

Question 1: Antisymmetrizer and Slater determinants

The normalized, two electron ($n = 2$) wave function $\Phi(1, 2)$ may be written using a Slater determinant

$$\Phi(1, 2) = \frac{1}{\sqrt{n!}} |\phi_1 \bar{\phi}_1|, \quad (1)$$

or by using the anti-symmetrizer $\hat{\mathcal{A}}$

$$\Phi(1, 2)' = \sqrt{n!} \hat{\mathcal{A}} \psi_1(1) \psi_2(2), \quad (2)$$

where the spin-orbitals ψ_i are given by $\psi_1(j) = \phi_1(j)\alpha(j)$ and $\psi_2(j) = \phi_1(j)\beta(j)$, with spatial orbital ϕ_1 and electron spin functions α and β . The anti-symmetrizer is given by a sum over all $n!$ permutations \hat{P} , with parities $(-1)^p$,

$$\hat{\mathcal{A}} = \frac{1}{n!} \sum_P (-1)^p \hat{P}. \quad (3)$$

For $n = 2$ this sum contains two permutations, $\hat{P} = \hat{\mathbf{1}}$ (the identity operator) and $\hat{P} = \hat{P}_{1,2}$, the operator that interchanges labels 1 and 2.

1a. Evaluate both $\Phi(1, 2)$ and $\Phi(1, 2)'$ and show that they are identical.

Answer:

$$\Phi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix} = \phi_1(1)\phi_1(2) \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$$

and

$$\begin{aligned} \Phi(1, 2)' &= \frac{\sqrt{2}}{2} (\hat{\mathbf{1}} - \hat{P}_{1,2}) \psi_1(1) \psi_2(2) = \frac{1}{\sqrt{2}} [\psi_1(1) \psi_2(2) - \psi_2(1) \psi_1(2)] \\ &= \phi_1(1)\phi_1(2) \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}. \end{aligned}$$

The antisymmetrizer satisfies, for each permutation \hat{P}

$$\hat{P} \hat{\mathcal{A}} = (-1)^p \hat{\mathcal{A}}. \quad (4)$$

1b. Verify this expression for $n = 2$ and $\hat{P} = \hat{\mathbf{1}}$ and for $\hat{P} = \hat{P}_{1,2}$.

Answer: For $\hat{P} = \hat{\mathbf{1}}$, $p=\text{even}$:

$$\hat{\mathbf{1}} \hat{\mathcal{A}} = \hat{\mathcal{A}}$$

and for $\hat{P} = \hat{P}_{1,2}$, $p=\text{odd}$:

$$\hat{P}_{1,2} \hat{\mathcal{A}} = \frac{1}{2} \hat{P}_{1,2} (\hat{\mathbf{1}} - \hat{P}_{1,2}) = \frac{1}{2} (\hat{P}_{1,2} - \hat{P}_{1,2}^2) = -\frac{1}{2} (\hat{\mathbf{1}} - \hat{P}_{1,2}) = -\hat{\mathcal{A}}.$$

In the before last step we used $\hat{P}_{1,2}^2 = \hat{\mathbf{1}}$.

The antisymmetrizer also satisfies

$$\hat{\mathcal{A}}^2 = \hat{\mathcal{A}}. \quad (5)$$

1c. Prove Eq. (5) for arbitrary n , using Eqs. (3) and (4).

Answer:

$$\begin{aligned}\hat{\mathcal{A}}^2 &= \frac{1}{n!} \left(\sum_P (-1)^P \hat{P} \right) \hat{\mathcal{A}} = \frac{1}{n!} \sum_P (-1)^P \hat{P} \hat{\mathcal{A}} \\ &= \frac{1}{n!} \sum_P (-1)^P (-1)^P \hat{\mathcal{A}} = \frac{1}{n!} \sum_P \hat{\mathcal{A}} = \frac{1}{n!} \hat{\mathcal{A}} \sum_P 1 \\ &= \frac{n!}{n!} \hat{\mathcal{A}} = \hat{\mathcal{A}}.\end{aligned}$$

In the before last step we used the fact that there are $n!$ permutations for n labels.

Question 2: Coulomb and exchange integrals

The Coulomb integral is given by

$$J_{i,j} = \iint \frac{\psi_i(1)^* \psi_j(2)^* \psi_i(1) \psi_j(2)}{r_{12}} d\tau_1 d\tau_2.$$

The exchange integral is given by

$$K_{i,j} = \iint \frac{\psi_i(1)^* \psi_j(2)^* \psi_j(1) \psi_i(2)}{r_{12}} d\tau_1 d\tau_2.$$

Here, $\psi_i(j)$ are spin-orbitals, and the integrals are over spatial and spin-coordinates

Hint(1): for any function of two electrons $f(1,2)$ one may use

$$\iint f(1,2) d\tau_1 d\tau_2 = \iint f(2,1) d\tau_2 d\tau_1 = \iint f(2,1) d\tau_1 d\tau_2.$$

The first step is allowed because the integration variable may be renamed. For the second equal sign we must assume that the order of integration does not matter.

Hint(2): for any functions of two electrons $f(1,2)$ and $g(1,2)$ one may use

$$\iint f(1,2) g(1,2) d\tau_1 d\tau_2 = \iint g(1,2) f(1,2) d\tau_1 d\tau_2,$$

and in general factors in a product of functions may be reordered.

2a. Show that $J_{i,i} = K_{i,i}$.

Answer:

$$\begin{aligned}J_{i,i} &= \iint \frac{\psi_i(1)^* \psi_i(2)^* \psi_i(1) \psi_i(2)}{r_{12}} d\tau_1 d\tau_2 \\ K_{i,i} &= \iint \frac{\psi_i(1)^* \psi_i(2)^* \psi_i(1) \psi_i(2)}{r_{12}} d\tau_1 d\tau_2 = J_{i,i}.\end{aligned}$$

2b. Show that $J_{i,j} = J_{j,i}$.

Answer:

$$J_{j,i} = \iint \frac{\psi_j(1)^* \psi_i(2)^* \psi_j(1) \psi_i(2)}{r_{12}} d\tau_1 d\tau_2$$

[with Hint(1), change $1 \rightarrow 2$ and $2 \rightarrow 1$]

$$= \iint \frac{\psi_j(2)^* \psi_i(1)^* \psi_j(2) \psi_i(1)}{r_{12}} d\tau_1 d\tau_2$$

[with Hint(2)]

$$= \iint \frac{\psi_i(1)^* \psi_j(2)^* \psi_i(1) \psi_j(2)}{r_{12}} d\tau_1 d\tau_2 = J_{i,j}.$$

2c. Show that $J_{i,j}^* = J_{i,j}$.

Answer:

$$J_{i,j}^* = \iint \frac{\psi_i(1) \psi_j(2) \psi_i(1)^* \psi_j(2)^*}{r_{12}^*} d\tau_1^* d\tau_2^*$$

(r_{12} , $d\tau_1$ and $d\tau_2$ are real)

$$= \iint \frac{\psi_i(1) \psi_j(2) \psi_i(1)^* \psi_j(2)^*}{r_{12}} d\tau_1 d\tau_2$$

[with Hint(2)]

$$= \iint \frac{\psi_i(1)^* \psi_j(2)^* \psi_i(1) \psi_j(2)}{r_{12}} d\tau_1 d\tau_2 = J_{i,j}.$$

2d. Show that $K_{i,j} = K_{j,i}$.

Answer:

$$K_{j,i} = \iint \frac{\psi_j(1)^* \psi_i(2)^* \psi_i(1) \psi_j(2)}{r_{12}} d\tau_1 d\tau_2$$

[with Hint(1), change $1 \rightarrow 2$ and $2 \rightarrow 1$]

$$= \iint \frac{\psi_j(2)^* \psi_i(1)^* \psi_i(2) \psi_j(1)}{r_{12}} d\tau_1 d\tau_2$$

[with Hint(2)]

$$= \iint \frac{\psi_i(1)^* \psi_j(2)^* \psi_j(1) \psi_i(2)}{r_{12}} d\tau_1 d\tau_2 = K_{i,j}.$$

2e. Show that $K_{i,j}^* = K_{i,j}$.

Answer:

$$K_{i,j}^* = \iint \frac{\psi_i(1)\psi_j(2)\psi_j(1)^*\psi_i(2)^*}{r_{12}^*} d\tau_1^* d\tau_2^*$$

(r_{12} , $d\tau_1$ and $d\tau_2$ are real)

$$= \iint \frac{\psi_i(1)\psi_j(2)\psi_j(1)^*\psi_i(2)^*}{r_{12}} d\tau_1 d\tau_2$$

[with Hint(2)]

$$= \iint \frac{\psi_j(1)^*\psi_i(2)^*\psi_i(1)\psi_j(2)}{r_{12}} d\tau_1 d\tau_2 = K_{j,i} = K_{i,j}.$$

Question 3: Energy expressions for Slater determinants

Two closed shell electronic wave functions are given

$$\begin{aligned}\Phi_1 &= \frac{1}{\sqrt{2}}|\phi_1\bar{\phi}_1| \\ \Phi_2 &= \frac{1}{\sqrt{4!}}|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2|.\end{aligned}$$

The energy expression based on spin-orbitals (n -electron):

$$E = \sum_{i=1}^n h_{i,i} + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n [J_{i,j} - K_{i,j}] + V_{N,N}.$$

The energy expression based on spatial orbitals for closed-shell configurations:

$$E = 2 \sum_{k=1}^{n/2} \tilde{h}_{k,k} + \sum_{k=1}^{n/2} \sum_{l=1}^{n/2} [2\tilde{J}_{k,l} - \tilde{K}_{k,l}] + V_{N,N}.$$

(The tilde indicates integrals over spatial orbitals.)

3a. What is $V_{N,N}$ and why is it boring here?

Answer: *It is the nuclear repulsion and there just a constant.*

3b. Write out the energy expression for Φ_1 using the spatial-orbital expression.

Answer:

$$E = 2\tilde{h}_{1,1} + 2\tilde{J}_{1,1} - \tilde{K}_{1,1} + V_{N,N}$$

[with $\tilde{J}_{i,i} = \tilde{K}_{i,i}$]

$$= 2\tilde{h}_{1,1} + \tilde{J}_{1,1} + V_{N,N}.$$

3c. Derive the same expression for the energy of Φ_1 starting from the spin-orbital expression.

Answer:

$$E = h_{1,1} + h_{2,2} + \frac{1}{2}(J_{1,1} - K_{1,1} + J_{1,2} - K_{1,2} + J_{2,1} - K_{2,1} + J_{2,2} - K_{2,2}) + V_{N,N}$$

[with $J_{i,i} = K_{i,i}$, $J_{i,j} = J_{j,i}$ and $K_{i,j} = K_{j,i}$]

$$= h_{1,1} + h_{2,2} + J_{1,2} - K_{1,2} + V_{N,N}$$

[with $K_{1,2} = 0$, $J_{1,2} = \tilde{J}_{1,1}$, $h_{1,1} = h_{2,2} = \tilde{h}_{1,1}$]

$$= 2\tilde{h}_{1,1} + \tilde{J}_{1,1} + V_{N,N}.$$

3d. Write out the energy expression for Φ_2 using the spatial-orbital expression.

Answer:

$$E = 2(\tilde{h}_{1,1} + \tilde{h}_{2,2}) + (2\tilde{J}_{1,1} - \tilde{K}_{1,1}) + (2\tilde{J}_{1,2} - \tilde{K}_{1,2}) + (2\tilde{J}_{2,1} - \tilde{K}_{2,1}) + (2\tilde{J}_{2,2} - \tilde{K}_{2,2}) + V_{N,N}$$

[with $\tilde{J}_{i,i} = \tilde{K}_{i,i}$, $\tilde{J}_{i,j} = \tilde{J}_{j,i}$ and $\tilde{K}_{i,j} = \tilde{K}_{j,i}$]

$$= 2\tilde{h}_{1,1} + 2\tilde{h}_{2,2} + \tilde{J}_{1,1} + \tilde{J}_{2,2} + 4\tilde{J}_{1,2} - 2\tilde{K}_{1,2} + V_{N,N}.$$

3e. Derive the same expression for the energy of Φ_2 starting from the spin-orbital expression.

Answer: with $J_{i,i} = K_{i,i}$, $J_{i,j} = J_{j,i}$ and $K_{i,j} = K_{j,i}$ the two-electron part may be rewritten as

$$\frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n [J_{i,j} - K_{i,j}] = \sum_{i < j} [J_{i,j} - K_{i,j}]$$

and so

$$\begin{aligned} E &= h_{1,1} + h_{2,2} + h_{3,3} + h_{4,4} + V_{N,N} \\ &\quad + J_{1,2} - K_{1,2} + J_{1,3} - K_{1,3} + J_{1,4} - K_{1,4} \\ &\quad + J_{2,3} - K_{2,3} + J_{2,4} - K_{2,4} + J_{3,4} - K_{3,4} \end{aligned}$$

[with $h_{1,1} = h_{2,2} = \tilde{h}_{1,1}$, $h_{3,3} = h_{4,4} = \tilde{h}_{2,2}$,
 $J_{1,2} = \tilde{J}_{1,1}$, $J_{1,3} = \tilde{J}_{1,2}$, $J_{1,4} = \tilde{J}_{1,2}$, $J_{2,3} = \tilde{J}_{1,2}$, $J_{2,4} = \tilde{J}_{1,2}$, $J_{3,4} = \tilde{J}_{2,2}$,
 $K_{1,2} = 0$, $K_{1,3} = \tilde{K}_{1,2}$, $K_{1,4} = 0$, $K_{2,3} = 0$, $K_{2,4} = \tilde{K}_{1,2}$, and $K_{3,4} = 0$]

$$= 2\tilde{h}_{1,1} + 2\tilde{h}_{2,2} + \tilde{J}_{1,1} + \tilde{J}_{2,2} + 4\tilde{J}_{1,2} - 2\tilde{K}_{1,2} + V_{N,N}.$$