Chem221a : Solution Set 6

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Problem 1

(a) Although we'll use this expression in the case where the n-fold commutator terminates exactly, its trucated form is used in coupled-cluster theory (electronic structure). It is called the Hadamard formula, and is an example of a Baker-Campbell-Hausdorff expansion.

First we're going to consider the Taylor expansion of $F(\lambda) = e^{-\lambda B} A e^{\lambda B}$ around 0.

$$F(\lambda) = F(0) + F'(0)\lambda + F''(0)\frac{\lambda^2}{2} + \cdots \tag{1}$$

$$= \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} F^{(n)}(0) \tag{2}$$

From this, we see that we want to show that $F^{(n)}(0) = [B, A]_n$. We'll do this in two steps. First we'll posit (and prove) a general recursion relation for derivatives of $F(\lambda)$.[1] It should be clear that the λ will always be in the exponents, so in order to get the desired results for $F^{(n-1)}$, we need to find something that looks like

$$F^{(n)}(\lambda) = e^{\lambda B} \left[B, A\right]_n e^{-\lambda B} \tag{3}$$

Now let's suppose that this holds for some order n. We want to show that it also hold for $n+1$. That just involves taking the derivative:

$$F^{(n+1)}(\lambda) = \frac{\mathrm{d}}{\mathrm{d}\lambda} e^{\lambda B} \left[B, A\right]_n e^{-\lambda B} \tag{4}$$

$$= B e^{\lambda B} \left[B, A\right]_n e^{-\lambda B} + e^{\lambda B} \left[B, A\right]_n (-B) e^{-\lambda B} \tag{5}$$

$$= e^{\lambda B} \left(B \left[B, A\right]_n - \left[B, A\right]_n B\right) e^{-\lambda B} \tag{6}$$

$$= e^{\lambda B} \left[B, \left[B, A\right]_n\right] e^{-\lambda B} \tag{7}$$

$$= e^{\lambda B} \left[B, A\right]_{n+1} e^{-\lambda B} \tag{8}$$

where we've used the fact that B commutes with $e^{\pm\lambda B}$. This result means that if the expression (3) holds true for *any* value of n, then it will hold for all subsequent values of n.

[1] You may be asking "How the heck would I come up with that?" It's really not as bad as you'd fear. First, we know we have to show this for an infinite set of derivatives, so proof by induction is a likely tool. To guess the specific formula, just look at the first few orders. Equivalently, you could show that $\frac{\mathrm{d}}{\mathrm{d}\lambda} e^{-\lambda B} g(A, B) e^{\lambda B} = e^{-\lambda B} [B, g(A, B)] e^{\lambda B}$ for any function $g(A, B)$, and you'd be able to make the create the recursion formula.

Note that this alone is not sufficient to complete our proof. We showed that *if* equation (3) is true for any n, then it is true for all later n. But it doesn't show that there is any n for which it is true. Now we have to show that.

Perhaps the easiest way to do this would be to show that it is satisfied for $n = 1$ (the math is similar to what is shown above). However, I'm going to instead show that $[B, A]_0 = A$.

The recursive definition of the n-fold commutator is

$$[B, A]_n = [B, [B, A]_{n-1}] \tag{9}$$

Let's replace n with 1 in the above:

$$[B, A]_1 = [B, [B, A]_0] \tag{10}$$

Of course, $[B, A]_1 = [B, A]$, so we can identify $[B, A]_0 = A$. Finally, we use the fact that

$$F^{(0)}(\lambda) = F(\lambda) = e^{\lambda B} A e^{-\lambda B} = e^{\lambda B} [B, A]_0 e^{-\lambda B} \tag{11}$$

So our recursion relation holds fold $n = 0$, and it holds for any $n > 0$. Plugging $\lambda = 0$ into equation (3):

$$F^{(n)}(0) = [B, A]_n \tag{12}$$

Putting that back into our Taylor expansion, we see that we have shown

$$e^{\lambda B} A e^{-\lambda B} = \sum_n [B, A]_n \frac{\lambda^n}{n!} \tag{13}$$

One of the tricks with this expansion is that it terminates for certain operators. For example, the commutator of $\hat{p}$ with $\hat{x}$ is a constant. But any operator commutes with a constant, giving a commutator of zero for the next n in the n-fold commutator.

(b) Let's call our tranlated state $|\psi_a\rangle$. We know that

$$|\psi_a\rangle = T(a) |\psi\rangle = e^{-i\hat{p}a/\hbar} |\psi\rangle \tag{14}$$

$$\langle\psi_a| = \langle\psi| T^\dagger(a) = \langle\psi| e^{i\hat{p}a/\hbar} \tag{15}$$

We'll start by looking at the expectation value of $\hat{p}$ in the translated state. By definition, this is

$$\langle\hat{p}\rangle = \langle\psi_a|\hat{p}|\psi_a\rangle \tag{16}$$

$$= \left\langle \psi \middle| e^{i\hat{p}a/\hbar} \hat{p} e^{-i\hat{p}a/\hbar} \middle| \psi \right\rangle \tag{17}$$

Since $e^{\pm i\hat{p}a/\hbar}$ is a function of only the operator $\hat{p}$, it will commute with $\hat{p}$. That gives us:

$$\langle\hat{p}\rangle = \left\langle \psi \middle| \hat{p} e^{i\hat{p}a/\hbar} e^{-i\hat{p}a/\hbar} \middle| \psi \right\rangle \tag{18}$$

$$= \langle\psi|\hat{p}|\psi\rangle \tag{19}$$

$$= p_0 \tag{20}$$

where the last equality invoked the problem set's definition of p_0.

Now for the expectation value of $\hat{x}$:

$$\langle x \rangle = \langle \psi_a | \hat{x} | \psi_a \rangle \tag{21}$$

$$= \left\langle \psi \middle| e^{i\hat{p}a/\hbar} \hat{x} e^{-i\hat{p}a/\hbar} \middle| \psi \right\rangle \tag{22}$$

We notice that if we define $\lambda = ia/\hbar$, $B = \hat{p}$, and $A = \hat{x}$, we recover the expression from part (a). As mentioned above, the n-fold commutator of $\hat{x}$ and $\hat{p}$ is zero above a certain order. To show this exactly:

$$[\hat{p}, \hat{x}]_1 = [\hat{p}, \hat{x}] = -i\hbar \tag{23}$$

$$[\hat{p}, \hat{x}]_2 = [\hat{p}, [\hat{p}, \hat{x}]] \tag{24}$$

$$= [\hat{p}, -i\hbar] = 0 \tag{25}$$

In general, $[A, 0] = 0$, so all higher orders will also be zero. putting this together with the expectation value of $\hat{x}$ in the translated state, we get:

$$\langle x \rangle = \left\langle \psi \middle| \sum_{n=0}^{\infty} \frac{(ia/\hbar)^n}{n!} [\hat{p}, \hat{x}]_n \middle| \psi \right\rangle \tag{26}$$

$$= \left\langle \psi \middle| \hat{x} + \frac{ia}{\hbar}(-i\hbar) + \sum_{n=2}^{\infty} \frac{(ia/\hbar)^n}{n!} [\hat{p}, \hat{x}]_n \middle| \psi \right\rangle \tag{27}$$

We've already shown that $[\hat{p}, \hat{x}]_n = 0$ for $n \geq 2$, so this becomes:

$$\langle x \rangle = \langle \psi | \hat{x} + a + 0 | \psi \rangle \tag{28}$$

$$= \langle \psi | \hat{x} | \psi \rangle + \langle \psi | a | \psi \rangle \tag{29}$$

$$= x_0 + a \tag{30}$$

Problem 2

(a) We're to find $FC(n_2 \leftarrow 0)$, so let's start off by getting that expressed in Dirac notation:

$$FC(n_2 \leftarrow 0) = \left| \int_{\mathbb{R}} \mathrm{d}x \, \psi_{n_2}^{(b)*}(x) \psi_0^{(a)}(x) \right|^2 \tag{31}$$

$$= \left| \int_{\mathbb{R}} \mathrm{d}x \, \left\langle \psi_{n_2}^{(b)} \middle| x \right\rangle \left\langle x \middle| \psi_0^{(a)} \right\rangle \right|^2 \tag{32}$$

$$= \left| \left\langle \psi_{n_2}^{(b)} \middle| \psi_0^{(a)} \right\rangle \right|^2 \tag{33}$$

Now the trick is going to be to describe the (a) states in terms of the (b) states, or vice versa. These form two equivalent lines of reasoning; I'm only going to step through the reasoning involved in finding the (b) states with respect to the (a) states.

The potentials from the two curves are only different in that the (b) potential is shifting in energy by E (which doesn't change the wavefunction) and shifted in x by x_0. So the wavefunctions for the (b) states are given by the translation of the (a) states by x_0. Mathematically:

$$\left|\psi_n^{(b)}\right\rangle = T(x_0)\left|\psi_n^{(a)}\right\rangle = e^{-i\hat{p}x_0/\hbar}\left|\psi_n^{(a)}\right\rangle \tag{34}$$

Now I'm going to switch notation slightly: all kets will be labeled according to the value of n for the state, and all kets will be taken to be representing (a) states. In this case, the Franck-Condon factor becomes:

$$FC(n_2 \leftarrow 0) = \left|\left\langle n_2\middle|T^\dagger(x_0)\middle|0\right\rangle\right|^2 \tag{35}$$

$$= \left|\left\langle n_2\middle|e^{i\hat{p}x_0/\hbar}\middle|0\right\rangle\right|^2 \tag{36}$$

$$= \left|\left\langle n_2\middle|e^{i^2\sqrt{m\hbar\omega/2}(a^\dagger - a)x_0/\hbar}\middle|0\right\rangle\right|^2 \tag{37}$$

$$= \left|\left\langle n_2\middle|e^{-\lambda x_0 a^\dagger + \lambda x_0 a}\middle|0\right\rangle\right|^2 \tag{38}$$

As we showed in problem 1, the 2-fold commutator of $\hat{x}$ and $\hat{p}$ is zero. So we use the "useful identity" given in the problem:

$$FC(n_2 \leftarrow 0) = \left|\left\langle n_2\middle|e^{-\lambda x_0 a^\dagger}e^{\lambda x_0 a}e^{-\frac{1}{2}[-\lambda x_0 a^\dagger, \lambda x_0 a]}\middle|0\right\rangle\right|^2 \tag{39}$$

$$= \left|\left\langle n_2\middle|e^{-\lambda x_0 a^\dagger}e^{\lambda x_0 a}e^{\frac{1}{2}\lambda^2 x_0^2[a^\dagger, a]}\middle|0\right\rangle\right|^2 \tag{40}$$

$$= \left|\left\langle n_2\middle|e^{-\lambda x_0 a^\dagger}e^{\lambda x_0 a}e^{-\frac{1}{2}\lambda^2 x_0^2}\middle|0\right\rangle\right|^2 \tag{41}$$

$$= \left|e^{-\frac{1}{2}\lambda^2 x_0^2}\left\langle n_2\middle|e^{-\lambda x_0 a^\dagger}e^{\lambda x_0 a}\middle|0\right\rangle\right|^2 \tag{42}$$

Now we'll start doing the series expansions of the operators. Let's begin with the lowering operator, a:

$$FC(n_2 \leftarrow 0) = \left|e^{-\frac{1}{2}\lambda^2 x_0^2}\left\langle n_2\middle|e^{-\lambda x_0 a^\dagger}\sum_{i=0}^{\infty}\frac{(\lambda x_0 a)^i}{i!}\middle|0\right\rangle\right|^2 \tag{43}$$

However, the lowering operator acting one or more times on the ket $|0\rangle$ gives zero, and thus no contribution to the sum. The only term which survives is when $i = 0$. Thus $e^{\lambda x_0 a}|0\rangle = |0\rangle$. We use that, and then expand the sum for the raising operator:

$$FC(n_2 \leftarrow 0) = \left|e^{-\frac{1}{2}\lambda^2 x_0^2}\left\langle n_2\middle|e^{-\lambda x_0 a^\dagger}\middle|0\right\rangle\right|^2 \tag{44}$$

$$= \left|e^{-\frac{1}{2}\lambda^2 x_0^2}\left\langle n_2\middle|\sum_{j=0}^{\infty}\frac{(-\lambda x_0 a^\dagger)^j}{j!}\middle|0\right\rangle\right|^2 \tag{45}$$

$$= \left|e^{-\frac{1}{2}\lambda^2 x_0^2}\sum_{j=0}^{\infty}\frac{(-\lambda x_0)^j}{j!}\left\langle n_2\middle|a^{\dagger j}\middle|0\right\rangle\right|^2 \tag{46}$$

We can either thing of $a^\dagger$ as lowering to the left or raising on the right. I will treat it as a raising operator on the right, although the two analyses are equivalent:

$$FC(n_2 \leftarrow 0) = \left| e^{-\frac{1}{2}\lambda^2 x_0^2} \sum_{j=0}^{\infty} \frac{(-\lambda x_0)^j}{j!} \left\langle n_2 \middle| \sqrt{j!} \middle| j \right\rangle \right|^2 \tag{47}$$

$$= \left| e^{-\frac{1}{2}\lambda^2 x_0^2} \sum_{j=0}^{\infty} \frac{(-\lambda x_0)^j}{\sqrt{j!}} \langle n_2 | j \rangle \right|^2 \tag{48}$$

$$= \left| e^{-\frac{1}{2}\lambda^2 x_0^2} \frac{(-\lambda x_0)^{n_2}}{\sqrt{n_2!}} \right|^2 \tag{49}$$

where we have used the fact that $\langle n_2 | j \rangle$ acts as the Kronecker delta $\delta_{n_2,j}$. Simplifying:

$$FC(n_2 \leftarrow 0) = e^{-\lambda^2 x_0^2} \frac{(\lambda x_0)^{2n_2}}{n_2!} \left((-1)^2\right)^n \tag{50}$$

$$= e^{-\lambda^2 x_0^2} \frac{(\lambda x_0)^{2n_2}}{n_2!} \tag{51}$$

(b) Let's plug the appropriate numbers into the equations for λ and x_0. We begin with the reduced mass for I_2:

$$\mu = \frac{m_{\mathrm{I}}}{2} = \frac{126.9 \text{ amu}}{2} \cdot \frac{1.66054 \times 10^{-27} \text{ kg}}{\text{amu}} = 1.054 \times 10^{-21} \text{ kg} \tag{52}$$

We also want the energy $\hbar\omega$ (when ω is reported in units of energy, we really mean $\hbar\omega$):

$$\hbar\omega = 126 \text{ cm}^{-1} \cdot \frac{1.9864 \times 10^{-23} \text{ J}}{\text{cm}^{-1}} = 2.503 \times 10^{-21} \text{ J} \tag{53}$$

Now let's do the entirety of λ:

$$\lambda = \sqrt{\frac{\mu\omega}{2\hbar}} = \sqrt{\frac{\mu(\hbar\omega)}{2\hbar^2}} = \sqrt{\frac{(1.054 \text{ kg})(2.503 \times 10^{-21} \text{ J})}{2(1.504 \times 10^{-34} \text{ J} \cdot \text{s})^2}} \tag{54}$$

$$= \sqrt{1.252 \times 10^{22} \frac{\text{kg}}{\text{J} \cdot \text{s}^2}} = \sqrt{1.252 \times 10^{22} \frac{\text{kg}}{(\text{kg} \cdot \text{m}^2/\text{s}^2) \cdot \text{s}^2}} \tag{55}$$

$$= 1.119 \times 10^{11} \text{ m}^{-1} \tag{56}$$

Finally, let's determine x_0:

$$x_0 = 3.204 \text{ Å} - 2.666 \text{ Å} = 5.38 \times 10^{-11} \text{ m} \tag{57}$$

This means that the quantity λx_0 is unitless (it had better be, if it shows up as thew argument of an exponential) and is given by $\lambda x_0 = 6.02$. Plugging all of this into the equation for the Franck-Condon factors, we obtain the expression:

$$FC(n_2 \leftarrow 0) = e^{-(\lambda x_0)^2} \frac{(\lambda x_0)^{2n_2}}{n_2!} = e^{-36.2} \frac{(36.2)^{n_2}}{n_2!} \tag{58}$$

The energies for each excited state level will be given by the term energy plus n_2 times the energy level spacing:

$$E(n_2) = T_e + n_2\hbar\omega \tag{59}$$

$$= 15769 \text{ cm}^{-1} + n_2(126 \text{ cm}^{-1}) \tag{60}$$

This properly accounts for the zero point energy, since the ZPEs are the same in both states (in this rough harmonic oscillator approximation we've made). The plot of the Franck-Condon intensities is given in 1. The strongest transition corresponds to $n_2 = 36$ which gives energy $E = 20305 \text{ cm}^{-1} = 4.033 \times 10^{-19}$ J.

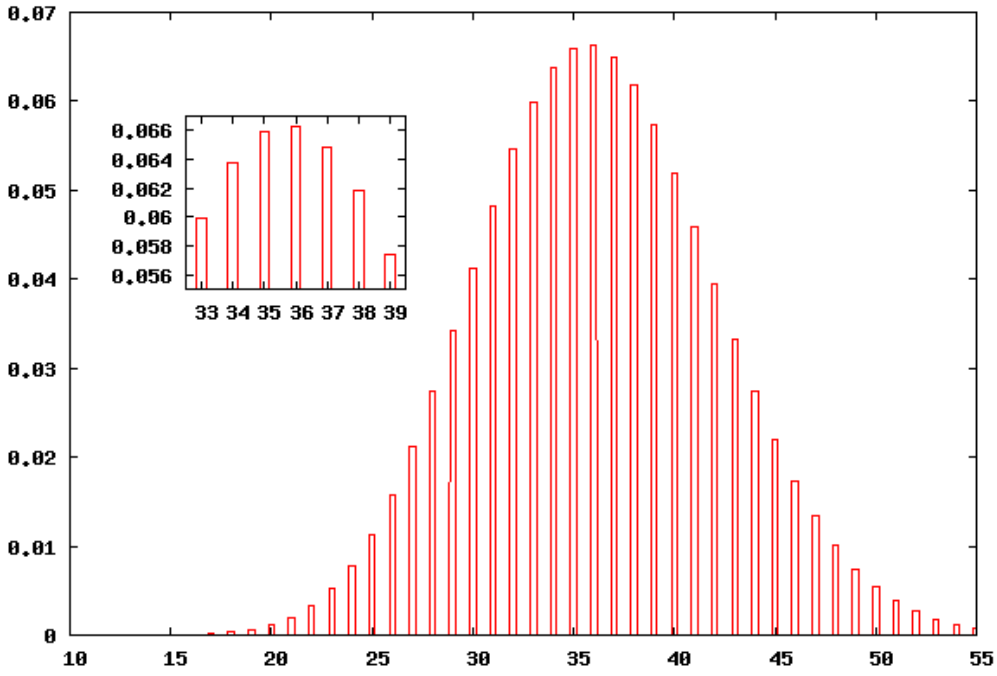

Figure 1: Plot of Franck-Condon intensities for a rough approximation to the I_2 $B \leftarrow X$ vibronic transition. The inset gives a close-up near the peak, in order to identify the maximum value of n_2.

Problem 3

(a) Let's start out by expanding the potential: this should make it easier for us to take the derivatives:

$$V = \frac{1}{2}k_1\left((x_2 - x_1)^2 + (x_3 - x_2)^2\right) + \frac{1}{2}k_2\left((y_1 + y_3 - 2y_2)^2 + (z_1 + z_3 - 2z_2)^2\right) \tag{61}$$

$$\begin{aligned} &= \frac{1}{2}\left(k_1\left(2x_2^2 + x_1^2 - 2x_1x_2 + x_3^2 - 2x_2x_3\right)\right. \\ &\quad +k_2\left(y_1^2 + y_3^2 + 4y_2^2 + 2y_1y_3 - 4y_1y_2 - 4y_2y_3\right) \\ &\quad \left.+k_2\left(z_1^2 + z_3^2 + 4z_2^2 + 2z_1z_3 - 4z_1z_2 - 4z_2z_3\right)\right) \end{aligned} \tag{62}$$

The first derivatives are in figure 2. By grouping the derivatives in the order x_1, x_2, x_3, y_1, ..., z_3, the matrix of second derivatives gives $\mathbf{U}$ as shown in figure 3, where we have used $\mathbf{U}_{ij} = V_{ij}/\sqrt{m_i m_j}$. Finally, we note that $m_1 = m_3 = m_O$ and $m_2 = m_C$, which gives us the matrix for $\mathbf{U}$ as shown in figure 4.

$$\begin{array}{lll} \dfrac{\partial V}{\partial x_1} = k_1(x_1 - x_2) & \dfrac{\partial V}{\partial x_2} = k_1(2x_2 - x_1 - x_3) & \dfrac{\partial V}{\partial x_3} = k_1(x_3 - x_2) \\ \dfrac{\partial V}{\partial y_1} = k_2(y_1 + y_3 - 2y_2) & \dfrac{\partial V}{\partial y_2} = 2k_2(2y_2 - y_1 - y_3) & \dfrac{\partial V}{\partial y_3} = k_2(y_1 + y_3 - 2y_2) \\ \dfrac{\partial V}{\partial z_1} = k_2(z_1 + z_3 - 2z_2) & \dfrac{\partial V}{\partial z_2} = 2k_2(2z_2 - z_1 - z_3) & \dfrac{\partial V}{\partial z_3} = k_2(z_1 + z_3 - 2z_2) \end{array}$$

Figure 2: First derivatives of the potential.

$$\mathbf{U} = \begin{pmatrix} \frac{k_1}{m_1} & \frac{-k_1}{\sqrt{m_1m_2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{-k_1}{\sqrt{m_1m_2}} & \frac{2k_1}{m_2} & \frac{-k_1}{\sqrt{m_2m_3}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{-k_1}{\sqrt{m_2m_3}} & \frac{k_1}{m_3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{k_2}{m_1} & \frac{-2k_2}{\sqrt{m_1m_2}} & \frac{k_2}{\sqrt{m_1m_3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{-2k_2}{\sqrt{m_1m_2}} & \frac{4k_2}{m_2} & \frac{-2k_2}{\sqrt{m_2m_3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{k_2}{\sqrt{m_1m_3}} & \frac{-2k_2}{\sqrt{m_2m_3}} & \frac{k_2}{m_3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{k_2}{m_1} & \frac{-2k_2}{\sqrt{m_1m_2}} & \frac{k_2}{\sqrt{m_1m_3}} \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{-2k_2}{\sqrt{m_1m_2}} & \frac{4k_2}{m_2} & \frac{-2k_2}{\sqrt{m_2m_3}} \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{k_2}{\sqrt{m_1m_3}} & \frac{-2k_2}{\sqrt{m_2m_3}} & \frac{k_2}{m_3} \end{pmatrix}$$

Figure 3: Second derivatives of the potential, with mass weightings.

Fortunately, that matrix is block diagonal, so we can diagonalize each of the 3×3 blocks instead of the whole 9×9 mess. In addition, the lower two blocks are identical, so we only need to diagonalize them once!

$$\mathbf{U} = \begin{pmatrix} \frac{k_1}{m_O} & \frac{-k_1}{\sqrt{m_O m_C}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{-k_1}{\sqrt{m_O m_C}} & \frac{2k_1}{m_C} & \frac{-k_1}{\sqrt{m_C m_O}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{-k_1}{\sqrt{m_C m_O}} & \frac{k_1}{m_O} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{k_2}{m_O} & \frac{-2k_2}{\sqrt{m_O m_C}} & \frac{k_2}{m_O} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{-2k_2}{\sqrt{m_O m_C}} & \frac{4k_2}{m_C} & \frac{-2k_2}{\sqrt{m_C m_O}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{k_2}{m_O} & \frac{-2k_2}{\sqrt{m_C m_O}} & \frac{k_2}{m_O} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{k_2}{m_O} & \frac{-2k_2}{\sqrt{m_O m_C}} & \frac{k_2}{m_O} \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{-2k_2}{\sqrt{m_O m_C}} & \frac{4k_2}{m_C} & \frac{-2k_2}{\sqrt{m_C m_O}} \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{k_2}{m_O} & \frac{-2k_2}{\sqrt{m_C m_O}} & \frac{k_2}{m_O} \end{pmatrix}$$

Figure 4: Second derivatives of the potential, with masses labelled by atom associated.

Before we start on this diagonalization procedure, let's make some predictions: we know that we should get 5 eigenvalues of zero. Since the matrix is block diagonal (and the degree is small enough) we can predict how many zero eigenvalues each block should have. Each block will have 3 eigenvalues total. Since the bottom two blocks are identical, they must have the same eigenvalues. So either they have 2 zero eigenvalues and the top block has 1 zero eigenvalue (to make 5 total), or the bottom blocks have 1 zero eigenvalue and the top has 3 zero eigenvalues. Since the top block isn't the zero matrix, we don't expect the latter case to occur. Therefore, we already know that we're looking for two eigenvalues of zero for the bottom two blocks, and one eigenvalue of zero for the top block.

By far, it is easiest to calculate these eigenvalues and eigenvectors using a computer algebra system. However, I want to show you some tricks to do this by hand. Then I'll check my results using Maxima.

The main idea is to find ways to rename variables such that the system looks less intimidating. Once you've got that, it's just a matter of diagonalizing a 3x3 matrix. We'll start with the upper block.

We'll start by taking out a factor of k_1/m_O from the upper block matrix:

$$U_{\text{top}} = \begin{pmatrix} \frac{k_1}{m_O} & \frac{-k_1}{\sqrt{m_O m_C}} & 0 \\ \frac{-k_1}{\sqrt{m_O m_C}} & \frac{2k_1}{m_C} & \frac{-k_1}{\sqrt{m_C m_O}} \\ 0 & \frac{-k_1}{\sqrt{m_C m_O}} & \frac{k_1}{m_O} \end{pmatrix} = \frac{k_1}{m_O} \begin{pmatrix} 1 & -\sqrt{\frac{m_O}{m_C}} & 0 \\ -\sqrt{\frac{m_O}{m_C}} & 2\frac{m_O}{m_C} & -\sqrt{\frac{m_O}{m_C}} \\ 0 & -\sqrt{\frac{m_O}{m_C}} & 1 \end{pmatrix} \tag{63}$$

We'll call the factored matrix $U^{(1)}_{\text{top}}$ and note how its eigenvalues λ compare to the eigenvalues

of U_{top}, which we'll call λ'. Suppose we have an eigenvector $x_{\lambda'}$ such that:

$$U_{\text{top}} x_{\lambda'} = \lambda' x_{\lambda'} \tag{64}$$

$$\left(\frac{k_1}{m_O}\right) U^{(1)}_{\text{top}} x_{\lambda'} = \tag{65}$$

$$U^{(1)}_{\text{top}} x_{\lambda'} = \frac{m_O}{k_1} \lambda' x_{\lambda'} \tag{66}$$

So $U^{(1)}_{\text{top}}$ has the same eigenvectors as U_{top} with eigenvalues $\lambda = \frac{m_O}{k_1}\lambda'$. If we solve the eigenequation for one matrix, we have the solution for the other.

Looking at the form of $U^{(1)}_{\text{top}}$, we see that it will look simpler if we define $b = \sqrt{\frac{m_O}{m_C}}$. Then the matrix becomes:

$$U^{(1)}_{\text{top}} = \begin{pmatrix} 1 & -b & 0 \\ -b & 2b^2 & -b \\ 0 & -b & 1 \end{pmatrix} \tag{67}$$

That doesn't look so scary. Let's find its eigenvalues:

$$0 = \det \begin{pmatrix} \lambda - 1 & b & 0 \\ b & \lambda - 2b^2 & b \\ 0 & b & \lambda - 1 \end{pmatrix} \tag{68}$$

$$= (\lambda - 1)^2 \left(\lambda - 2b^2\right) - 2b^2 (\lambda - 1) \tag{69}$$

$$= \lambda^3 - 2\lambda^2 + \lambda - 2b^2\lambda^2 + 4b^2\lambda - 2b^2 - 2b^2\lambda + 2b^2 \tag{70}$$

$$= \lambda^3 - 2(1 + b^2)\lambda^2 + (1 + 2b^2)\lambda \tag{71}$$

$$= \lambda \left(\lambda^2 - 2(1 + b^2)\lambda + (1 + 2b^2)\right) \tag{72}$$

So we have found one eigenvalue of $\lambda = 0$. We know that this is not one of the vibrational modes, so we're not going to worry about it. When λ is non-zero, we'll have:

$$\lambda = \frac{2(1 + b^2) \pm \sqrt{4(1 + b^2)^2 - 4(1 + 2b^2)}}{2} \tag{73}$$

$$= 1 + b^2 \pm \sqrt{(1 + b^2)^2 - 1 - 2b^2} \tag{74}$$

$$= 1 + b^2 \pm \sqrt{1 + 2b^2 + b^4 - 1 - 2b^2} \tag{75}$$

$$= 1 + b^2 \pm b^2 \tag{76}$$

So this means that $\lambda = 1$ or $\lambda = 1 + 2b^2$. Translating this back to λ', the eigenvalues of our actual matrix, we obtain either

$$\lambda' = \frac{k_1}{m_O}(1) = \frac{k_1}{m_O} \tag{77}$$

or

$$\lambda' = \frac{k_1}{m_O}(1+2b^2) \tag{78}$$

$$= \frac{k_1}{m_O}\left(1+2\frac{m_O}{m_C}\right) = \frac{k_1}{m_O}\frac{m_C+2m_O}{m_C} \tag{79}$$

$$= k_1\frac{m_C+2m_O}{m_O m_C} \tag{80}$$

$$= k_1\frac{M}{m_O m_C} \tag{81}$$

where M is the total mass of the carbon dioxide molecule.

The eigenvalues give us the force constants, and therefore they are proportional to the square root of the frequency. That means that we can use this to identify which modes these are even before getting their eigenvalues. We already know to expect that the modes from this matrix will be the symmetric and antisymmetric stretch (two reasons: this matrix is associated with motion along the molecular axis, as are those modes; also, we know that the two eigenvalues from the bottom blocks have to be the same and therefore represent the degenerate bending modes).

Taking the ratio of the second eigenvalue to the first, we find:

$$\sqrt{\frac{k_1 M/(m_O m_C)}{k_1/m_O}} = \sqrt{\frac{M}{m-C}} \approx 1.9 \tag{82}$$

This is near the ratio of ν_3 to ν_1.[2] Therefore we expect that the first eigenvalue will be associated with the symmetric stretch and that the second eigenvalue will be associated with antisymmetric stretch.

Now let's actually find the eigenvectors associated with each eigenvalue. Since the eigenvectors are identical for U_{top} and $U^{(1)}_{\text{top}}$, we'll use the latter to find the eigenvectors.

First we'll find the eigenvector associated with $\lambda = 1$ ($\lambda' = \frac{k_1}{m_O}$):

$$\begin{pmatrix} 0 & b & 0 \\ b & 1-2b^2 & b \\ 0 & b & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \tag{83}$$

This immediately gives us two equations:

$$0 = x_2 \tag{84}$$

$$0 = bx_1 + (1-2b^2)x_2 + bx_2 \tag{85}$$

Plugging the first of those equations into the second, we find that the (normalized) eigenvector is:

$$x_{\lambda=1} = \begin{pmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{pmatrix} \tag{86}$$

[2]The fact that it isn't all *that* close indicates the weakness of this potential as an approximation.

As we expected, this gives us the symmetric stretch. We can read this vector as saying that the two oxygen atoms are moving opposite directions with equal magnitudes of forces acting on them, and that the carbon atom isn't moving with respect to the center of mass. Since these represent the x components of the vectors, all the motion is along the x direction. This is exactly what we would expect in order to describe the symmetric stretch of CO_2. Note that the masses don't show up in the eigenvector. This doesn't mean that the motion is independent of mass, however: the eigenvalue is in terms of the masses.

Now let's get the eigenvector for $\lambda = 1 + 2b^2$ (or $\lambda' = k_1 \frac{M}{m_O m_C}$):

$$\begin{pmatrix} 2b^2 & b & 0 \\ b & 1 & b \\ 0 & b & 2b^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \tag{87}$$

From this, we obtain the equations:

$$0 = 2b^2 x_1 + b x_2 \tag{88}$$

$$0 = b x_1 + x_2 + b x_3 \tag{89}$$

The first of these gives us

$$x_2 = -2b x_1 \tag{90}$$

Plugging equation (90) into equation (89), we obtain:

$$0 = b x_1 - 2b x_1 + b x_3 \tag{91}$$

$$x_3 = x_1 \tag{92}$$

Hence we find our unnormalized eigenvector to be

$$x_{\lambda=1+2b^2} = \begin{pmatrix} A \\ -2Ab \\ A \end{pmatrix} \tag{93}$$

Finding the normalization constant:

$$A = \left(1^2 + (-2b)^2 + 1^2\right)^{-1/2} \tag{94}$$

$$= \left(2 + 4b^2\right)^{-1/2} \tag{95}$$

Plugging in the definition of b, we obtain

$$A = \left(2 + 4\frac{m_O}{m_C}\right)^{-1/2} \tag{96}$$

$$= \left(\frac{2m_C + 4m_O}{m_C}\right)^{-1/2} \tag{97}$$

$$= \sqrt{\frac{m_C}{2(m_C + 2m_O)}} \tag{98}$$

$$= \sqrt{\frac{m_C}{2M}} \tag{99}$$

Now we'll put the normalization constant into the unnormalized eigenvector we found in equation (93):

$$x_{\lambda=1+2b^2} = \sqrt{\frac{m_C}{2M}} \begin{pmatrix} 1 \\ -2\sqrt{\frac{m_O}{m_C}} \\ 1 \end{pmatrix} \tag{100}$$

$$= \frac{1}{\sqrt{2M}} \begin{pmatrix} \sqrt{m_C} \\ -2\sqrt{m_O} \\ \sqrt{m_C} \end{pmatrix} \tag{101}$$

This is the antisymmetric stretch. It represents motion in the x direction, with the oxygen atoms moving the same direction with the same magnitude, and the carbon atom moving in the opposite direction with a magnitude weighted by the masses. The weighting comes into play because the center of mass has to remain constant.

We can use a similar process for the bottom block matrices. We already know that these will contribute the two bend modes, so let's go ahead and see how those look:

$$U^{(1)}_{\text{bottom}} = \frac{m_O}{k_2} U_{\text{bottom}} \tag{102}$$

$$= \begin{pmatrix} 1 & -2\sqrt{\frac{m_O}{m_C}} & 1 \\ -2\sqrt{\frac{m_O}{m_C}} & 4\frac{m_O}{m_C} & -2\sqrt{\frac{m_O}{m_C}} \\ 1 & -2\sqrt{\frac{m_O}{m_C}} & 1 \end{pmatrix} \tag{103}$$

$$= \begin{pmatrix} 1 & -2b & 1 \\ -2b & 4b^2 & -2b \\ 1 & -2b & 1 \end{pmatrix} \tag{104}$$

Finding the eigenvalues:

$$0 = \det \begin{pmatrix} \lambda - 1 & 2b & -1 \\ 2b & 4b^2 - \lambda & 2b \\ -1 & 2b & \lambda - 1 \end{pmatrix} \tag{105}$$

$$= (\lambda - 1)^2(\lambda - 4b^2) - 8b^2 - 8b^2(\lambda - 1) - (\lambda - 4b^2) \tag{106}$$

$$= \lambda^3 - 2\lambda^2 + \lambda - 4b^2\lambda^2 + 8b^2\lambda - 4b^2 - 8b^2 - 8b^2\lambda + 8b^2 - \lambda + 4b^2 \tag{107}$$

$$= \lambda^3 - 2\lambda^2 - 4b^2\lambda^2 \tag{108}$$

$$= \lambda^2(\lambda - (2 + 4b^2)) \tag{109}$$

Therefore either $\lambda = 0$ or $\lambda = 2 + 4b^2$. The former case is uninteresting to us (not a vibrational mode), but let's look more carefully at the latter:

$$\lambda' = \frac{k_2}{m_O} \left(2 + 4\frac{m_O}{m_C}\right) \tag{110}$$

$$= 2k_2 \left(\frac{m_C + 2m_O}{m_C m_O}\right) \tag{111}$$

$$= 2k_2 \left(\frac{M}{m_C m_O}\right) \tag{112}$$

Now let's find its associated eigenvector:

$$\begin{pmatrix} 1+4b^2 & 2b & -1 \\ 2b & 2 & 2b \\ -1 & 2b & 1+4b^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \tag{113}$$

This gives us the equations

$$0 = (1+4b^2)x_1 + 2bx_2 - x_3 \tag{114}$$
$$0 = bx_1 + x_2 + bx_3 \tag{115}$$

The first of these equations gives us $x_3 = 2bx_2 + (1+4b^2)x_1$, which we'll plug into the second equation in order to get an expression for x_2 in terms of x_1:

$$0 = bx_1 + x_2 + b(2bx_2 + (1+4b^2)x_1) \tag{116}$$
$$= (1+2b^2)x_2 + 2b(1+2b^2)x_1 \tag{117}$$
$$x_2 = -2bx_1 \tag{118}$$

Now we plug that result for x_2 back into the second equation to get x_3 in terms of x_1:

$$0 = bx_1 - 2bx_1 + bx_3 \tag{119}$$
$$x_3 = x_1 \tag{120}$$

So our unnormalized vector is

$$x_{\lambda=2+4b^2} = \begin{pmatrix} A \\ -2bA \\ A \end{pmatrix} \tag{121}$$

The normalization constant is easily shown to be

$$A = \left(2+4b^2\right)^{-1/2} \tag{122}$$
$$= \sqrt{\frac{m_C}{2M}} \tag{123}$$

So, finally, the eigenvector is

$$x_{\lambda=2+4b^2} = \frac{1}{\sqrt{2M}} \begin{pmatrix} \sqrt{m_C} \\ -2\sqrt{m_O} \\ \sqrt{m_C} \end{pmatrix} \tag{124}$$

These correspond to the bends in either the y direction or the z direction. Both oxygen atoms move in the same direction with the same magnitude, and the carbon atom moves in the opposite direction with magnitude weighted to keep the center of mass constant.

If you're wondering why it is that (within the directional subspace) the bends have the same eigenvectors as the asymmetric stretch, the reason is that both types of modes have essentially the same description if you ignore direction: the oxygen atoms move in the same direction

with equal magnitude, and the carbon atom moves in the other direction with a magnitude that keeps the center of mass constant.

I've given these eigenvectors in their subspaces. The actual eigenvectors should by 9-dimensional. Since most of those will be zeros, I've left them out. The symmetric and antisymmetric modes should have the given values in the first three places, then six zeros following them. The bend in the y direction should have the given vector with three zeros before and three zeros after. The bend in the z direction should be preceded by six zeros.

(b) Pretty much the only reasonable way to do this part is with a computer's help (there's no interesting math to learn from it). It's a good chance to learn how to use a spreadsheet for simple programs: make a column each for n_1, n_2, and n_3. Create an energy column which calculates $E = \hbar(\omega_1(n_1 + 1/2) + \omega_2(n_2 + 1) + \omega_3(n_3 + 1/2))$. The n_2 has 1 added to it, instead of 1/2, to account for both of the equivalent bend modes. Sort by the energy column, and there's your answer (just make sure you allowed enough excitations — at least 4 — in each mode).

Level	(n_1, n_2, n_3)	E_n
1	(0, 0, 0)	2545.5
2	(0, 1, 0)	3217.5
3	(0, 2, 0)	3889.5
4	(1, 0, 0)	3896.5
5	(0, 3, 0)	4561.5
6	(1, 1, 0)	4568.5
7	(0, 0, 1)	4941.5
8	(0, 4, 0)	5233.5
9	(1, 2, 0)	5240.5
10	(2, 0, 0)	5247.5

Table 1: List of 10 lowest energy states (with zero point energy) of the CO_2 oscillator, with number of quanta of excitation in each normal mode