Problem Set 2

Chemical Bonding, Thermal Expansion, Normal Modes, Phonons and Tightbinding 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.

(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!). 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

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

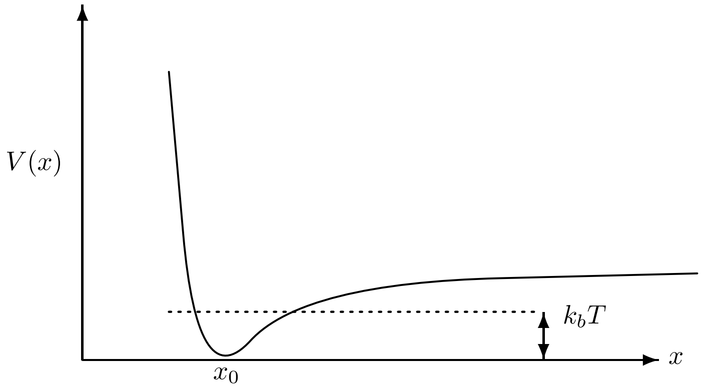
(why can we write V_{cross} and t equivalently using either one of the expressions given on the right hand side?). Show that the eigenvalues of our Schroedinger equation Eq. 1 are given by

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

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

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

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) **Classical model:** 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, one can expand the exponentials as

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

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. In what temperature range is the above expansion valid?

(b) **Quantum model:** In quantum mechanics we write a Hamiltonian

$$H = H_0 + V$$

where

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

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 here?

(i)** (Note: You can solve parts ii and iii below even if you cannot solve this part).

Use perturbation theory to show that to lowest order in κ_3

$$\langle n|x|n\rangle = x_0 + E_n\kappa_3/(2\kappa^2) \qquad (2)$$

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 $\omega = \sqrt{\kappa/m}$.

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

(iii)* Use, Eq. 2 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 *a* 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?

(c) 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?

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.2.3. 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.

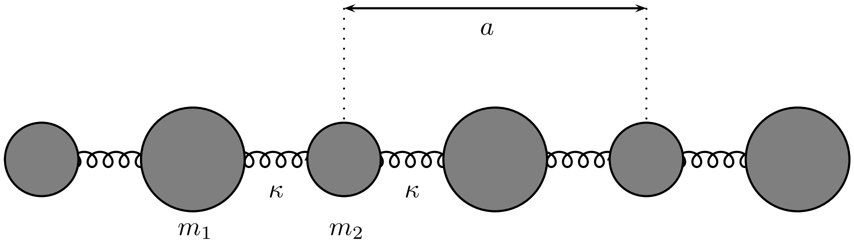
(b)‡ Derive the dispersion relation for the longitudinal oscillations of a one dimensional mass-and-spring crystal with N identical atoms of mass m, lattice spacing a, and spring constant κ. (Motion of the masses is restricted to be in one dimension).

(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).

(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 energies of the acoustic and optical modes at $k = 0$ as well as at the Brillioun 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.

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

2.7. **One Dimensional Tight Binding Model**

(a) **Monatomic Solid:** Consider a one-dimensional tight binding model of electrons hopping between atoms. Let the distance between atoms be called a, and here let us label the atomic orbital on atom n as $|n\rangle$ for $n = 1 \ldots N$ (and you may assume periodic boundary conditions). Suppose there is an on-site energy ϵ and a hopping matrix element $-t$. In other words, suppose $\langle n|H|m\rangle = \epsilon$ for $n = m$ and $\langle n|H|m\rangle = -t$ for $n = m \pm 1$. Derive and sketch the dispersion curve for electrons. (Hint: Use the effective Schroedinger equations of problem 2.2.a) How many different eigenstates are there in this system? What is the effective mass of the electron near the bottom of this band? What is the density of states? If each atom is monovalent (it donates a single electron) what is the density of states at the fermi surface? What then is the Pauli paramagentic (spin) susceptibility of the system? (See problem 1.6.). What is the spin susceptibility if each atom is divalent?

(b) **Diatomic Solid:** Now consider a model of a diatomic solid as such

$$-A-B-A-B-A-B-$$

Suppose that the onsite energy of type A is different from the onsite energy of type B. I.e, $\langle n|H|n\rangle$ is ϵ_A for n being on a site of type A and is ϵ_B for n being on a site of type B. (All hopping matrix elements $-t$ are still identical to each other). Calculate the new dispersion relation. Sketch this dispersion relation in both the reduced and extended zone schemes. What happens in the "atomic" limit when t becomes very small. What is the effective mass of an electron near the bottom of the lower band? If each atom (of either type) is monovalent, is the system a metal or an insulator?