Physics 221B: Solution to HW # 6

1) Born-Oppenheimer for Coupled Harmonic Oscillators

This problem is meant to convince you of the validity of the Born-Oppenheimer (BO) Approximation through a toy model of coupled 1D harmonic oscillators. Since we know how to solve the system exactly we can compare the exact solution to BO.

The 1D Hamiltonian we will investigate is

$$H = \frac{p_1^2}{2M} + \frac{p_2^2}{2M} + \frac{p_3^2}{2m} + \frac{1}{2}k(x_3 - x_1 - d)^2 + \frac{1}{2}k(x_2 - x3 - d)^2 \qquad (1)$$

a) Born-Oppenheimer Approximation

In the BO approximation we are first taking $M \to \infty$, leaving only x_3 as a dynamical degree of freedom. Then, once we solve the problem for x_3 we use x_3's energy levels as a potential for x_1 and x_2.

Sending $M \to \infty$ we can ignore the kinetic energy terms for x_1 and x_2, which fixes their values. just to remind ourselves that x_1 and x_2 are fixed, we will call them X_1 and X_2. Rewriting (1), the Hamiltonian is now

$$H = \frac{p_3^2}{2m} + \frac{1}{2}k(x_3 - X_1 - d)^2 + \frac{1}{2}k(X_2 - x3 - d)^2.$$

Combining into one harmonic oscillator we get

$$H = \frac{p_3^2}{2m} + \frac{1}{2}2k\left(x_3 - \frac{X_1 + X_2}{2}\right)^2 + k\left(X_2 - X3 - d\right)^2.$$

The second term is the left-over constant from completing the square. We know the solution is

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) + k\left(X_2 - X1 - d\right)^2 \qquad \text{with} \qquad \omega = \sqrt{\frac{2k}{m}} \qquad (2)$$

Now we can treat M as a finite mass, freeing X_1 and X_2 to be x_1 and x_2, and use Eq. (2) as the potential for the heavy particles. The Hamiltonian is now

$$H_n = \frac{p_1^2}{2M} + \frac{p_2^2}{2M} + \hbar\omega\left(n + \frac{1}{2}\right) + k\left(x_2 - x1 - d\right)^2.$$

This has a well known solution as well. we can go to the center of mass frame, defining

$$x = x_1 - x_2 \qquad \mu = \frac{M}{2}$$

to get

$$H_n = \frac{P^2}{2(2M)} + \frac{p^2}{2\mu)} + +\hbar\omega\left(n + \frac{1}{2}\right) + \frac{1}{2}(2k)(x-d)^2$$

where P is the momentum of the center of mass. If we set $P = 0$ the energy is

$$E_{n,n'} = \hbar\omega\left(n + \frac{1}{2}\right) + \hbar\omega'\left(n' + \frac{1}{2}\right)$$

$$\text{with} \qquad \omega' = \sqrt{\frac{k/2}{\mu}} = \sqrt{\frac{k}{M}}$$

$$\text{and} \qquad \omega = \sqrt{\frac{2k}{m}}$$

The BO approximation is a simple illustration of an important concept in physics called an effective theory. When a system contains two very different frequencies (two different energy scales) we can treat them separately i.e. solve for the high frequency modes alone ('integrate them out' of the theory[1]). Once we solve for the high frequency modes, those degrees of freedom are no longer in our system, but they have left their mark by changing the potential for the low modes.

b)

We can solve this problem exactly by diagonalizing the Hamiltonian the way we do in classical mechanics and then apply our knowledge on the harmonic oscillator in quantum mechanics. There are several equivalent approaches to doing this— I chose to work with the classical equations of motion. Writing Hamilton's equations (and combining them) we get

$$M\ddot{x}_1 = k(x_3 - x_1)$$
$$M\ddot{x}_2 = k(x_3 - x_2)$$
$$m\ddot{x}_3 = k(x_1 + x_2 - 2x_3)$$

[1]This is called 'integrating out' because in the path integral formulation we are performing the integral over paths with high frequency, leaving an integral over low frequency paths with a different (effective) action.

Rewriting this in matrix form,

$$\ddot{\vec{X}} \equiv \begin{pmatrix} \ddot{x}_1 \\ \ddot{x}_2 \\ \ddot{x}_3 \end{pmatrix} = \begin{pmatrix} -\frac{k}{M} & 0 & \frac{k}{M} \\ 0 & -\frac{k}{M} & \frac{k}{M} \\ \frac{k}{m} & \frac{k}{m} & -\frac{2k}{m} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \equiv K\vec{X} \tag{3}$$

Assume a solution of the form $x_i \propto e^{i\omega t}$. Plugging this in (4) and rearranging gives a homogeneous equation for $\vec{X}$

$$\begin{pmatrix} -\frac{k}{M} + \omega^2 & 0 & \frac{k}{M} \\ 0 & -\frac{k}{M} + \omega^2 & \frac{k}{M} \\ \frac{k}{m} & \frac{k}{m} & -\frac{2k}{m} + \omega^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = 0 \tag{4}$$

which comes down to solving for the eigenvalues of the matrix K defined above. The eigenvalue and their eigenvectors vectors come out to be:

$$\begin{aligned} &\omega_1 = 0 && \text{with} && \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \\ &\omega_2 = \sqrt{\tfrac{k}{M}} && \text{with} && \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix} \\ &\omega_3 = \sqrt{\tfrac{2k}{m} + \tfrac{k}{M}} && \text{with} && \begin{pmatrix} 1 \\ 1 \\ -2\frac{M}{m} \end{pmatrix} \end{aligned}$$

The first term is just the center of mass motion, and the other two are the two vibrational modes we would have guessed. There is no real need to work out the kinetic terms because having diagonalized the Hamiltonian we know we will get the regular $p^2/2m$ for the new modes.

Finally we get the exact solution for the energy spectrum

$$\begin{aligned} &E_{n_2,n_3} = \hbar\omega_2 \left(n_2 + \frac{1}{2}\right) + \hbar\omega_3 \left(n_3 + \frac{1}{2}\right) \\ &\text{with} \qquad \omega_2 = \sqrt{\frac{k}{M}} \\ &\text{and} \qquad \omega_3 = \sqrt{\frac{2k}{m} + \frac{k}{M}} \end{aligned}$$

c)

Comparing the results of a) and b), we can identify ω' of part a) with ω_2 of part b) exactly. We can explain this by noting that in the second mode of our exact solution the light mass does not move at all. Therefore, the BO approximation that separates the motion of the heavy and the light masses doesn't miss anything, regarding this mode.

When we take the $M \to \infty$ limit again we see that $\omega_3 \to \omega$. So the BO approximation is missing corrections of $O(m/M)$.

2) Chemistry[2]

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

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

a)

$$\begin{aligned}(2p_x) &= \tfrac{1}{\sqrt{2}}((2p_-)-(2p_+)) = \tfrac{1}{4\sqrt{2\pi}}\,xe^{-r/2}\\ (2p_y) &= \tfrac{i}{\sqrt{2}}((2p_-)+(2p_+)) = \tfrac{1}{4\sqrt{2\pi}}\,ye^{-r/2}\end{aligned}$$

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

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

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

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

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

[2]Once again, I thank Ed Boyda.

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

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

See the Mathematica file for plots. Three dimensional models that aided in visualization got extra credit.