages of the CI approach is that the number of excitations grows very quickly with the number of molecular orbitals, even if the expansion (8) is truncated after the double excitations. Because of this, the CI methods are usually limited to small molecules with modest basis sets.

9) How can we compute the exact energy? We denote the complete set of determinants $\{|\Phi_0\rangle, |\Phi_i^a\rangle, |\Phi_{ij}^{ab}\rangle, \ldots\}$ as $\{|\Phi_I\rangle\}$ where I indexes every determinant starting from 0 (the Hartree-Fock determinant). Using this notation, we can rewrite the exact wavefunction (8) in the general form:

$$|\Psi\rangle = \sum_I c_I |\Phi_I\rangle \tag{11}$$

The electronic Schrödinger equation can be written in the following form:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{12}$$

$$\sum_I c_I \hat{H}|\Phi_I\rangle = E\sum_I c_I |\Phi_I\rangle \tag{13}$$

$$\sum_I c_I \langle\Phi_J|\hat{H}|\Phi_I\rangle = Ec_J \tag{14}$$

$$\sum_I H_{JI}c_I = c_J E \tag{15}$$

$$\mathbf{Hc} = \mathbf{cE} \tag{16}$$

where we used the fact that the Slater determinants are orthonormal $\langle\Phi_I|\Phi_J\rangle = \delta_{IJ}$. Thus, *to compute the exact energy we must diagonalize the* **H** *matrix, which is the matrix representation of the electronic Hamiltonian in the basis of all Slater determinants*. Obviously, in the complete spin-orbital basis, the matrix **H** has infinite dimensions, and the diagonalization problem is impossible to solve. In a finite one-electron basis set, the Hamiltonian matrix has finite dimensions ($\mathrm{N_{FCI}} \times \mathrm{N_{FCI}}$ where $\mathrm{N_{FCI}}$ is given by Eq. (9)), and the diagonalization is possible for one-electron basis sets with small n. In practice, solving the eigenvalue problem (16) for $n > 18$ becomes prohibitively expensive computationally, unless special techniques are used.

10) To solve the eigenvalue problem (16), we must know how to evaluate the matrix elements $H_{IJ} = \langle\Phi_I|\hat{H}|\Phi_J\rangle$ with respect to any pair of Slater determinants I and J. These matrix elements can be evaluated in terms of the one- and two-electron integrals using the so-called **Slater rules**. These rules can be summarized as follows:

Rule 1. Determinants are the same ($|\Phi_I\rangle = |\Phi_J\rangle = |\Phi\rangle$).

$$\langle\Phi|\hat{H}|\Phi\rangle = \sum_{m}^{occ} \langle m|\hat{h}|m\rangle + \sum_{m>n}^{occ} \langle mn||mn\rangle \tag{17}$$

where summations run over the spin-orbitals $|\psi_m\rangle$ that are occupied in $|\Phi\rangle$.

Rule 2. Determinants are different by one spin-orbital ($|\Phi_I\rangle = |\Phi\rangle$, $|\Phi_J\rangle = |\Phi_i^a\rangle$).

$$\langle\Phi|\hat{H}|\Phi_i^a\rangle = \langle i|\hat{h}|a\rangle + \sum_{m}^{occ} \langle im||am\rangle \tag{18}$$

where $|\Phi_J\rangle$ is different from $|\Phi_I\rangle$ by substituting $|\psi_i\rangle$ with $|\psi_a\rangle$ and the summation runs over the spin-orbitals occupied in both determinants.

Rule 3. Determinants are different by two spin-orbitals ($|\Phi_I\rangle = |\Phi\rangle$, $|\Phi_J\rangle = |\Phi_{ij}^{ab}\rangle$).

$$\langle\Phi|\hat{H}|\Phi_{ij}^{ab}\rangle = \langle ij||ab\rangle \tag{19}$$

where $|\Phi_J\rangle$ is different from $|\Phi_I\rangle$ by replacing $|\psi_i\rangle$ and $|\psi_j\rangle$ with $|\psi_a\rangle$ and $|\psi_b\rangle$.

Rule 4. Determinants are different by more than two spin-orbitals ($|\Phi_I\rangle = |\Phi\rangle$, $|\Phi_J\rangle = |\Phi_{ij\ldots}^{ab\ldots}\rangle$).

$$\langle\Phi|\hat{H}|\Phi_{ij\ldots}^{ab\ldots}\rangle = 0 \tag{20}$$

The last rule is the result of the fact that the electronic Hamiltonian contains only up to two-body terms. Although we did not derive Slater rules, their derivation is very similar to the derivation of the Hartree-Fock energy expression that we considered in detail. In fact, the Hartree-Fock energy expression is just a special case of the Slater Rule 1.

11) The ground-state energy E obtained from the full CI procedure is the lowest ground-state energy that is possible to obtain for a given finite basis set. The difference between this exact energy and the Hartree-Fock ground-state energy E_0 computed using the same basis set is called the **correlation energy**:

$$E_{corr} = E - E_0 \tag{21}$$

Note that $E_{corr} < 0$ is guaranteed by the variational principle. The correlation energy is a measure of the importance of **electron correlation**, which arises when the motion of one electron in a molecule is influenced by the presence of all other electrons. Since Hartree-Fock theory describes the interaction between two electrons only through a one-particle (Fock) operator, it does not capture electron correlation between electrons with opposite spins. Hartree-Fock does capture correlation between electrons with the same spins because it satisfies Pauli principle that prohibits two electrons with the same spins to occupy the same position in space. Therefore, the correlation energy is mainly the measure of electron correlation between electrons with the opposite spins.