Chem 442: Homework for lecture L20

(only turn in **BOLD** assignment first lecture next week of classes; do <u>all</u> assignments)

1. Turn in. 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 Ψ 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 Ψ 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.

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 $c_n = \langle n|\psi\rangle$.

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 ψ.

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 $\sum_n \varphi_n(x)\int dx\,\varphi_n{}^*(x)\_\_$ in ordinary function notation.

b. Now apply (a) to $\psi(x)$ to show that you get the same function back. [Hint: the overlap integral $\int dx\,\varphi_n{}^*(x)\psi(x)$ is just c_n.]