

HW #7 Solutions (221B)

1)

Since this problem admits an exact solution, it gives some sense of how accurate the Born-Oppenheimer approximation is. The Hamiltonian is

$$H = \frac{p_1^2}{2M} + \frac{p_2^2}{2M} + \frac{p_3^2}{2m} + \frac{1}{2}k(x_3 - x_1 - d)^2 + \frac{1}{2}k(x_2 - x_3 - d)^2.$$

a)

When we fix the positions of the heavy particles, the Hamiltonian becomes

$$H_{M=\infty} = \frac{p_3^2}{2m} + \frac{1}{2}k(x_3 - x_1 - d)^2 + \frac{1}{2}k(x_2 - x_3 - d)^2.$$

Thinking physically, this is just a harmonic oscillator centered around the center of mass of the heavy particles, $x_{cm} = \frac{x_2+x_1}{2}$, whose position coordinate is the deviation from the center point, $\Delta x = x_3 - x_{cm}$. In terms of the Δx coordinate, the Hamiltonian is

$$H_{M=\infty} = \frac{p_{\Delta x}^2}{2m} + k\Delta x^2 + k\left(\frac{x_2 - x_1}{2} - d\right)^2,$$

whence the energies are

$$E_{M=\infty} = \hbar\omega\left(n + \frac{1}{2}\right) + k\left(\frac{x_2 - x_1}{2} - d\right)^2, \quad (\omega = \sqrt{2k/m}).$$

The heavy particles move according to the Hamiltonian

$$H_{heavy} = \frac{p_1^2}{2M} + \frac{p_2^2}{2M} + k\left(\frac{x_2 - x_1}{2} - d\right)^2.$$

Choosing coordinates x_{cm} and $x_{osc} = \frac{x_2-x_1}{2} - d$,

$$H_{heavy} = \frac{p_{cm}^2}{4M} + \frac{p_{osc}^2}{4M} + kx_{osc}^2,$$

so that

$$E_{heavy} = \frac{\hbar^2 K^2}{4M} + \hbar\Omega\left(m + \frac{1}{2}\right), \quad (\Omega = \sqrt{k/M}).$$

The first contribution is the usual center of mass translation, the second the expected harmonic oscillator behavior. The total Born-Oppenheimer energy is

$$E_{Born-Opp} = \frac{\hbar^2 K^2}{4M} + \hbar\Omega\left(m + \frac{1}{2}\right) + \hbar\omega\left(n + \frac{1}{2}\right), \quad (1)$$

$$(\Omega = \sqrt{k/M}, \omega = \sqrt{2k/m}, K \in \mathbb{R}, m, n \in \mathbb{Z}^+).$$

b)

One way to find the oscillation modes is to diagonalize the equations of motion in the form

$$-\omega^2 \vec{x} = M^{-1} K \vec{x},$$

where

$$\vec{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}, \quad M = \begin{pmatrix} M & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix}, \quad K = \begin{pmatrix} -k & 0 & k \\ 0 & -k & k \\ k & k & -2k \end{pmatrix},$$

and we can assume time dependence $\vec{x} \sim e^{-i\omega t}$ by time translation invariance. Mathematica can do this problem (e.g. “Eigenvalues[]” and “Eigenvectors[]”), giving eigenvalues and -vectors

$$\omega_1^2 = 0 \leftrightarrow \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \quad \omega_2^2 = \frac{k}{M} \leftrightarrow \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}, \quad \omega_3^2 = \frac{km + 2kM}{mM} \leftrightarrow \begin{pmatrix} -1 \\ -1 \\ \frac{2M}{m} \end{pmatrix}.$$

The quantum mechanical energies of the system are then clearly

$$E_{exact} = \frac{\hbar^2 K^2}{2(2M + m)} + \hbar\omega_2(m + \frac{1}{2}) + \hbar\omega_3(n + \frac{1}{2}). \quad (2)$$

Comparing with the Born-Oppenheimer result (1), we see that the energies are equal at zeroth order in m/M , since $\omega_3 = \sqrt{2k/m} + O(m/M)$ and the kinetic energy term is $E_{kin} = \hbar^2 K^2(1/4M + O(m/M))$.

We could have course rewritten the Hamiltonian in terms of the normal modes. Write

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = q_1 \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} + q_2 \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix} + q_3 \begin{pmatrix} -1 \\ -1 \\ \frac{2M}{m} \end{pmatrix}$$

and then back solve for the q_i in terms of the x_i :

$$q_1 = \frac{Mx_1 + Mx_2 + mx_3}{2M + m}, \quad q_2 = \frac{x_2 - x_1}{2}, \quad q_3 = (x_3 - \frac{x_2 + x_1}{2}) \frac{m}{2M + m}.$$

The first coordinate marks the center of mass, the second the relative motion of the heavy blocks, and the third the motion of the light block relative to the heavy blocks. The relationships to the coordinates used in part (a) should be clear. Rewriting the Hamiltonian in terms of the q_i will put it in exactly the right form to yield energies (2).

2) Chemistry

We choose to make orthonormal mixed orbitals. For reference, the wavefunctions in atomic units are

$$\begin{aligned}(2s) &= \frac{1}{2\sqrt{2\pi}} \left(1 - \frac{r}{2}\right) e^{-r/2} \\(2p_0) &= \frac{1}{4\sqrt{2\pi}} r e^{-r/2} \cos \theta = \frac{1}{4\sqrt{2\pi}} z e^{-r/2} \\(2p_{\pm}) &= \mp \frac{1}{8\sqrt{\pi}} r e^{-r/2} \sin \theta e^{\pm i\phi}\end{aligned}$$

The chemically-oriented people in the class suffered much less pain than the rest of us in doing this problem, so I'm going to share their solutions:

a)

$$\begin{aligned}(2p_x) &= \frac{1}{\sqrt{2}}((2p_-) - (2p_+)) = \frac{1}{4\sqrt{2\pi}} x e^{-r/2} \\(2p_y) &= \frac{i}{\sqrt{2}}((2p_-) + (2p_+)) = \frac{1}{4\sqrt{2\pi}} y e^{-r/2}\end{aligned}$$

b)

The $(2s)$ is spherically symmetric so won't affect the direction of the peak of the wavefunction. To achieve angles of $\phi = 0, 2\pi/3, 4\pi/3$, the non- $(2s)$ parts of the wavefunctions should go as

$$(2p_x), \quad \sqrt{3}(2p_y) - (2p_x), \quad -\sqrt{3}(2p_y) - (2p_x).$$

Adding in the $(2s)$ contributions and orthonormalizing,

$$\begin{aligned}(sp^2)_{\phi=0} &= \frac{1}{\sqrt{3}}((2s) + \sqrt{2}(2p_x)) \\(sp^2)_{\phi=2\pi/3} &= \frac{1}{\sqrt{6}}(\sqrt{2}(2s) + \sqrt{3}(2p_y) - (2p_x)) \\(sp^2)_{\phi=4\pi/3} &= \frac{1}{\sqrt{6}}(\sqrt{2}(2s) - \sqrt{3}(2p_y) - (2p_x)).\end{aligned}$$

The $(2s)$ pieces appear with the same weight in all three wavefunctions, as we would hope.

c)

Rather than take the top of the tetrahedron along the z -axis, the wily chemists make a tetrahedron toward the 4 corners of a cube whose faces are centered about the x, y, z axes. (Take the four corners in the $(xyz) =$

(+++), (---), (-+-), (+--) octants). Adding the (2s) piece to achieve orthonormality, the sp^3 orbitals are

$$\begin{aligned}(sp^3)_{+++} &= \frac{1}{2}((2s) + (2p_x) + (2p_y) + (2p_z)) \\(sp^3)_{---} &= \frac{1}{2}((2s) - (2p_x) - (2p_y) + (2p_z)) \\(sp^3)_{-+-} &= \frac{1}{2}((2s) - (2p_x) + (2p_y) - (2p_z)) \\(sp^3)_{+--} &= \frac{1}{2}((2s) + (2p_x) - (2p_y) - (2p_z)).\end{aligned}$$

See the mathematica file for plots.