The full CI equations and Slater rules

4.1 The FCI equations and their solution

In this section we will derive the equations that determine the coefficients in the FCI wave function. In this chapter, **we always assume that the spin orbital basis is orthonormal**, that is $\langle \psi_i | \psi_j \rangle = \delta_{ij}$, and that there are $2K$ spin orbitals formed from a set of K spatial orbitals $\{\phi_j\}$. For convenience, we will introduce a short-hand notation for a Slater determinant $\Phi_{ijk\ldots}(x_1, x_2, \ldots, x_N)$ where we condense all the orbital indices $ijk\cdots$ to a multi-index $I = \{i_1, i_2, i_3, \cdots\}$ with $i_1 < i_2 < i_3 < \ldots$, so that we can write determinants with only one label as Φ_I.[1] Then the FCI wave function can be written as

[1]The index I is also called a *string* of indices $I = \{i_1, i_2, \ldots, i_N\}$ that indicate the occupied spin orbitals.

$$|\Psi_{\text{FCI}}\rangle = \sum_I c_I |\Phi_I\rangle. \tag{4.1}$$

To derive the FCI equations we first have to establish the properties of the basis of Slater determinant. Recall that a determinant may be written as

$$
\Phi_{i_1 i_2 \cdots i_N}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}}
\begin{vmatrix}
\psi_{i_1}(x_1) & \psi_{i_1}(x_2) & \cdots & \psi_{i_1}(x_N) \\
\psi_{i_2}(x_1) & \psi_{i_2}(x_2) & \cdots & \psi_{i_2}(x_N) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_{i_N}(x_1) & \psi_{i_N}(x_2) & \cdots & \psi_{i_N}(x_N)
\end{vmatrix}
$$

$$
= \frac{1}{\sqrt{N!}} \sum_\pi^{N!} (-1)^{p_\pi} P_\pi \left[\psi_{i_1}(x_1) \psi_{i_2}(x_2) \cdots \psi_{i_N}(x_N) \right], \tag{4.2}
$$

where π labels a permutation, $(-1)^{p_\pi}$ is the parity of the permutation π, and P_π is a permutation operator that acts on the electron coordinates.[2]

[2]For example, for two indices $\pi = [(1, 2), (2, 1)]$ and $p_\pi = [0, 1]$.

The overlap integral $\langle \Phi_I | \Phi_I \rangle$ for a generic determinant Φ_I may be written as

$$
\langle \Phi_I | \Phi_I \rangle = \frac{1}{N!} \sum_\pi^{N!} \sum_{\pi'}^{N!} (-1)^{p_\pi + p_{\pi'}} \int dx_1 dx_2 \cdots dx_N
$$
$$
P_\pi \left[\psi_{i_1}^*(x_1) \cdots \psi_{i_N}^*(x_N) \right] P_\pi \left[\psi_{i_1}(x_1) \cdots \psi_{i_N}(x_N) \right]. \tag{4.3}
$$

Since the spin-orbital basis is assumed to be orthonormal, the integrals for each separate variable must contain the square of the same spin orbital to get a non-zero result. This happens when the two permutations coincide, $\pi = \pi'$, in which case the integral simplifies to:

$$
\int dx_1 dx_2 \cdots dx_N P_\pi \left[|\psi_{i_1}(x_1)|^2 |\psi_{i_2}(x_2)|^2 \cdots |\psi_{i_N}(x_N)|^2 \right] = 1. \tag{4.4}
$$

Summing over all permutations we have

$$\langle \Phi_I | \Phi_I \rangle = \frac{1}{N!} \sum_{\pi}^{N!} 1 = \frac{N!}{N!} = 1. \tag{4.5}$$

Problem 4.1.1 — Orthogonality of Slater determinants. Show that two determinants Φ_I and Φ_J that differ by one or more spin orbital have zero overlap

$$\langle \Phi_I | \Phi_J \rangle = 0. \tag{4.6}$$

To do so, plug in the definition of Slater determinants in $\langle \Phi_I | \Phi_J \rangle$, break down this integral as a product of one-electron integrals, and then show that each term contains one integral that is always zero.

The orthonormality condition for the Slater determinants may be summarized as:

$$\langle \Phi_I | \Phi_J \rangle = \delta_{IJ}. \tag{4.7}$$

We can now proceed to derive the FCI equations. Plugging in the FCI wave function in the Schrödinger equation we obtain

$$\hat{H} \sum_I c_I | \Phi_I \rangle = E \sum_I c_I | \Phi_I \rangle. \tag{4.8}$$

Projecting onto the left with $\langle \Phi_J |$ and rearranging terms we get

$$\sum_I \langle \Phi_J | \hat{H} | \Phi_I \rangle c_I = E \sum_I \underbrace{\langle \Phi_J | \Phi_I \rangle}_{\delta_{IJ}} c_I, \tag{4.9}$$

which may be simplified to

$$\sum_I H_{IJ} c_I = E c_J, \tag{4.10}$$

with the matrix elements H_{IJ} defined as $H_{IJ} = \langle \Phi_J | \hat{H} | \Phi_I \rangle$. This is an eigenvalue problem that can be written compactly as

$$\mathbf{HC} = \mathbf{CE}, \tag{4.11}$$

where $\mathbf{H}$ is a matrix of dimension $N_{\text{FCI}} \times N_{\text{FCI}}$, where N_{FCI} is the number of FCI determinants. To solve this equation we have to derive equations for the matrix elements of the Hamiltonian operator $H_{IJ} = \langle \Phi_J | \hat{H} | \Phi_I \rangle$. The set of rules that determine the value of these matrix elements are called **Slater rules**.

4.2   Slater rules

In this section we look at how can we compute matrix elements of the Hamiltonian $\langle \Phi_I | \hat{H} | \Phi_J \rangle$, where Φ_I and Φ_J are two determinants built out of the same orthonormal spin orbital basis.[3] For convenience we will write the electronic Hamiltonians as

[3]More general rules exist for nonorthonormal spin orbitals, and when Φ_I and Φ_J use different set of spin orbitals.

$$\hat{H} = V_{\text{NN}} + \hat{H}_1 + \hat{H}_2, \tag{4.12}$$

where

$$V_{\mathrm{NN}} = \sum_{A}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{r_{AB}} \tag{4.13}$$

$$\hat{H}_1 = -\frac{1}{2} \sum_{i}^{N} \nabla_i^2 - \sum_{i}^{N} \sum_{A}^{M} \frac{Z_A}{r_{iA}} = \sum_{i} \hat{h}(i) \tag{4.14}$$

$$\hat{H}_2 = \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} = \sum_{i}^{N} \sum_{j>i}^{N} \hat{v}(i,j). \tag{4.15}$$

4.2.1 Matrix elements of the scalar term

The simplest matrix element is that of the scalar term (V_{NN}), which can be derived using only the orthonormality condition of the Slater determinant basis

$$\langle \Phi_I | V_{\mathrm{NN}} | \Phi_J \rangle = V_{\mathrm{NN}} \langle \Phi_I | \Phi_J \rangle = V_{\mathrm{NN}} \delta_{IJ}. \tag{4.16}$$

4.2.2 Matrix elements of the one-electron Hamiltonian

Let us consider the matrix element of the one-body operator:

$$\langle \Phi_I | \hat{H}_1 | \Phi_I \rangle = \frac{1}{N!} \sum_{\pi \pi'}^{N!} \sum_{j} (-1)^{p_\pi + p_{\pi'}} \int dx_1 dx_2 \cdots dx_N \tag{4.17}$$

$$P_\pi \left[\psi_{i_1}^*(x_1) \cdots \psi_{i_N}^*(x_N) \right] \hat{h}(x_j) P_{\pi'} \left[\psi_{i_1}(x_1) \cdots \psi_{i_N}(x_N) \right].$$

In this case the only permutations that give nonzero contributions are those for which $\pi = \pi'$. Otherwise, there would be one or more mismatched spin orbitals. For example, consider the case of a permutation π' that swaps coordinates $x_1 \leftrightarrow x_2$ while π is the identity. The term with the operator $\hat{h}(x_1)$

$$\int dx_1 dx_2 \cdots \psi_{i_1}^*(x_2) \psi_{i_2}^*(x_1) \cdots \hat{h}(x_1) \psi_{i_1}(x_1) \psi_{i_2}(x_2) \cdots$$

$$= \int dx_1 \, \psi_{i_2}^*(x_1) \hat{h}(x_1) \psi_{i_1}(x_1) \times \underbrace{\int dx_2 \, \psi_{i_1}^*(x_2) \psi_{i_2}(x_2)}_{=0} \times \cdots = 0. \tag{4.18}$$

We also get zero if the permutation mixes two variables not involved with the operator $\hat{h}$ as in the case of the permutation $\pi' \equiv (x_2 \leftrightarrow x_3)$

$$\int dx_1 dx_2 \cdots \psi_{i_1}^*(x_1) \psi_{i_3}^*(x_2) \cdots \hat{h}(x_1) \psi_{i_1}(x_1) \psi_{i_2}(x_2) \cdots$$

$$= \int dx_1 \, \psi_{i_1}^*(x_1) \hat{h}(x_1) \psi_{i_1}(x_1) \times \underbrace{\int dx_2 \, \psi_{i_3}^*(x_2) \psi_{i_2}(x_2)}_{=0} \times \cdots = 0. \tag{4.19}$$

Since for any permutation $P_\pi \sum_j \hat{h}(x_j) = \sum_j \hat{h}(x_j)$, we may combine the permutation operators into a single term

$$\langle \Phi_I | \hat{H}_1 | \Phi_I \rangle = \frac{1}{N!} \sum_{\pi}^{N!} \int dx_1 dx_2 \cdots dx_N$$

$$P_\pi \left\{ \psi_{i_1}^*(x_1) \cdots \psi_{i_N}^*(x_N) \left[\sum_j \hat{h}(x_j) \right] \psi_{i_1}(x_1) \cdots \psi_{i_N}(x_N) \right\}. \tag{4.20}$$

Each permutation of the integral will give a contribution equal to:

$$\sum_j^N \int dx\, \psi_{i_j}^*(x)\hat{h}(x)\psi_{i_j}(x) = \sum_j^N \langle \psi_{i_j}|\,\hat{h}\,|\psi_{i_j}\rangle = \sum_i^{\text{occ}} \langle \psi_i|\,\hat{h}\,|\psi_i\rangle , \qquad (4.21)$$

and since there are $N!$ permutations, we find that

$$\langle \Phi_I|\,\hat{H}_1\,|\Phi_I\rangle = \frac{1}{N!}\sum_\pi^{N!}\sum_i^{\text{occ}} \langle \psi_i|\,\hat{h}\,|\psi_i\rangle = \sum_i^{\text{occ}} \langle i|\,\hat{h}\,|i\rangle . \qquad (4.22)$$

In the last term we introduced the abbreviated notation $\langle i|\,\hat{h}\,|i\rangle \equiv \langle \psi_i|\,\hat{h}\,|\psi_i\rangle$.

4.2.3   Matrix elements of the two-electron Hamiltonian

The derivation of the two-electron contribution is more involved, and it gives the following result:

$$\langle \Phi_I|\,\hat{H}_2\,|\Phi_I\rangle = \sum_i \sum_{j<i} \left[\langle ij|ij\rangle - \langle ij|ji\rangle\right], \qquad (4.23)$$

where the quantity $\langle ij|kl\rangle$ is a two-electron integral in **physicist notation**:

$$\langle ij|kl\rangle = \int dx_1 dx_2 \psi_i^*(x_1)\psi_j^*(x_2)\hat{v}(x_1,x_2)\psi_k(x_1)\psi_l(x_2). \qquad (4.24)$$

If we introduce the antisymmetrized two-electron integral:

$$\langle ij||kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle , \qquad (4.25)$$

then it is possible to rewrite as an unconstrained double sum

$$\langle \Phi_I|\,\hat{H}_2\,|\Phi_I\rangle = \sum_i \sum_{j<i} \langle ij||ij\rangle = \frac{1}{2}\sum_{ij} \langle ij||ij\rangle , \qquad (4.26)$$

[4]This is simple to see: $\langle ii||ii\rangle = \langle ii|ii\rangle - \langle ii|ii\rangle = 0.$ since the term that corresponds to $i=j$ is null[4] and $\langle ji||ji\rangle = \langle ij||ij\rangle$.

4.2.4   Slater rule for a diagonal matrix element

In summary we can express the diagonal element of the Hamiltonian matrix as

$$\begin{aligned}\langle \Phi_I|\,\hat{H}\,|\Phi_I\rangle &= V_{\text{NN}} + \sum_i^{\text{occ}} \langle i|\,\hat{h}\,|i\rangle + \frac{1}{2}\sum_{ij}^{\text{occ}} \langle ij||ij\rangle , \\ &= V_{\text{NN}} + \sum_i^{\text{occ}} \langle i|\,\hat{h}\,|i\rangle + \sum_{i<j}^{\text{occ}} \langle ij||ij\rangle ,\end{aligned} \qquad (4.27)$$

where each sum is over the set of occupied molecular orbitals in Φ_I [also denoted as $\text{occ}(\Phi_I)$].

■ **Example 4.2.1 | Energy of a single electron.**
Consider the determinant for a single electron:

$$|\psi_1\rangle . \qquad (4.28)$$

The energy is then given by:

$$\langle \psi_1|\,\hat{H}\,|\psi_1\rangle = \langle 1|\,\hat{h}\,|1\rangle + \frac{1}{2}\underbrace{\langle 11||11\rangle}_{=0} = \langle 1|\,\hat{h}\,|1\rangle . \qquad (4.29)$$

■

■ **Example 4.2.2 | Energy of a pair of electrons in a closed-shell configuration.**
Let us consider the determinant:
$$|\Phi_I\rangle = |\psi_1\psi_{\bar{1}}\rangle \tag{4.30}$$

The energy is given by:

$$\langle\Phi_I|\,\hat{H}\,|\Phi_I\rangle = \langle\psi_1|\,\hat{h}\,|\psi_1\rangle + \langle\psi_{\bar{1}}|\,\hat{h}\,|\psi_{\bar{1}}\rangle$$

$$+ \frac{1}{2}\left[\langle\psi_1\psi_1||\psi_1\psi_1\rangle + \langle\psi_1\psi_{\bar{1}}||\psi_1\psi_{\bar{1}}\rangle + \langle\psi_{\bar{1}}\psi_1||\psi_{\bar{1}}\psi_1\rangle + \langle\psi_{\bar{1}}\psi_{\bar{1}}||\psi_{\bar{1}}\psi_{\bar{1}}\rangle\right]$$

$$= 2\langle\phi_1|\,\hat{h}\,|\phi_1\rangle + \langle\phi_1\phi_1|\phi_1\phi_1\rangle, \tag{4.31}$$

where we have eliminated two-electron integrals that are zero due to a mismatch in the spin function.
■

To simplify this notation, sometimes we will use the **Coulomb integral** (J_{ij})

$$J_{ij} = \langle ij|ij\rangle = \int dx_1 dx_2 \frac{|\psi_i(x_1)|^2|\psi_j(x_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = \int dx_1 dx_2 \frac{|\phi_i(\mathbf{r}_1)|^2|\phi_j(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{4.32}$$

which is just Coulomb's law for a two charges with density distribution $\rho_i(\mathbf{r}) = |\phi_i(\mathbf{r})|^2$ and $\rho_j(\mathbf{r}) = |\phi_j(\mathbf{r})|^2$. We can also define the **exchange** integral (K_{ij}) as

$$K_{ij} = \langle ij|ji\rangle = \int dx_1 dx_2 \frac{\psi_i^*(x_1)\psi_j^*(x_1)\psi_j(x_2)\psi_i(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{4.33}$$

Using these two quantities the energy of a determinant may be written as

$$\langle\Phi_I|\,\hat{H}\,|\Phi_I\rangle = V_{NN} + \sum_i^{\text{occ}(\Phi_I)} \langle i|\,\hat{h}\,|i\rangle + \frac{1}{2}\sum_{ij}^{\text{occ}(\Phi_I)} (J_{ij} - K_{ij}). \tag{4.34}$$

4.3 Slater rules for off-diagonal terms

For matrix elements between two Slater determinants with different spin orbitals we have to consider different case.

4.3.1 Single replacement

First, we consider two determinants that differ in the occupation of one spin orbital. For example, consider the two determinants

$$|\Phi_I\rangle = |\psi_1\cdots\psi_i\cdots\psi_N\rangle \tag{4.35}$$
$$|\Phi_J\rangle = |\psi_1\cdots\psi_a\cdots\psi_N\rangle, \tag{4.36}$$

where the spin orbital ψ_i is replaced by ψ_a. In this case we say that the two determinant have been brought to have maximum coincidence in the order of the spin orbitals. The matrix elements between $|\Phi_I\rangle$ and $|\Phi_J\rangle$ is given by

$$\langle\Phi_I|\,\hat{H}\,|\Phi_J\rangle = \langle i|\,\hat{h}\,|a\rangle + \sum_k^{\text{occ}(\Phi_I)} \langle ik||ak\rangle. \tag{4.37}$$

This expression contains contributions from both the one- and two-electron operator.

4.3.2   Double replacement

Next, we consider two determinants that when brought to have maximum coincidence still differ in the occupation of two spin orbitals, for example

$$|\Phi_I\rangle = |\psi_1 \cdots \psi_i \psi_j \cdots \psi_N\rangle \tag{4.38}$$

$$|\Phi_J\rangle = |\psi_1 \cdots \psi_a \psi_b \cdots \psi_N\rangle . \tag{4.39}$$

The matrix elements between $|\Phi_I\rangle$ and $|\Phi_J\rangle$ is given by a single element of the two-electron integrals

$$\langle \Phi_I | \hat{H} | \Phi_J \rangle = \langle ij || ab \rangle . \tag{4.40}$$

Equations (4.27), (4.37), and (4.40) are called Slater's rules and account for all nonzero matrix elements of a two-body Hamiltonian. When two determinants differ by more than two spin orbitals then a matrix element is automatically zero.

4.4   Structure of the FCI wave function and Hamiltonian

In many cases, the FCI wave function is well approximated by a single Slater determinant, say Φ_0, where

$$|\Phi_0\rangle = |\psi_1 \psi_2 \cdots \psi_N\rangle . \tag{4.41}$$

This is called the **reference** determinant and it plays an important role because we can define all other Slater determinants in the FCI expansion in terms of **excitations** of electrons starting from Φ_0. These excitations promote electrons from the occupied orbitals in Φ_0

$$\text{occupied} = \{\psi_1, \psi_2, \cdots, \psi_N\}, \tag{4.42}$$

to those that are unoccupied

$$\text{unoccupied} = \{\psi_{N+1}, \psi_{N+2}, \cdots, \psi_{2K}\}. \tag{4.43}$$

Determinants that differ from Φ_0 by one spin orbital, for example, by replacing $\psi_N \to \psi_{N+1}$

$$|\psi_1 \psi_2 \cdots \psi_{N-1} \psi_{N+1}\rangle , \tag{4.44}$$

are called **singly excited**. We can similarly define determinants with two, three, etc. spin orbital replaced as doubly, triply, etc. excited determinants. In physics, especially in the field of condensed matter, occupied orbitals are also called **holes** while the unoccupied orbitals are called **particles**. This language is consistent with the view that an excited determinant can be seen as combination of creating holes (by removing electrons from occupied orbitals) and particles (by adding electrons to the unoccupied orbitals). Therefore, excited determinants are also referred to as **particle-hole** excitations.[5]

This classification of determinants allows us to rearrange the FCI wave function as

$$|\Psi_{\text{FCI}}\rangle = c_0 |\Phi_0\rangle + \sum_S c_S |\Phi_S\rangle + \sum_D c_D |\Phi_D\rangle + \sum_T c_T |\Phi_T\rangle + \ldots, \tag{4.45}$$

where summations over the indices S, D, and T, indicate singly, doubly, and triply excited determinants. For an N-electron system this series truncates when we reach at most N-tuply excited determinants.

Often, the FCI wave function may be expressed assuming **intermediate normalization**. This means that we scale the coefficients so that $c_0 = 1$

$$|\Psi_{\text{FCI}}\rangle = |\Phi_0\rangle + \sum_S c_S |\Phi_S\rangle + \sum_D c_D |\Phi_D\rangle + \sum_T c_T |\Phi_T\rangle + \ldots. \tag{4.46}$$

[5]In band theory another convention is used. Occupied orbitals are referred to as **valence bands** while unoccupied ones as **conduction bands**.

Note that assuming this normalization of the wave function we have that

$$\langle \Psi_0 | \Phi_{\text{FCI}} \rangle = 1, \tag{4.47}$$

and the wave function is not normalized

$$\langle \Psi_{\text{FCI}} | \Phi_{\text{FCI}} \rangle \neq 1. \tag{4.48}$$

Note also that in intermediate normalization we have that

$$\langle \Phi_0 | \hat{H} | \Psi_{\text{FCI}} \rangle = \langle \Phi_0 | E | \Psi_{\text{FCI}} \rangle = E \langle \Phi_0 | \Psi_{\text{FCI}} \rangle = E. \tag{4.49}$$

Writing this expression as $E = \langle \Phi_0 | \hat{H} | \Psi_{\text{FCI}} \rangle$ and plugging in the definition of Ψ_{FCI} in intermediate normalization [Eq. (4.46)] we can express the energy in terms of only FCI coefficients for single and double excitations
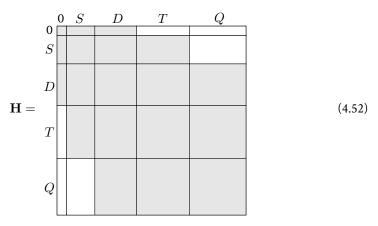
$$E = \langle \Phi_0 | \hat{H} | \Psi_{\text{FCI}} \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \sum_S c_S \langle \Phi_0 | \hat{H} | \Phi_S \rangle + \sum_D c_D \langle \Phi_0 | \hat{H} | \Phi_D \rangle. \tag{4.50}$$

Terms like $\langle \Phi_0 | \hat{H} | \Phi_T \rangle$ that arise in this expansion are zero due to Slater rules (Φ_T and Φ_0 differ by more than two spin orbitals!).

Applying a similar logic, we can map out the general structure of the FCI Hamiltonian matrix. In this case several blocks will be zero due to difference in more than two spin orbitals. For example the terms that couple the singly (Φ_S) and quadruply (Φ_Q) excited determinants

$$H_{SQ} = \langle \Phi_S | \hat{H} | \Phi_Q \rangle = 0, \tag{4.51}$$

because Φ_S and Φ_Q differ by more than two spin orbitals. The general structure of the Hamiltonian matrix is indicated below

$$\tag{4.52}$$

As you can see, only the diagonal blocks and determinant connected by two or less substitutions are nonzero. This means that the FCI matrix is very sparse. To be more precise, for each row of the matrix, there will be as many elements as the number of singly and doubly substituted determinants, which is of the order of (neglecting spin and spatial symmetry)

$$N(2K - N) + \frac{1}{4} N^2 (2K - N)^2. \tag{4.53}$$

Since the number of rows contains of the order of $\binom{2K}{N}$ elements, we can see that the number of nonzero elements divided by the number of matrix elements is

$$\text{fraction of nonzero elements} = \frac{N(2K - N) + \frac{1}{4} N^2 (2K - N)^2}{\binom{2K}{N}}. \tag{4.54}$$

This quantity becomes smaller as N and K increase showing that $\mathbf{H}$ is mostly empty.

4.5   Iterative solution of the FCI equations

In practical applications of FCI, it is impossible to store the full Hamiltonian matrix. Instead, one uses a **direct** diagonalization algorithm that requires storage of only several trial coefficient vectors. To see how direct algorithms work, suppose that we have a good initial guess to the FCI vector, $\tilde{\mathbf{c}}$, and that the exact eigenvector can be written as

$$\mathbf{c} = \tilde{\mathbf{c}} + \delta\mathbf{c}. \tag{4.55}$$

From this approximate eigenvector we can compute an approximate energy $\tilde{E}$

$$\tilde{E} = \frac{\tilde{\mathbf{c}}^T \mathbf{H} \tilde{\mathbf{c}}}{\tilde{\mathbf{c}}^T \tilde{\mathbf{c}}} \tag{4.56}$$

and write $E = \tilde{E} + \delta E$, where δE is the energy error with respect to the eigenvalue E. Substitute these quantity in the Schrödinger equation ($\mathbf{H}\mathbf{c} = E\mathbf{c}$) gives

$$\mathbf{H}(\tilde{\mathbf{c}} + \delta\mathbf{c}) = E(\tilde{\mathbf{c}} + \delta\mathbf{c}), \tag{4.57}$$

from which we get

$$(\mathbf{H} - \tilde{E} - \delta E)\delta\mathbf{c} = -(\mathbf{H} - \tilde{E} - \delta E)\tilde{\mathbf{c}} = -(\mathbf{H} - \tilde{E})\tilde{\mathbf{c}} + \delta E\tilde{\mathbf{c}}. \tag{4.58}$$

Ignoring δE, we can write an equation for $\delta\mathbf{c}$ that reads as

$$\delta\mathbf{c} = -(\mathbf{H} - \tilde{E})^{-1}(\mathbf{H} - \tilde{E})\tilde{\mathbf{c}}. \tag{4.59}$$

The inverse $(\mathbf{H} - \tilde{E})^{-1}$ can be simplified by retaining only the diagonal part of $\mathbf{H}$ ($\mathbf{H}_{\mathrm{d}}$) to get

$$\delta\mathbf{c} = -(\mathbf{H}_{\mathrm{d}} - \tilde{E})^{-1}(\mathbf{H} - \tilde{E})\tilde{\mathbf{c}}. \tag{4.60}$$

This equation shows that if we want to improve the trial eigenvector, we just need to evaluate an expression in which only the product, $\mathbf{H}\tilde{\mathbf{c}}$, appears. This quantity is usually called the **sigma vector** and it is indicated with $\boldsymbol{\sigma} = \mathbf{H}\tilde{\mathbf{c}}$. Approaches based on direct diagonalization methods have extended the domain of FCI from several thousand determinants to several billions.

> ■ **Advanced topic** | **Deriving the FCI equations using the Lagrangian approach.**
> In this section we will derive the FCI equations using a different approach based on the formalism of Lagrange multipliers. In this approach we seek to minimize the Rayleigh–Ritz functional
>
> $$E_{\mathbf{RR}}[\Psi] = \frac{\langle\Psi|\,\hat{H}\,|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{4.61}$$
>
> Note that the denominator $\langle\Psi|\Psi\rangle$ is necessary to guarantee that the functional is valid irrespective of the way we normalize the wave function Ψ. If the smallest eigenvalue of the Hamiltonian (E_0) is bound, that is, $E_0 > -\infty$, then minimization of $E_{\mathrm{RR}}[\Psi]$ with respect to Ψ will give the lowest eigenvalue and eigenstate (Ψ_0) of the Hamiltonian
>
> $$\min_{\Psi} E_{\mathbf{RR}}[\Psi] = E_0. \tag{4.62}$$
>
> The minimum of $E_{\mathrm{RR}}[\Psi]$ is obtained by solving the set of equations
>
> $$\frac{\partial E_{\mathrm{RR}}[\Psi]}{\partial c_I} = 0. \tag{4.63}$$
>
> This approach is a bit clumsy because the expression that we want to minimize contains the quantity $\langle\Psi|\Psi\rangle$ in the denominator.
>
>   The Lagrangian approach offers a more direct way to find the FCI equations. To begin with, we write a Lagrangian, that is a function that contains the quantity that we want to minimize and the constraints that we need to satisfy.

The FCI Lagrangian is given by the energy minus the normalization constraint

$$\mathcal{L}[\Psi] = \underbrace{\langle \Psi | \hat{H} | \Psi \rangle}_{\text{energy}} - \underbrace{\lambda(\langle \Psi | \Psi \rangle - 1)}_{\text{normalization constraint}}$$

$$= \sum_{IJ} c_I^* H_{IJ} c_J - \lambda(\sum_I |c_I^2| - 1). \quad (4.64)$$

Taking the derivative of $\mathcal{L}[\Psi]$ with respect to c_I^* gives

$$\frac{\partial \mathcal{L}[\Psi]}{\partial c_I^*} = \sum_J H_{IJ} c_J - \lambda c_I, \quad (4.65)$$

from which we conclude that the FCI vector $\mathbf{c}$ must satisfy the eigenvalue equation

$$\sum_J H_{IJ} c_J = \lambda c_I. \quad (4.66)$$

∎

■ **Example 4.5.1 | Minimization of a function of two variables with a constraint.**

Let us consider the problem of minimizing the function $f(x, y) = x^2 + 2y^2$ with the constraint that $x + y = 2$. We rewrite the constraint as a function $g(x, y) = x + y - 2$ and we will try to impose $g(x, y) = 0$. Consider the Lagrangian function of three independent variables (x, y, λ):

$$\mathcal{L}(x, y, \lambda) = f(x, y) - \lambda g(x, y) = x^2 + 2y^2 - \lambda(x + y - 2). \quad (4.67)$$

The stationary point of $\mathcal{L}(x, y, \lambda)$ with respect to the variables x, y, and λ corresponds to:

$$\frac{\partial \mathcal{L}(x, y, \lambda)}{\partial x} = 2x - \lambda = 0 \quad (4.68)$$

$$\frac{\partial \mathcal{L}(x, y, \lambda)}{\partial y} = 4y - \lambda = 0 \quad (4.69)$$

$$\frac{\partial \mathcal{L}(x, y, \lambda)}{\partial \lambda} = g(x, y) = 0. \quad (4.70)$$

From Eqs. (4.68) and (4.69) we obtain:

$$x = 2y, \quad (4.71)$$

which combined with Eq. (4.70) gives:

$$g(2y, y) = 2y + y - 2 = 0 \quad \Rightarrow \quad y = \frac{2}{3}, \quad (4.72)$$

and $x = \frac{4}{3}$. ∎

Study Questions

1. What is the value of $\langle \Phi_I | \Phi_J \rangle$ for two arbitrary Slater determinants Φ_I and Φ_J?
2. What is the equation that determines the FCI energy and eigenvector?
3. What are Slater rules?
4. What is a one-electron integral?
5. What is a two-electron integral?
6. What is the expectation value of the Hamiltonian for a Slater determinant?
7. What are Slater rules for off-diagonal terms?
8. What is a reference determinant?
9. What is an excited determinant?
10. How do we write the FCI wave function using singly, doubly, etc. excited determinants?

11. What is the structure of the Hamiltonian matrix?

12. What are direct diagonalization methods?