

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.,

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

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.,

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

is an orthonormal set.

Solution 2.1

It is easy to verify the normalization of any χ_{2i-1} or χ_{2j} ,

$$\langle \chi_{2i-1} | \chi_{2j-1} \rangle = \int d\mathbf{x} \chi_{2i-1}^*(\mathbf{x}) \chi_{2j-1}(\mathbf{x}) = \int d\mathbf{r} \psi_i^{\alpha*}(\mathbf{r}) \psi_j^\alpha(\mathbf{r}) \int d\omega \alpha^*(\omega) \alpha(\omega) = \delta_{ij} \times 1 = \delta_{ij}, \quad (2.1)$$

$$\langle \chi_{2i} | \chi_{2j} \rangle = \int d\mathbf{x} \chi_{2i}^*(\mathbf{x}) \chi_{2j}(\mathbf{x}) = \int d\mathbf{r} \psi_i^{\beta*}(\mathbf{r}) \psi_j^\beta(\mathbf{r}) \int d\omega \beta^*(\omega) \beta(\omega) = \delta_{ij} \times 1 = \delta_{ij}. \quad (2.2)$$

and the orthogonalization between χ_{2i-1} and χ_{2j} ,

$$\langle \chi_{2i-1} | \chi_{2j} \rangle = \int d\mathbf{x} \chi_{2i-1}^*(\mathbf{x}) \chi_{2j}(\mathbf{x}) = \int d\mathbf{r} \psi_i^{\alpha*}(\mathbf{r}) \psi_j^\beta(\mathbf{r}) \int d\omega \alpha^*(\omega) \beta(\omega) = S_{ij} \times 0 = 0, \quad (2.3)$$

$$\langle \chi_{2i} | \chi_{2j-1} \rangle = \int d\mathbf{x} \chi_{2i}^*(\mathbf{x}) \chi_{2j-1}(\mathbf{x}) = \int d\mathbf{r} \psi_i^{\beta*}(\mathbf{r}) \psi_j^\alpha(\mathbf{r}) \int d\omega \beta^*(\omega) \alpha(\omega) = S_{ij}^* \times 0 = 0. \quad (2.4)$$

Thus, we can conclude that the set $\{\chi_i\}$ is an orthonormal set.

2.2.2 Hartree Products

Exercise 2.2

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

Solution 2.2

Verification is easy.

$$\mathcal{H}\Psi^{\text{HP}} = \left(\sum_{i=1}^N h(i) \right) \Psi^{\text{HP}} = \sum_{i=1}^N (h(i)\Psi^{\text{HP}}) = \sum_{i=1}^N \varepsilon_i \Psi^{\text{HP}} = \left(\sum_{i=1}^N \varepsilon_i \right) \Psi^{\text{HP}}. \quad (2.5)$$

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

Verification is easy, too.

$$\begin{aligned} \langle \Psi | \Psi \rangle &= \int d\vec{x} \langle \Psi | \vec{x} \rangle \langle \vec{x} | \Psi \rangle \\ &= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \frac{1}{\sqrt{2}} [\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)]^* \frac{1}{\sqrt{2}} [\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)] \\ &= \frac{1}{2}(1 + 0 + 0 + 1) = 1. \end{aligned} \quad (2.6)$$

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 $\mathcal{H} = h(1) + h(2)$ (c.f. Eq.(2.28)) and have the same eigenvalue namely, $\varepsilon_i + \varepsilon_j$.

Solution 2.4

Firstly, we check the Hartree product of χ_i and χ_j .

$$\begin{aligned} \mathcal{H}|\Psi_{12}^{\text{HP}}\rangle &= (h(1) + h(2)) \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) = h(1)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) + h(2)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \\ &= [h(1)\chi_i(\mathbf{x}_1)]\chi_j(\mathbf{x}_2) + \chi_i(\mathbf{x}_1)[h(2)\chi_j(\mathbf{x}_2)] = \varepsilon_i\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) + \varepsilon_j\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \\ &= (\varepsilon_i + \varepsilon_j)\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) = (\varepsilon_i + \varepsilon_j)|\Psi_{12}^{\text{HP}}\rangle. \end{aligned} \quad (2.7)$$

Similarly, we can find

$$\mathcal{H}|\Psi_{21}^{\text{HP}}\rangle = (\varepsilon_i + \varepsilon_j)|\Psi_{21}^{\text{HP}}\rangle. \quad (2.8)$$

Thus, the eigenvalue of a Hartree product of χ_i and χ_j is irrelevant to the order of electrons, which does not violate the indistinguishability of electrons and physically meaningful. Note that

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

We find that

$$\begin{aligned} \mathcal{H}|\Psi\rangle &= \mathcal{H} \frac{1}{\sqrt{2}} (|\Psi_{12}^{\text{HP}}\rangle - |\Psi_{21}^{\text{HP}}\rangle) = \frac{1}{\sqrt{2}} (\mathcal{H}|\Psi_{12}^{\text{HP}}\rangle - \mathcal{H}|\Psi_{21}^{\text{HP}}\rangle) \\ &= \frac{1}{\sqrt{2}} [(\varepsilon_i + \varepsilon_j)|\Psi_{12}^{\text{HP}}\rangle - (\varepsilon_i + \varepsilon_j)|\Psi_{21}^{\text{HP}}\rangle] = (\varepsilon_i + \varepsilon_j) \frac{1}{\sqrt{2}} (|\Psi_{12}^{\text{HP}}\rangle - |\Psi_{21}^{\text{HP}}\rangle) = (\varepsilon_i + \varepsilon_j)|\Psi\rangle. \end{aligned} \quad (2.9)$$

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 $\mathcal{H} = h(1) + h(2)$ (c.f. Eq.(2.28)) and have the same eigenvalue namely, $\varepsilon_i + \varepsilon_j$.

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,

$$\begin{aligned} \langle K|L\rangle &= \int d\vec{x} \langle K|\vec{x}\rangle \langle \vec{x}|L\rangle \\ &= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \frac{1}{\sqrt{2}} [\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)]^* \frac{1}{\sqrt{2}} [\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) - \chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2)] \\ &= \frac{1}{2} \left[\int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) - \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2) \right. \\ &\quad \left. - \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) + \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_1)\chi_i^*(\mathbf{x}_2)\chi_l(\mathbf{x}_1)\chi_k(\mathbf{x}_2) \right] \\ &= \frac{1}{2} (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} - \delta_{jk}\delta_{il} + \delta_{jl}\delta_{ik}) = \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il} \equiv \delta_{ij}^{kl}. \end{aligned} \quad (2.10)$$

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 $|L\rangle = |\chi_j \chi_i\rangle = -|K\rangle$ and the overlap is -1 .
- Otherwise, the overlap is 0.

2.2.4 The Hartree-Fock Approximation

2.2.5 The Minimal Basis H₂ Model

Exercise 2.6

Show that ψ_1 and ψ_2 form an orthonormal set.

Solution 2.6

Similar to Solution 2.1, we have to verify the normalization of any ψ_1 or ψ_2 , with $S_{ij} = S_{ij}^* = S_{ji}$,

$$\begin{aligned} \langle \psi_1|\psi_1\rangle &= \int d\mathbf{r} \psi_1^*(\mathbf{r})\psi_1(\mathbf{r}) = \int d\mathbf{r} \frac{1}{\sqrt{2(1+S_{12})}} (\phi_1(\mathbf{r}) + \phi_2(\mathbf{r}))^* \frac{1}{\sqrt{2(1+S_{12})}} (\phi_1(\mathbf{r}) + \phi_2(\mathbf{r})) \\ &= \frac{1}{2(1+S_{12})} (1 + S_{12} + S_{21} + 1) = 1, \end{aligned} \quad (2.11)$$

$$\begin{aligned} \langle \psi_2|\psi_2\rangle &= \int d\mathbf{r} \psi_2^*(\mathbf{r})\psi_2(\mathbf{r}) = \int d\mathbf{r} \frac{1}{\sqrt{2(1-S_{12})}} (\phi_1(\mathbf{r}) - \phi_2(\mathbf{r}))^* \frac{1}{\sqrt{2(1-S_{12})}} (\phi_1(\mathbf{r}) - \phi_2(\mathbf{r})) \\ &= \frac{1}{2(1-S_{12})} (1 - S_{12} - S_{21} + 1) = 1, \end{aligned} \quad (2.12)$$

and the orthogonalization between ψ_1 and ψ_2 ,

$$\begin{aligned}\langle\psi_1|\psi_2\rangle &= \int d\mathbf{r} \psi_1^*(\mathbf{r})\psi_2(\mathbf{r}) = \int d\mathbf{r} \frac{1}{\sqrt{2(1+S_{12})}} (\phi_1(\mathbf{r}) + \phi_2(\mathbf{r}))^* \frac{1}{\sqrt{2(1-S_{12})}} (\phi_1(\mathbf{r}) - \phi_2(\mathbf{r})) \\ &= \frac{1}{2\sqrt{(1-(S_{12})^2)}} (1 - S_{12} + S_{12} - 1) = 0 = \langle\psi_2|\psi_1\rangle^*.\end{aligned}\quad (2.13)$$

Thus, we can 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

Firstly, there are in total 42 electrons in a benzene molecule. Here, each carbon atom delivers 6 electrons while each hydrogen atom delivers only 1 electron.

Secondly, the minimal basis set of benzene includes 36 spatial orbitals. Here, each carbon atom delivers its 1s, 2s and three 2p orbitals (i.e., $2p_x$, $2p_y$ and $2p_z$) while each hydrogen atom delivers its 1s orbital. 36 spatial orbitals can be used to construct 72 spin orbitals, as shown in Exercise 2.1.

Thirdly, consider that a spin orbital can contain only one electron, there are 42 occupied spin orbitals and 30 unoccupied spin orbitals.

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.

Moreover, there are $\binom{42}{2}\binom{30}{2} = 374535$ doubly excited determinants.

2.3 Operators and Matrix Elements

2.3.1 Minimal Basis H_2 Matrix Elements

Exercise 2.8

Show that

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

and

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

Solution 2.8

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

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

Its first part is

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

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

Similarly, we can obtain

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

Thus,

$$\langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = \frac{1}{2} (\langle 3|h|3 \rangle + \langle 4|h|4 \rangle) + \frac{1}{2} (\langle 3|h|3 \rangle + \langle 4|h|4 \rangle) = \langle 3|h|3 \rangle + \langle 4|h|4 \rangle. \quad (2.14)$$

Besides, in the same way,

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

and

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

Therefore,

$$\langle \Psi_{12}^{34} | h(1) | \Psi_{12}^{34} \rangle = \langle \Psi_{12}^{34} | h(1) | \Psi_0 \rangle + \langle \Psi_{12}^{34} | h(2) | \Psi_0 \rangle = 0 + 0 = 0, \quad (2.15)$$

and

$$\langle \Psi_0 | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = \langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_0 \rangle^* = 0^* = 0. \quad (2.16)$$

Exercise 2.9

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

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

and that is it Hermitian.

Solution 2.9

From Eq.(2.92), we know

$$\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \langle 1|h|1 \rangle + \langle 2|h|2 \rangle + \langle 12|12 \rangle - \langle 12|21 \rangle. \quad (2.17)$$

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

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

Besides,

$$\begin{aligned} & \langle \Psi_0 | \mathcal{O}_2 | \Psi_{12}^{34} \rangle \\ &= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \frac{1}{\sqrt{2}} [\chi_1(1) \chi_2(2) - \chi_2(1) \chi_1(2)]^* r_{12}^{-1} \frac{1}{\sqrt{2}} [\chi_3(1) \chi_4(2) - \chi_4(1) \chi_3(2)] \\ &= \frac{1}{2} \left[\int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_1^*(1) \chi_2^*(2) r_{12}^{-1} \chi_3(1) \chi_4(2) - \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_1^*(1) \chi_2^*(2) r_{12}^{-1} \chi_4(1) \chi_3(2) \right. \\ & \quad \left. - \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_2^*(1) \chi_1^*(2) r_{12}^{-1} \chi_3(1) \chi_4(2) + \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_2^*(1) \chi_1^*(2) r_{12}^{-1} \chi_4(1) \chi_3(2) \right] \\ &= \frac{1}{2} (\langle 12|34 \rangle - \langle 12|43 \rangle - \langle 21|34 \rangle + \langle 21|43 \rangle) = \frac{1}{2} (\langle 12|34 \rangle - \langle 12|43 \rangle - \langle 12|43 \rangle + \langle 12|34 \rangle) \end{aligned}$$

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

Thus,

$$\langle \Psi_0 | \mathcal{H} | \Psi_{12}^{34} \rangle = \langle \Psi_0 | \mathcal{O}_1 | \Psi_{12}^{34} \rangle + \langle \Psi_0 | \mathcal{O}_2 | \Psi_{12}^{34} \rangle = 0 + \langle 12|34 \rangle - \langle 12|43 \rangle = \langle 12|34 \rangle - \langle 12|43 \rangle. \quad (2.18)$$

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

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

Moreover,

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

Hence,

$$\langle \Psi_{12}^{34} | \mathcal{H} | \Psi_{12}^{34} \rangle = \langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_{12}^{34} \rangle + \langle \Psi_{12}^{34} | \mathcal{O}_2 | \Psi_{12}^{34} \rangle = \langle 3|h|3 \rangle + \langle 4|h|4 \rangle + \langle 34|34 \rangle - \langle 34|43 \rangle. \quad (2.19)$$

In conclusion, we have proved that

$$\mathcal{H} = \begin{pmatrix} \langle 1|h|1 \rangle + \langle 2|h|2 \rangle + \langle 12|12 \rangle - \langle 12|21 \rangle & \langle 12|34 \rangle - \langle 12|43 \rangle \\ \langle 34|12 \rangle - \langle 34|21 \rangle & \langle 3|h|3 \rangle + \langle 4|h|4 \rangle + \langle 34|34 \rangle - \langle 34|43 \rangle \end{pmatrix}. \quad (2.20)$$

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

2-10 so

Exercise 2.11

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

2-11 so

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

2-12 so

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

2-13 so

Exercise 2.14

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

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

To show the power and simplicity of the mnemonic device introduced in this subsection, let us derive the above result without doing any algebra. Consider the representation of $|{}^N \Psi_0\rangle$ in Fig. 2.4. If we remove an electron from χ_a , we lose the “one-electron energy” contribution $\langle a | h | a \rangle$ to ${}^N E_0$. Moreover, we lose the pair-wise contributions arising from the “interaction” of the electron in χ_a with the remaining electrons $\left(\text{i.e., } \sum_{b \neq a}^N \langle ab || ab \rangle \right)$. Because $\langle aa || aa \rangle = 0$, the above result follows immediately.

Solution 2.14

2-14 so

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), $\mathcal{H} = \sum_{i=1}^N h(i)$, with an eigenvalue $\varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$. *Hint:* Since \mathcal{H} is invariant to permutations of the electron labels, it commutes with the permutation operator \mathcal{P}_n .

Solution 2.15

2-15 so

Exercise 2.16

A different procedure for deriving the above matrix elements uses the theorem that $\langle K | \mathcal{H} | L \rangle = (N!)^{1/2} \langle K^{\text{HP}} | \mathcal{H} | L \rangle$ where $|K^{\text{HP}}\rangle$ 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

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

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

Solution 2.16

2-16 so

2.3.5 Transition from Spin Orbitals to Spatial Orbitals

Exercise 2.17

By integrating out spin, show that the full CI matrix for minimal basis H_2 (see Exercise 2.9) is

$$\mathbf{H} = \begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix}.$$

Solution 2.17

2-17 so

Exercise 2.18

In Chapter 6, where we consider perturbation theory, we show that the leading correction to the Hartree-Fock ground state energy is

$$E_{\text{H}}^{[2]} = \frac{1}{4} \sum_{abrs} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}.$$

Show that for a closed-shell system (where $\varepsilon_i = \varepsilon_{\bar{i}}$) this becomes

$$E_{\text{H}}^{[2]} = \sum_{a,b=1}^{N/2} \sum_{r,s=(N/2+1)}^K \frac{\langle ab||rs\rangle(2\langle rs||ab\rangle - \langle rs||ba\rangle)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}.$$

Solution 2.18

2-18 so

2.3.6 Coulomb and Exchange Integrals

Exercise 2.19

Prove the following properties of coulomb and exchange integrals

$$\begin{aligned} J_{ii} &= K_{ii}, & J_{ij}^* &= J_{ij}, & K_{ij}^* &= K_{ij}, \\ J_{ij} &= J_{ji}, & K_{ij} &= K_{ji}. \end{aligned}$$

Solution 2.19

2-19 so

fff

fff

fff

Exercise 2.20

Show that for *real* spatial orbitals

$$K_{ij} = (ij|ij) = (ji|ji) = \langle ii|jj\rangle = \langle jj|ii\rangle.$$

Solution 2.20

2-20 so

Exercise 2.21

Show that the full CI matrix for minimal basis H_2 (see Exercise 2.17) is

$$\mathbf{H} = \begin{pmatrix} 2h_{11} + J_{11} & K_{12} \\ K_{12} & 2h_{22} + J_{22} \end{pmatrix}.$$

The spatial molecular orbitals of this model are real because they were constructed as linear combinations of real atomic orbitals (see Eqs.(2.54), (2.55), (2.57), and (2.58)).

Solution 2.21

2-21 so

Exercise 2.22

Show that the energies of the Hartree products

$$\Psi_{\uparrow\downarrow}^{\text{HP}} = \psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_2(\mathbf{r}_2)\beta(\omega_2)$$

and

$$\Psi_{\downarrow\uparrow}^{\text{HP}} = \psi_1(\mathbf{r}_1)\beta(\omega_1)\psi_2(\mathbf{r}_2)\alpha(\omega_2)$$

are the same and equal to $E(\uparrow\downarrow)$ as to be expected since the motion of electrons with parallel spin in not correlated within the Hartree product approximation to the wave function.

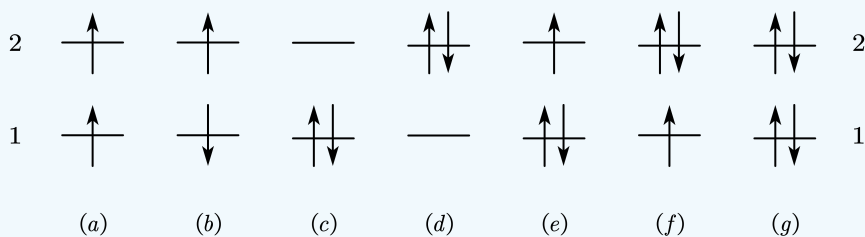
Solution 2.22

2-22 so

fff

2.3.7 Pseudo-Classical Interpretation of Determinantal Energies**Exercise 2.23**

Verify the energies of the following determinants by inspection.



- a. $h_{11} + h_{22} + J_{12} - K_{12}$.
- b. $h_{11} + h_{22} + J_{12}$.
- c. $2h_{11} + J_{11}$.
- d. $2h_{22} + J_{22}$.
- e. $2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12}$.
- f. $2h_{22} + h_{11} + J_{22} + 2J_{12} - K_{12}$.
- g. $2h_{11} + 2h_{22} + J_{11} + J_{22} + 4J_{12} - 2K_{12}$.

Solution 2.23

2-23 so

2.4 Second Quantization

2.4.1 Creation and Annihilation Operators and Their Anticommutation Relations

Exercise 2.24

Show, using the properties of determinants, that

$$(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)|K\rangle = 0$$

for every $|K\rangle$ in set $\{|\chi_1\chi_2\rangle, |\chi_1\chi_3\rangle, |\chi_1\chi_4\rangle, |\chi_2\chi_3\rangle, |\chi_2\chi_4\rangle, |\chi_3\chi_4\rangle\}$.

Solution 2.24

2-24 so
fff

Exercise 2.25

Show, using the properties of determinants, that

$$(a_1 a_2^\dagger + a_2^\dagger a_1)|K\rangle = 0,$$

$$(a_1 a_1^\dagger + a_1^\dagger a_1)|K\rangle = |K\rangle$$

for every $|K\rangle$ in set $\{|\chi_1\chi_2\rangle, |\chi_1\chi_3\rangle, |\chi_1\chi_4\rangle, |\chi_2\chi_3\rangle, |\chi_2\chi_4\rangle, |\chi_3\chi_4\rangle\}$.

Solution 2.25

2-25 so

Exercise 2.26

Show using second quantization that $\langle\chi_i|\chi_j\rangle = \delta_{ij}$.

Solution 2.26

2-26 so

Exercise 2.27

Given a state

$$|K\rangle = |\chi_1\chi_2\cdots\chi_N\rangle = a_1^\dagger a_2^\dagger \cdots a_N^\dagger| \rangle,$$

show that $\langle K|a_i^\dagger a_j|K\rangle = 1$ if $i = j$ and $i \in \{1, 2, \dots, N\}$, but is zero otherwise.

Solution 2.27

2-27 so

Exercise 2.28

Let $|\Psi_0\rangle = |\chi_1\cdots\chi_a\chi_b\cdots\chi_N\rangle$ be the Hartree-Fock ground state wave function. Show that

- $a_r|\Psi_0\rangle = 0 = \langle\Psi_0|a_r^\dagger$.
- $a_a^\dagger|\Psi_0\rangle = 0 = \langle\Psi_0|a_a$.
- $|\Psi_a^r\rangle = a_r^\dagger a_a|\Psi_0\rangle$.
- $\langle\Psi_a^r| = \langle\Psi_0|a_a^\dagger a_r$.
- $|\Psi_{ab}^{rs}\rangle = a_s^\dagger a_b a_r^\dagger a_a|\Psi_0\rangle = a_r^\dagger a_s^\dagger a_b a_a|\Psi_0\rangle$.
- $\langle\Psi_{ab}^{rs}| = \langle\Psi_0|a_a^\dagger a_r a_b^\dagger a_s = \langle\Psi_0|a_a^\dagger a_b^\dagger a_s a_r$.

Solution 2.28

2-28 so

2.4.2 Second-Quantized Operators and Their Matrix Elements**Exercise 2.29**

Let $|\Psi_0\rangle = |\chi_1\chi_2\rangle = a_1^\dagger a_2^\dagger| \rangle$ be the Hartree-Fock wave function for minimal basis H_2 . Show using second quantization that

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_{ij} \langle i|h|j\rangle \langle\Psi_0|a_2a_1a_i^\dagger a_j a_1^\dagger a_2^\dagger|\Psi_0\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle.$$

Solution 2.29

2-29 so

Exercise 2.30

Show that

$$\langle\Psi_a^r|\mathcal{O}_1|\Psi_0\rangle = \sum_{ij} \langle i|h|j\rangle \langle\Psi_0|a_a^\dagger a_r a_i^\dagger a_j|\Psi_0\rangle = \langle r|h|a\rangle$$

by moving a_a^\dagger and a_r to the right.

Solution 2.30

2-30 so

Exercise 2.31

Show that

$$\langle\Psi_a^r|\mathcal{O}_2|\Psi_0\rangle = \sum_b^N \langle rb||ab\rangle.$$

Hint: first show that

$$\begin{aligned} \langle\Psi_0|a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k|\Psi_0\rangle &= \delta_{rj}\delta_{al}\langle\Psi_0|a_i^\dagger a_k|\Psi_0\rangle - \delta_{rj}\delta_{ak}\langle\Psi_0|a_i^\dagger a_l|\Psi_0\rangle \\ &\quad + \delta_{ri}\delta_{ak}\langle\Psi_0|a_j^\dagger a_l|\Psi_0\rangle - \delta_{ri}\delta_{al}\langle\Psi_0|a_j^\dagger a_k|\Psi_0\rangle \end{aligned}$$

then refer to Exercise 2.27.

Solution 2.31

2-31 so

2.5 Spin-Adapted Configurations**2.5.1 Spin Operators****Exercise 2.32**

a) Derive (2.247) from (2.245); b) Derive (2.248).

Solution 2.32

2-32 so

Exercise 2.33

Find the 2×2 matrix representations of s^2 , s_z , s_+ , and s_- in the basis $|\alpha\rangle$, $|\beta\rangle$. Verify the identities analogous to (2.248a,b) for these matrix representations.

Solution 2.33

2-33 so

Exercise 2.34

Using the commutation relations (2.242), show that $[s^2, s_z] = 0$.

Solution 2.34

2-34 so

Exercise 2.35

Consider an operator \mathcal{A} that commutes with the Hamiltonian. Suppose $|\Phi\rangle$ is an eigenfunction of \mathcal{H} with eigenvalue E . Show that $\mathcal{A}|\Phi\rangle$ is also an eigenfunction of \mathcal{H} with eigenvalue E . Thus if $|\Phi\rangle$ is (energetically) nondegenerate, then $\mathcal{A}|\Phi\rangle$ is at most a constant multiple of $|\Phi\rangle$ (i.e., $\mathcal{A}|\Phi\rangle = a|\Phi\rangle$) and hence $|\Phi\rangle$ is an eigenfunction of \mathcal{A} . In case of degeneracies, we can always construct appropriate linear combinations of the degenerate eigenfunctions of \mathcal{H} that are also eigenfunctions of \mathcal{A} .

Solution 2.35

2-35 so

Exercise 2.36

Given two nondegenerate eigenfunctions of a hermitian operator \mathcal{A} that commutes with \mathcal{H} , i.e., $\mathcal{A}|\Psi_1\rangle = a_1|\Psi_1\rangle$, $\mathcal{A}|\Psi_2\rangle = a_2|\Psi_2\rangle$, $a_1 \neq a_2$, show that $\langle\Psi_1|\mathcal{H}|\Psi_2\rangle = 0$. Thus the matrix element of the Hamiltonian between, say, singlet and triplet spin-adapted configurations is zero.

Solution 2.36

2-36 so

Exercise 2.37

Prove Eq.(2.254). *Hint:* Use expansion (2.115) for a Slater determinant and note that \mathcal{S}_z , since it is invariant to any permutation of the electron labels, commutes with \mathcal{P}_n .

Solution 2.37

2-37 so

2.5.2 Restricted Determinants and Spin-Adapted Configurations**Exercise 2.38**

Prove Eq.(2.256). *Hint:* 1) $\mathcal{S}^2 = \mathcal{S}_-\mathcal{S}_+ + \mathcal{S}_z + \mathcal{S}_z^2$, 2) as a result of Eq.(2.254) it is sufficient to show $\mathcal{S}_+|\psi_i\bar{\psi}_i\cdots\rangle = 0$, 3) use expansion (2.115) for the determinant, and note the \mathcal{S}_+ commutes with the permutation operator, 4) $s_+\psi_\alpha = 0$, 5) finally, $s_+\psi_\beta = \psi_\alpha$, but the determinant vanishes because it has two identical columns.

Solution 2.38

2-38 so

Exercise 2.39

Using $\mathcal{S}^2 = \mathcal{S}_-\mathcal{S}_+ + \mathcal{S}_z + \mathcal{S}_z^2$, show that $|^1\Psi_1^2\rangle$ is a singlet while $|^3\Psi_1^2\rangle$, $|\Psi_1^{\bar{2}}\rangle$ and $|\Psi_1^2\rangle$ are triplets.

Solution 2.39

2-39 so

Exercise 2.40

Show that

$$\begin{aligned}\langle {}^1\Psi_1^2 | \mathcal{H} | {}^1\Psi_1^2 \rangle &= h_{11} + h_{22} + J_{12} + K_{12}, \\ \langle {}^3\Psi_1^2 | \mathcal{H} | {}^3\Psi_1^2 \rangle &= h_{11} + h_{22} + J_{12} - K_{12}.\end{aligned}$$

Note that the energy of the triplet is lower than the energy of the singlet. Why is this to be expected from the space parts of the two wave functions?

Solution 2.40

2-40 so

2.5.3 Unrestricted Determinants**Exercise 2.41**

Consider the determinant $|K\rangle = |\psi_1^\alpha \bar{\psi}_1^\beta\rangle$ formed from *nonorthogonal* spatial orbitals, $\langle \psi_1^\alpha | \psi_1^\beta \rangle = S_{11}^{\alpha\beta}$.

- Show that $|K\rangle$ is an eigenfunction of \mathcal{S}^2 only if $\psi_1^\alpha = \psi_1^\beta$.
- Show that $\langle K | \mathcal{S}^2 | K \rangle = 1 - |S_{11}^{\alpha\beta}|^2$ in agreement with Eq.(2.271).

Solution 2.41

2-41 so