Problem Set 2

Chemical Bonding, Thermal Expansion, Normal Modes, Phonons in 1d

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2.1. Chemical Bonding

(a) Qualitatively describe five different types of chemical bonds and why they occur.

▷ Describe which combinations of what types of atoms are expected to form which types of bonds (make reference to location on the periodic table).

▷ Describe some of the qualitative properties of materials that have these types of bonds.

(Yes, you can just copy the table out of the notes, but the point of this exercise is to learn the information in the table!)

(b) Describe qualitatively the phenomenon of Van der Waals forces. Explain why the force is attractive and proportional to $1/R^7$ where R is the distance between two atoms.

2.2. Covalent Bonding in Detail*

(a) **Linear Combination of Atomic Orbitals (LCAO)** In class we considered two atoms each with a single atomic orbital. We called the orbital $|1\rangle$ around nucleus 1 and $|2\rangle$ around nucleus 2. More generally we may consider any set of wavefunctions $|n\rangle$ for $n = 1, \ldots, N$. For simplicity, let us assume this basis is orthonormal $\langle n|m\rangle = \delta_{n,m}$

Let us write a trial wavefunction for our ground state as

$$|\Psi\rangle = \sum_n \phi_n |n\rangle$$

This is known as a linear combination of atomic orbitals (LCAO). We would like to find the lowest energy wavefunction we can construct in this form, that is the best approximation to the actual ground state wavefunction. (The more states we use in our basis, generally, the more accurate our results will be).

We claim that the the ground state is given by the solution of the effective Schroedinger equation

$$\mathcal{H}\,\boldsymbol{\phi} = E\,\boldsymbol{\phi} \tag{1}$$

where $\boldsymbol{\phi}$ is the vector of N coefficients ϕ_n, and $\mathcal{H}$ is the N by N matrix

$$\mathcal{H}_{n,m} = \langle n|H|m\rangle$$

with H the Hamiltonian of the full system we are considering.

To prove this, let us construct the energy

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

▷ Show that minimizing this energy with respect to each ϕ_n gives the same eigenvalue equation, Eq. 1. (Caution: ϕ_n is generally complex! If you are not comfortable with complex differentiation, write everything in terms of real and imaginary parts of each ϕ_n). Similarly, the second eigenvalue of the effective Schroedinger equation will be an approximation to the first excited state of the system.

This technique is know as the molecular orbital approach, or the LCAO (linear combination of atomic orbitals) approach. It is used heavily in numerical simulation of molecules. However, more generally, one cannot assume that the basis set of orbitals is orthonormal. In problem A.2.1. we properly consider a non-orthonormal basis.

(b) **Two-orbital covalent bond** Let us return to the case where there are only two orbitals in our basis. This pertains to a case where we have two identical nuclei and a single electron which will be shared between them to form a covalent bond. We write the full Hamiltonian as

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r} - \mathbf{R_1}) + V(\mathbf{r} - \mathbf{R_2}) = K + V_1 + V_2$$

where V is the Coulomb interaction between the electron and the nucleus, R_1 is the position of the first nucleus and R_2 is the position of the second nucleus. Let ϵ be the energy of the atomic orbital around one nucleus in the absence of the other. In other words

$$\begin{aligned}(K + V_1)|1\rangle &= \epsilon|1\rangle \\ (K + V_2)|2\rangle &= \epsilon|2\rangle\end{aligned}$$

Define also the cross-energy element

$$V_{cross} = \langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle$$

and the hopping matrix element

$$t = -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle$$

These are not typos!

▷ Why can we write V_{cross} and t equivalently using either one of the expressions given on the right hand side?

▷ Show that the eigenvalues of our Schroedinger equation Eq. 1 are given by

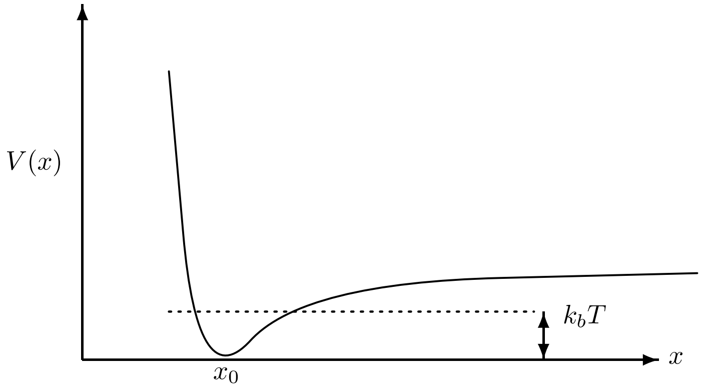
$$E = \epsilon + V_{cross} \pm |t|$$

▷ Argue (perhaps using Gauss's law) that V_{cross} should roughly cancel the repulsion between nuclei, so that, in the lower eigenstate the total energy is indeed lower when the atoms are closer together.

▷ This approximation must fail when the atoms get sufficiently close. Why?

2.3. Thermal Expansion

As a model of thermal expansion, we study the distance between two nearest neighbor atoms in an anharmonic potential that looks roughly like this



where x is the distance between the two neighboring atoms. This potential can be expanded around its minimum as

$$V(x) = \frac{\kappa}{2}(x - x_0)^2 - \frac{\kappa_3}{3!}(x - x_0)^3 + \ldots \tag{2}$$

where the minimum is at position x_0 and $\kappa_3 > 0$. For small energies, we can truncate the series at the cubic term.

(a) A very accurate approximate form for inter-atomic potentials (particularly for inert atoms such as Helium or Argon) is given by the so-called Lennard-Jones potential

$$V(x) = 4\epsilon \left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6} \right] \tag{3}$$

where ϵ and σ are constants that depend on the particular atoms we are considering.

$\triangleright$ What is the meaning of the exponent 6 in the second term of this expression. (i.e., why is the exponent necessarily chosen to be 6).

$\triangleright$ By expanding Eq. 3 around its minimum, and comparing to Eq. 2, calculate the values of the coefficients x_0, κ, and κ_3 for the Lennard-Jones potential in terms of the constants ϵ and σ. We will need these results below.

(b) **Classical model:**

(i) In classical statistical mechanics, we write the expectation of x as

$$\langle x \rangle_\beta = \frac{\int dx\, x\, e^{-\beta V(x)}}{\int dx\, e^{-\beta V(x)}}$$

Although one cannot generally do such integrals for arbitrary potential $V(x)$ as in Eq. 2, one can expand the exponentials as

$$e^{-\beta V(x)} = e^{-\frac{\beta\kappa}{2}(x-x_0)^2} \left[1 + \frac{\beta\kappa_3}{6}(x - x_0)^3 + \ldots \right]$$

and let limits of integration go to $\pm\infty$

$\triangleright$ Why is this expansion of the exponent and the extension of the limits of integration allowed?

$\triangleright$ Use this expansion to derive $\langle x \rangle_\beta$ to lowest order in κ_3, and hence show that the coefficient of thermal expansion is

$$\alpha = \frac{1}{L}\frac{dL}{dT} \approx \frac{1}{x_0}\frac{d\langle x \rangle_\beta}{dT} = \frac{1}{x_0}\frac{k_b\,\kappa_3}{2\kappa^2}$$

with k_b Boltzmann's constant.

$\triangleright$ In what temperature range is the above expansion valid?

(ii) For Argon, the the Lennard-Jones constants ϵ from Eq. 3 is given by $\epsilon = 10\text{meV}$

$\triangleright$ Estimate the thermal expansion coefficient α of Argon. Note: *You can do this part even if you got stuck on some of the above parts!*

The actual thermal expansion coefficient of Argon is approximately $\alpha = 2 \times 10^{-3}/\text{K}$ at about 80 K. However at lower temperature α drops quickly. We will use a more sophisticated quantum model to understand why this is so.

(iii) While this model of thermal expansion in a solid is valid if there are only two atoms, why is it invalid for the case of a many-atom chain? (Although it is not so bad as an approximation!)

(c) **Quantum model:**

(i) In quantum mechanics we write a Hamiltonian

$$H = H_0 + V$$

where

$$H_0 = \frac{p^2}{2m} + \frac{\kappa}{2}(x - x_0)^2 \tag{4}$$

is the Hamiltonian for the free Harmonic oscillator, and V is the perturbation

$$V = -\frac{\kappa_3}{6}(x - x_0)^3 + \ldots$$

where we will throw out quartic and higher terms.

▷ What value of m should be used in Eq. 4?

Using perturbation theory it can be shown that, to lowest order in κ_3 the following equation holds

$$\langle n|x|n\rangle = x_0 + E_n \kappa_3/(2\kappa^2) \tag{5}$$

where $|n\rangle$ is the eigenstate of the Harmonic oscillator whose energy is

$$E_n = \hbar\omega(n + \frac{1}{2}) + \mathcal{O}(\kappa_3) \qquad n \geq 0$$

with $\omega = \sqrt{\kappa/m}$. In (iii) below we will prove Eq. 5. For now, take it as given.

▷ Note that even when the oscillator is in its ground state, the expectation of x deviates from x_0. Physically why is this?

(ii)* Use, Eq. 5 to calculate the quantum expectation of x at any temperature. We write

$$\langle x\rangle_\beta = \frac{\sum_n \langle n|x|n\rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

▷ Derive the coefficient of thermal expansion.

▷ Examine the high temperature limit and show that it matches that of part b above.

▷ In what range of temperatures is our perturbation expansion valid?

▷ In light of the current quantum calculation, when is the above classical calculation valid?

▷ Why does the thermal expansion coefficient drop at low temperature.

(iii)** Prove Eq. 5 above by using lowest order perturbation theory.

It is easiest to perform this calculation by using raising and lowering (ladder) operators. Recall that one can define operators a and $a^\dagger$ such that $[a, a^\dagger] = 1$ and

$$\begin{aligned} a^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle \\ a|n\rangle &= \sqrt{n}|n-1\rangle \end{aligned}$$

In terms of these operators, we have the operator $x - x_0$ given by

$$x - x_0 = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger)$$

2.4. **Classical Normal Modes to Quantum Eigenstates**

In class we stated, without proof that a classical normal mode becomes a quantum eigenstate. Here we prove this fact for a simple diatomic molecule in a potential well. (See also problem A.1.1.)

Consider two particles, each of mass m in one dimension, connected by a spring (K), at the bottom of a potential well (with spring constant k). We write the potential energy as

$$U = \frac{k}{2}(x_1^2 + x_2^2) + \frac{K}{2}(x_1 - x_2)^2$$

▷ Write the classical equations of motion.

▷ Transform into relative $x_{rel} = (x_1 - x_2)$ and center of mass $x_{cm} = (x_1 + x_2)/2$ coordinates.

(a) Show that in these transformed coordinates, the system decouples, thus showing that the two normal modes have frequencies

$$\begin{aligned} \omega_{cm} &= \sqrt{k/m} \\ \omega_{rel} &= \sqrt{(k+2K)/m} \end{aligned}$$

Note that since there are two initial degrees of freedom, there are two normal modes.

Now consider the quantum mechanical version of the same problem. The Hamiltonian is

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U(x_1, x_2)$$

▷ Again transform into relative and center of mass coordinates.

Define the corresponding momenta are given by $p_{rel} = (p_1 - p_2)/2$ and $p_{cm} = (p_1 + p_2)$.

(b) Show that $[p_\alpha, x_\gamma] = -i\hbar\delta_{\alpha,\gamma}$ where α and γ take the values *cm* or *rel*.

(c) In terms of these new coordinates show that the Hamiltonian decouples into two independent harmonic oscillators with the same eigenfrequencies ω_{cm} and ω_{rel}. Conclude that the spectrum of this system is

$$E_{n_{rel}, n_{cm}} = \hbar\omega_{rel}(n_{rel} + \frac{1}{2}) + \hbar\omega_{cm}(n_{cm} + \frac{1}{2})$$

where n_{cm} and n_{rel} are nonnegative integers.

(d) At temperature T what is the expectation of the energy of this system?

In problem A.2.4. the principle that normal modes become quantum eigenstates is proven in more generality.

2.5. **Normal Modes of a One Dimensional Monatomic Chain**

(a)‡ Explain what is meant by “normal mode” and by “phonon”.

▷ Explain briefly why phonons obey Bose statistics.

(b)‡ Derive the dispersion relation for the longitudinal oscillations of a one dimensional mass-and-spring crystal with N identical atoms of mass m, lattice spacing a, and spring constant κ. (Motion of the masses is restricted to be in one dimension).

(c)‡ Show that the mode with wavevector k has the same pattern of mass displacements as the the mode with wavevector $k + 2\pi/a$. Hence show that the dispersion relation is periodic in reciprocal space (k-space).

▷ How many *different* normal modes are there.

(d)‡ Derive the phase and group velocities and sketch them as a function of k.

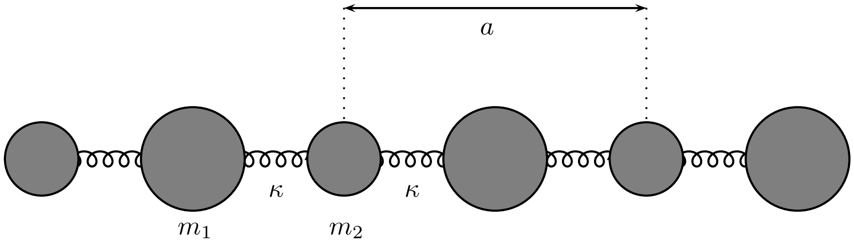
▷ What is the sound velocity?

▷ Show that the the sound velocity is also given by $v_s = \sqrt{\beta^{-1}/\rho}$ where ρ is the chain density and β is the compressibility.

(e) Find the expression for $g(\omega)$, the density of states of modes per angular frequency.

▷ Sketch $g(\omega)$.

2.6. Normal modes of a One Dimensional Diatomic Chain*



(a) What is the difference between an acoustic mode and an optical mode.

▷ Describe how particles move in each case.

(b) Derive the dispersion relation for the longitudinal oscillations of a one dimensional *diatomic* mass-and-spring crystal where the unit cell is of length a and each unit cell contains one atom of mass m_1 and one atom of mass m_2 connected together by springs with spring constant κ (all springs are the same, and motion of particles is in one dimension only).

(c) Determine the frequencies of the acoustic and optical modes at $k = 0$ as well as at the Brillouin zone boundary.

▷ Determine the sound velocity and show that the group velocity is zero at the zone boundary.

▷ Show that the the sound velocity is also given by $v_s = \sqrt{\beta^{-1}/\rho}$ where ρ is the chain density and β is the compressibility.

(d) Sketch the dispersion in both reduced and extended zone scheme.

▷ If there are N unit cells, how many different normal modes are there?

▷ How many *branches* of excitations are there? (I.e., in reduced zone scheme, how many modes are there there at each k).

(e) What happens when $m_1 = m_2$?

2.7. One more problem

Problem 3.8. really belongs to this problem set, but this set is too long already, so I pushed it to the next problem set. If you have extra time, give it a shot.