Many Electron Wave Functions and Operators

2.1 The Electron Problem

2.1.1 Atomic Units

2.1.2 The Born-Oppenheimer Approximation

2.1.3 The Antisymmetry or Pauli Exclusion Principle

2.2 Orbitals, Slater Determinants, and Basis Functions

2.2.1 Spin Orbitals and Spatial Orbitals

Exercise 2.1

Given a set of K orthonormal spatial functions, $\{\psi_i^\alpha(\mathbf{r})\}$, and another set of K orthonormal functions, $\{\psi_i^\beta(\mathbf{r})\}$, such that the first set is not orthogonal to the second set, i.e.,

$$\int \mathrm{d}\mathbf{r}\, \psi_i^{\alpha*}(\mathbf{r})\psi_j^\beta(\mathbf{r}) = S_{ij}$$

where $\mathbf{S}$ is an overlap matrix, show that the set $\{\chi_i\}$ of $2K$ spin orbitals, formed by multiplying $\psi_i^\alpha(\mathbf{r})$ by the α spin function and $\psi_i^\beta(\mathbf{r})$ by the β spin function, i.e.,

$$\left.\begin{array}{l} \chi_{2i-1}(\mathbf{x}) = \psi_i^\alpha(\mathbf{r})\alpha(\omega) \\[2mm] \chi_{2i}(\mathbf{x}) = \psi_i^\beta(\mathbf{r})\beta(\omega) \end{array}\right\} i = 1, 2, \ldots, K$$

is an orthonormal set.

Solution 2.1

It is easy to verify the normalization of any χ_{2i-1} or χ_{2j}, where $i = 1, 2, \ldots, K$ and $j = 1, 2, \ldots, K$,

$$\langle \chi_{2i-1}|\chi_{2j-1}\rangle = \int \mathrm{d}\mathbf{x}\, \chi_{2i-1}^*(\mathbf{x})\chi_{2j-1}(\mathbf{x}) = \int \mathrm{d}\mathbf{r}\, \psi_i^{\alpha*}(\mathbf{r})\psi_j^\alpha(\mathbf{r}) \int \mathrm{d}\omega\, \alpha^*(\omega)\alpha(\omega) = \delta_{ij} \times 1 = \delta_{ij},$$

$$\langle \chi_{2i}|\chi_{2j}\rangle = \int \mathrm{d}\mathbf{x}\, \chi_{2i}^*(\mathbf{x})\chi_{2j}(\mathbf{x}) = \int \mathrm{d}\mathbf{r}\, \psi_i^{\beta*}(\mathbf{r})\psi_j^\beta(\mathbf{r}) \int \mathrm{d}\omega\, \beta^*(\omega)\beta(\omega) = \delta_{ij} \times 1 = \delta_{ij}.$$

and the orthogonality between χ_{2i-1} and χ_{2j}, where $i = 1, 2, \ldots, K$ and $j = 1, 2, \ldots, K$,

$$\langle \chi_{2i-1}|\chi_{2j}\rangle = \int \mathrm{d}\mathbf{x}\, \chi_{2i-1}^*(\mathbf{x})\chi_{2j}(\mathbf{x}) = \int \mathrm{d}\mathbf{r}\, \psi_i^{\alpha*}(\mathbf{r})\psi_j^\beta(\mathbf{r}) \int \mathrm{d}\omega\, \alpha^*(\omega)\beta(\omega) = S_{ij} \times 0 = 0,$$

$$\langle \chi_{2i}|\chi_{2j-1}\rangle = \int \mathrm{d}\mathbf{x}\, \chi_{2i}^*(\mathbf{x})\chi_{2j-1}(\mathbf{x}) = \int \mathrm{d}\mathbf{r}\, \psi_i^{\beta*}(\mathbf{r})\psi_j^\alpha(\mathbf{r}) \int \mathrm{d}\omega\, \beta^*(\omega)\alpha(\omega) = S_{ji}^* \times 0 = 0.$$

Thus, we can that the set $\{\chi_i\}$ of $2K$ spin orbitals is an orthonormal set.

2.2.2 Hartree Products

Exercise 2.2

Show that the Hartree product of (2.30) is an eigenfunction of $\mathscr{H} = \sum\limits_{i=1}^{N} h(i)$ with an eigenvalue given by (2.32).

Solution 2.2

The verification is easy. With (2.29), we find that

$$\mathscr{H}\Psi^{\mathrm{HP}} = \left(\sum_{i=1}^{N} h(i)\right)\left[\prod_{j=1}^{N} \chi_{j'}(\mathbf{x}_j)\right] = \sum_{i=1}^{N}\prod_{j=1}^{N} h(i)\chi_{j'}(\mathbf{x}_j) = \sum_{i=1}^{N}\prod_{j=1}^{N} \varepsilon_i \chi_{j'}(\mathbf{x}_j) = \sum_{i=1}^{N} \varepsilon_i \prod_{j=1}^{N} \chi_{j'}(\mathbf{x}_j).$$

$$(2.2\text{-}1)$$

2.2.3 Slater Determinants

Exercise 2.3

Show that $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ of Eq.(2.34) is normalized.

Solution 2.3

The verification is direct, viz.,

$$\langle\Psi|\Psi\rangle = \int d\vec{\mathbf{x}}\,\langle\Psi|\vec{\mathbf{x}}\rangle\langle\vec{\mathbf{x}}|\Psi\rangle$$

$$= \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \frac{1}{\sqrt{2}}\left[\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\right]^* \frac{1}{\sqrt{2}}\left[\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\right]$$

$$= \frac{1}{2}\left(\int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\right.$$

$$\left. - \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) + \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\right)$$

$$= \frac{1}{2}(1 - 0 - 0 + 1) = 1.$$

Exercise 2.4

Suppose the spin orbitals χ_i and χ_j are eigenfunctions of a one-electron operator h with eigenvalues ε_i and ε_j as in Eq.(2.29). Show that the Hartree products in Eqs.(2.33a, b) and the antisymmetrized wave function in Eq.(2.34) are eigenfunctions of the independent-particle Hamiltonian $\mathscr{H} = h(1) + h(2)$ (c.f. Eq.(2.28)) and have the same eigenvalue namely, $\varepsilon_i + \varepsilon_j$.

Solution 2.4

Firstly, we check the Hartree products of χ_i and χ_j. With the conclusion of Exercise 2.2, we get that

$$\mathscr{H}|\Psi_{12}^{\mathrm{HP}}\rangle = (\varepsilon_i + \varepsilon_j)|\Psi_{21}^{\mathrm{HP}}\rangle,$$
$$\mathscr{H}|\Psi_{21}^{\mathrm{HP}}\rangle = (\varepsilon_j + \varepsilon_i)|\Psi_{21}^{\mathrm{HP}}\rangle = (\varepsilon_i + \varepsilon_j)|\Psi_{21}^{\mathrm{HP}}\rangle.$$

Thus, the eigenvalue of the Hartree product of χ_i and χ_j is irrelevant to their order. Note that

$$\Psi = \frac{1}{\sqrt{2}}\left[\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\right] = \frac{1}{\sqrt{2}}\left(\Psi_{12}^{\mathrm{HP}} - \Psi_{21}^{\mathrm{HP}}\right),$$

we find that

$$\mathscr{H}|\Psi\rangle = \mathscr{H}\frac{1}{\sqrt{2}}\left(|\Psi_{12}^{\mathrm{HP}}\rangle - |\Psi_{21}^{\mathrm{HP}}\rangle\right) = \frac{1}{\sqrt{2}}\left(\mathscr{H}|\Psi_{12}^{\mathrm{HP}}\rangle - \mathscr{H}|\Psi_{21}^{\mathrm{HP}}\rangle\right)$$

$$= \frac{1}{\sqrt{2}} \left[(\varepsilon_i + \varepsilon_j) | \Psi_{12}^{HP} \rangle - (\varepsilon_i + \varepsilon_j) | \Psi_{21}^{HP} \rangle \right]$$

$$= (\varepsilon_i + \varepsilon_j) \frac{1}{\sqrt{2}} \left(| \Psi_{12}^{HP} \rangle - | \Psi_{21}^{HP} \rangle \right) = (\varepsilon_i + \varepsilon_j) | \Psi \rangle.$$

Thus, we have proved that the Hartree products in Eqs.(2.33a, b) and the antisymmetrized wave function in Eq.(2.34) are eigenfunctions of the independent-particle Hamiltonian $\mathcal{H} = h(1) + h(2)$ and have the same eigenvalue $\varepsilon_i + \varepsilon_j$.

Exercise 2.5

Consider the Slater determinants

$$|K\rangle = |\chi_i \chi_j\rangle, \quad |L\rangle = |\chi_k \chi_l\rangle.$$

Show that

$$\langle K | L \rangle = \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}.$$

Note that the overlap is zero unless: 1) $k = i$ and $l = j$, in which case $|L\rangle = |K\rangle$ and the overlap is unity and 2) $k = j$ and $l = i$ in which case $|L\rangle = |\chi_j \chi_i\rangle = -|K\rangle$ and the overlap is minus one.

Solution 2.5

We calculate the inner product firstly,

$$\langle K | L \rangle = \int d\vec{\mathbf{x}} \, \langle K | \vec{\mathbf{x}} \rangle \langle \vec{\mathbf{x}} | L \rangle$$

$$= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \frac{1}{\sqrt{2}} \left[\chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) \right]^* \frac{1}{\sqrt{2}} \left[\chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) - \chi_l(\mathbf{x}_1) \chi_k(\mathbf{x}_2) \right]$$

$$= \frac{1}{2} \left[\int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) - \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \chi_l(\mathbf{x}_1) \chi_k(\mathbf{x}_2) \right.$$

$$\left. - \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_j^*(\mathbf{x}_1) \chi_i^*(\mathbf{x}_2) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) + \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_j^*(\mathbf{x}_1) \chi_i^*(\mathbf{x}_2) \chi_l(\mathbf{x}_1) \chi_k(\mathbf{x}_2) \right]$$

$$= \frac{1}{2} \left(\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{jk} \delta_{il} + \delta_{jl} \delta_{ik} \right) = \delta_{ik} \delta_{jl} - \delta_{jk} \delta_{il}.$$

The conclusion is obvious.

- When $k = i$ and $l = j$, in which case $|L\rangle = |K\rangle$ and the overlap is 1.

- When $k = j$ and $l = i$ in which case $|L\rangle = |\chi_k \chi_l\rangle = |\chi_j \chi_i\rangle = -|K\rangle$ and the overlap is -1.

- Otherwise, the overlap is 0.

2.2.4 The Hartree-Fock Approximation

2.2.5 The Minimal Basis H_2 Model

Exercise 2.6

Show that ψ_1 and ψ_2 form an orthonormal set.

Solution 2.6

Similar to Exercise 2.1, verify the normalization of ψ_1 or ψ_2, with $S_{12} = S_{21}$,

$$\langle \psi_1 | \psi_1 \rangle = \int d\mathbf{r} \, \psi_1^*(\mathbf{r}) \psi_1(\mathbf{r}) = \int d\mathbf{r} \, \frac{1}{\sqrt{2(1 + S_{12})}} (\phi_1(\mathbf{r}) + \phi_2(\mathbf{r}))^* \frac{1}{\sqrt{2(1 + S_{12})}} (\phi_1(\mathbf{r}) + \phi_2(\mathbf{r}))$$

$$= \frac{1}{2(1 + S_{12})} (1 + S_{12} + S_{21} + 1) = 1,$$

$$\langle \psi_2 | \psi_2 \rangle = \int d\mathbf{r} \, \psi_2^*(\mathbf{r}) \psi_2(\mathbf{r}) = \int d\mathbf{r} \, \frac{1}{\sqrt{2(1 - S_{12})}} \left(\phi_1(\mathbf{r}) - \phi_2(\mathbf{r}) \right)^* \frac{1}{\sqrt{2(1 - S_{12})}} \left(\phi_1(\mathbf{r}) - \phi_2(\mathbf{r}) \right)$$

$$= \frac{1}{2(1 - S_{12})} (1 - S_{12} - S_{21} + 1) = 1,$$

and the orthogonality between ψ_1 and ψ_2,

$$\langle \psi_1 | \psi_2 \rangle = \int d\mathbf{r} \, \psi_1^*(\mathbf{r}) \psi_2(\mathbf{r}) = \int d\mathbf{r} \, \frac{1}{\sqrt{2(1 + S_{12})}} \left(\phi_1(\mathbf{r}) + \phi_2(\mathbf{r}) \right)^* \frac{1}{\sqrt{2(1 - S_{12})}} \left(\phi_1(\mathbf{r}) - \phi_2(\mathbf{r}) \right)$$

$$= \frac{1}{2\sqrt{(1 - (S_{12})^2)}} (1 - S_{12} + S_{21} - 1) = 0 = \langle \psi_2 | \psi_1 \rangle^*.$$

Thus, we conclude that ψ_1 and ψ_2 form an orthonormal set.

2.2.6   Excited Determinants

2.2.7   Form of the Exact Wave Function and Configuration Interaction

Exercise 2.7

A minimal basis set for benzene consists of 72 spin orbitals. Calculate the size of the full CI matrix if it would be formed from determinants. How many singly excited determinants are there? How many doubly excited determinants are there?

Solution 2.7

To begin with, a benzene molecule consists of 6 carbon atoms, each contributing 6 electrons, and 6 hydrogen atoms, each contributing 1 electron. Consequently, the total number of electrons in a benzene molecule is calculated as $6 \times 6 + 6 \times 1 = 42$ electrons. Namely, $N = 42$.

Secondly, the minimal basis set of benzene includes 36 spatial orbitals. Each carbon atom provides its $1s$, $2s$, and three $2p$ orbitals (i.e., $2p_x$, $2p_y$, and $2p_z$), while each hydrogen atom contributes its $1s$ orbital. These 36 spatial orbitals can be used to construct 72 spin orbitals. Namely, $2K = 72$.

Thus, there are $\binom{72}{42} = 164307576757973059488$ determinants in full CI calculation. Besides, there are $\binom{42}{1}\binom{30}{1} = 1260$ singly excited determinants and $\binom{42}{2}\binom{30}{2} = 374535$ doubly excited determinants.

2.3   Operators and Matrix Elements

2.3.1   Minimal Basis H_2 Matrix Elements

Exercise 2.8

Show that
$$\langle \Psi_{12}^{34} | \mathscr{O}_1 | \Psi_{12}^{34} \rangle = \langle 3 | h | 3 \rangle + \langle 4 | h | 4 \rangle$$
and
$$\langle \Psi_0 | \mathscr{O}_1 | \Psi_{12}^{34} \rangle = \langle \Psi_{12}^{34} | \mathscr{O}_1 | \Psi_0 \rangle = 0.$$

Solution 2.8

For $\langle \Psi_{12}^{34} | \mathscr{O}_1 | \Psi_{12}^{34} \rangle$, it can be divided into two parts, too, viz.,

$$\langle \Psi_{12}^{34} | \mathscr{O}_1 | \Psi_{12}^{34} \rangle = \langle \Psi_{12}^{34} | h(1) | \Psi_{12}^{34} \rangle + \langle \Psi_{12}^{34} | h(2) | \Psi_{12}^{34} \rangle.$$

Its first part is

$$\langle \Psi_{12}^{34} | h(1) | \Psi_{12}^{34} \rangle$$
$$= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \frac{1}{\sqrt{2}} [\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]^* h(1) \frac{1}{\sqrt{2}} [\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]$$

$$
= \frac{1}{2} \left[\int d\mathbf{x}_1 \, \chi_3^*(1)h(1)\chi_3(1) \int d\mathbf{x}_2 \, \chi_4^*(2)\chi_4(2) - \int d\mathbf{x}_1 \, \chi_3^*(1)h(1)\chi_4(1) \int d\mathbf{x}_2 \, \chi_4^*(2)\chi_3(2) \right.
$$

$$
\left. - \int d\mathbf{x}_1 \, \chi_4^*(1)h(1)\chi_3(1) \int d\mathbf{x}_2 \, \chi_3^*(2)\chi_4(2) + \int d\mathbf{x}_1 \, \chi_4^*(1)h(1)\chi_4(1) \int d\mathbf{x}_2 \, \chi_3^*(2)\chi_3(2) \right]
$$

$$
= \frac{1}{2} \left[\int d\mathbf{x}_1 \, \chi_3^*(1)h(1)\chi_3(1) + 0 + 0 + \int d\mathbf{x}_1 \, \chi_4^*(1)h(1)\chi_4(1) \right] = \frac{1}{2} \left(\langle 3|h|3\rangle + \langle 4|h|4\rangle \right).
$$

Similarly, we can obtain that

$$
\langle \Psi_{12}^{34}|h(2)|\psi_{12}^{34}\rangle = \frac{1}{2} \left(\langle 3|h|3\rangle + \langle 4|h|4\rangle \right).
$$

Thus,

$$
\langle \Psi_{12}^{34}|\mathscr{O}_1|\Psi_{12}^{34}\rangle = \frac{1}{2} \left(\langle 3|h|3\rangle + \langle 4|h|4\rangle \right) + \frac{1}{2} \left(\langle 3|h|3\rangle + \langle 4|h|4\rangle \right) = \langle 3|h|3\rangle + \langle 4|h|4\rangle. \tag{2.8-1}
$$

Besides, in the same way, we obtain that

$$
\langle \Psi_{12}^{34}|h(1)|\Psi_0\rangle
$$

$$
= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \frac{1}{\sqrt{2}} [\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]^* h(1) \frac{1}{\sqrt{2}} [\chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)]
$$

$$
= \frac{1}{2} \left[\int d\mathbf{x}_1 \, \chi_3^*(1)h(1)\chi_1(1) \int d\mathbf{x}_2 \, \chi_4^*(2)\chi_2(2) - \int d\mathbf{x}_1 \, \chi_3^*(1)h(1)\chi_2(1) \int d\mathbf{x}_2 \, \chi_4^*(2)\chi_1(2) \right.
$$

$$
\left. - \int d\mathbf{x}_1 \, \chi_4^*(1)h(1)\chi_1(1) \int d\mathbf{x}_2 \, \chi_3^*(2)\chi_2(2) + \int d\mathbf{x}_1 \, \chi_4^*(1)h(1)\chi_2(1) \int d\mathbf{x}_2 \, \chi_3^*(2)\chi_1(2) \right]
$$

$$
= \frac{1}{2} [0 - 0 - 0 + 0] = 0.
$$

and

$$
\langle \Psi_{12}^{34}|h(2)|\Psi_0\rangle = 0,
$$

Therefore,

$$
\langle \Psi_{12}^{34}|h(1)|\Psi_{12}^{34}\rangle = \langle \Psi_{12}^{34}|h(1)|\Psi_0\rangle + \langle \Psi_{12}^{34}|h(2)|\Psi_0\rangle = 0 + 0 = 0, \tag{2.8-2}
$$

and

$$
\langle \Psi_0|\mathscr{O}_1|\Psi_{12}^{34}\rangle = \langle \Psi_{12}^{34}|\mathscr{O}_1|\Psi_0\rangle^* = 0^* = 0. \tag{2.8-3}
$$

Exercise 2.9

Using the above approach, show that the full CI matrix for minimal basis H_2 is

$$
\mathscr{H} = \begin{pmatrix} \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle & \langle 12|34\rangle - \langle 12|43\rangle \\ \langle 34|12\rangle - \langle 34|21\rangle & \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle \end{pmatrix}.
$$

and that it is Hermitian.

Solution 2.9

From (2.92), we know that

$$
\langle \Psi_0|\mathscr{H}|\Psi_0\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle.
$$

For $\langle \Psi_0|\mathscr{H}|\Psi_{12}^{34}\rangle$, from Exercise 2.8, we know

$$
\langle \Psi_0|\mathscr{O}_1|\Psi_{12}^{34}\rangle = 0.
$$

Besides,

$$
\langle \Psi_0|\mathscr{O}_2|\Psi_{12}^{34}\rangle
$$

$$
= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \frac{1}{\sqrt{2}} [\chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)]^* r_{12}^{-1} \frac{1}{\sqrt{2}} [\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]
$$

$$= \frac{1}{2}\left[\int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_1^*(1)\chi_2^*(2)r_{12}^{-1}\chi_3(1)\chi_4(2) - \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_1^*(1)\chi_2^*(2)r_{12}^{-1}\chi_4(1)\chi_3(2)\right.$$

$$\left. - \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_2^*(1)\chi_1^*(2)r_{12}^{-1}\chi_3(1)\chi_4(2) + \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_2^*(1)\chi_1^*(2)r_{12}^{-1}\chi_4(1)\chi_3(2)\right]$$

$$= \frac{1}{2}\left(\langle 12|34\rangle - \langle 12|43\rangle - \langle 21|34\rangle + \langle 21|43\rangle\right) = \frac{1}{2}\left(\langle 12|34\rangle - \langle 12|43\rangle - \langle 12|43\rangle + \langle 12|34\rangle\right)$$

$$= \langle 12|34\rangle - \langle 12|43\rangle.$$

Thus, we know that

$$\langle \Psi_0|\mathscr{H}|\Psi_{12}^{34}\rangle = \langle \Psi_0|\mathscr{O}_1|\Psi_{12}^{34}\rangle + \langle \Psi_0|\mathscr{O}_2|\Psi_{12}^{34}\rangle = 0 + \langle 12|34\rangle - \langle 12|43\rangle = \langle 12|34\rangle - \langle 12|43\rangle, \qquad (2.9\text{-}1)$$

and

$$\langle \Psi_{12}^{34}|\mathscr{H}|\Psi_0\rangle = (\langle \Psi_0|\mathscr{H}|\Psi_{12}^{34}\rangle)^* = \langle 34|12\rangle - \langle 34|21\rangle. \qquad (2.9\text{-}2)$$

At last, for $\langle \Psi_{12}^{34}|\mathscr{H}|\Psi_{12}^{34}\rangle$, from Exercise 2.8,

$$\langle \Psi_{12}^{34}|\mathscr{O}_1|\Psi_{12}^{34}\rangle = \langle 3|h|3\rangle + \langle 4|h|4\rangle.$$

Moreover,

$$\langle \Psi_{34}^{12}|\mathscr{O}_2|\Psi_{12}^{34}\rangle$$

$$= \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \frac{1}{\sqrt{2}}[\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]^* r_{12}^{-1} \frac{1}{\sqrt{2}}[\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]$$

$$= \frac{1}{2}\left[\int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_3^*(1)\chi_4^*(2)r_{12}^{-1}\chi_3(1)\chi_4(2) - \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_3^*(1)\chi_4^*(2)r_{12}^{-1}\chi_4(1)\chi_3(2)\right.$$

$$\left. - \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_4^*(1)\chi_3^*(2)r_{12}^{-1}\chi_3(1)\chi_4(2) + \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_4^*(1)\chi_3^*(2)r_{12}^{-1}\chi_4(1)\chi_3(2)\right]$$

$$= \frac{1}{2}\left(\langle 34|34\rangle - \langle 34|43\rangle - \langle 43|34\rangle + \langle 43|43\rangle\right) = \frac{1}{2}\left(\langle 34|34\rangle - \langle 34|43\rangle - \langle 34|43\rangle + \langle 34|34\rangle\right)$$

$$= \langle 34|34\rangle - \langle 34|43\rangle.$$

Hence,

$$\langle \Psi_{12}^{34}|\mathscr{H}|\Psi_{12}^{34}\rangle = \langle \Psi_{12}^{34}|\mathscr{O}_1|\Psi_{12}^{34}\rangle + \langle \Psi_{12}^{34}|\mathscr{O}_2|\Psi_{12}^{34}\rangle = \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle. \qquad (2.9\text{-}3)$$

In conclusion, we have proved that

$$\mathscr{H} = \begin{pmatrix} \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle & \langle 12|34\rangle - \langle 12|43\rangle \\ \langle 34|12\rangle - \langle 34|21\rangle & \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle \end{pmatrix}. \qquad (2.9\text{-}4)$$

Obviously, it is Hermitian.

2.3.2 Notations for One- and Two-Electron Integrals

2.3.3 General Rules for Matrix Elements

Exercise 2.10

Derive Eq.(2.110) from Eq.(2.107).

Solution 2.10

We derive Eqs.(2.109a, b) firstly, then derive other equations. Note that

$$\langle mm||mm\rangle = \langle mm|mm\rangle - \langle mm|mm\rangle = 0. \qquad (2.10\text{-}1)$$

Thus (2.109a) has been proved. Besides, note that

$$\langle mn||mn\rangle = \langle mn|mn\rangle - \langle mn|nm\rangle = \langle nm|nm\rangle - \langle nm|mn\rangle = \langle nm||nm\rangle. \qquad (2.10\text{-}2)$$

Thus, (2.109b) has been proved. From Eq.(2.107), with $\langle mm||mm\rangle = 0$, we find that

$$\langle K|\mathcal{H}|K\rangle = \sum_m^N \langle m|h|m\rangle + \frac{1}{2}\sum_m^N\sum_n^N \langle mn||mn\rangle$$

$$= \sum_m^N \langle m|h|m\rangle + \frac{1}{2}\sum_m^N\sum_{n>m}^N \langle mn||mn\rangle + \frac{1}{2}\sum_n^N\sum_{m>n}^N \langle mn||mn\rangle$$

$$= \sum_m^N \langle m|h|m\rangle + \frac{1}{2}\sum_m^N\sum_{n>m}^N \langle mn||mn\rangle + \frac{1}{2}\sum_m^N\sum_{n>m}^N \langle nm||nm\rangle$$

$$= \sum_m^N \langle m|h|m\rangle + \sum_m^N\sum_{n>m}^N \langle mn||mn\rangle.$$

The first line of (2.110) has been verified. Then,

$$\langle K|\mathcal{H}|K\rangle = \sum_m^N \langle m|h|m\rangle + \sum_m^N\sum_{n>m}^N \langle mn||mn\rangle = \sum_m^N \langle m|h|m\rangle + \sum_m^N\sum_{n>m}^N \langle mn|mn\rangle - \langle mn|nm\rangle$$

$$= \sum_m^N [m|h|m] + \sum_m^N\sum_{n>m}^N [mm|nn] - [mn|nm].$$

If $|K\rangle = |\chi_1\chi_2\chi_3\rangle$ show that

$$\langle K|\mathcal{H}|K\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 3|h|3\rangle + \langle 12||12\rangle + \langle 13||13\rangle + \langle 23||23\rangle.$$

Solution 2.11

From the conclusion of Exercise 2.10, we immediately obtain that

$$\langle K|\mathcal{H}|K\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 3|h|3\rangle + \langle 12||12\rangle + \langle 13||13\rangle + \langle 23||23\rangle.$$

Exercise 2.12

Evaluate the matrix elements that occur in the minimal basis H_2 full CI matrix (Eq.(2.79)) using the rules. Compare with the result obtained in Exercise 2.9.

Solution 2.12

$\langle\Psi_0|\mathcal{H}|\Psi_0\rangle$ has been delivered by (2.111) and (2.114). Applying the rules, we get that

$$\langle\Psi_0|\mathcal{H}|\Psi_{12}^{34}\rangle = \langle\Psi_0|\mathcal{O}_1|\Psi_{12}^{34}\rangle + \langle\Psi_0|\mathcal{O}_2|\Psi_{12}^{34}\rangle = 0 + \langle 12||34\rangle = \langle 12||34\rangle,$$

$$\langle\Psi_{12}^{34}|\mathcal{H}|\Psi_0\rangle = \langle\Psi_{12}^{34}|\mathcal{O}_1|\Psi_0\rangle + \langle\Psi_{12}^{34}|\mathcal{O}_2|\Psi_0\rangle = 0 + \langle 34||12\rangle = \langle 34||12\rangle,$$

$$\langle\Psi_{12}^{34}|\mathcal{H}|\Psi_{12}^{34}\rangle = \langle\Psi_{12}^{34}|\mathcal{O}_1|\Psi_{12}^{34}\rangle + \langle\Psi_{12}^{34}|\mathcal{O}_2|\Psi_{12}^{34}\rangle = \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34||34\rangle.$$

This result equals that of Exercise 2.9.

Exercise 2.13

Show that

$$\langle\Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = \begin{cases} 0, & \text{if } a \neq b, \, r \neq s; \\ \langle r|h|s\rangle, & \text{if } a = b, \, r \neq s; \\ -\langle b|h|a\rangle, & \text{if } a \neq b, \, r = s; \\ \sum_c^N \langle c|h|c\rangle - \langle a|h|a\rangle + \langle r|h|r\rangle & \text{if } a = b, \, r = s. \end{cases}$$

Solution 2.13

Note that this result is not correct until the two determinants are in maximum coincidence! We talk about the final result according to the different occupation of the bra and the ket.

- When $a \neq b$ and $r \neq s$, the two determinants differ by two spin orbitals, and thus

$$\langle \Psi_a^r | \mathscr{O}_1 | \Psi_b^s \rangle = 0.$$

- When $a = b$ and $r \neq s$, the two determinants differ by one spin orbital, and thus

$$\langle \Psi_a^r | \mathscr{O}_1 | \Psi_b^s \rangle = \langle \Psi_a^r | \mathscr{O}_1 | \Psi_a^s \rangle = \langle r | h | s \rangle.$$

- When $a \neq b$ and $r = s$, the two determinants differ by one spin orbital, and thus $\langle \Psi_a^r | \mathscr{O}_1 | \Psi_b^s \rangle = \langle \Psi_a^r | \mathscr{O}_1 | \Psi_b^r \rangle$. Note that

$$\langle \Psi_a^r | \mathscr{O}_1 | \Psi_b^r \rangle = \langle \cdots \chi_r \chi_b \cdots | \mathscr{O}_1 | \cdots \chi_a \chi_r \cdots \rangle = -\langle \cdots \chi_r \chi_b \cdots | \mathscr{O}_1 | \cdots \chi_r \chi_a \cdots \rangle = -\langle r | h | a \rangle.$$

- When $a = b$ and $r = s$, the two determinants are the same, and thus

$$\langle \Psi_a^r | \mathscr{O}_1 | \Psi_b^s \rangle = \langle \Psi_a^r | \mathscr{O}_1 | \Psi_a^r \rangle = \langle \cdots \chi_{a \to r} \cdots | \mathscr{O}_1 | \cdots \chi_{a \to r} \cdots \rangle = \sum_{c \neq a} \langle c | h | c \rangle + \langle r | h | r \rangle.$$

  In other words,
$$\langle \Psi_a^r | \mathscr{O}_1 | \Psi_b^s \rangle = \sum_c \langle c | h | c \rangle - \langle a | h | a \rangle + \langle r | h | r \rangle.$$

In conclusion, we get that

$$\langle \Psi_a^r | \mathscr{O}_1 | \Psi_b^s \rangle = \begin{cases} 0, & \text{if } a \neq b, \, r \neq s; \\ \langle r | h | s \rangle, & \text{if } a = b, \, r \neq s; \\ -\langle b | h | a \rangle, & \text{if } a \neq b, \, r = s; \\ \displaystyle\sum_c^N \langle c | h | c \rangle - \langle a | h | a \rangle + \langle r | h | r \rangle & \text{if } a = b, \, r = s. \end{cases} \qquad \text{(2.13-1)}$$

Exercise 2.14

The Hartree-Fock ground state energy for an N-electron system is ${}^N E_0 = \langle {}^N \Psi_0 | \mathscr{H} | {}^N \Psi_0 \rangle$. Consider a state of the ionized system (in which an electron has been removed from spin orbital χ_a) with energy ${}^{N-1} E_a = \langle {}^{N-1} \Psi_a | \mathscr{H} | {}^{N-1} \Psi_a \rangle$, where $| {}^{N-1} \Psi_a \rangle$ is a single determinant with all spin orbitals but χ_a occupied,

$$| {}^{N-1} \Psi_a \rangle = | \chi_1 \chi_2 \cdots \chi_{a-1} \chi_{a+1} \cdots \chi_N \rangle.$$

Show, using the rules in the tables, that the energy required for this ionization process is

$${}^N E_0 - {}^{N-1} E_a = \langle a | h | a \rangle + \sum_b^N \langle ab || ab \rangle.$$

Solution 2.14

The verification is direct.

$$
{}^N E_0 - {}^{N-1} E_0 = \left[\sum_b^N \langle b | h | b \rangle + \frac{1}{2} \sum_c^N \sum_d^N \langle cd || cd \rangle \right] - \left[\sum_{b \neq a}^N \langle b | h | b \rangle + \frac{1}{2} \sum_{c \neq a}^N \sum_{d \neq a}^N \langle cd || cd \rangle \right]
$$

$$
= \left[\sum_b^N \langle b | h | b \rangle - \sum_{b \neq a}^N \langle b | h | b \rangle \right] + \frac{1}{2} \left[\sum_c^N \sum_d^N \langle cd || cd \rangle - \sum_{c \neq a}^N \sum_{d \neq a}^N \langle cd || cd \rangle \right]
$$

$$
= \langle a | h | a \rangle + \frac{1}{2} \left[\sum_d^N \langle ad || ad \rangle + \sum_c^N \langle ca || ca \rangle - \langle aa || aa \rangle \right]
$$

$$= \langle a|h|a\rangle + \frac{1}{2}\left[\sum_b^N \langle ab||ab\rangle + \sum_b^N \langle ab||ab\rangle\right] = \langle a|h|a\rangle + \sum_b^N \langle ab||ab\rangle.$$

2.3.4 Derivation of the Rules for Matrix Elements

Exercise 2.15

Generalize the result of Exercise 2.4 to N-electron Slater determinants. Show that the Slater determinant $|\chi_i\chi_j\cdots\chi_k\rangle$ formed from spin orbitals, which are eigenfunctions of the one-electron operator h as in Eq.(2.29), is an eigenfunction of the independent-electron Hamiltonian (2.28), $\mathscr{H} = \sum_{i=1}^{N} h(i)$, with an eigenvalue $\varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$. *Hint*: Since $\mathscr{H}$ is invariant to permutations of the electron labels, it commutes with the permutation operator $\mathscr{P}_n$.

Solution 2.15

Note that a Slater determinant is a linear combination of $N!$ Hartree product. With the conclusion of Exercise 2.2 and the truth that $\mathscr{H}$ commutes with the permutation operator $\mathscr{P}_n$, we find that

$$\mathscr{H}\Psi = \mathscr{H}\frac{1}{\sqrt{N!}}\sum_n^{N!}(-1)^{p_n}\mathscr{P}_n\prod_{j=1}^{N}\chi_{j'}(\mathbf{x}_j) = \frac{1}{\sqrt{N!}}\sum_n^{N!}(-1)^{p_n}\mathscr{P}_n\mathscr{H}\prod_{j=1}^{N}\chi_{j'}(\mathbf{x}_j)$$

$$= \frac{1}{\sqrt{N!}}\sum_n^{N!}(-1)^{p_n}\mathscr{P}_n\sum_{i=1}^{N}\varepsilon_i\prod_{j=1}^{N}\chi_{j'}(\mathbf{x}_j) = \sum_{i=1}^{N}\varepsilon_i\frac{1}{\sqrt{N!}}\sum_n^{N!}(-1)^{p_n}\mathscr{P}_n\prod_{j=1}^{N}\chi_{j'}(\mathbf{x}_j) = \sum_{i=1}^{N}\varepsilon_i\Psi.$$

Exercise 2.16

A different procedure for deriving the above matrix elements uses the theorem that $\langle K|\mathscr{H}|L\rangle = (N!)^{1/2}\langle K^{\mathrm{HP}}|\mathscr{H}|L\rangle$ where $|K^{\mathrm{HP}}\rangle$ is the Hartree product corresponding to the determinant $|K\rangle$, i.e.,

$$|K\rangle = |\chi_m(\mathbf{x}_1)\chi_n(\mathbf{x}_2)\cdots\rangle$$

and

$$|K^{\mathrm{HP}}\rangle = \chi_m(\mathbf{x}_1)\chi_n(\mathbf{x}_2)\cdots.$$

Prove this theorem. Use it to derive the matrix elements of a sum of one-electron operators.

Solution 2.16

Firstly, note that for a general permutation operator $\mathscr{P}_k$ and a general ket $|L\rangle$, due to the antisymmetry of the ket, we have that

$$(-1)^{p_k}\mathscr{P}_k\langle K^{\mathrm{HP}}|\mathscr{H}|L\rangle = \langle K^{\mathrm{HP}}|\mathscr{H}|L\rangle.$$

Thus, we find that

$$\langle K|\mathscr{H}|L\rangle = \frac{1}{\sqrt{N!}}\sum_{k=1}^{N!}(-1)^{p_k}\mathscr{P}_k\langle K^{\mathrm{HP}}|\mathscr{H}|L\rangle = \frac{1}{\sqrt{N!}}\sum_{k=1}^{N!}\langle K^{\mathrm{HP}}|\mathscr{H}|L\rangle$$

$$= \frac{1}{\sqrt{N!}}N!\langle K^{\mathrm{HP}}|\mathscr{H}|L\rangle = \sqrt{N!}\langle K^{\mathrm{HP}}|\mathscr{H}|L\rangle.$$

Hence, for the operator $\mathscr{O}_1$, which is a sum of one-electron operators o, we get that

$$\langle K|\mathscr{O}_1|L\rangle = \sqrt{N!}\langle K^{\mathrm{HP}}|\mathscr{O}_1|L\rangle$$

$$= \frac{\sqrt{N!}}{\sqrt{N!}}\sum_j(-1)^{p_j}\int d\mathbf{x}_1\int d\mathbf{x}_2\cdots\int d\mathbf{x}_N\{\chi_m^*(1)\chi_n^*(2)\cdots\chi_l^*(N)\}\sum_i o(i)\mathscr{P}_j\{\chi_p(1)\chi_q(2)\cdots\chi_r(N)\}$$

$$= \sum_i\sum_j(-1)^{p_j}\int d\mathbf{x}_1\int d\mathbf{x}_2\cdots\int d\mathbf{x}_N\{\chi_m^*(1)\chi_n^*(2)\cdots\chi_l^*(N)\}o(i)\mathscr{P}_j\{\chi_p(1)\chi_q(2)\cdots\chi_r(N)\}.$$

Here, for a given Hartree product K^{HP}, the maximum coincidence is dependent of the number of spin orbitals which $|K\rangle$ and $|L\rangle$ differ.

- When $|K\rangle$ and $|L\rangle$ are the same, at this time, there are N ways for the maximum coincidence and all of them are using an even permutation, thus,

$$\langle K|\mathscr{O}_1|L\rangle = \sum_i \int \mathrm{d}\mathbf{x}_i \chi_m^*(i)o(i)\chi_m(i) \int \mathrm{d}\mathbf{x}_1 \chi_n^*(1)\chi_n(1) \cdots \int \mathrm{d}\mathbf{x}_N \chi_l^*(N)\chi_l(N) = \sum_i \langle i|o|i\rangle.$$

- When $|K\rangle$ and $|L\rangle$ differ by one spin orbital, at this time, there is only one way for the maximum coincidence and it is using an even permutation, viz.,

$$\langle K|\mathscr{O}_1|L\rangle = \sum_i \int \mathrm{d}\mathbf{x}_i \chi_m^*(i)o(i)\chi_p(i) \int \mathrm{d}\mathbf{x}_1 \chi_n^*(1)\chi_n(1) \cdots \int \mathrm{d}\mathbf{x}_N \chi_l^*(N)\chi_l(N) = \langle m|o|p\rangle.$$

- When $|K\rangle$ and $|L\rangle$ differ by more than one spin orbital, at this time, there is no way for the maximum coincidence and thus,
$$\langle K|\mathscr{O}_1|L\rangle = 0.$$

In conclusion, we have derived the matrix elements of a sum of one-electron operators using $\langle K|\mathscr{H}|L\rangle = (N!)^{1/2}\langle K^{\mathrm{HP}}|\mathscr{H}|L\rangle$.

2.3.5   Transition from Spin Orbitals to Spatial Orbitals