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

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

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 $\mathscr{H} = \sum_{i=1}^{N} h(i)$ 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

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

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

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,

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

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

$$\begin{aligned}
\langle\psi_1|\psi_1\rangle &= \int \mathrm{d}\mathbf{r}\,\psi_1^*(\mathbf{r})\psi_1(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\,\frac{1}{\sqrt{2(1+S_{12})}}\left(\phi_1(\mathbf{r})+\phi_2(\mathbf{r})\right)^* \frac{1}{\sqrt{2(1+S_{12})}}\left(\phi_1(\mathbf{r})+\phi_2(\mathbf{r})\right) \\
&= \frac{1}{2(1+S_{12})}(1 + S_{12} + S_{21} + 1) = 1, \qquad (2.1)
\end{aligned}$$

$$\begin{aligned}\langle\psi_2|\psi_2\rangle &= \int \mathrm{d}\mathbf{r}\,\psi_2^*(\mathbf{r})\psi_2(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\,\frac{1}{\sqrt{2(1-S_{12})}}\left(\phi_1(\mathbf{r})-\phi_2(\mathbf{r})\right)^*\frac{1}{\sqrt{2(1-S_{12})}}\left(\phi_1(\mathbf{r})-\phi_2(\mathbf{r})\right)\\ &= \frac{1}{2(1-S_{12})}(1-S_{12}-S_{21}+1) = 1,\end{aligned}\tag{2.2}$$

and the orthogonalization between ψ_1 and ψ_2,

$$\begin{aligned}\langle\psi_1|\psi_2\rangle &= \int \mathrm{d}\mathbf{r}\,\psi_1^*(\mathbf{r})\psi_2(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\,\frac{1}{\sqrt{2(1+S_{12})}}\left(\phi_1(\mathbf{r})+\phi_2(\mathbf{r})\right)^*\frac{1}{\sqrt{2(1-S_{12})}}\left(\phi_1(\mathbf{r})-\phi_2(\mathbf{r})\right)\\ &= \frac{1}{2\sqrt{(1-(S_{12})^2)}}(1-S_{12}+S_{12}-1) = 0 = \langle\psi_2|\psi_1\rangle^*.\end{aligned}\tag{2.3}$$

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