Chem 442: Homework for lecture L22

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

1. Show that if $\hat{H}$ is an operator with real eigenvalues ("hermitian"), then

$$\langle A|\hat{H}|B\rangle = \langle B|\hat{H}|A\rangle^*$$

[Hint: it's just a slightly more general version of question (2) on H21]

2. Turn in Diagonalize the matrix

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$

explicitly and find its eigenvectors. Some helpful hints are given below.

a) Recall the equation $H\vec{v} = E\vec{v}$, and write down the matrix equation and its determinant that you need to get a quadratic equation for the two eigenvalues. Use your result from problem (1) to simplify the determinant (i.e. H_{AB} is not independent of H_{BA}).
b) Solve the quadratic equation for the eigenvalues E (there will be two of them).
c) Next, substitute each value of E back into the matrix equation $\hat{H}\vec{v} - E\vec{v} = 0$ and solve the equation to find the coefficients of the vector $\vec{v}$. This procedure gives an eigenvector for each eigenvalue E. Make sure your final eigenvectors are normalized.

Note an important difference between the matrix in homework H21 and here: the Hamiltonian is hermitian, and its eigenvalues are real; the matrix M from H21 was not hermitian, and its eigenvalues are complex.

3. In class, you saw the form of the hydrogen ion Hamiltonian. When the H^+ nuclei are moved closer together, eventually the energy of the ground state goes up. Which of the 4 terms in the Hamiltonian is responsible for this effect, and why?

4. Consider the ∞ dimensional Hilbert space formed by the solutions of the Schrödinger equation of a molecule rotating in the plane: exp[iMφ] where M= …, -2, -1, 0, 1, 2.… ANY normalizable function y(φ) over the angle φ=0…2π should be expressible in terms of this basis. At a first glance, it may not be obvious that $y=\sin^2\varphi$ (a product, not a sum of trig functions) can be expressed as a SUM over the basis functions. Show that it can.