

Problem Set 9: Solutions

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

$$\text{PE} = -\frac{ke^2}{r} + \frac{b}{r^9} \quad (1)$$

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 $r_o = 0.279$ 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:

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

$$ke^2 r_o^8 = 9b \quad (3)$$

$$b = \frac{1}{9} ke^2 r_o^8 \quad (4)$$

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:

$$\text{PE} = U(r) = -\frac{ke^2}{r} + \frac{ke^2 r_o^8}{9r^9} \quad (5)$$

Evaluating at equilibrium, $r_o = 0.279$ nm,

$$U(r_o) = -\frac{ke^2}{r_o} + \frac{ke^2}{9r_o} = -\frac{8ke^2}{9r_o} \approx -4.59 \text{ eV} \quad (6)$$

The frequency of small oscillations can be found by Taylor expanding the potential about equilib-

rium for small displacements from equilibrium:

$$U(\mathbf{r} - \mathbf{r}_o) \approx U(\mathbf{r}_o) + U'(\mathbf{r}_o) (\mathbf{r} - \mathbf{r}_o) + \frac{1}{2}U''(\mathbf{r}_o) (\mathbf{r} - \mathbf{r}_o)^2 \quad (7)$$

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 \mathbf{b} , after all). The third term is quadratic in displacement, just as it would be for a simple harmonic oscillator, $U = \frac{1}{2}k (\mathbf{r} - \mathbf{r}_o)^2$. 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.

$$\frac{1}{2}k = \frac{1}{2}U''(\mathbf{r}_o) \quad (8)$$

$$k = U''(\mathbf{r}_o) = -\frac{2ke^2}{r_o^3} \frac{90b}{r_o^{11}} = \frac{8ke^2}{r_o^3} \approx 84.9 \text{ N/m} \quad (9)$$

$$\omega = \sqrt{\frac{k}{\mu}} = 2\pi f \quad (10)$$

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

$$\mu = \frac{m_K m_{Cl}}{m_K + m_{Cl}} \approx 3.09 \times 10^{-26} \text{ kg} \quad (11)$$

which gives the frequency of oscillation f as

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

The accepted valueⁱ is 281 cm^{-1} , in excellent agreement with our simple model.

2. Energetics of diatomic systems II. An expression for the potential energy of two neutral atoms as a function of their separation r is given by the *Morse potential*,

$$\text{PE} = P_o \left[1 - e^{-\alpha(r-r_o)} \right]^2 \quad (13)$$

(a) Find the equilibrium spacing and dissociation energy. **(b)** Calculate the force constant for small oscillations about $r=r_o$.

ⁱNIST, see <http://cccbdb.nist.gov/compvibs3.asp?casno=7447407&charge=0&method=14&basis=9>

Solution: As in the previous problem, equilibrium is characterized by $dU/dr=0$.

$$\frac{dU}{dr} = 2P_o \left[1 - e^{-\alpha(r-r_o)} \right] \left(\alpha e^{-\alpha(r-r_o)} \right) = 0 \quad (14)$$

Either of the terms in brackets could be zero. The latter only leads to the trivial solution of $r \rightarrow \infty$, meaning there is no molecule in the first place. Setting the former term in brackets to zero,

$$0 = 1 - e^{-\alpha(r-r_o)} \quad \implies \quad r = r_o \quad (15)$$

The dissociation energy is defined as the amount of energy required to take the system from equilibrium at $r=r_o$ to complete breakup for $r \rightarrow \infty$. Thus,

$$(\text{dissociation energy}) = \left[\lim_{r \rightarrow \infty} U(r) \right] - U(r_o) = P_o - 0 = P_o \quad (16)$$

In other words, an amount of work P_o is required to bring about an infinite separation of the atoms, and this defines the dissociation energy.

If we wish to calculate a force constant, it is necessary to show that the force at least approximately obeys Hooke's law for small displacements, i.e., for a small displacement δ from equilibrium, $\delta = r - r_o$, $F(r_o + \delta) \approx k\delta$ where k is the force constant.ⁱⁱ We have already calculated the force versus displacement:

$$\begin{aligned} F(r) &= -\frac{dU}{dr} = -2P_o \left[1 - e^{-\alpha(r-r_o)} \right] \left(\alpha e^{-\alpha(r-r_o)} \right) = -2P_o \alpha \left(e^{-\alpha(r-r_o)} - e^{-2\alpha(r-r_o)} \right) \\ F(r_o + \delta) &= -2P_o \alpha \left(e^{-\alpha\delta} - e^{-2\alpha\delta} \right) \end{aligned} \quad (17)$$

For small δ , we may make use of the approximation $e^\delta \approx 1 + \delta + \frac{1}{2}\delta^2 + \dots$. Retaining terms only up to first order,

$$F(r_o + \delta) \approx -2P_o \alpha (1 - \alpha\delta - 1 + 2\alpha\delta) = - (2P_o \alpha^2) \delta \quad \implies \quad k = 2P_o \alpha^2 \quad (18)$$

Thus, for small displacements from equilibrium, we may treat the molecule as a mass-spring system, with an effective force constant k . Note that we could have equivalently used the method from the last problem, $k=U''$, but it is worth seeing how to approach the problem in a different way. For further information, the Wikipedia article is quite informative:

http://en.wikipedia.org/wiki/Morse_potential

ⁱⁱEquivalently, we could show $U(\delta) \approx \frac{1}{2}k\delta^2$.

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

$$E[\psi] = \frac{\int \psi^* H \psi dV}{\int |\psi|^2 dV} \quad (19)$$

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.

For a hydrogen-like ion, with Z protons and a single electron, the energy operator may be written as

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Zke^2}{r} \quad (20)$$

if we presume that the wave function of such an ion in its lowest energy state is functionally the same as the hydrogen atom,

$$\psi = c_1 e^{-c_2 r} \quad (21)$$

where c_1 and c_2 are adjustable constants.

(a) Use the variational principle and normalization to find the values of c_1 and c_2 that give the minimum energy for this trial wave function.

(b) For a He^+ ion ($Z = 2$), compare the ground state energy with the values of c_1 and c_2 you determine to the second ionization energy of He, -54.5 eV . Note that since the trial function is spherically symmetric, $dV = 4\pi r^2 dr$ and $\nabla^2 \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right)$.

Solution: The solution is somewhat lengthy, so it is best to tackle it systematically, step by step. First, let us calculate $\nabla^2 \psi$:

$$\nabla^2 \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} (-r^2 c_1 c_2 e^{-c_2 r}) = \frac{1}{r^2} (-2rc_1 c_2 e^{-c_2 r} + r^2 c_1 c_2^2 e^{-c_2 r}) \quad (22)$$

$$= c_1 c_2 e^{-c_2 r} \left(c_2 - \frac{2}{r} \right) \quad (23)$$

With that in hand, we can calculate $H\psi$, the energy operator H operating on the wave function ψ

$$H\psi = -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Zke^2}{r}\psi = -\frac{\hbar^2}{2m}c_1^2c_2e^{-2c_2r}\left(c_2 - \frac{2}{r}\right) - \frac{kZe^2}{r}c_1^2e^{-2c_2r} \quad (24)$$

Finally, we can calculate $\psi H\psi$ by multiplying through by the wavefunction:

$$\psi H\psi = -\frac{\hbar^2}{2m}c_1^2c_2e^{-2c_2r}\left(c_2 - \frac{2}{r}\right) - \frac{kZe^2}{r}c_1^2e^{-2c_2r} \quad (25)$$

Next, we must integrate this over all space to find the numerator in our energy expression. Since the wavefunction is spherically symmetric, we may use $dV=4\pi r^2$ and let r run from 0 to ∞ :

$$\int \psi H\psi dV = -\frac{2\pi\hbar^2}{m}c_1^2 \int_0^\infty e^{-2c_2r} r^2 \left(c_2 - \frac{2c_2}{r}\right) dr - 4\pi Zke^2c_1^2 \int_0^\infty r e^{-2c_2r} dr \quad (26)$$

$$= -\frac{2\pi\hbar^2}{m}c_1^2 \left(c_2^2 \frac{2}{(2c_2)^3} - \frac{2c_2}{(2c_2)^2}\right) - Zke^2c_1^2 \frac{\pi}{(2c_2)^2} = \frac{\pi\hbar^2c_2}{2mc^2} - \frac{Zke^2\pi c_1^2}{c_2^2} \quad (27)$$

The denominator of our energy expression is just the normalization condition:

$$\int \psi^2 dV = \int_0^\infty 4\pi r^2 c_1^2 e^{-2c_2r} dr = \frac{\pi c_1^2}{c_2^3} \quad (28)$$

Combining,

$$E[\psi] = \frac{\int \psi^* H\psi dV}{\int |\psi|^2 dV} = \frac{c_2^3}{\pi c_1^2} \left(\frac{\pi\hbar^2c_2}{2mc^2} - \frac{Zke^2\pi c_1^2}{c_2^2}\right) = \frac{\hbar^2c_2^2}{2m} - Zke^2c_2 \quad (29)$$

The best we can do with this wave function is to minimize the energy with respect to our parameters c_1 and c_2 . The energy does not explicitly depend on c_1 – sensible, since it is only a normalization constant – so we can minimize with respect to c_2 to find the minimum ground state energy with this trial wave function:

$$\frac{\partial E}{\partial c_2} = \frac{\hbar^2c_2}{m} - Zke^2 = 0 \quad \implies \quad c_2 = \frac{Zke^2m}{\hbar^2} = \frac{Z}{a_0} \quad (30)$$

Here a_0 is the Bohr radius. This is a sensible result: the larger that Z is, the stronger the attraction of the electron to the nucleus, and the more short-range the wave function becomes. We can find c_1 from normalization, which gives

$$c_1 = \sqrt{\frac{Z^3}{\pi a_0^3}} \quad (31)$$

The best-case trial wavefunction is thus

$$\psi = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0} \quad (32)$$

Given our value of c_2 , we may find the energy of the ground state:

$$E = \frac{\hbar^2 c_2^2}{2m} - Zke^2 c_2 = \frac{\hbar^2 Z^2}{2ma_0^2} - \frac{kZ^2 e^2}{a_0} \quad (33)$$

For He^+ , with $Z = 2$, we find $E \approx -54 \text{ eV}$, in very good agreement with experiment and exact calculations.ⁱⁱⁱ

4. *Variational Principle II.* Pretend we didn't know the ground state wave function for hydrogen, but attempted a trial solution of

$$\psi = c_1 e^{-c_2 r^2} \quad (34)$$

How far off is the ground state energy using this trial wavefunction?

Solution: We follow the same procedure we did for the previous problem, calculate step by step. First, $\nabla^2 \psi$:

$$\nabla^2 \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) = 4c_1 c_2^2 r^2 e^{-c_2 r^2} - 6c_1 c_2 e^{-c_2 r^2} \quad (35)$$

Using the energy operator from the previous problem with $Z=1$ for hydrogen,

$$H\psi = -\frac{\hbar^2}{2m} \left(4c_1 c_2^2 r^2 e^{-c_2 r^2} - 6c_1 c_2 e^{-c_2 r^2} \right) - \frac{ke^2}{r} c_1 e^{-c_2 r^2} \quad (36)$$

Multiplying through by the wave function,

$$\psi H\psi = -\frac{\hbar^2}{2m} c_1^2 e^{-2c_2 r^2} (4c_2^2 r^2 - 6c_2) - \frac{ke^2}{r} c_1^2 e^{-2c_2 r^2} \quad (37)$$

Integrating over all space (noting again that the wave function is spherically symmetric),

ⁱⁱⁱWe should not be too surprised, since our 'trial wavefunction' was exactly the right one. The next problem shows how close one can get if the trial wavefunction is not chosen quite as cleverly.

$$\int \psi H \psi dV = \int_0^{\infty} -\frac{4\pi\hbar^2 c_1^2}{m} (2c_2^2 r - 3c_2 r^2) e^{-2c_2 r^2} - 4\pi k e^2 c_1^2 r e^{-2c_2 r^2} dr \quad (38)$$

$$= -\frac{4\pi\hbar^2 c_1^2}{m} \left(2c_2^2 \frac{3\sqrt{\pi}}{8(2c_2)^{3/2}} - 3c_2 \frac{\sqrt{\pi}}{4} \frac{1}{(2c_2)^{3/2}} \right) - \frac{\pi k e^2 c_1^2}{c_2} \quad (39)$$

$$= \frac{3\pi^{3/2}\hbar^2 c_1^2}{2^{5/2}m\sqrt{c_2}} - \frac{\pi k e^2 c_1^2}{c_2} \quad (40)$$

The denominator in our energy expression gives

$$\int \psi^2 dV = \int_0^{\infty} 4\pi r^2 c_1^2 e^{-2c_2 r^2} dr = \frac{\sqrt{\pi}}{4} \frac{4\pi c_1^2}{(2c_2)^{3/2}} = \frac{c_1^2 \pi^{3/2}}{2^{3/2} c_2^{3/2}} \quad (41)$$

Combining, we have our energy:

$$E[\psi] = \frac{2^{3/2} c_2^{3/2}}{c_1^2 \pi^{3/2}} \left(\frac{3\pi^{3/2}\hbar^2 c_1^2}{2^{5/2}m\sqrt{c_2}} - \frac{\pi k e^2 c_1^2}{c_2} \right) = \frac{3\hbar^2 c_2}{2m} - \frac{2^{3/2} k e^2 \sqrt{c_2}}{\sqrt{\pi}} \quad (42)$$

Again, the energy does not depend on the normalization constant c_1 . Minimizing with respect to c_2 ,

$$\frac{\partial E}{\partial c_2} = \frac{3\hbar^2}{2m} - \sqrt{\frac{2}{\pi}} \frac{k e^2}{\sqrt{c_2}} = 0 \quad \implies \quad \sqrt{c_2} = \frac{2k e^2 m}{3\hbar^2} \sqrt{\frac{2}{\pi}} \quad (43)$$

Plugging this back into our energy expression,

$$E = \frac{3\hbar^2}{2m} \frac{4k^2 e^4 m}{9\hbar^4} - \frac{3\hbar^2 k e^2}{2k e^2 m} = \frac{4k^2 e^4 m}{3\pi\hbar^2} - \frac{8k^2 e^4 m}{3\pi\hbar^2} = -\frac{8}{3\pi} \left(\frac{k^2 e^4 m}{2\hbar^2} \right) = \frac{8}{3\pi} E_1 \quad (44)$$

Recognizing that $E_1 = \frac{k^2 e^4 m}{2\hbar^2}$ is the correct $n=1$ ground state energy for Hydrogen, our trial wave function is just a factor of $8/3\pi$ off (or about 15%) at $E \approx -11.5$ eV

5. Consider two equal bodies (not affected by gravity), each of mass, m , attached to three springs, each with spring constant, k . They are attached in the manner depicted below. (a) Find the possible frequencies of stable vibrations. We can use this system as a reasonable model for several types of molecular vibrations.

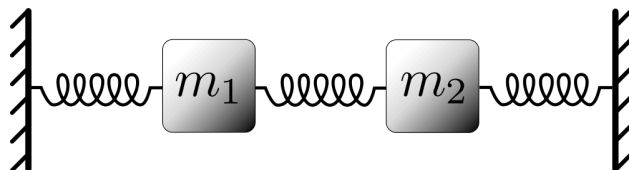


Figure 1: From http://en.wikipedia.org/wiki/Normal_mode.

(b) A diatomic molecule (figure (a) below) has only one mode of vibration. Find its frequency, assuming that the masses of A and B are different.

(c) 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, find their frequencies.

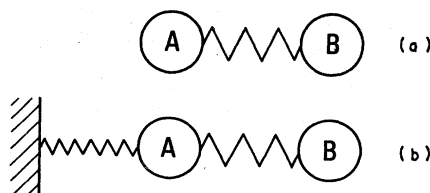


FIG. 1. (a) Classical model for vibrating free-space AB diatomic molecule; (b) same molecule adsorbed onto a surface.

Figure 2: From http://prb.aps.org/abstract/PRB/v19/i10/p5355_1.

Solution: We will solve the more general problem of three different springs (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, but solves all three problems posed: by setting $k_1 = k_2 = k_3$ and $m_1 = m_2$ we solve problem (a), setting $k_1 = k_3 = 0$ we solve problem (b), and setting $k_3 = 0$ we solve problem (c).

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.^{iv} 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 $-k_1 x_1$ on mass m_1 . Similarly, spring 3 is compressed only by mass 2, so it reacts with a force $-k_3 x_2$ on mass m_2 . Spring 2 is connected to both masses m_1 and m_2 , and its net change in length

^{iv}It makes no difference which direction we call $+x$, so long as we are consistent.

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 .

$$F_1 = m_1 \frac{d^2 x_1}{dt^2} = -k_1 x_1 + k_2 (x_2 - x_1) \quad (45)$$

$$F_2 = m_2 \frac{d^2 x_2}{dt^2} = -k_3 x_2 + k_2 (x_1 - x_2) \quad (46)$$

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

$$x_1 = A_1 e^{i\omega t} \quad (47)$$

$$x_2 = A_2 e^{i\omega t} \quad (48)$$

Plugging this trial solution into our equations of motion above,

$$-m_1 \omega^2 A_1 e^{i\omega t} = -k_1 A_1 e^{i\omega t} + k_2 (A_2 - A_1) e^{i\omega t} \quad (49)$$

$$-m_2 \omega^2 A_2 e^{i\omega t} = -k_3 A_2 e^{i\omega t} + k_2 (A_1 - A_2) e^{i\omega t} \quad (50)$$

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

$$-m_1 \omega^2 A_1 = -k_1 A_1 + k_2 (A_2 - A_1) \quad (51)$$

$$-m_2 \omega^2 A_2 = -k_3 A_2 + k_2 (A_1 - A_2) \quad (52)$$

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

$$(m_1\omega^2 - k_1 - k_2) A_1 + k_2 A_2 = 0 \quad k_2 A_1 + (m_2\omega^2 - k_3 - k_2) A_2 = 0 \quad (53)$$

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:

$$\begin{bmatrix} (m_1\omega^2 - k_1 - k_2) & k_2 \\ k_2 & (m_2\omega^2 - k_3 - k_2) \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad (54)$$

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

$$\begin{vmatrix} (m_1\omega^2 - k_1 - k_2) & k_2 \\ k_2 & (m_2\omega^2 - k_3 - k_2) \end{vmatrix} = 0 = (m_1\omega^2 - k_1 - k_2) (m_2\omega^2 - k_3 - k_2) - k_2^2 \quad (55)$$

Expanding,

$$m_1 m_2 \omega^4 - [(k_2 + k_3) m_1 + (k_1 + k_2) m_2] \omega^2 + (k_1 + k_2) (k_2 + k_3) - k_2^2 = 0 \quad (56)$$

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

$$\begin{aligned} \omega^2 &= \frac{(k_2 + k_3) m_1 + (k_1 + k_2) m_2 \pm \sqrt{((k_2 + k_3) m_1 + (k_1 + k_2) m_2)^2 - 4 m_1 m_2 [(k_1 + k_2) (k_2 + k_3) - k_2^2]}}{2 m_1 m_2} \\ \omega^2 &= \frac{(k_2 + k_3) m_1 + (k_1 + k_2) m_2 \pm \sqrt{((k_2 + k_3) m_1 - (k_1 + k_2) m_2)^2 + 4 m_1 m_2 k_2^2}}{2 m_1 m_2} \end{aligned} \quad (57)$$

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

(a) For the problem as stated, we let $k_1 = k_2 = k_3 \equiv k$ and $m_1 = m_2 \equiv m$. Our expression above then simplifies to

$$\omega^2 = \frac{4km \pm 2km}{2m^2} = \left\{ \frac{3k}{m}, \frac{k}{m} \right\} \quad (58)$$

Physically, this makes sense. We have the symmetric mode ($\omega = \sqrt{k/m}$) in which the central spring remains uncompressed, and the vibrations are only due to each mass m interacting independently with the spring k that connects it to the wall. The antisymmetric mode has the exterior springs

being compressed by each mass during half the 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 $\omega = \sqrt{3k/m}$ mode.

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

$$\omega^2 = \frac{k m_1 + k m_2 \pm \sqrt{(k m_1 - k m_2)^2 + 4 m_1 m_2 k^2}}{2 m_1 m_2} = \frac{k (m_1 + m_2) \pm k (m_1 + m_2)}{2 m_1 m_2} \quad (59)$$

$$\omega^2 = \frac{k (m_1 + m_2)}{m_1 + m_2} = \frac{k}{\mu} \quad (60)$$

Here $\mu = m_1 m_2 / (m_1 + m_2)$ 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:

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

$$\omega^2 = \frac{k_1 + 2k_2 \pm \sqrt{4k_2^2 + k_1^2}}{2m} \quad (61)$$

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

$$\omega^2 = \frac{(3 \pm \sqrt{5}) k}{2 m} \quad (62)$$

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, $k_1 \ll k_2$,

$$\omega^2 = \frac{k_1 + 2k_2 \pm \sqrt{4k_2^2 + k_1^2}}{2m} = \frac{k_1 + 2k_2 \pm 2k_2 \sqrt{1 + \frac{k_1^2}{4k_2^2}}}{2m} \approx \frac{k_1 + 2k_2 \pm 2k_2 \left(1 + \frac{k_1^2}{8k_2^2}\right)}{2m} \quad (63)$$

$$\omega^2 \approx \left\{ \frac{k_1 - \frac{k_1^2}{4k_2}}{2m}, \frac{k_1 + 4k_2 + \frac{k_1^2}{4k_2}}{2m} \right\} \approx \left\{ \frac{k_1}{2m}, \frac{2k_2}{m} + \frac{k_1}{2m} \right\} \quad (64)$$

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

$$\omega^2 = \left\{ \frac{k_1}{2m}, \frac{2k_2}{m} + \frac{k_1}{2m} \right\} = \{\delta\omega, \omega_o + \delta\omega\} \quad (65)$$

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.