

Homework H23 Solution

1. Use the link given below

http://www.mathstools.com/section/main/system_equations_solver#.VRR1N1qprzK

to numerically diagonalize the matrices

$$\begin{pmatrix} -10 & 4 \\ 4 & -10 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} -5 & 4 \\ 4 & -15 \end{pmatrix}$$

Use the eigenvalues you get for each matrix to find the eigenvectors of said matrix (you will have to do this by hand). Which matrix is more like the H_2^+ problem? Which matrix is more like the HeH^+ problem? How is this reflected in the eigenvectors?

Solution:

a. Using the app in the link provided, we find that the eigenvalues of the first matrix are

$$E_{lo} = -14.0 \quad \text{and} \quad E_{hi} = -6.0$$

We continue by finding the eigenvectors in the usual way (this should be getting *very* familiar by now, so the abridged version is provided here). For E_{lo} we have

$$\begin{pmatrix} 4 & 4 \\ 4 & 4 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

which results in two identical equations, both of the form

$$4c_1 + 4c_2 = 0$$

Letting $c_1 = 1$ results in $c_2 = -1$, leading to the normalized eigenvector

$$v_{E_{lo}} = \frac{1}{\sqrt{1^2 + (-1)^2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

For E_{hi} we have

$$\begin{pmatrix} -4 & 4 \\ 4 & -4 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

which results in the two equations

$$-4c_1 + 4c_2 = 0$$

$$4c_1 - 4c_2 = 0$$

Letting $c_1 = 1$ in the first equation gives $c_2 = 1$, leading to the normalized eigenvector

$$v_{E_{hi}} = \frac{1}{\sqrt{1^2 + 1^2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Using the app to find the eigenvalues of the second matrix, we have

$$E_{lo} = -16.4031 \quad \text{and} \quad E_{hi} = -3.5969$$

We continue by finding the eigenvalues in the usual way (again, presenting the abridged version). For E_{lo} we have

$$\begin{pmatrix} 11.4031 & 4 \\ 4 & 1.4031 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

which results in the two equations

$$11.4031c_1 + 4c_2 = 0$$

$$4c_1 + 1.4031c_2 = 0$$

Letting $c_1 = 1$ in equation 1 results in $c_2 = -2.851$, leading to the normalized e.vec.

$$v_{E_{lo}} = \frac{1}{\sqrt{1^2 + (-2.851)^2}} \begin{pmatrix} 1 \\ -2.851 \end{pmatrix} = \begin{pmatrix} 0.331 \\ -0.9436 \end{pmatrix}$$

For E_{hi} we have

$$\begin{pmatrix} -1.4031 & 4 \\ 4 & -11.4031 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

which results in the two equations

$$-1.4031c_1 + 4c_2 = 0$$

$$4c_1 - 11.4031c_2 = 0$$

Letting $c_1 = 1$ in the first equation gives $c_2 = 0.351$, leading to the normalized eigenvector

$$v_{E_{hi}} = \frac{1}{\sqrt{1^2 + 0.351^2}} \begin{pmatrix} 1 \\ 0.351 \end{pmatrix} = \begin{pmatrix} 0.9436 \\ 0.331 \end{pmatrix}$$

We see in the original matrices that the first matrix is more like the H_2^+ problem in that the diagonal elements (corresponding to H_{AA} and H_{BB}) are identical. The eigenvectors are symmetrical combinations of the basis functions. The second matrix is more like the HeH^+ problem in that the diagonal elements are different, with the lower right entry (corresponding to H_{BB}) being significantly lower than the upper left entry (H_{AA}). This observation is consistent with the Hamiltonian matrix for the HeH^+ ion. The eigenvectors of the first matrix are the same as for the H_2^+ problem, while the eigenvectors of the second matrix are very similar (though perhaps not exactly the same) to those of the HeH^+ problem. Again, this is due to the form of the matrices we are diagonalizing being similar to those of H_2^+ and HeH^+ .

b. Again using the app in the link provided, the eigenvalues of the 3x3 matrix are approximately -0.082, 3.035 and 100.046. Note that the energy levels at 1 and 2 repelled each other to ≈ 0 and ≈ 3 ; the level at 100 is far away, and does not shift much. The eigenvalues of the truncated 2x2 matrix are approximately -0.081 and 3.081. Those numbers are not very different from the lowest eigenvalues of the original matrix, but they are slightly larger than before as predicted by the variational principle. 3.081 and 3.035 differ by $\sim 1.5\%$, so the truncation is not quite accurate to 1%, but close.

2. Turn in

Questions:

- In the interactive energy diagram, zoom (in Mac, by scrolling) to observe the plotted energy levels of the molecular orbitals. What is the energy level, in Hartree units, of the sigma and sigma* orbitals? Now go to this website (<http://www.unitconversion.org/energy/hartree-energy-to-electron-volts-conversion.html>) and convert the energy of the sigma orbital to eV. Compared to the energy of hydrogen atom 1s orbital which is -13.6 eV, is the energy of the sigma orbital greater or lower? How does this explain the natural occurrence of hydrogen gas as a stable molecule?
- What is the bond distance of the UFF minimization that you did (click on bonds in menu to left).
- What atomic orbitals form the two empty molecular orbitals above the LUMO (the σ^* lowest empty orbital) and HOMO (the σ orbital occupied by 2 electrons)?

Solution:

A reminder about energy units: 1 hartree = 27.2 eV = $4.35 \cdot 10^{-18}$ J. Quantum mechanics researchers generally prefer the smaller units of hartree or eV (electron-volt) over Joules. Even the giant particle accelerators that smash subatomic particles together with TeV (tera-electron volt) energy reach only microJoule energy for the particles. A human body consumes about 10,000 microJoules per second.

- a. $E_{\sigma} = -0.606$ hartrees ~ -16.49 eV < -13.6 eV = E_{1s} ; $E_{\sigma^*} = 0.247$ hartrees. Naturally, the hydrogen element is found in diatomic form (H_2 gas). The extra stability gained by the bond formation between two H atoms justifies this fact.
- b. The bond distance of the UFF minimization is 0.70793 Angstrom (Click on bonds in menu and look at the bottom left corner). Experiments measure 0.74 Å, and if you ran a geometry optimization with the large 6-311G+ basis set in IQmol, that's also the answer you would get. The "quicker" UFF force field is not as accurate as the big basis set quantum calculation.
- c. The one p orbital from each hydrogen atom forms the two empty molecular orbitals above the LUMO and HOMO. These two MOs are usually left out of context in organic textbooks because of their irrelevance in chemical reactions between hydrogen gas and other compounds (they have no electrons and are too high in energy). They are there, however, and the H_2 molecule will absorb deep UV light to go to the Pi state (the ground state is a Sigma state).
- d. Be sure to have turned in your own ".FChk" file to the TA for full credit. This is one of the files downloaded by IQMol after it runs the calculations for you and returns the results.