PH253: Introduction to molecules and bonds

Patrick R. LeClair

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Introduction to Molecules and Bonds

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What we learned so far is that an isolated proton and an isolated electron can gain 13.6 eV (about 1300 kJ/mol) by joining together to form a hydrogen atom. That is, it is energetically favorable for them to bind together, so given a chance that is what they do. We also know that larger numbers of protons and electrons can lower their energy by forming heavier atoms, and all of them can combine in various energetically-favored ways to form stable molecules. Two hydrogen atoms can lower their overall energy by forming an H_2 molecule.

Combining atoms like this forms *chemical bonds*, leading to substances potentially very different than their constituents. For example, a violently reactive metal (Na) can combine with a poisonous gas (Cl_2) to form common table salt. Our goal now is to figure out how this happens, and what the energy levels of molecules look like. First we can look at the problem very generally and see what the energetics look like and what we can predict on general grounds. Next, we'll need approximate methods to say something concrete about molecular energy levels - we already know we can't solve Schrödinger's equation exactly even for Helium, for multiple atoms the situation is even worse. We'll use the *variational method*, which will lead us to the linear combination of atomic orbitals (LCAO) scheme you probably saw in intro chemistry. At that point, the real challenge will be to extend our understanding to solids - really interesting things happen when you put *lots* of atoms together.

Is this then not just chemistry? There is more to the world than reductionism. (Relevant article) Complexity brings interesting new things we didn't expect from the sum of the parts - like getting salt from a poisonous gas and an explosively-reactive metal. We need quantum physics and electrodynamics to understand how bonds work, and then the *really* complicated things get started. The rest is certainly not stamp collecting, as the saying goes, and there is no rigid boundary between chemistry and physics (or engineering, etc). Our job is to learn about interesting and practical things, what someone wants to call it is their business. (Relevant comic.)

1.1   General mechanical properties of bonds

Clearly, there must be an attractive force for a bond to form, and we know this must be the Coulomb interaction. We've already reasoned that bonds should form when electrons could be "shared." For example, Na desperately wants to give up its outer electron to reach a closed shell (like Ne), while Cl desperately wants one more electron to reach a closed shell (like Ar). It makes sense they would want to combine. What is less obvious is why they still stay some distance apart. Why do Na and Cl stay about a quarter of a nanometer apart rather than pulling even closer together?

$E(r)$
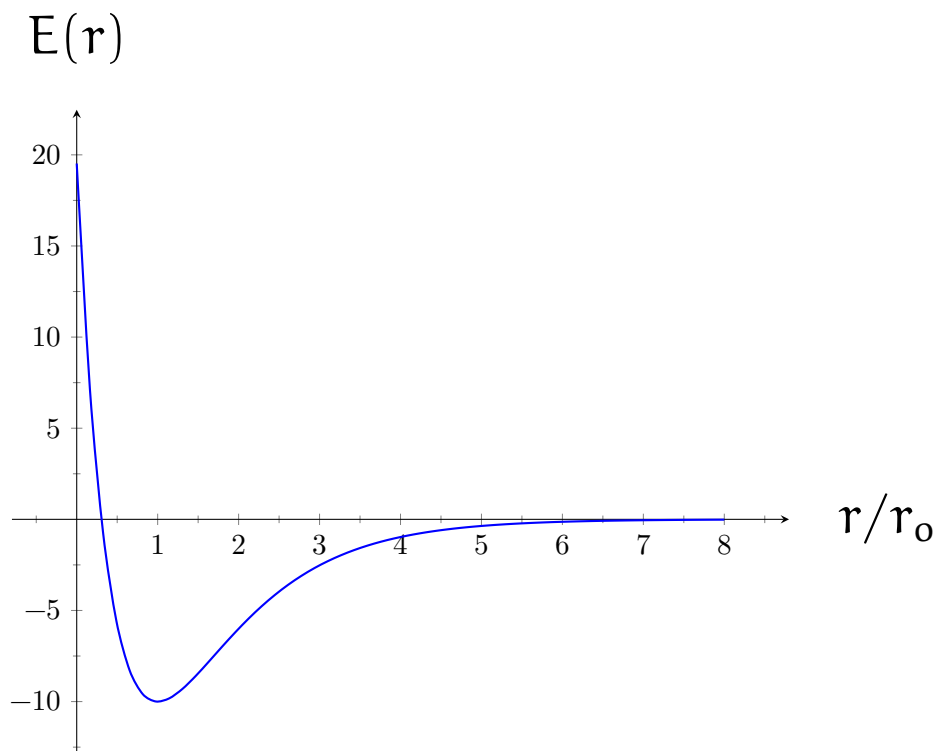
Figure 1.1: *Schematic energy vs. separation for a diatomic molecule*

The answer is that there must be a repulsive force at short ranges for an equilibrium spacing to exist. When the ions get very close together, the electron clouds are distorted, and the nuclei "see" each other a little better and repel each other. Long story short: there is a very short-range repulsive force in addition to the longer-ranging attractive force that leads to an equilibrium spacing of the atoms forming a bond. Figure 1.1 is a schematic of what the energy versus separation looks like for a pair of atoms forming a bond.

A few key aspects. First, the energy E goes to zero for large r, as it must. Second, is attractive ($E < 0$) in a region above a critical radius $r_c < r < \infty$. Third, at the equilibrium radius r_o the energy is minimum, a gain of E_c below the value for infinite separation. Fourth, below the critical radius, the situation is energetically unfavorable, and the reaction is repulsive. Recall that $F(r) = -dE/dr$, so a large negative slope means a large positive (repulsive) force. Finally, at the equilibrium radius the force is zero (zero slope), the energy minimal, and for any displacements the force is restoring - displacements lead to a force pushing the system back to equilibrium.

The exact mathematical form of $E(r)$ is not so interesting right now. There are various models one can use and parameterize to do calculations, but for now only the general properties outlined above are of interest. As it turns out, just knowing the basic properties is enough for us to answer interesting questions about mechanical properties, such as "what happens when we try to squish something."

1.1.1 Compression of solids

Let's say we have a cube of a solid material, with sides of length a. Each atom is at an equilibrium distance r_o from the others, with N atoms per unit volume. For each atom, its energy as a function of position is $E(r)$ (a function which looks like the one in Fig. 1.1) which is minimum at r_o. To this cube, we will apply uniform pressure (isotropic compression) on every face by using a force F, or more conveniently a *stress* (force per unit area) of $\sigma = F/A = F/a^2$ on each side. What happens to our cube?

The energy of the cube in equilibrium is the number of atoms multiplied by the energy per atom. The number of atoms per unit volume is N and the volume is a^3, so

$$E_{\text{tot, eq}} = Na^3 E(r_o) \tag{1.1}$$

If we compress the cube such that each atom is Δr closer to the others in every direction, the new energy is

$$E_{\text{tot, compr.}} = Na^3 E(r_o - \Delta r) \tag{1.2}$$

If we presume $\Delta r \ll r$, then the difference in energy is easily found from a Taylor series:

$$E(r_o - \Delta r) \approx E(r_o) + \left(\frac{\partial E}{\partial r}\right)\bigg|_{r_o} \Delta r + \frac{1}{2}\left(\frac{\partial^2 E}{\partial r^2}\right)\bigg|_{r_o} (\Delta r)^2 + \ldots \tag{1.3}$$

$$\Delta E = E(r_o - \Delta r) - E(r_o) \approx \left(\frac{\partial E}{\partial r}\right)\bigg|_{r_o} \Delta r + \frac{1}{2}\left(\frac{\partial^2 E}{\partial r^2}\right)\bigg|_{r_o} (\Delta r)^2 + \ldots \tag{1.4}$$

The *change* in energy ΔE due to the compression, for small Δr is relatively simple. But it is even simpler than it looks. First, $E(r_o)$ is a constant, which we could easily define to be zero if we like. Second, $\frac{\partial E}{\partial r}\big|_{r_o} = -F(r_o)$ is just the force on at atom in equilibrium, which is by definition zero. Only the second order term survives:

$$\Delta E = E(r_o - \Delta r) - E(r_o) \approx \frac{1}{2}\left(\frac{\partial^2 E}{\partial r^2}\right)\bigg|_{r_o} (\Delta r)^2 \tag{1.5}$$

The result looks just like $U = \frac{1}{2}kx^2$ for a simple harmonic oscillator, which indicates that *the response of the material is elastic*. Our little cube of stuff behaves like a network of masses and springs. This makes sense given that the shape of the energy curve is concave up around the equilibrium point - a nudge in any direction gives a force trying to push the system back to equilibrium. All the math is saying that because $E(r)$ is concave up with a minimum at r_o, the lowest order approximation near equilibrium is a parabola, just as it would be for mass-spring system. The more important message is that the effective spring constant k is proportional to $\partial^2 E/\partial r^2$ - if we can find $E(r)$, we

can calculate the mechanical properties of a pure crystal, e.g., the speed of sound, bulk modulus, etc..[i]

1.2   Bulk modulus and other properties

We can get a bit further by comparing the change in energy of the crystal to the work done in compressing it. In general, if the force increases from $0 \to F$ while the distance changes from $0 \to D$, we can write for an elastic medium where $F = k\Delta x$

$$W = \int_0^D F(r)\, dr = \int_0^D kr\, dr = \frac{1}{2}kD^2 = \frac{1}{2}kD \cdot D = \frac{1}{2}FD \tag{1.6}$$

The work done is the average force times the displacement. Remember that the stress and force relate via $F = \sigma A = \sigma a^2$. What is the distance? Each atom moves by Δr, so the change in the side of the cube's length would be the fractional change for a single atom times the original length of the side:

$$\text{net movement of one side toward the other} = \frac{\Delta r}{r_o}a \tag{1.7}$$

However, each side moves closer to the other by half this amount, so the distance each side moves is

$$D = \frac{\Delta r}{r_o}\frac{a}{2} \tag{1.8}$$

Since there are 6 faces, the net work done in squishing the cube is

$$W = 6 \cdot \frac{1}{2}FD = 3\sigma a^2 \frac{\Delta r}{r_o}\frac{a}{2} = \frac{3}{2}\sigma a^3 \frac{\Delta r}{r_o} \tag{1.9}$$

Compare this to our expression for ΔE, and we can identify the stress

$$\sigma = \frac{1}{3r_o}\left.\frac{\partial^2 E}{\partial r^2}\right|_{r_o}\left(\frac{\Delta r}{r_o}\right) \tag{1.10}$$

This tells us the stress is related to the bond energy function $E(r)$ and linearly related to the strain $\epsilon = \Delta r/r_o$. If you are a mechanical engineer, you already knew this.

From the stress and strain, we can get the *bulk modulus* K which relates stress and volume change. By definition,

$$K = \frac{\text{stress}}{\text{fractional volume change}} = \frac{\sigma}{\Delta V/V} \tag{1.11}$$

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[i]Which is wildly different than finding the properties of a real material, where defects and microstructure can dominate the mechanical properties. But it is a start.

If $\Delta V/V \ll 1$, which it will be since we already assumed $\Delta r/r_o \ll 1$, we can approximate it as

$$\frac{\Delta V}{V} \approx \frac{\Delta x}{x} + \frac{\Delta y}{y} + \frac{\Delta y}{y} = \frac{3\Delta x}{x} \tag{1.12}$$

Here the last step is due to the material being isotropic, so the x, y, and z directions are all the same. This leads to

$$K \approx \frac{\sigma}{3\Delta x/x} = \frac{1}{9r_o}\left.\frac{\partial^2 E}{\partial r^2}\right|_{r_o} = \frac{E}{3(1-2\nu)} \tag{1.13}$$

Here in the last step E is Young's modulus and ν is Poisson's ratio. You don't really need to know that part, but it will be familiar for some of the engineers. The main point is, again, that from $E(r)$ we can predict mechanical properties for solids. The next step is to figure out how to find $E(r)$ by approximate (but respectable) methods, in our case, the Variational method. These days, one can do this for almost all materials to fantastic accuracy with numerical methods, but those techniques are beyond the scope of this course.

1.3   Bond types

The discussion so far is relatively generic - the only real assumption is the form of $E(r)$. We should think a bit more about the bonding mechanisms before moving on. As a friend of mine put it glibly on facebook, the atoms involved are playing games with electrons: "ionic bonding is keep away, covalent is tug of war, metallic is hot potato." And he's got a Ph.D. in chemistry, so he knows this stuff.[ii]

1.3.1   Ionic bonds

The first one we have already discussed: ionic bonding. As noted above, one atom gains electron(s) and another loses electron(s). As Dr. Burgess notes, one atom is playing "keep away" with another's electron(s). Sodium ionizes to Na^+, chlorine to Cl^- by trading an electron, and the pair are then electrostatically bound. What are the energetics like?

Na^+ and Cl^- ions form a an alternating cubic lattice like this:
The atoms are about $0.28\,nm$ apart along an edge. Once the ionization is accomplished, which is favorable for both atoms since it results in a closed shell, the energy is now an electrostatics problem. Each Na^+ has 6 Cl^- nearest neighbors at a distance a, so the electrostatic energy is

$$E_{nn} = -\frac{ke^2}{a} \cdot 6 \tag{1.14}$$

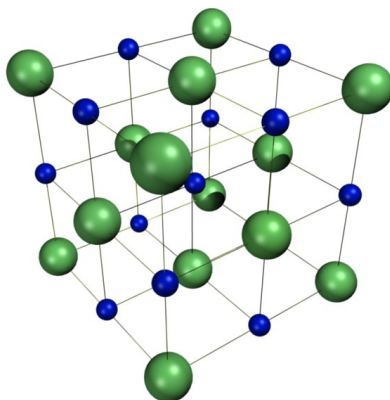
[ii]Dr. James Burgess, facebook comment on 25 March 2020.

Figure 1.2: *From* `https://commons.wikimedia.org/wiki/File:Nacl-structure.jpg`; *see link for license and attribution.*

That's about $-30\,\mathrm{eV}$, which is great! However, there are 12 Na+ next-nearest neighbors at a distance $a\sqrt{2}$ which give an unfavorable contribution to the energy.

$$E_{nnn} = -\frac{ke^2}{a\sqrt{2}} \cdot 12 \tag{1.15}$$

This contribution is about $+44\,\mathrm{eV}$, so overall the first two sets of neighbors add up to be unfavorable. You can keep doing this for the 8 Cl atoms at $a\sqrt{3}$ and sum the whole thing up over sets of increasingly-distant neighbors:

$$E = -\frac{ke^2}{a}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} + \dots\right) = -M\frac{ke^2}{a} \tag{1.16}$$

Two things happen. One, the sum is overall proportional to the Na-Cl pair energy $\frac{-ke^2}{a}$, the term in brackets is just a constant. Two, it converges *very* slowly, amounting to $M \approx 1.748$. That means the entire crystal gains an energy per Na-Cl pair of about 1.75 times the pair energy or nearly $9\,\mathrm{eV}$, which is *huge*, so *creating the crystal is favorable even compared to individual pairs of Na-Cl*, which was already more favorable than the individual atoms. Crystals form over isolated pairs of atoms because the collective is energetically favorable, another example where the whole is more interesting than the sum of its parts. The constant M, the "Madelung constant" is characteristic for each type of crystal lattice, the larger it is the more stable the crystal is.

As a result of the large energy gain, ionic bonds are quite strong, making materials that tend to be brittle. Given the ionization that happens and the resulting segregation of positive and negative charges, there are really no free mobile charges to speak of. Put another way, since both atoms end up with a filled outer shell, all electrons are fairly tightly bound to their host atom, leaving no loosely bound electrons to conduct electricity. Brittle, insulating, and sometimes, tasty.

1.3.2 Metallic bonding

Metallic bonding will have to wait until we've learned enough to understand why there are metals in the first place. And *that* will require getting past molecules to think more carefully about large collections of atoms in a crystal. The gist of it is that there is some similarity with ionic bonding, but the negative charges are electrons, not ions, and the positive charges are comparatively immobile ions. That is, a lattice of positive ions fixed in place, and a "sea" of mobile (outer shell) electrons that can zip around through the crystal from atom to atom, hence conducting electricity and heat. Another view is that the electron sea is like a fluid able to flow through the crystal lattice, albeit not without resistance. Metals, as a result, are generally ductile and malleable in addition to being conductors. As Dr. Burgess said: hot potato - the electrons jump from site to site, and given a thermal or electrical potential gradient, one can induce a net flow of them (a current).

1.3.3 Covalent bonding

Bonding so far has involved charge transfer of some kind, followed by unlike charges attracting each other. This picture doesn't work at all for a crystal of Si or C. What holds them together? Why is there an energy gain for a bunch of Si atoms to form a crystal? Further, Si is *partly* conducting, not really consistent metallic or ionic bonding. The bonds in Si and C are also very strong and highly directional (i.e., they break preferentially along certain directions) like ionic bonds.

Covalent bonding is extremely important in organic chemistry, and inexplicable without quantum mechanics. It is a difficult topic; for now we will just go over the basics. Covalent bonds involve *pairs* of electrons, usually one from each atom participating in the bond. The electrons' density tends to be partly localized in the region between the two nuclei to screen them from one another, and the spins tend to be antiparallel.[iii] Let's take H_2 as an example.

H_2 has two protons and two electrons. The two protons will settle some distance apart - about three quarters of a nanometer as it turns out - for reasons discussed earlier. Where will the electrons go? They will repel each other, but will also want to shield the protons from each other since both raise the overall energy. The idea is that the two electrons will spread their density out such that a good share of it is between the two protons to shield them from each other, but with just enough of it on the opposite sides of the protons to keep the electron-electron repulsion energy minimized and the electron-proton attraction energy optimized. We talked about that already.

There is another way to view it though. Both H atoms want one more electron to complete the $1s$ shell, but they don't have enough between them. You could also say then that the two electrons in H_2 are trying to spread themselves out as much as possible to do their best to fill the outer shells

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[iii]As we discussed earlier in the course, one aspect of the Pauli principle is that like spins tend to avoid each other spatially, while unlike spins can congregate. It is a bit more complicated than that, but the idea is that since the two electrons in the bond have to be close together, they end up with antiparallel spins.

of both H atoms. That is, rather than thinking of the electron clouds as spatially distributed, you could imagine that they are sharing their *time*. Imagine one electron sat in the middle, and the other jumped back and forth between the opposite sides. Half the time one atom is perfectly happy, while the other is moderately distressed, and vice versa. If the two atoms share the electrons, they can be 100% happy 50% of the time, and so long as they are better than 50% happy the rest of the time, it is a win. As Dr. Burgess says, "tug of war" - or take turns with the electrons, pulling them back and forth.

Carbon, Silicon, and Germanium are all in the same row of the periodic table (see page 9) and all 4 electrons short of a filled shell:

- C: $1s^2 2s^2 p^2$

- Si: $1s^2 2s^2 p^6 3s^2 p^2$

- Ge: $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^2$

That's too many to steal or give away, generally speaking, so ionic bonding is hard to pull off. On the other hand, if four carbon atoms could share their electrons, it could work. Even better would be to form a lattice of some kind so some of the bonds can be shared. Or sprinkle in some H atoms to donate an electron here and there and you have hydrocarbons. The way we think about elements in this column is that they each have four "dangling bonds" to share - they want add or subtract four electrons to complete their outer or inner shell, and they are willing to share with other atoms. This means that there are no electrons left to wander around and conduct electricity or heat, so covalently-bonded materials tend to be poor conductors or insulators.

However. Let's say we added an element like phosphorous (P) that only wants 3 electrons, not 4. It doesn't need to share quite as much, meaning the electrons associated with P are a bit more loosely bound. Adding just a bit of P to Si makes it much more conductive by effectively adding loosely bound electrons. Going the other way, boron (B) wants to gain 5 electrons, which seems greedy, or give up 3. Either way, it isn't sharing enough, which leads to effectively fewer electrons than necessary. Surprisingly, this *also* increases the conductivity, but the reasons for this we will have to discuss after we've gone a bit further in the course. The main point of this being that covalently bonded systems are incredibly flexible. Silicon's primary value is not so much that it is a great conductor or a insulator, but that it is so flexible: it can be either with some gentle prodding. That's how we make transistors, diodes, computers, and cell phones, which we should be able to explain by the end of the course. Well, at least the gist of it.

Periodic Table

Via http://www.texample.net/media/tikz/examples/TEX/periodic-table-of-chemical-elements.tex

(Mendeleev's) Periodic Table of Chemical Elements via Ti*k*Z

Legend:
- Alkali Metal
- Alkaline Earth Metal
- Metal
- Metalloid
- Non-metal
- Halogen
- Noble Gas
- Lanthanide/Actinide

Z mass
Symbol
Name

man-made

Problems

1. *Energetics of diatomic systems* An approximate expression for the potential energy of two ions as a function of their separation is (treating the problem one dimensionally),

$$V = -\frac{ke^2}{x} + \frac{b}{x^9} \tag{1.17}$$

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)** What is the equilibrium spacing x_o? **(b)** Find b as a function of the equilibrium spacing x_o. **(c)** For NaCl, with an equilibrium spacing of $r_o = 0.236$ nm, calculate the frequency of small oscillations about $x = x_o$. *Hint: do a Taylor expansion of the potential energy to make it look like a harmonic oscillator for small $x = x_o$.*

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

$$F(r_o) = -\frac{dU}{dr}\bigg|_{r=r_o} = 0 = \frac{ke^2}{r_o^2} - \frac{9b}{r_o^{10}} \tag{1.18}$$

$$ke^2 r_o^8 = 9b \tag{1.19}$$

$$b = \frac{1}{9}ke^2 r_o^8 \tag{1.20}$$

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:

$$PE = U(r) = -\frac{ke^2}{r} + \frac{ke^2 r_o^8}{9r^9} \tag{1.21}$$

Evaluating at equilibrium, $r_o = 0.279$ nm,

$$U(r_o) = -\frac{ke^2}{r_o} + \frac{ke^2}{9r_o} = -\frac{8ke^2}{9r_o} \approx -5.42\,\text{eV} \tag{1.22}$$

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

$$U(r - r_o) \approx U(r_o) + U'(r_o)(r - r_o) + \frac{1}{2}U''(r_o)(r - r_o)^2 \tag{1.23}$$

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

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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:

$$\mu = \frac{m_{Na} m_{Cl}}{m_{Na} + m_{Cl}} \approx 13.95\,\text{u} = 2.32 \times 10^{-26}\,\text{kg} \tag{1.24}$$

That is, the diatomic molecule looks like two masses coupled by a spring.

$$\frac{1}{2}k = \frac{1}{2}U''(r_o) \tag{1.25}$$

$$k = U''(r_o) = -\frac{2ke^2}{r_o^3} \frac{90b}{r_o^{11}} = \frac{8ke^2}{r_o^3} \approx 140\,\text{N/m} \tag{1.26}$$

$$\omega = \sqrt{\frac{k}{\mu}} = 2\pi f \tag{1.27}$$

The frequency of oscillation f is then

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \approx 1.24 \times 10^{13}\,\text{Hz} \approx 414\,\text{cm}^{-1} \tag{1.28}$$

A reliable experimental value is about $365\,\text{cm}^{-1}$, in good agreement with our simple model.[iv]

2. (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.

(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.
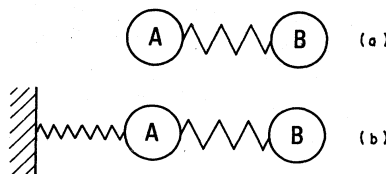

FIG. 1. (a) Classical model for vibrating free-space
AB diatomic molecule; (b) same molecule adsorbed onto
a surface.

Figure 1.3: *From http://prb.aps.org/abstract/PRB/v19/i10/p5355_1.*

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

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[iv]See http://scitation.aip.org/content/aip/journal/jpcrd/36/2/10.1063/1.2436891.

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.
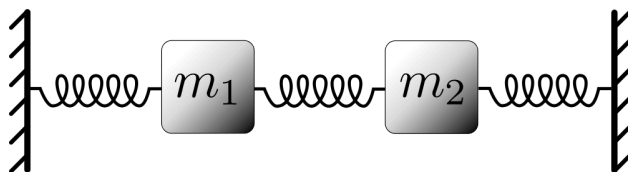
Figure 1.4: *From http://en.wikipedia.org/wiki/Normal_mode.*

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.[v] 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 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.

$$F_1 = m_1 \frac{d^2 x_1}{dt^2} = -k_1 x_1 + k_2 \left(x_2 - x_1 \right) \tag{1.29}$$

$$F_2 = m_2 \frac{d^2 x_2}{dt^2} = -k_3 x_2 + k_2 \left(x_1 - x_2 \right) \tag{1.30}$$

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

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

$$x_1 = A_1 e^{i\omega t} \tag{1.31}$$

$$x_2 = A_2 e^{i\omega t} \tag{1.32}$$

Plugging this trial solution into our equations of motion above,

$$-m_1 \omega^2 A_1 e^{i\omega t} = -k_1 A_1 e^{i\omega t} + k_2 \left(A_2 - A_1\right) e^{i\omega t} \tag{1.33}$$

$$-m_2 \omega^2 A_2 e^{i\omega t} = -k_3 A_2 e^{i\omega t} + k_2 \left(A_1 - A_2\right) e^{i\omega t} \tag{1.34}$$

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

$$-m_1 \omega^2 A_1 = -k_1 A_1 + k_2 \left(A_2 - A_1\right) \tag{1.35}$$

$$-m_2 \omega^2 A_2 = -k_3 A_2 + k_2 \left(A_1 - A_2\right) \tag{1.36}$$

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

$$\left(m_1 \omega^2 - k_1 - k_2\right) A_1 + k_2 A_2 = 0 k_2 A_1 + \left(m_2 \omega^2 - k_3 - k_2\right) A_2 \qquad = 0 \tag{1.37}$$

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:

$$\begin{bmatrix} \left(m_1 \omega^2 - k_1 - k_2\right) & k_2 \\ k_2 & \left(m_2 \omega^2 - k_3 - k_2\right) \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{1.38}$$

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

$$\begin{vmatrix} \left(m_1 \omega^2 - k_1 - k_2\right) & k_2 \\ k_2 & \left(m_2 \omega^2 - k_3 - k_2\right) \end{vmatrix} = 0 = \left(m_1 \omega^2 - k_1 - k_2\right)\left(m_2 \omega^2 - k_3 - k_2\right) - k_2^2 \tag{1.39}$$

Expanding,

$$m_1 m_2 \omega^4 - \left[\left(k_2 + k_3\right) m_1 + \left(k_1 + k_2\right) m_2\right] \omega^2 + \left(k_1 + k_2\right)\left(k_2 + k_3\right) - k_2^2 = 0 \tag{1.40}$$

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

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

$$\omega^2 = \frac{(k_2 + k_3)\, m_1 + (k_1 + k_2)\, m_2 \pm \sqrt{((k_2 + k_3)\, m_1 - (k_1 + k_2)\, m_2)^2 + 4m_1 m_2 k_2^2}}{2m_1 m_2} \tag{1.41}$$

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

$$\omega^2 = \frac{4km \pm 2km}{2m^2} = \left\{ \frac{3k}{m}, \frac{k}{m} \right\} \tag{1.42}$$

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

$$\omega^2 = \frac{km_1 + km_2 \pm \sqrt{(km_1 - km_2)^2 + 4m_1 m_2 k^2}}{2m_1 m_2} = \frac{k\,(m_1 + m_2) \pm k\,(m_1 + m_2)}{2m_1 m_2} \tag{1.43}$$

$$\omega^2 = \frac{k\,(m_1 + m_2)}{m_1 m_2} = \frac{k}{\mu} \tag{1.44}$$

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:

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

$$\omega^2 = \frac{k_1 + 2k_2 \pm \sqrt{4k_2^2 + k_1^2}}{2m} \tag{1.45}$$

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

$$\omega^2 = \frac{\left(3 \pm \sqrt{5}\right)}{2} \frac{k}{m} \tag{1.46}$$

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, $k_1 \ll k_2$,

$$\omega^2 = \frac{k_1 + 2k_2 \pm \sqrt{4k_2^2 + k_1^2}}{2m} = \frac{k_1 + 2k_2 \pm 2k_2 \sqrt{1 + \frac{k_1^2}{4k_2^2}}}{2m} \approx \frac{k_1 + 2k_2 \pm 2k_2 \left(1 + \frac{k_1^2}{8k_2^2}\right)}{2m} \tag{1.47}$$

$$\omega^2 \approx \left\{ \frac{k_1 - \frac{k_1^2}{4k_2}}{2m}, \frac{k_1 + 4k_2 + \frac{k_1^2}{4k_2}}{2m} \right\} \approx \left\{ \frac{k_1}{2m}, \frac{2k_2}{m} + \frac{k_1}{2m} \right\} \tag{1.48}$$

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

$$\omega^2 = \left\{ \frac{k_1}{2m}, \frac{2k_2}{m} + \frac{k_1}{2m} \right\} = \{\delta\omega, \omega_o + \delta\omega\} \tag{1.49}$$

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.

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?

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

(a)   (b)
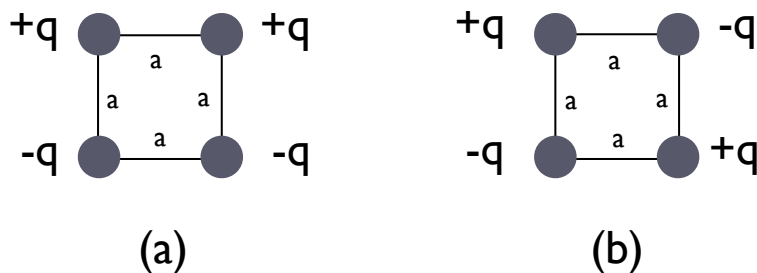
of charges, both of magnitude q, separated by a distance d is just:

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

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

$$q_1 q_2, q_1 q_3, q_1 q_4$$
$$q_2 q_3, q_2 q_4$$
$$q_3 q_4$$

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 $q_2 q_4$ and $q_1 q_3$, which are separated by a distance $a\sqrt{2}$, all others are separated by a distance a. Thus,

$$PE = \frac{k_e q_1 q_2}{a} + \frac{k_e q_1 q_3}{a\sqrt{2}} + \frac{k_e q_1 q_4}{a} + \frac{k_e q_2 q_3}{a} + \frac{k_e q_2 q_4}{a\sqrt{2}} + \frac{k_e q_3 q_4}{a} \tag{1.50}$$

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:

$$PE_a = \frac{k_e q^2}{a} + \frac{k_e \left(-q^2\right)}{a\sqrt{2}} + \frac{k_e \left(-q^2\right)}{a} + \frac{k_e \left(-q^2\right)}{a} + \frac{k_e \left(-q^2\right)}{a\sqrt{2}} + \frac{k_e q^2}{a} \tag{1.51}$$

$$= \frac{k_e q^2}{a} \left(-\frac{2}{\sqrt{2}}\right) = -\sqrt{2}\frac{k_e q^2}{a} \approx -1.414\frac{k_e q^2}{a} \tag{1.52}$$

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

$$PE = \frac{k_e\left(-q^2\right)}{a} + \frac{k_e q^2}{a\sqrt{2}} + \frac{k_e\left(-q^2\right)}{a} + \frac{k_e\left(-q^2\right)}{a} + \frac{k_e q^2}{a\sqrt{2}} + \frac{k_e\left(-q^2\right)}{a} \tag{1.53}$$

$$= \frac{k_e q^2}{a}\left(-4 + \frac{2}{\sqrt{2}}\right) = \frac{k_e q^2}{a}\left(-4 + \sqrt{2}\right) \approx -2.586\frac{k_e q^2}{a} \tag{1.54}$$

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 II.* An approximate expression for the potential energy of two ions as a function of their separation is

$$U(r) = -\frac{ke^2}{r} + \frac{b}{r^9} \tag{1.55}$$

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)** Calculate the potential energy of KCl at its equilibrium spacing ($r_o = 0.279$ nm).

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

$$F(r_o) = -\frac{dU}{dr}\bigg|_{r=r_o} = 0 = \frac{ke^2}{r_o^2} - \frac{9b}{r_o^{10}} \tag{1.56}$$

$$ke^2 r_o^8 = 9b \tag{1.57}$$

$$b = \frac{1}{9}ke^2 r_o^8 \tag{1.58}$$

Substituting this result back into our potential energy expression,

$$PE = U(r) = -\frac{ke^2}{r} + \frac{ke^2 r_o^8}{9r^9} \tag{1.59}$$

Evaluating at equilibrium,

$$U(r_o) = -\frac{ke^2}{r_o} + \frac{ke^2}{9r_o} = -\frac{8ke^2}{9r_o} \approx -4.59\,\text{eV} \tag{1.60}$$

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

$$PE = U(r) = P_o\left[1 - e^{-a(r-r_o)}\right]^2 \tag{1.61}$$

(a) Show that r_o is the atomic spacing and P_o the dissociation energy. **(b)** Calculate the force constant for small oscillations about $r = r_o$.

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

$$\frac{dU}{dr} = 2P_o \left[1 - e^{-a(r-r_o)}\right] \left(ae^{-a(r-r_o)}\right) = 0 \tag{1.62}$$

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

$$0 = 1 - e^{-a(r-r_o)} \qquad \Longrightarrow \qquad r = r_o \tag{1.63}$$

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 $r \to \infty$. Thus,

$$(\text{dissociation energy}) = \left[\lim_{r \to \infty} U(r)\right] - U(r_o) = P_o - 0 = P_o \tag{1.64}$$

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.[vi] We have already calculated the force versus displacement:

$$F(r) = -\frac{dU}{dr} = -2P_o \left[1 - e^{-a(r-r_o)}\right] \left(ae^{-a(r-r_o)}\right) = -2P_o a \left(e^{-a(r-r_o)} - e^{-2a(r-r_o)}\right)$$
$$F(r_o + \delta) = -2P_o a \left(e^{-a\delta} - e^{-2a\delta}\right) \tag{1.65}$$

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

$$F(r_o + \delta) \approx -2P_o a \left(1 - a\delta - 1 + 2a\delta\right) = -\left(2P_o a^2\right)\delta \qquad \Longrightarrow \qquad k = 2P_o a^2 \tag{1.66}$$

Thus, for small displacements from equilibrium, we may treat the molecule as a mass-spring system, with an effective force constant k.

6. *Energetics of diatomic systems IV.* In the potassium iodide molecule, presume that the K and I atoms bond ionically by the transfer of one electron from K to I. **(a)** The ionization energy of K is 4.34 eV, and the electron affinity of I is 3.06 eV. What energy is needed to transfer an electron from K to I, to form K^+ and I^- ions from neutral atoms? This is sometimes called the activation energy E_a. **(b)** Another model potential energy function for the KI molecule is the Lennard-Jones

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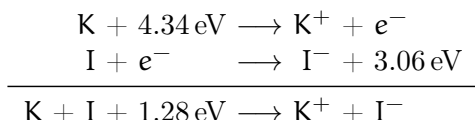[vi]Equivalently, we could show $U(\delta) \approx \frac{1}{2}k\delta^2$.

potential:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] + E_a \tag{1.67}$$

where r is the internuclear separation distance, and σ and ϵ are adjustable parameters. The E_a term is added to ensure correct asymptotic behavior at large r. At the equilibrium separation distance $r = r_o = 0.305\,\text{nm}$, $U(r)$ is a minimum, and $U(r_o) = -3.37\,\text{eV}$ is the negative of the dissociation energy. Evaluate σ and ϵ. **(c)** Calculate the force needed to break up a KI molecule. **(d)** Calculate the force constant for small oscillations about $r = r_o$. *Hint: Set $r = r_o + \delta$, where $\delta/r_o \ll 1$ and expand $U(r)$ in powers of δ/r_o up to second-order terms.*

In order to transfer an electron, we must add the ionization energy of K to remove its electron, but we will gain back the electron affinity of I once it has an extra electron. Thus, the net energy required is

$$(\text{ionization energy K}) - (\text{electron affinity I}) = 4.34\,\text{eV} - 3.06\,\text{eV} = 1.28\,\text{eV} \tag{1.68}$$

Put another way, the following two reactions must occur and balance:

$$
\begin{aligned}
\text{K} + 4.34\,\text{eV} &\longrightarrow \text{K}^+ + e^- \\
\text{I} + e^- &\longrightarrow \text{I}^- + 3.06\,\text{eV} \\
\hline
\text{K} + \text{I} + 1.28\,\text{eV} &\longrightarrow \text{K}^+ + \text{I}^-
\end{aligned}
$$

Thus, an activation energy of $1.28\,\text{eV}$ is required.

We can find σ by enforcing the condition $\frac{dU}{dr}\big|_{r=r_o} = 0$:

$$\frac{dU}{dr}\bigg| r = r_o = 4\epsilon \left[\frac{12\sigma^{12}}{r_o^{13}} - \frac{6\sigma^6}{r_o^7} \right] = 0 \tag{1.69}$$

$$\frac{12\sigma^{12}}{r_o^{13}} = \frac{6\sigma^6}{r_o^7} \tag{1.70}$$

$$2\sigma^6 = r_o^6 \tag{1.71}$$

$$\sigma = 2^{-1/6} r_o \approx 0.272\,\text{nm} \tag{1.72}$$

Knowing σ, we can find ϵ by evaluating $U(r_o)$, since we are given $U(r_o) = -E_{\text{diss}} = -3.37\,\text{eV}$.

$$U(r_o) = 4\epsilon \left[\left(2^{-1/6} \right)^{12} - \left(2^{-1/6} \right)^6 \right] + E_a = -\epsilon + E_a = -E_{\text{diss}} \tag{1.73}$$

$$\implies \quad \epsilon = -(E_{\text{diss}} + E_a) \approx 4.65\,\text{eV} \tag{1.74}$$

In order to find the force required to break up the molecule, we should first calculate the maximum restoring force that the molecule is able to respond with. If we exceed that force, the molecule will

be broken.

$$F = -\frac{dU}{dr} = 4\epsilon \left[\frac{12\sigma^{12}}{r^{13}} - \frac{6\sigma^6}{r^7} \right] \tag{1.75}$$

This function has a clear maximum, which we can find by setting $dF/dr = 0$:

$$\frac{dF}{dr} = 4\epsilon \left[\frac{-156\sigma^{12}}{r^{14}} + \frac{42\sigma^6}{r^8} \right] = \frac{4\epsilon}{\sigma^2} \left[-156 \left(\frac{\sigma}{r} \right)^{14} + 42 \left(\frac{\sigma}{r} \right)^8 \right] = 0$$

$$\implies \quad r = \left(\frac{156}{42} \right)^{1/6} \sigma \approx 0.338 \, \text{nm} \tag{1.76}$$

Applying the second derivative test, or quick graph, will verify that this is a maximum. Thus,

$$F_{\text{max}} = F\left(\left(\frac{156}{42} \right)^{1/6} \sigma \right) = 4\epsilon \left[12 \left(\frac{42}{156} \right)^{13/6} - \left(\frac{42}{156} \right)^{7/6} \right] \approx 6.55 \, \text{nN} \tag{1.77}$$

Thus, the molecule can apply a maximum restoring force of about $6.55 \, \text{nN}$, so exceeding this force will break up the molecule.

In order to find the force constant for small oscillations, we must either show that $F(r_o + \delta) \approx -k\delta$ or $U(r_o + \delta) \approx \frac{1}{2}k\delta^2$ for small displacements δ from equilibrium. The basic tactic is always the same: if the displacement is small compared to the equilibrium distance, $\delta/r_o \ll 1$, then we should write the potential or force in such a way to use an expansion in δ/r_o.

Starting from the potential:

$$U(r_o + \delta) = 4\epsilon \left[\left(\frac{\sigma}{r_o + \delta} \right)^{12} - \left(\frac{\sigma}{r_o + \delta} \right)^6 \right] + E_a = 4\epsilon \left[\left(\frac{2^{-1/6}r_o}{r_o + \delta} \right)^{12} - \left(\frac{2^{-1/6}r_o}{r_o + \delta} \right)^6 \right] + E_a$$

$$= 4\epsilon \left[\frac{1}{4} \left(\frac{r_o}{r_o + \delta} \right)^{12} - \frac{1}{2} \left(\frac{r_o}{r_o + \delta} \right)^6 \right] + E_a$$

$$= 4\epsilon \left[\frac{1}{4} \left(\frac{1}{1 + \frac{\delta}{r_o}} \right)^{12} - \frac{1}{2} \left(\frac{1}{1 + \frac{\delta}{r_o}} \right)^6 \right] + E_a \tag{1.78}$$

Since $\delta/r_o \ll 1$, we may use the binomial expansion to simplify, viz., $(1 + \delta/r_o)^n \approx 1 + n\delta/r_o + \frac{1}{2}n(n-1)\delta^2/r_o^2$, keeping terms up to 2nd order.

$$U(r_o + \delta) = 4\epsilon \left[\frac{1}{4} \left(\frac{1}{1 + \frac{\delta}{r_o}} \right)^{12} - \frac{1}{2} \left(\frac{1}{1 + \frac{\delta}{r_o}} \right)^6 \right] + E_a$$

$$\approx 4\epsilon \left[\frac{1}{4} \left(1 - 12\frac{\delta}{r_o} + \frac{12 \cdot 11}{2}\frac{\delta^2}{r_o^2} \right) - \frac{1}{2} \left(1 - 6\frac{\delta}{r_o} + \frac{6 \cdot 5}{2}\frac{\delta^2}{r_o^2} \right) \right] + E_a$$

$$\approx \epsilon \left[-1 + 36\frac{\delta^2}{r_o^2} \right] + E_a = (E_a - \epsilon) + \frac{1}{2} \left(\frac{72\epsilon}{r_o^2} \right) \delta^2 = U(r_o) + \frac{1}{2} \left(\frac{72\epsilon}{r_o^2} \right) \delta^2 \qquad (1.79)$$

Thus, $k = 72\epsilon/r_o^2 \approx 3600\,\text{eV/nm} \approx 576\,\text{N/m}$. One can just as easily start with the force expression to arrive at the same result, except that now we need only keep terms to first order in the binomial expansion:

$$F(r_o + \delta) = 4\epsilon \left[\frac{12\sigma^{12}}{(r_o + \delta)^{13}} - \frac{6\sigma^6}{(r_o + \delta)^7} \right] = 4\epsilon \left[12\frac{\frac{1}{4}r_o^{12}}{(r_o + \delta)^{13}} - 6\frac{\frac{1}{2}r_o^6}{(r_o + \delta)^7} \right]$$

$$= 4\epsilon \left[\frac{3}{r_o} \left(1 + \frac{\delta}{r_o} \right)^{-13} - \frac{3}{r_o} \left(1 + \frac{\delta}{r_o} \right)^{-7} \right]$$

$$\approx 4\epsilon \left[\frac{3}{r_o} \left(1 - 13\frac{\delta}{r_o} \right) - \frac{3}{r_o} \left(1 - 7\frac{\delta}{r_o} \right) \right] = - \left(\frac{72\epsilon}{r_o^2} \right) \delta \qquad (1.80)$$

Again, the conclusion is $k = 72\epsilon/r_o^2$.

7. *Crystal lattice energy.* Consider a one-dimensional chain of alternating positive and negative ions. Show that the potential energy associated with one of the ions and its interactions with the rest of this hypothetical crystal is

$$U(r) = -k_e \alpha \frac{e^2}{r} \qquad (1.81)$$

where the Madelung constant is $\alpha = 2\ln 2$ and r is the interionic spacing. *Hint: the series expansion for* $\ln(1 + x)$ *may prove useful in evaluating an infinite sum.*

Pick any positive ion $+e$ as the origin. Immediately to the right at a distance r, we have a negative ion $-e$. The potential energy of this pair is $-ke^2/r$. One more lattice spacing to the right, a distance $2r$ from the origin, is another negative ion, whose potential energy with the ion at the origin is $ke^2/2r$. Continuing in this way, all ions to the right-hand side of the ion at the origin give us a potential energy

$$U_{\text{RHS}} = -\frac{ke^2}{r} + \frac{ke^2}{2r} - \frac{ke^2}{3r} + \ldots = \frac{ke^2}{r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} = -\frac{ke^2}{r} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \qquad (1.82)$$

To the left-hand side of the origin, there are just as many ions in the same arrangement, giving us

the same contribution to the potential energy. Thus,

$$U_{\text{tot}} = 2U_{\text{RHS}} = -2\frac{ke^2}{r}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} \tag{1.83}$$

The series we must evaluate is then

$$\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} \tag{1.84}$$

This is known as the *alternating harmonic series*, and is known to evaluate to $\ln 2$. This can be seen readily from the Taylor expansion for $\ln(1+x)$:

$$\ln(1+x) = \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}x^n \qquad \Longrightarrow \qquad \ln(2) = \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} \tag{1.85}$$

Thus, the potential energy is

$$U_{\text{tot}} = 2U_{\text{RHS}} = -2\frac{ke^2}{r}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} = -k_e\alpha\frac{e^2}{r} \qquad \text{with} \qquad \alpha = 2\ln 2 \tag{1.86}$$

8. A phenomenological expression for the potential energy of a bond as a function of spacing is given by

$$U(r) = \frac{A}{r^n} - \frac{B}{r^m} \tag{1.87}$$

For a stable bond, $m < n$. Show that the molecule will break up when the atoms are pulled apart to a distance

$$r_b = \left(\frac{n+1}{m+1}\right)^{1/(n-m)} r_o \tag{1.88}$$

where r_o is the equilibrium spacing between the atoms. Be sure to note your criteria for breaking used to derive the above result.

The potential $U(r)$ has an associated force, the molecule's restoring force:

$$F(r) = -\frac{dU}{dr} \tag{1.89}$$

The molecule will break when its maximum restoring force is reached, when $dF/dr = -d^2U/dr^2 = 0$. Equilibrium is when $F = -dU/dr = 0$. At the equilibrium spacing r_o, the force is zero, or equivalently, the potential is at a minimum.

$$F(r_o) = -\left.\frac{dU}{dr}\right|_{r_o} = \frac{nA}{r_o^{n+1}} - \frac{mB}{r_o^{m+1}} = 0 \tag{1.90}$$

$$\frac{nA}{mB} = \frac{r_o^{n+1}}{r_o^{m+1}} = r_o^{n-m} \tag{1.91}$$

$$r_o = \left(\frac{nA}{mB}\right)^{\frac{1}{n-m}} \tag{1.92}$$

Is this really a minimum for U? We can check with the second derivative test: if $d^2U/dr^2 = -dF/dr > 0$ at r_o, have a maximum. We will need dF/dr shortly anyway. You didn't really need to do this on your homework, but it is instructive:

$$-\frac{dF}{dr} = \frac{d^2U}{dr^2} = \frac{n(n+1)A}{r^{n+2}} - \frac{m(m+1)B}{r^{m+2}} \tag{1.93}$$

$$\left.\frac{d^2U}{dr^2}\right|_{r_o} = n(n+1)A\left(\frac{mB}{nA}\right)^{\frac{n+2}{n-m}} - m(m+1)B\left(\frac{mB}{nA}\right)^{\frac{m+2}{n-m}} \tag{1.94}$$

$$= \left(\frac{mB}{nA}\right)^2\left[n(n+1)A\left(\frac{mB}{nA}\right)^{\frac{n}{n-m}} - m(m+1)B\left(\frac{mB}{nA}\right)^{\frac{m}{n-m}}\right] \tag{1.95}$$

$$= \left(\frac{mB}{nA}\right)^2\left(\frac{mB}{nA}\right)^{\frac{n}{n-m}}\left[n(n+1)A - m(m+1)B\left(\frac{mB}{nA}\right)^{\frac{m-n}{n-m}}\right] \tag{1.96}$$

$$= \left(\frac{mB}{nA}\right)^2\left(\frac{mB}{nA}\right)^{\frac{n}{n-m}}\left[n(n+1)A - m(m+1)B\left(\frac{nA}{mB}\right)\right] \tag{1.97}$$

$$= \left(\frac{mB}{nA}\right)^{\frac{n+2}{n-m}}\left[n(n+1)A - n(m+1)A\right] \tag{1.98}$$

$$= nA\left(\frac{mB}{nA}\right)^{\frac{n+2}{n-m}}\left[n-m\right] > 0 \tag{1.99}$$

Clearly, the only way this expression will be positive is if $n > m$, which means stable bonds have $n > m$ as the problem states. This means that the repulsive force has a higher index than the attractive force, and it is of shorter range.

What about breaking the molecule? For distances smaller than r_o, the force is repulsive, while for distances greater than r_o it is attractive – in either case, it serves to try and restore the equilibrium position. However, the competition between the shorter-range repulsive force and longer-range attractive force means that there is a critical distortion of the molecule for $r > r_o$ at which the force is maximum, and any stronger force (or larger displacement) will separate the constituents to an arbitrarily large distance – the molecule will be broken.

We have the force between the molecular constituents above:

$$F(r) = \frac{nA}{r^{n+1}} - \frac{mB}{r^{m+1}} \tag{1.100}$$

so we can readily calculate the maximum force with which the bond may try to restore its equilibrium. The force above is the force with which the molecule will respond if we push or pull on it. The maximum force will occur when $dF/dr=0$, at a radius r_b

$$\frac{dF}{dr}\Bigg|_{r_b} = \frac{n(n+1)A}{r_b^{n+2}} - \frac{m(m+1)B}{r_b^{m+2}} = 0 \tag{1.101}$$

$$\frac{n(n+1)A}{m(m+1)B} = \frac{r_b^{n+2}}{r_b^{m+2}} = r_b^{n-m} \tag{1.102}$$

$$r_b = \left(\frac{n(n+1)}{m(m+1)B}\right)^{\frac{1}{n-m}} = \left(\frac{nA}{mB}\right)^{\frac{1}{n-m}} \left(\frac{n+1}{m+1}\right)^{\frac{1}{n-m}} \tag{1.103}$$

Now, how do we know this is the *maximum* force, and not a minimum force? We grind through another derivative ... we must have $d^2F/dr^2 > 0$ for a maximum:

$$\frac{d^2F}{dr^2} = \frac{n(n+1)(n+2)A}{r^{n+3}} - \frac{m(m+1)(m+2)B}{r^{m+3}} = r^{n+3}\left[n(n+1)(n+2)A - \frac{m(m+1)(m+2)B}{r^{m-n}}\right]$$

$$\frac{d^2F}{dr^2}\Bigg|_{r_b} = r_o^{n+3}\left(\frac{n+1}{m+1}\right)^{\frac{n+3}{n-m}}\left[n(n+1)(n+2)A - m(m+1)(m+2)Br_o^{n-m}\left(\frac{n+1}{m+1}\right)^{\frac{n-m}{n-m}}\right]$$

$$= r_o^{n+3}\left(\frac{n+1}{m+1}\right)^{\frac{n+3}{n-m}}\left[n(n+1)(n+2)A - m(m+1)(m+2)Br_o^{n-m}\right] \tag{1.104}$$

$$= r_o^{n+3}\left(\frac{n+1}{m+1}\right)^{\frac{n+3}{n-m}}\left[n(n+1)(n+2)A - m(n+1)(m+2)B\left(\frac{nA}{mB}\right)\right] \tag{1.105}$$

$$= r_o^{n+3}\left(\frac{n+1}{m+1}\right)^{\frac{n+3}{n-m}}\left[n(n+1)(n+2)A - n(n+1)(m+2)A\right] \tag{1.106}$$

$$= An(n+1)r_o^{n+3}\left(\frac{n+1}{m+1}\right)^{\frac{n+3}{n-m}}\left[n-m\right] > 0 \tag{1.107}$$

For the second to last line, we noted that $r_o^{n-m} = nA/mB$. Once again, if $n > m$, the second derivative is positive, and thus the force is maximum at r_b. Applying a force sufficiently strong to stretch the bond to a separation r_b will serve to break it. Incidentally, the maximum force required is

$$F(r_b) = \frac{nA}{r_o^{n+1}} \left(\frac{n+1}{m+1}\right)^{\frac{n+1}{m-n}} - \frac{mB}{r_o^{m+1}} \left(\frac{n+1}{m+1}\right)^{\frac{m+1}{m-n}} = \left(\frac{n+1}{m+1}\right)^{\frac{n+1}{m-n}} \left[\frac{nA}{r_o^{n+1}} - \frac{mB}{r_o^{m+1}} \left(\frac{n+1}{m+1}\right)\right]$$

$$= \left(\frac{n+1}{m+1}\right)^{\frac{n+1}{m-n}} \left[nA \left(\frac{nA}{mB}\right)^{\frac{n+1}{m-n}} - mB \left(\frac{nA}{mB}\right)^{\frac{m+1}{m-n}} \left(\frac{n+1}{m+1}\right)\right] \tag{1.108}$$

$$= \left(\frac{n+1}{m+1}\right)^{\frac{n+1}{m-n}} \left(\frac{nA}{mB}\right)^{\frac{n+1}{m-n}} \left[nA - nA \left(\frac{n+1}{m+1}\right)\right] \tag{1.109}$$

$$= nA \left(\frac{n+1}{m+1}\right)^{\frac{n+1}{m-n}} \left(\frac{nA}{mB}\right)^{\frac{n+1}{m-n}} \left(\frac{m-n}{m+1}\right) = \frac{nA}{r_b^{n+1}} \left(\frac{m-n}{m+1}\right) \tag{1.110}$$