CHAPTER 2

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.,

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

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 $j = 1, 2, \ldots, K$,

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

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

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

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 $\mathscr{H} = \sum_{i=1}^{N} h(i)$ with an eigenvalue given by (2.32).

Solution 2.2

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

$$\mathscr{H}\Psi^{\mathrm{HP}} = \left(\sum_{i=1}^{N} h(i)\right)\left[\prod_{j=1}^{N}\chi_{j'}(\mathbf{x}_j)\right] = \sum_{i=1}^{N}\prod_{j=1}^{N} h(i)\chi_{j'}(\mathbf{x}_j) = \sum_{i=1}^{N}\prod_{j=1}^{N}\varepsilon_i\chi_{j'}(\mathbf{x}_j) = \sum_{i=1}^{N}\varepsilon_i\prod_{j=1}^{N}\chi_{j'}(\mathbf{x}_j). \tag{2.2-1}$$

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.,

$$\begin{aligned}
&\langle\Psi|\Psi\rangle = \int \mathrm{d}\vec{\mathbf{x}}\,\langle\Psi|\vec{\mathbf{x}}\rangle\langle\vec{\mathbf{x}}|\Psi\rangle \\
&= \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2 \frac{1}{\sqrt{2}}\left[\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\right]^* \frac{1}{\sqrt{2}}\left[\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\right] \\
&= \frac{1}{2}\Bigg(\int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2) \\
&\qquad - \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) + \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\Bigg) \\
&= \frac{1}{2}(1 - 0 - 0 + 1) = 1.
\end{aligned}$$

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

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

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

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

$$
\begin{aligned}
&= \frac{1}{\sqrt{2}}\left[(\varepsilon_i+\varepsilon_j)|\Psi_{12}^{\mathrm{HP}}\rangle - (\varepsilon_i+\varepsilon_j)|\Psi_{21}^{\mathrm{HP}}\rangle\right] \\
&= (\varepsilon_i+\varepsilon_j)\frac{1}{\sqrt{2}}\left(|\Psi_{12}^{\mathrm{HP}}\rangle - |\Psi_{21}^{\mathrm{HP}}\rangle\right) = (\varepsilon_i+\varepsilon_j)|\Psi\rangle.
\end{aligned}
$$

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 $\mathscr{H} = h(1) + h(2)$ 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,

$$
\begin{aligned}
\langle K|L\rangle &= \int \mathrm{d}\vec{\mathbf{x}}\, \langle K|\vec{\mathbf{x}}\rangle\langle\vec{\mathbf{x}}|L\rangle \\
&= \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \frac{1}{\sqrt{2}}\left[\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)\right]^* \frac{1}{\sqrt{2}}\left[\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) - \chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2)\right] \\
&= \frac{1}{2}\left[\int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) - \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2)\right. \\
&\qquad \left. - \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) + \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2)\right] \\
&= \frac{1}{2}\left(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} - \delta_{jk}\delta_{il} + \delta_{jl}\delta_{ik}\right) = \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}.
\end{aligned}
$$

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 $S_{12} = S_{21}$,

$$
\begin{aligned}
\langle\psi_1|\psi_1\rangle = \int \mathrm{d}\mathbf{r}\, \psi_1^*(\mathbf{r})\psi_1(\mathbf{r}) &= \int \mathrm{d}\mathbf{r}\, \frac{1}{\sqrt{2(1+S_{12})}}\left(\phi_1(\mathbf{r}) + \phi_2(\mathbf{r})\right)^* \frac{1}{\sqrt{2(1+S_{12})}}\left(\phi_1(\mathbf{r}) + \phi_2(\mathbf{r})\right) \\
&= \frac{1}{2(1+S_{12})}(1 + S_{12} + S_{21} + 1) = 1,
\end{aligned}
$$

$$\langle\psi_2|\psi_2\rangle = \int \mathrm{d}\mathbf{r}\, \psi_2^*(\mathbf{r})\psi_2(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\, \frac{1}{\sqrt{2(1-S_{12})}}\left(\phi_1(\mathbf{r}) - \phi_2(\mathbf{r})\right)^* \frac{1}{\sqrt{2(1-S_{12})}}\left(\phi_1(\mathbf{r}) - \phi_2(\mathbf{r})\right)$$
$$= \frac{1}{2(1-S_{12})}(1 - S_{12} - S_{21} + 1) = 1,$$

and the orthogonality between ψ_1 and ψ_2,

$$\langle\psi_1|\psi_2\rangle = \int \mathrm{d}\mathbf{r}\, \psi_1^*(\mathbf{r})\psi_2(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\, \frac{1}{\sqrt{2(1+S_{12})}}\left(\phi_1(\mathbf{r}) + \phi_2(\mathbf{r})\right)^* \frac{1}{\sqrt{2(1-S_{12})}}\left(\phi_1(\mathbf{r}) - \phi_2(\mathbf{r})\right)$$
$$= \frac{1}{2\sqrt{(1-(S_{12})^2)}}(1 - S_{12} + S_{21} - 1) = 0 = \langle\psi_2|\psi_1\rangle^*.$$

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

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

$$
\begin{aligned}
&= \frac{1}{2}\left[\int \mathrm{d}\mathbf{x}_1\, \chi_3^*(1)h(1)\chi_3(1)\int \mathrm{d}\mathbf{x}_2\, \chi_4^*(2)\chi_4(2) - \int \mathrm{d}\mathbf{x}_1\, \chi_3^*(1)h(1)\chi_4(1)\int \mathrm{d}\mathbf{x}_2\, \chi_4^*(2)\chi_3(2)\right.\\
&\qquad \left. - \int \mathrm{d}\mathbf{x}_1\, \chi_4^*(1)h(1)\chi_3(1)\int \mathrm{d}\mathbf{x}_2\, \chi_3^*(2)\chi_4(2) + \int \mathrm{d}\mathbf{x}_1\, \chi_4^*(1)h(1)\chi_4(1)\int \mathrm{d}\mathbf{x}_2\, \chi_3^*(2)\chi_3(2)\right]\\
&= \frac{1}{2}\left[\int \mathrm{d}\mathbf{x}_1\, \chi_3^*(1)h(1)\chi_3(1) + 0 + 0 + \int \mathrm{d}\mathbf{x}_1\, \chi_4^*(1)h(1)\chi_4(1)\right] = \frac{1}{2}\left(\langle 3|h|3\rangle + \langle 4|h|4\rangle\right).
\end{aligned}
$$

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

$$
\begin{aligned}
&\langle \Psi_{12}^{34}|h(1)|\Psi_0\rangle\\
&= \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \frac{1}{\sqrt{2}}[\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]^* h(1)\frac{1}{\sqrt{2}}[\chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)]\\
&= \frac{1}{2}\left[\int \mathrm{d}\mathbf{x}_1\, \chi_3^*(1)h(1)\chi_1(1)\int \mathrm{d}\mathbf{x}_2\, \chi_4^*(2)\chi_2(2) - \int \mathrm{d}\mathbf{x}_1\, \chi_3^*(1)h(1)\chi_2(1)\int \mathrm{d}\mathbf{x}_2\, \chi_4^*(2)\chi_1(2)\right.\\
&\qquad \left. - \int \mathrm{d}\mathbf{x}_1\, \chi_4^*(1)h(1)\chi_1(1)\int \mathrm{d}\mathbf{x}_2\, \chi_3^*(2)\chi_2(2) + \int \mathrm{d}\mathbf{x}_1\, \chi_4^*(1)h(1)\chi_2(1)\int \mathrm{d}\mathbf{x}_2\, \chi_3^*(2)\chi_1(2)\right]\\
&= \frac{1}{2}\left[0 - 0 - 0 + 0\right] = 0.
\end{aligned}
$$

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

$$\langle \Psi_0|\mathscr{H}|\Psi_0\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle. \tag{2.1}$$

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,

$$
\begin{aligned}
&\langle \Psi_0|\mathscr{O}_2|\Psi_{12}^{34}\rangle\\
&= \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \frac{1}{\sqrt{2}}[\chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)]^* r_{12}^{-1}\frac{1}{\sqrt{2}}[\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{2}\left[\int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_1^*(1)\chi_2^*(2)r_{12}^{-1}\chi_3(1)\chi_4(2) - \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_1^*(1)\chi_2^*(2)r_{12}^{-1}\chi_4(1)\chi_3(2)\right.\\
&\qquad \left. - \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_2^*(1)\chi_1^*(2)r_{12}^{-1}\chi_3(1)\chi_4(2) + \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_2^*(1)\chi_1^*(2)r_{12}^{-1}\chi_4(1)\chi_3(2)\right]\\
&= \frac{1}{2}\left(\langle 12|34\rangle - \langle 12|43\rangle - \langle 21|34\rangle + \langle 21|43\rangle\right) = \frac{1}{2}\left(\langle 12|34\rangle - \langle 12|43\rangle - \langle 12|43\rangle + \langle 12|34\rangle\right)\\
&= \langle 12|34\rangle - \langle 12|43\rangle.
\end{aligned}
$$

Thus, we know that

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

and

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

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,

$$
\begin{aligned}
&\langle \Psi_{34}^{12}|\mathscr{O}_2|\Psi_{12}^{34}\rangle\\
&= \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \frac{1}{\sqrt{2}}[\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]^* r_{12}^{-1} \frac{1}{\sqrt{2}}[\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]\\
&= \frac{1}{2}\left[\int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_3^*(1)\chi_4^*(2)r_{12}^{-1}\chi_3(1)\chi_4(2) - \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_3^*(1)\chi_4^*(2)r_{12}^{-1}\chi_4(1)\chi_3(2)\right.\\
&\qquad \left. - \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_4^*(1)\chi_3^*(2)r_{12}^{-1}\chi_3(1)\chi_4(2) + \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_4^*(1)\chi_3^*(2)r_{12}^{-1}\chi_4(1)\chi_3(2)\right]\\
&= \frac{1}{2}\left(\langle 34|34\rangle - \langle 34|43\rangle - \langle 43|34\rangle + \langle 43|43\rangle\right) = \frac{1}{2}\left(\langle 34|34\rangle - \langle 34|43\rangle - \langle 34|43\rangle + \langle 34|34\rangle\right)\\
&= \langle 34|34\rangle - \langle 34|43\rangle.
\end{aligned}
$$

Hence,

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

In conclusion, we have proved that

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

Obviously, it is Hermitian.

2.3.2 Notations for One- and Two-Electron Integrals

2.3.3 General Rules for Matrix Elements