# Homework H20 Solution

**Turn in 1:** The molecule $H_2^-$ contains 3 electrons. The wave function can be written approximately as a product over individual electron wavefunctions, or $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \Psi_a(\mathbf{r}_1)\cdot\Psi_b(\mathbf{r}_2)\cdot\Psi_c(\mathbf{r}_3)$.

a. Show that this function does not satisfy $\hat{P}_{23}\Psi = -\Psi$.

b. Convince yourself of (a) with a numerical example. The table below shows some values of the one-electron wavefunctions along the x axis (y=z=0 for simplicity)

| | x=0.7 Å | x=1.1 Å | x=1.7 Å |
|---|---|---|---|
| $\Psi_a(x)$ | 0.02 | -0.14 | 0.04 |
| $\Psi_b(x)$ | 1.3 | 0.8 | 0.23 |
| $\Psi_c(x)$ | -0.3 | 0 | 0.1 |

What is the value of $\Psi$ when electron #1 is in state "a" at $x_1$=1.1 Å, electron #2 in state "b" at $x_2$=0.7 Å, and electron 3 in state "c" at $x_3$=1.7 Å? Now apply $\hat{P}_{23}$ switching electrons 2 and 3 (i.e. $x_2$ and $x_3$). What is the value of $\Psi$ now? Is it $-\Psi$?

c. Write down the correct determinant form of the wavefunction $\Psi_a(\mathbf{r}_1)\cdot\Psi_b(\mathbf{r}_2)\cdot\Psi_c(\mathbf{r}_3)$.

d. Evaluate this 3x3 determinant. How many terms do you get? How many are positive? How many are negative?

e. Show that this function does satisfy $\hat{P}_{23}\Psi = -\Psi$.

Basically, the idea of the determinant is to produce all possible permutations of the electrons among states "a", "b" and "c", with a minus sign whenever a pair of electrons is switched (two switches gives (-)*(-)=(+)). This automatically makes sure that the wavefunction is antisymmetric under exchange of identical fermions.

**Solution:**

a.

$$\Psi = \Psi_a(r_1)\Psi_b(r_2)\Psi_c(r_3)$$

$$\hat{P}_{23}\Psi = \Psi_a(r_1)\Psi_b(r_3)\Psi_c(r_2) \neq -\Psi$$

b.

$$\Psi = (-0.14) * (1.3) * (0.1) = -0.0182$$

Now,

$$\hat{P}_{23}\Psi = \Psi_a(r_1)\Psi_b(r_3)\Psi_c(r_2)$$

$$= (-0.14) * (0.23) * (-0.3) = 0.00966 \neq -\Psi$$

c. The correct determinant form of the wavefunction is the one that ensures all possible combinations of the electrons in the available states.

$$\Psi = \frac{1}{\sqrt{3!}}\begin{vmatrix} \Psi_a(r_1) & \Psi_b(r_1) & \Psi_c(r_1) \\ \Psi_a(r_2) & \Psi_b(r_2) & \Psi_c(r_2) \\ \Psi_a(r_3) & \Psi_b(r_3) & \Psi_c(r_3) \end{vmatrix}$$

d. Evaluating the determinant gives you,

$$\Psi = \Psi_a(r_1)[\Psi_b(r_2)\Psi_c(r_3) - \Psi_b(r_3)\Psi_c(r_2)] - \Psi_b(r_1)[\Psi_a(r_2)\Psi_c(r_3) - \Psi_a(r_3)\Psi_c(r_2)] + \Psi_c(r_1)[\Psi_a(r_2)\Psi_b(r_3) - \Psi_a(r_3)\Psi_b(r_2)]$$

$$= \Psi_a(r_1)\Psi_b(r_2)\Psi_c(r_3) - \Psi_a(r_1)\Psi_b(r_3)\Psi_c(r_2) - \Psi_b(r_1)\Psi_a(r_2)\Psi_c(r_3) + \Psi_b(r_1)\Psi_a(r_3)\Psi_c(r_2) + \Psi_c(r_1)\Psi_a(r_2)\Psi_b(r_3) - \Psi_c(r_1)\Psi_a(r_3)\Psi_b(r_2)$$

Thus we get 6 terms, of which 3 are positive and 3 are negative.

e.

$$\hat{P}_{23}\Psi = \Psi_a(r_1)\Psi_b(r_3)\Psi_c(r_2) - \Psi_a(r_1)\Psi_b(r_2)\Psi_c(r_3) - \Psi_b(r_1)\Psi_a(r_3)\Psi_c(r_2) + \Psi_b(r_1)\Psi_a(r_2)\Psi_c(r_3) + \Psi_c(r_1)\Psi_a(r_3)\Psi_b(r_2) - \Psi_c(r_1)\Psi_a(r_2)\Psi_b(r_3)$$

$$= -\Psi$$

2. It was shown a long time back that any wavefunction can be written as a linear combination of basis functions, $\psi(x) = \sum_n c_n\varphi_n(x)$. In "bra-ket" notation, this is expressed as $|\psi\rangle = \sum_n c_n|n\rangle$.
a. Prove explicitly the analogy of functions to vectors stated in class by Gruebele, namely that $c_n = \int dx\varphi_n^*(x)\psi(x)$.
b. Now do the same in bracket notation, and prove explicitly the analogy of kets to vectors stated in class by Gruebele, namely that $c_n = \langle n|\psi\rangle$.

Solution:

a. Expanding the summation, we get

$$\psi(x) = c_1\varphi_1(x) + c_2\varphi_2(x) + \cdots + c_n\varphi_n(x) + c_{n+1}\varphi_{n+1}(x) + \cdots$$

Now multiply both sides by ${\varphi_n}^*(x)$ and integrate over space,

$$\int dx\,\varphi_n^*(x)\,\psi(x) = c_1\int dx\varphi_n^*(x)\,\varphi_1(x) + c_2\int dx\varphi_n^*(x)\,\varphi_2(x) + \cdots + c_n\int dx\varphi_n^*(x)\,\varphi_n(x) + \cdots$$

We know (or rather ensured ) that the basis functions are orthonormal, that is,

$$\int dx\varphi_n^*(x)\,\varphi_m(x) = 0\,, if\ m \neq n$$
$$= 1, if\ m = n$$

Thus, in the above expansion, only the integral with $c_n$ survives, the rest are 0.

Thus $\int dx\ \varphi_n^*(x)\ \psi(x) = c_n$

This is the standard technique employed to obtain the coefficient of a particular basis in a wavefunction, in other words, the projection of a wavefunction onto a basis function.

b. Expanding the summation for the linear superposition of the wavefunction,

$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle + \cdots + c_n|n\rangle + c_{n+1}|n+1\rangle + \cdots$$

Now multiply both sides by $< n|$ to integrate,

$$\langle n|\psi\rangle = c_1\langle n|1\rangle + c_2\langle n|2\rangle + \cdots + c_n\langle n|n\rangle + c_{n+1}\langle n|n+1\rangle + \cdots$$

$= c_n$ [Since the basis states are orthonormal, i.e., $\langle m|n\rangle = 0$ if $m \neq n,$
$= 1\ if\ m = n$

3. Remember from basic matrix algebra that multiplying any vector by the identity matrix, leaves the vector unchanged. Show explicitly that the identity operator works in a similar fashion, that is $\hat{I}\ \psi(x) = \ \psi(x)$ for any wavefunction $\psi$.
a. You learned in lecture that the identity operator is given by $\hat{I} = \sum_n |n\rangle\langle n|$ in Dirac notation; show by analogy that it can be written as $\sum_n \psi_n(x) \int dx\ \psi_n{}^*(x)\_\_$ in ordinary function notation.
b. Now apply it to $\psi(x)$ to show that you get the same function back. [Hint: the overlap integral $\int dx\ \psi_n{}^*(x)\psi(x)$ is just $c_n$.]

Solution:

a. First we write the wavefunction as a linear superposition of basis states,

$$\psi = c_1\psi_1 + c_2\psi_2 + \cdots + c_n\psi_n = \psi_1 c_1 + \psi_2 c_2 + \cdots \psi_n c_n$$

You proved in Problem 2 that $c_n = \langle n|\psi\rangle = \int dx\ \psi_n^*(x)\ \psi(x)$

So, $\psi(x) = \psi_1 \int dx\ \psi_1^*(x)\ \psi(x) + \psi_2 \int dx\ \psi_2^*(x)\ \psi(x) + \cdots + \psi_n \int dx\ \psi_n^*(x)\ \psi(x)$

$$or, \psi(x) = \left(\sum_n \psi_n \int dx\ \psi_n^*(x)\right) \psi(x)$$

Thus, $\sum_n \psi_n \int dx\ \psi_n^*(x)\_\_$ is the identity operator for functions, since it leaves any function $\Psi$ unchanged.

b. $$\hat{I}\psi(x) = \left(\sum_n \psi_n \int dx\, \psi_n^*(x)\_\_\right) \psi(x)$$

$$= \sum_n \psi_n \int dx\, \psi_n^*(x)\psi(x)$$

$$= \sum_n c_n \psi_n(x) \quad = \psi(x)$$

Thus, the identity operator does indeed leave any function unchanged.