PH 253 / LeClair Spring 2013

Problem Set 7: Solutions

1. *Variational Principle I.* The energy of a system with wave function ψ is given by

$$E[\psi] = \frac{\int \psi^* H\psi \, dV}{\int |\psi|^2 \, dV} \tag{1}$$

where H is the energy operator. The variational principle is a method by which we guess a trial form for the wave function ψ, with adjustable parameters, and minimize the resulting energy with respect to the adjustable parameters. This essentially chooses a "best fit" wave function based on our guess. Since the energy of the system with the correct wave function will always be minimum, our guess will always lead to an energy which is slightly too high, but the variational principle allows us to get as close as possible to the correct energy with our trial wave function.

Pretend we don't know the ground state wave function for hydrogen, but decided to guess the following form for ψ:

$$\psi(r) = \frac{\beta}{\alpha^2 + r^2} \tag{2}$$

(a) Use the variational principle and normalization to find the values of α and β that give the minimum energy for this trial wave function. *Note that since the trial function is spherically symmetric,* $dV = 4\pi r^2 \, dr$ *and* $\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right)$.
(b) Compare this result to the correct ground state energy of hydrogen and sketch/plot your best guess for ψ with the correct ground state wave function.

Solution: Let there be no confusion: this variational stuff is messy. Highly effective, but messy. Let's get started.

First, let us compute $H\psi$.

$$H\psi = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) - \frac{ke^2}{r}\psi = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\frac{\beta}{\alpha^2+r^2}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} \tag{3}$$

$$= -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{-2r\beta}{\left(\alpha^2+r^2\right)^2}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(\frac{-2r^3\beta}{\left(\alpha^2+r^2\right)^2}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} \tag{4}$$

$$= -\frac{\hbar^2}{2mr^2}\left(\frac{8r^4\beta}{\left(\alpha^2+r^2\right)^3} - \frac{6r^2\beta}{\left(\alpha^2+r^2\right)^2}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} \tag{5}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{8r^2\beta - 6\beta\alpha^2 - 6\beta^2}{\left(\alpha^2+r^2\right)^3}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} = -\frac{\hbar^2}{2m}\left(\frac{2r^2\beta - 6\beta\alpha^2}{\left(\alpha^2+r^2\right)^3}\right) - \frac{ke^2}{r}\frac{\beta}{\alpha^2+r^2} \tag{6}$$

Yes, that was just terrible. Now we multiply through by ψ again to get $\psi H\psi$. Since $\psi(x)$ is real for all x, we need not worry about complex conjugates and such.

$$\psi H\psi = -\frac{\hbar^2\beta}{2m}\left(\frac{2\beta r^2 - 6\beta\alpha^2}{\left(\alpha^2+r^2\right)^4}\right) - \frac{ke^2\beta^2}{r\left(\alpha^2+r^2\right)^2} \tag{7}$$

Now we integrate that over all space, using the volume element $4\pi r^2\,dr$ with r ranging from 0 to ∞. In this process, we either remember some obscure integrals or use Wolfram Alpha (`http://wolframalpha.com`).

$$\int \psi H \psi = \int_0^\infty -\frac{4\pi\hbar^2\beta^2}{2m}\left(\frac{2r^4-6\alpha^2r^2}{(\alpha^2+r^2)^4}\right) - \frac{4\pi k e^2\beta^2 r}{(\alpha^2+r^2)^2} \tag{8}$$

$$= -\frac{4\pi\hbar^2\beta^2}{m}\left(2\frac{\pi}{32\alpha^3} - 6\alpha^2\frac{\pi}{32\alpha^5}\right) - 4\pi k e^2\beta^2\frac{1}{2\alpha^2} \tag{9}$$

$$= -\frac{4\pi^2\hbar^2\beta^2}{2m}\left(\frac{1}{16\alpha^2} - \frac{3}{16\alpha^2}\right) - \frac{2\pi k e^2\beta^2}{\alpha^2} = \frac{\pi^2\hbar^2\beta^2}{4m\alpha^3} - \frac{2ke^2\beta^2}{\alpha^2} \tag{10}$$

Now the denominator in our energy expression:

$$\int |\psi|^2\,dV = \int_0^\infty \frac{4\pi\beta^2 r^2}{(\alpha^2+r^2)^2}\,dr = 4\pi\beta^2\frac{\pi}{4\alpha} = \frac{\pi^2\beta^2}{\alpha} \tag{11}$$

This implies that for the wave function to be normalized, such that $\int |\psi|^2\,dV = 1$, we require $\beta^2 = \alpha/\pi^2$. Putting it all together, we can find our expression for energy:

$$E = \frac{\alpha}{\pi^2\beta^2}\left(\frac{\pi^2\hbar^2\beta^2}{4m\alpha^3} - \frac{2\pi k e^2\beta^2}{\alpha^2}\right) = \frac{\hbar^2}{4m\alpha^2} - \frac{2ke^2}{\pi\alpha} \tag{12}$$

Note that the energy is independent of β, which makes some sense - β is just the normalization constant. Our variational condition is that this energy is minimized with respect to the parameter α, thus

$$0 = \frac{\partial E}{\partial \alpha} = 2\frac{2\hbar^2}{4m\alpha^3} = \frac{2ke^2}{\pi\alpha^2} \tag{13}$$

$$\frac{\hbar^2}{2m\alpha^3} = \frac{2ke^2}{\pi\alpha^2} \tag{14}$$

$$\alpha = \frac{\pi\hbar^2}{4mke^2} = \frac{\pi}{4}a_o \tag{15}$$

Here a_o is the Bohr radius, $a_o = \hbar^2/kme^2$. Thus, we can interpret α as a characteristic distance of the electron cloud, about 20% smaller than the exact solution gives us. Plugging this in our energy equation, we have

$$E = -\frac{-4\hbar^2}{\pi^2 m a_o^2} \approx -11.1\,\mathrm{eV} \tag{16}$$

This is about 19% off of the exact value for the ground state energy. The plots of ψ for the variational and correct ground state wavefunctions are left as an exercise for the reader ...

Finally, here are couple of useful tutorials you may have already come across:

`http://galileo.phys.virginia.edu/classes/752.mf1i.spring03/Variational_Methods.htm` `http://www.colorado.edu/physics/phys7440/phys7440_sp03/HOMEWORK/Homework/S2.htm`

2. *Variational Principle II.* The energy operator for a simple harmonic oscillator in *one dimension* is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \tag{17}$$

Presume we don't know the proper wave function, but guessed a wave function of the form

$$\psi(r) = \frac{\beta}{\alpha^2 + x^2} \tag{18}$$

(a) Use the variational principle and normalization to find the values of α and β that give the minimum energy for this trial wave function. *Since this is a one dimensional problem, take* $dV = dx$.
(b) Compare this result to the correct ground state energy of the simple harmonic oscillator and sketch/plot your best guess for ψ with the correct ground state wave function.

Solution: Much like the last one, except here $dV = dx$ and x runs from $-\infty$ to ∞, which changes all the integrals.

$$\begin{aligned}
H\psi &= -\frac{\hbar^2}{2m}\left(\frac{d}{dx}\frac{\beta}{\alpha^2 + x^2}\right) + \frac{1}{2}m\omega^2 x^2 \frac{\beta}{\alpha^2 + x^2} \qquad (19)\\
&= -\frac{\hbar^2}{2m}\left(\frac{-2\beta}{(\alpha^2 + x^2)^2} + \frac{8x^2\beta}{(\alpha^2 + x^2)^3}\right) + \frac{1}{2}\frac{m\omega^x \beta x^2}{\alpha^2 + x^2} \qquad (20)\\
&= -\frac{\hbar^2\beta}{2m}\left(\frac{3x^2 - \alpha^2}{(\alpha^2 + x^2)^3}\right) + \frac{1}{2}\frac{m\omega^x \beta x^2}{\alpha^2 + x^2} \qquad (21)
\end{aligned}$$

Now $H\psi H$:

$$\psi H\psi = -\frac{\hbar^2\beta^2}{m}\left(\frac{3x^2 - \alpha^2}{(\alpha^2 + x^2)^4}\right) + \frac{1}{2}\frac{m\omega^2\beta^2 x^2}{(\alpha^2 + x^2)^2} \tag{22}$$

And, the full numerator:

$$\begin{aligned}
\int \psi H\psi \, dx = \int_{-\infty} \frac{\hbar^2\beta^2}{m}\left(\frac{\alpha^2 - 3x^2}{(\alpha^2 + x^2)^4}\right) + \frac{1}{2}\frac{m\omega^x\beta^2 x^2}{(\alpha^2 + x^2)^2} &= \frac{\hbar^2\beta^2}{2m}\left(\frac{5\pi}{16\alpha^5} - \frac{3\pi}{16\alpha^5}\right) + \frac{m\omega^2\beta^2}{2}\frac{\pi}{2\alpha} \qquad (23)\\
&= \frac{\pi\beta^2\hbar^2}{8m\alpha^5} + \frac{\pi m\beta^2\omega^2}{4\alpha} \qquad (24)
\end{aligned}$$

And the denominator:

$$\int |\psi|^2 \, dx = \int_{-\infty}^{\infty} \frac{\beta^2}{(\alpha^2 + x^2)^2}\, dx = \frac{\pi\beta^2}{2\alpha^3} \tag{25}$$

This implies that for a normalized wavefunction we require $\beta^2 = 2\alpha^3/\pi$. Now the energy expression in full:

$$E = \frac{2\alpha^3}{\pi\beta^2}\left(\frac{\pi\beta^2\hbar^2}{8m\alpha^5} + \frac{\pi m\beta^2\omega^2}{4\alpha}\right) = \frac{\hbar^2}{4m\alpha^2} + \frac{\alpha^2 m\omega^2}{2} \tag{26}$$

Once again, the energy is independent of β as it should be, and the optimal solution is when $dE/d\alpha = 0$.

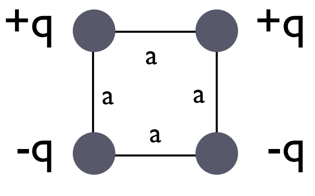
$$\frac{dE}{d\alpha} = 0 = -\frac{2\hbar^2}{4m\alpha^3} + m\alpha\omega^2 \qquad \Longrightarrow \qquad \alpha^2 = \frac{\hbar}{\sqrt{2}mw} \tag{27}$$

The minimum energy for this guess at the wavefunction is then

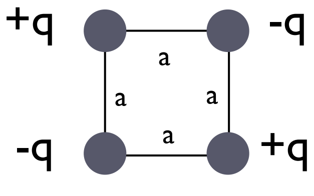
$$E = \frac{\hbar^2}{4m}\frac{\sqrt{2}m\omega}{\hbar} + \frac{m\omega^2}{2}\frac{\hbar}{\sqrt{2}m\omega} = \frac{\sqrt{2}}{2}\hbar\omega = \frac{1}{2}\hbar\omega\left(\sqrt{2}\right) \tag{28}$$

Our variational approach with a plausible guess at the wavefunction yields a ground state energy that is a factor $\sqrt{2}\approx 1.4$ times higher than the exact value. Not bad for a guess.

3. Two positive and two negative charges are arranged on a square lattice of side a in two different ways, shown below. Calculate the electrostatic potential energy of each configuration. Which configuration of charges is more stable? Why?



(a)



(b)

Solution: This is problem is straight from intro physics. Using the principle of superposition, we know that the potential energy of a system of charges is just the sum of the potential energies for all the unique pairs of charges. The problem is then reduced to figuring out how many different possible pairings of charges there are, and what the energy of each pairing is. The potential energy for a single pair of charges, both of magnitude q, separated by a distance d is just:

$$PE_{\text{pair}} = \frac{k_e q^2}{a}$$

We need figure out how many pairs there are, and for each pair, how far apart the charges are. Once we've done that, we need to figure out the two different arrangements of charges and run the numbers.

In this case, there are not many possibilities. Label the upper left charge in each diagram "1" and number the rest clockwise. The possible pairings are then only

$$q_1q_2, q_1q_3, q_1q_4$$
$$q_2q_3, q_2q_4$$
$$q_3q_4$$

Since there are the same number of possibilities for either crystal, the total potential energy in either case is just adding all of these pairs' contributions together. Except for pairs q_2q_4 and q_1q_3, which are separated by a distance $a\sqrt{2}$, all others are separated by a distance a. Thus,

$$\mathsf{PE} = \frac{k_e q_1 q_2}{a} + \frac{k_e q_1 q_3}{a\sqrt{2}} + \frac{k_e q_1 q_4}{a} + \frac{k_e q_2 q_3}{a} + \frac{k_e q_2 q_4}{a\sqrt{2}} + \frac{k_e q_3 q_4}{a} \tag{29}$$

First, consider configuration (a). All we need to do now is plug in $+q$ for q_1 and q_2, and $-q$ for q_3 and q_4:

$$\mathsf{PE}_a = \frac{k_e q^2}{a} + \frac{k_e\left(-q^2\right)}{a\sqrt{2}} + \frac{k_e\left(-q^2\right)}{a} + \frac{k_e\left(-q^2\right)}{a} + \frac{k_e\left(-q^2\right)}{a\sqrt{2}} + \frac{k_e q^2}{a} \tag{30}$$

$$= \frac{k_e q^2}{a}\left(-\frac{2}{\sqrt{2}}\right) = -\sqrt{2}\frac{k_e q^2}{a} \approx -1.414\frac{k_e q^2}{a} \tag{31}$$

For configuration (b), we need $+q$ for q_1 and q_3, and $-q$ for q_2 and q_4:

$$\mathsf{PE} = \frac{k_e\left(-q^2\right)}{a} + \frac{k_e q^2}{a\sqrt{2}} + \frac{k_e\left(-q^2\right)}{a} + \frac{k_e\left(-q^2\right)}{a} + \frac{k_e q^2}{a\sqrt{2}} + \frac{k_e\left(-q^2\right)}{a} \tag{32}$$

$$= \frac{k_e q^2}{a}\left(-4 + \frac{2}{\sqrt{2}}\right) = \frac{k_e q^2}{a}\left(-4 + \sqrt{2}\right) \approx -2.586\frac{k_e q^2}{a} \tag{33}$$

Configuration (b) has a lower potential energy, and is therefore more stable. Qualitatively, this makes sense: configuration (b) keeps the like charges as far away as possible, which also maximizes the number of favorable opposite pairings at close distance.

4. *Energetics of diatomic systems* An approximate expression for the potential energy of two ions as a function of their separation is

$$\mathsf{PE} = -\frac{ke^2}{r} + \frac{b}{r^9} \tag{34}$$

The first term is the usual Coulomb interaction, while the second term is introduced to account for the repulsive effect of the two ions at small distances. **(a)** Find b as a function of the equilibrium spacing r_o. **(b)** For KCl, with an equilibrium spacing of $r_o = 0.279\,\text{nm}$, calculate the frequency of small oscillations about $r = r_o$. *Hint: do a Taylor expansion of the potential energy to make it look like a harmonic oscillator for small* $r = r_o$.

Solution: The equilibrium spacing will be characterized by the net force between the ions being zero, or equivalently, the potential energy being zero:

$$F(r_o) = -\left.\frac{dU}{dr}\right|_{r=r_o} = 0 = \frac{ke^2}{r_o^2} - \frac{9b}{r_o^{10}} \tag{35}$$

$$ke^2 r_o^8 = 9b \tag{36}$$

$$b = \frac{1}{9}ke^2 r_o^8 \tag{37}$$

Substituting this result back into our potential energy expression, we can find the potential energy at equilibrium, how much energy is gained by the system of ions condensing into a crystal. First, the potential energy as a function of spacing:

$$\mathsf{PE} = \mathsf{U}(\mathsf{r}) = -\frac{\mathsf{ke}^2}{\mathsf{r}} + \frac{\mathsf{ke}^2\mathsf{r}_o^8}{9\mathsf{r}^9} \tag{38}$$

Evaluating at equilibrium, $r_o = 0.279\,\text{nm}$,

$$U(r_o) = -\frac{ke^2}{r_o} + \frac{ke^2}{9r_o} = -\frac{8ke^2}{9r_o} \approx -4.59\,\text{eV} \tag{39}$$

The frequency of small oscillations can be found by Taylor expanding the potential about equilibrium for small displacements from equilibrium:

$$U(r - r_o) \approx U(r_o) + U'(r_o)\,(r - r_o) + \frac{1}{2}U''(r_o)\,(r - r_o)^2 \tag{40}$$

The first term in the expansion is just the potential energy at equilibrium which we found above. The second term, linear in displacement, must vanish at equilibrium (which is exactly the condition we enforced to find b, after all). The third term is quadratic in displacement, just as it would be for a simple harmonic oscillator, $U = \frac{1}{2}k\,(r - r_o)^2$. Thus, the coefficient of the quadratic term must be $\frac{1}{2}k$, which means the frequency of small oscillations is $\omega = \sqrt{k/\mu}$, where μ is the reduced mass of the system (see the last problem for a derivation). That is, the diatomic molecule looks like two masses coupled by a spring.

$$\frac{1}{2}k = \frac{1}{2}U''(r_o) \tag{41}$$

$$k = U''(r_o) = -\frac{2ke^2}{r_o^3}\frac{90b}{r_o^{11}} = \frac{8ke^2}{r_o^3} \approx 84.9\,\text{N/m} \tag{42}$$

$$\omega = \sqrt{\frac{k}{\mu}} = 2\pi f \tag{43}$$

The reduced mass of the molecule in terms of the K and Cl atomic masses is

$$\mu = \frac{m_K m_{Cl}}{m_K + m_{Cl}} \approx 3.09 \times 10^{-26}\,\text{kg} \tag{44}$$

which gives the frequency of oscillation f as

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \approx 8.35 \times 10^{12}\,\text{Hz} \approx 278\,\text{cm}^{-1} \tag{45}$$

The accepted value[i] is $281\,\text{cm}^{-1}$, in excellent agreement with our simple model.

5. (a) A diatomic molecule has only one mode of vibration, and we may treat it as a pair of masses connected by a spring (figure (a) below). Find the vibrational frequency, assuming that the masses of A and B are different. Call them m_a and m_b, and let the spring have constant k.

---

[i] NIST, see `http://cccbdb.nist.gov/compvibs3.asp?casno=7447407&charge=0&method=14&basis=9`

(b) A diatomic molecule adsorbed on a solid surface (figure (b) below) has more possible modes of vibration. Presuming the two springs and masses to be equivalent this time, find their frequencies.

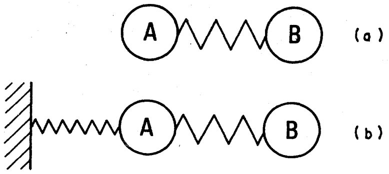


FIG. 1. (a) Classical model for vibrating free-space AB diatomic molecule; (b) same molecule adsorbed onto a surface.

Figure 1: *From* `http://prb.aps.org/abstract/PRB/v19/i10/p5355_1`.

Solution: Just because we can, we will solve the more general problem of three different springs shown below (k_1, k_2, and k_3 from left to right) and two different masses m_1 and m_2. Though it requires a bit more algebra, it solves both of our problems posed and several others. By setting $k_1=k_3=0$ we solve problem (a), and setting $k_3=0$ we solve problem (b). By setting $k_1=k_2=k_3$ we solve the simplest case of two coupled oscillators, a problem you will no doubt encounter again. So, for the purposes of illustration, we will drag this problem out in quite some detail.

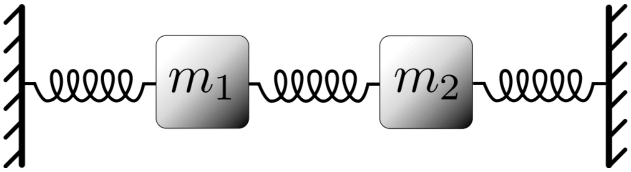


Figure 2: *From* `http://en.wikipedia.org/wiki/Normal_mode`.

Let mass m_1 be displaced from equilibrium by an amount x_1 and mass m_2 by an amount x_2, with positive x running to the right.[ii] Mass m_1 is connected to springs k_1 and k_2. Spring k_1 is compressed (or elongated) only by mass m_1 due to its displacement x_1, and it reacts with a force $-k_1x_1$ on mass m_1. Similarly, spring 3 is compressed only by mass 2, so it reacts with a force $-k_3x_2$ on mass m_2. Spring 2 is connected to both masses m_1 and m_2, and its net change in length from equilibrium is the *difference* between the displacements of masses m_1 and m_2, x_2-x_1. If both masses move in the same direction by the same amount, the net change in length is zero, whereas if both masses move in opposite directions in the same amount, the net change in length is twice as much. Spring 2 thus pushes back on both masses m_1 and m_2 with a force $k_2(x_2-x_1)$.

Putting all this together, we can write the net force on masses m_1 and m_2, making note of the fact that for mass m_1 the force from k_1 is opposite in direction to that of k_2, and similarly for the forces from k_3 and k_2 on mass m_2.

$$F_1 = m_1\frac{d^2x_1}{dt^2} = -k_1x_1 + k_2\left(x_2 - x_1\right) \tag{46}$$

$$F_2 = m_2\frac{d^2x_2}{dt^2} = -k_3x_2 + k_2\left(x_1 - x_2\right) \tag{47}$$

[ii] It makes no difference which direction we call $+x$, so long as we are consistent.

Now, what are the possible modes of oscillation? First, we seek only steady-state solutions. Since we have not included any damping, that means ones that involve both masses oscillating freely in a sinusoidal fashion. The symmetry of the problem dictates that only two modes should be possible: a symmetric one where both masses move in the same direction, and an antisymmetric one where the masses move in opposite directions. In the symmetric mode, in the limiting case that $k_1 = k_3$ and $m_1 = m_2$, we would have the masses moving in unison and the central spring k_2 would remain at its equilibrium length (and in this case the frequency should not depend on k_2). In the antisymmetric mode, a higher frequency vibration occurs where the masses move toward and away from each other. In any case: if we seek steady-state sinusoidal solutions, symmetric or antisymmetric, there is a single frequency governing each mode, and we may choose

$$x_1 = A_1 e^{i\omega t} \tag{48}$$

$$x_2 = A_2 e^{i\omega t} \tag{49}$$

Plugging this trial solution into our equations of motion above,

$$-m_1\omega^2 A_1 e^{i\omega t} = -k_1 A_1 e^{i\omega t} + k_2 \left(A_2 - A_1\right) e^{i\omega t} \tag{50}$$

$$-m_2\omega^2 A_2 e^{i\omega t} = -k_3 A_2 e^{i\omega t} + k_2 \left(A_1 - A_2\right) e^{i\omega t} \tag{51}$$

Simplifying, and canceling the common factor of $e^{i\omega t}$

$$-m_1\omega^2 A_1 = -k_1 A_1 + k_2 \left(A_2 - A_1\right) \tag{52}$$

$$-m_2\omega^2 A_2 = -k_3 A_2 + k_2 \left(A_1 - A_2\right) \tag{53}$$

We may write this as a system of two equations in terms of the two unknown amplitudes A_1 and A_2:

$$\left(m_1\omega^2 - k_1 - k_2\right) A_1 + k_2 A_2 = 0 k_2 A_1 + \left(m_2\omega^2 - k_3 - k_2\right) A_2 \qquad = 0 \tag{54}$$

Of course, we do not really wish to find the amplitudes, we wish to find ω. We may find ω by investigating the conditions under which a solution to the above equations exists. First, we write the equation above in matrix form:

$$\begin{bmatrix} \left(m_1\omega^2 - k_1 - k_2\right) & k_2 \\ k_2 & \left(m_2\omega^2 - k_3 - k_2\right) \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{55}$$

This system of equations has a solution only if the matrix of coefficients has a determinant of zero:

$$\begin{vmatrix} \left(m_1\omega^2 - k_1 - k_2\right) & k_2 \\ k_2 & \left(m_2\omega^2 - k_3 - k_2\right) \end{vmatrix} = 0 = \left(m_1\omega^2 - k_1 - k_2\right)\left(m_2\omega^2 - k_3 - k_2\right) - k_2^2 \tag{56}$$

Expanding,

$$m_1 m_2 \omega^4 - \left[\left(k_2 + k_3\right) m_1 + \left(k_1 + k_2\right) m_2\right] \omega^2 + \left(k_1 + k_2\right)\left(k_2 + k_3\right) - k_2^2 = 0 \tag{57}$$

This is a quadratic in ω^2, which we can readily solve:

$$\omega^2 = \frac{(k_2+k_3)\,m_1 + (k_1+k_2)\,m_2 \pm \sqrt{((k_2+k_3)\,m_1 + (k_1+k_2)\,m_2)^2 - 4m_1m_2\left[(k_1+k_2)(k_2+k_3) - k_2^2\right]}}{2m_1m_2}$$

$$\omega^2 = \frac{(k_2+k_3)\,m_1 + (k_1+k_2)\,m_2 \pm \sqrt{((k_2+k_3)\,m_1 - (k_1+k_2)\,m_2)^2 + 4m_1m_2k_2^2}}{2m_1m_2} \tag{58}$$

It doesn't simplify a lot more than this in the general case. Let us examine then the cases of interest.

FIrst, it instructive to keep the more general setup with three springs but consider the special case of identical masses and springs by letting $k_1 = k_2 = k_3 \equiv k$ and $m_1 = m_2 \equiv m$. Our expression above then simplifies to

$$\omega^2 = \frac{4km \pm 2km}{2m^2} = \left\{\frac{3k}{m}, \frac{k}{m}\right\} \tag{59}$$

Physically, this makes sense. We have the symmetric mode ($\omega = \sqrt{k/m}$) in which the two masses move in unison back and forth and the central spring remains uncompressed at all times. The second is an antisymmetric mode which has the two masses moving out of phase, both moving outward at the same time or both moving inward at the same time. The exterior springs are being compressed by each mass during half a cycle of oscillation, and during the other half the central spring is compressed by *both* masses (so twice as much), almost as if three springs are acting on each mass. This leads to the higher frequency of the antisymmetric $\omega = \sqrt{3k/m}$ mode.

(b) For the diatomic molecule, we set $k_1 = k_3 = 0$ and $k_2 \equiv k$ in the general solution, leading to

$$\omega^2 = \frac{km_1 + km_2 \pm \sqrt{(km_1 - km_2)^2 + 4m_1m_2k^2}}{2m_1m_2} = \frac{k\,(m_1+m_2) \pm k\,(m_1+m_2)}{2m_1m_2} \tag{60}$$

$$\omega^2 = \frac{k\,(m_1+m_2)}{m_1m_2} = \frac{k}{\mu} \tag{61}$$

Here $\mu = m_1m_2/(m_1+m_2)$ is the reduced mass of the system. The diatomic molecule has only one mode of vibration, the antisymmetric one, which is the same as that of a mass μ connected to a fixed point by a spring k. The symmetric mode in this case would correspond to a translation of the whole molecule, since it isn't anchored to anything. If the molecule is symmetric, $m_1 = m_2$, we have $\omega^2 = 2k/m$ – since the only mode is the one in which both atoms compress the spring together, we would expect the frequency to be twice as high as that of a single mass connected by a spring to a fixed point.

(c) For the symmetric diatomic molecule on a surface, we set $k_3 = 0$ and $m_1 = m_2 \equiv m$ in the general solution:

$$\omega^2 = \frac{(k_1+2k_2)\,m \pm \sqrt{(k_2m - (k_1+k_2)\,m)^2 + 4m^2k_2^2}}{2m^2} = \frac{(k_1+2k_2) \pm \sqrt{(k_2 - (k_1+k_2))^2 + 4k_2^2}}{2m}$$

$$\omega^2 = \frac{k_1 + 2k_2 \pm \sqrt{4k_2^2 + k_1^2}}{2m} \tag{62}$$

If the springs are equal – not very realistic for a molecule adsorbed on a surface – this simplifies to

$$\omega^2 = \frac{\left(3 \pm \sqrt{5}\right)}{2}\frac{k}{m} \tag{63}$$

While our free diatomic molecule has only a single mode of vibration, after bonding to the surface the system again has two vibrational modes, corresponding to symmetric and antisymmetric vibrations of the two masses.

Under the more realistic assumption that the "spring" coupling the molecule to the surface is much weaker than the interatomic bond, $k_1 \ll k_2$,

$$\omega^2 = \frac{k_1 + 2k_2 \pm \sqrt{4k_2^2 + k_1^2}}{2m} = \frac{k_1 + 2k_2 \pm 2k_2\sqrt{1 + \frac{k_1^2}{4k_2^2}}}{2m} \approx \frac{k_1 + 2k_2 \pm 2k_2\left(1 + \frac{k_1^2}{8k_2^2}\right)}{2m} \tag{64}$$

$$\omega^2 \approx \left\{\frac{k_1 - \frac{k_1^2}{4k_2}}{2m}, \frac{k_1 + 4k_2 + \frac{k_1^2}{4k_2}}{2m}\right\} \approx \left\{\frac{k_1}{2m}, \frac{2k_2}{m} + \frac{k_1}{2m}\right\} \tag{65}$$

If we write the isolated diatomic molecule's vibrational frequency as $\omega_o = \sqrt{2k_2/m}$,

$$\omega^2 = \left\{\frac{k_1}{2m}, \frac{2k_2}{m} + \frac{k_1}{2m}\right\} = \{\delta\omega, \omega_o + \delta\omega\} \tag{66}$$

Thus, for weak coupling to the surface, the fundamental mode is shifted upward by an amount $\delta\omega = \sqrt{k_1/2m}$, and a new low-frequency mode is introduced at $\delta\omega$. Spectroscopically, one can use this upward shift of the fundamental mode to detect the absorption of molecules on a surface and estimate the adsorption energy.