Additional Problems

More problems associated with Problem Set 1

A.1.1. **Diatomic Einstein Solid***

Having studied problem 1.1., consider now a solid made up of diatomic molecules. We can (very crudely) model this as a two particles in three dimensions, connected to each other with a spring, both in the bottom of a harmonic well.

$$H = \frac{\mathbf{p_1}^2}{2m_1} + \frac{\mathbf{p_2}^2}{2m_2} + \frac{k}{2}\mathbf{x_1}^2 + \frac{k}{2}\mathbf{x_2}^2 + \frac{K}{2}(\mathbf{x_1} - \mathbf{x_2})^2$$

Here k is the spring constant holding both particles in the bottom of the well, and K is the spring constant holding the two particles together. Assume that the two particles are distinguishable atoms.

(a) Analogous to problem 1.1. above, calculate the classical partition function and show that the heat capacity is again $3k_B$ per particle (i.e., $6k_B$ total).

(b)Analogous to problem 1.1. above, calculate the quantum partition function and find an expression for the heat capacity. Sketch the heat capacity as a function of temperature if $K \gg k$.

(c)** How does the result change if the atoms are indistinguishable?

For this problem you may find it useful to transform to relative and center-of-mass coordinates. If you find this difficult, for simplicity you may assume that $m_1 = m_2$.

A.1.2. **Another review of free electron theory**

What is the *free electron model* of a metal. Define *Fermi energy* and *Fermi temperature*.

Why do metals held at room temperature feel cold to the touch even though their Fermi temperatures are much higher than room temperature?

A d-dimensional sample with volume L^d contains N electrons and can be described as a free electron model. Show that the Fermi energy is given by

$$E_F = \frac{\hbar^2}{2mL^2}(Na_d)^{2/d}$$

Find the numerical values of a_d for $d = 1, 2$, and 3.

Show also that the density of states at the Fermi energy is given by

$$g(E_F) = \frac{Nd}{2L^d E_F}$$

Assuming the free electron model is applicable, estimate the Fermi energy and Fermi temperature of the following materials:

(a) Copper, a monovalent metal (with face-centered-cubic structure) having four atoms per unit cell, where the side of a unit cell has length 0.361 nm.

(b) A one dimensional organic conductor which has unit cell of length 0.8 nm, where each unit cell contributes one mobile electron.

A.1.3. **Heat Capacity of a Free Electron Gas****

In problem 1.6..a we approximated the heat capacity of a free electron gas (in 3d). Calculate an exact expression for the specific heat of a metal at low temperature. Caution, be careful to account for the fact that the chemical potential is a function of temperature. Note: you will run into some nasty integrals. If you cannot evaluate these integrals you can rewrite them as series whose summation is known.

More problems associated with Problem Set 2

A.2.1. **LCAO Done Right**

(a) In problem 2.2. we introduced the method of linear combination of Atomic orbitals. In that problem we assumed that our basis of orbitals is orthonormal. In this problem we will relax this assumption.

Consider now many orbitals on each atom (and potentially many atoms). Let us write

$$|\psi\rangle = \sum_{i=1}^{N} \phi_i |i\rangle$$

for an arbitrary number N of orbitals. Let us write the N by N overlap matrix $\mathcal{S}$ whose elements are

$$\mathcal{S}_{i,j} = \langle i|j\rangle$$

In this case do NOT assume that $\mathcal{S}$ is diagonal.

Using a similar method as in problem 2.2., derive the new "Schroedinger equation"

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

With the same notation for $\mathcal{H}$ and ϕ as in problem 2.2.. This equation is known as a "generalized eigenvalue problem" because of the $\mathcal{S}$ on the right hand side.

(b)** Let us now return to the situation with only two atoms and only one orbital on each atom but such that $\langle 1|2\rangle = \mathcal{S}_{1,2} \neq 0$. Without loss of generality we may assume $\langle i|i\rangle = 1$ and $S_{1,2}$ is real. If the atomic orbitals are s-orbitals then we may assume also that t is real and positive (why?).

Use the above Eq. 1 to derive the eigenenergies of the system. Argue again the the energy gained in the bonding orbital is sufficient to overcome the repulsion between nuclei.

A.2.2. **LCAO and the Ionic-Covalent Crossover**

(a) For problem 2.2..b consider now the case where the atomic orbitals $|1\rangle$ and $|2\rangle$ have unequal energies $\epsilon_{0,1}$ and $\epsilon_{0,2}$. As the difference in these two energies increases show that the bonding orbital becomes more localized on the lower energy atom. (For simplicity you may use the orthogonality assumption $\langle 1|2\rangle = 0$). Explain how this calculation can be used to describe a crossover between covalent and ionic bonding.

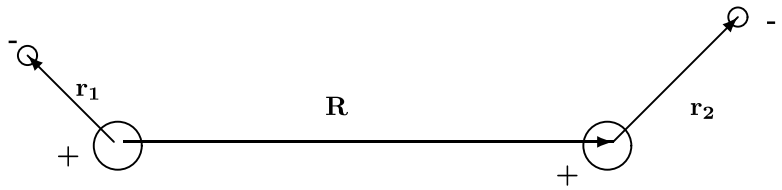
A.2.3. **Van der Waals Bonding in Detail***

(a) *Here we will do a much more precise calculation of the van der Waals force between two hydrogen atoms. First, let the position of the two nuclei be separated by a vector $\mathbf{R}$ as

shown in the figure. Let us write the Hamiltonian for both atoms (assuming fixed positions of nuclei) as

$$\begin{aligned} H &= H_0 + H_1 \\ H_0 &= \frac{\mathbf{p_1}^2}{2m} + \frac{\mathbf{p_2}^2}{2m} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r_1}|} - \frac{e^2}{4\pi\epsilon_0|\vec{r}_2|} \\ H_1 &= \frac{e^2}{4\pi\epsilon_0|\mathbf{R}|} + \frac{e^2}{4\pi\epsilon_0|\mathbf{R}+\mathbf{r_1}+\mathbf{r_2}|} - \frac{e^2}{4\pi\epsilon_0|\mathbf{R}+\mathbf{r_1}|} - \frac{e^2}{4\pi\epsilon_0|\mathbf{R}+\mathbf{r_2}|} \end{aligned}$$

as shown in the figure



Here H_0 is the Hamiltonian for two noninteracing hydrogen atoms, and H_1 is the interaction between the atoms.

Without loss of generality, let us assume that $\mathbf{R}$ is in the $\hat{x}$ direction. Show that for large $\vec{R}$ and small $\vec{r}_i$, the interaction Hamiltonian can be written as

$$H_1 = \frac{e^2}{4\pi\epsilon_0|\mathbf{R}|^3}(z_1z_2 + y_1y_2 - 2x_1x_2) + \mathcal{O}(1/R^4)$$

where x_i, y_i, z_i are the components of $\mathbf{r_i}$. Show that this is just the interaction between two dipoles.

(b) **Perturbation Theory:** The eigenvalues of H_0 can be given as the eigenvalues of the two atoms separately. Recall that the eigenstates of hydrogen are written in the usual notation as $|n, l, m\rangle$ and have energies $E_n = -\mathrm{Ry}/n^2$ with $\mathrm{Ry} = me^4/(32\pi^2\epsilon_0^2\hbar^2) = e^2/(8\pi\epsilon_0 a_0)$ the Rydberg (Here $l \geq 0$, $|m| \leq l$ and $n \geq l+1$). Thus the eigenstates of H_0 are written as $|n_1, l_l, m_1; n_2, l_2, m_2\rangle$ with energies $E_{n_1,n_2} = -\mathrm{Ry}(1/n_1^2 + 1/n_2^2)$. The ground state of H_0 is $|1,0,0;1,0,0\rangle$. Perturbing H_0 with the interaction H_1, show that to first order in H_1 there is no change in the ground state energy. Thus conclude that the leading correction to the energy ground state energy is proportional to $1/R^6$ (and hence the force is proportional to $1/R^7$). Recalling second order perturbation theory show that we have a correction to the total energy given by

$$\delta E = \sum_{n_1,n_2,l_1,l_2,m_1,m_2} \frac{|<1,0,0;1,0,0|\ H_1\ |n_1,l_l,m_1;n_2,l_2,m_2\rangle|^2}{E_{0,0} - E_{n_1,n_2}}$$

Show that the force must be attractive.

(c)* **Bounding the binding energy:** First, show that the numerator in this expression is zero if either $n_1 = 1$ or $n_2 = 1$. Thus the smallest E_{n_1,n_2} that appears in the denominator is $E_{2,2}$. If we replace E_{n_1,n_2} in the denominator with $E_{2,2}$ then the $|\delta E|$ we calculate will be greater than than the $|\delta E|$ in the exact calculation. On the other hand, if we replace E_{n_1,n_2} by 0, then we the $|\delta E|$ will always be less than the δE of the exact calculation. Make these replacements, and perform the remaining sum by identifying a complete set. Derive the bound

$$\frac{6e^2a_0^5}{4\pi\epsilon_0 R^6} \leq |\delta E| \leq \frac{8e^2a_0^5}{4\pi\epsilon_0 R^6}$$

You will need the matrix element for a hydrogen atom

$$\langle 1,0,0|x^2|1,0,0\rangle = a_0^2$$

where $a_0 = 4\pi\epsilon_0\hbar^2/(me^2)$ is the Bohr radius. (This last identity is easy to derive if you remember that the ground state wavefunction of a hydrogen atom is proportional to $e^{-r/2a_0}$).

A.2.4. **General Proof That Normal Modes Become Quantum Eigenstates** This proof generalizes the argument given in problem 2.4.. Consider a set of N particles $a = 1, \ldots N$ with masses m_p interacting via a potential

$$U = \frac{1}{2}\sum_{a,b} x_a V_{a,b} x_b$$

where x_a is the deviation of the position of particle a from its equilibrium position and V can be taken (without loss of generality) to be a symmetric matrix. (Here we consider a situation in 1d, however, we will see that to go to 3d we just need to keep track of 3 times as many coordinates).

(i) Defining $y_a = \sqrt{m_a}x_a$ show that the classical equations of motion may be written as

$$\ddot{y}_a = -\sum_b S_{a,b}\, y_b$$

where

$$S_{a,b} = \frac{1}{\sqrt{m_a}} V_{a,b} \frac{1}{\sqrt{m_b}}$$

Thus show that the solutions are

$$y_a^{(m)} = e^{-i\omega_m t} s_a^{(m)}$$

where ω_m is the m^{th} eigenvalue of the matrix S with corresponding eigenvector $s_a^{(m)}$. These are the N normal modes of the system.

(ii) Recall the orthogonality relations for eigenvectors of hermitian matrices

$$\sum_a [s_a^{(m)}]^* [s_a^{(n)}] = \delta_{m,n} \tag{2}$$

$$\sum_m [s_a^{(m)}]^* [s_b^{(m)}] = \delta_{a,b} \tag{3}$$

Since S is symmetric as well as hermitian, the eigenvectors can be taken to be real. Construct the transformed coordinates

$$Y^{(m)} = \sum_a s_a^{(m)} x_a \sqrt{m_a} \tag{4}$$

$$P^{(m)} = \sum_a s_a^{(m)} p_a/\sqrt{m_a} \tag{5}$$

show that these coordinates have canonical commutations

$$[P^{(m)}, Y^{(n)}] = -i\hbar\delta_{n,m} \tag{6}$$

and show that in terms of these new coordinates the Hamiltonian is rewritten as

$$H = \sum_m \left[\frac{1}{2}[P^{(m)}]^2 + \frac{1}{2}\omega_m^2 [Y^{(m)}]^2 \right] \tag{7}$$

Conclude that the quantum eigenfrequencies of the system are also ω_m. (Can you derive this result from the prior two equations?)

More problems associated with Problem Set 3

A.3.1. **And More X-ray scattering**

A sample of Aluminum powder is put in an Debye-Scherrer X-ray diffraction device. The incident X-ray radiation is from Cu-Ka Xray transition (this just means that the wavelength is l = 1.54 Angstrom)

The following scattering angles were observed:

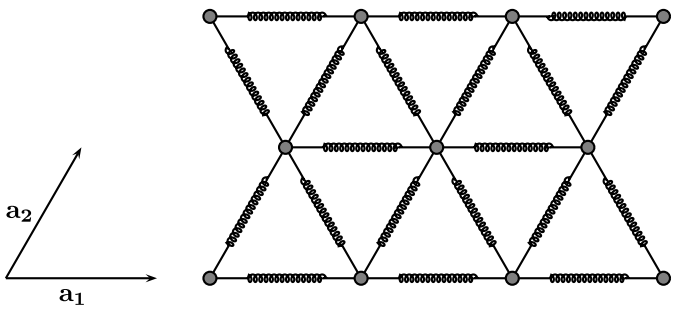
19.48° 22.64° 33.00° 39.68° 41.83° 50.35° 57.05° 59.42°

Given also that the atomic weight of Al is 27, and the density is 2.7 g/cm^3, use this information to calculate Avagadros number. How far off are you? What causes the error?

A.3.2. **Still More X-ray scattering**

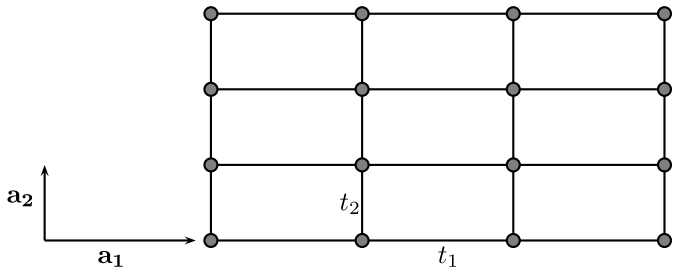
The unit cell dimension for a particular b.c.c. solid is 2.4 Angstrom. Two orders of diffraction are observed. What is the minimum Energy of the neutrons? At what T would such neutrons be dominant If the distribution is Maxwell Boltzmann.

A.3.3. **Phonons in 2d**



Consider a mass and spring model of a two dimensional triangular lattice (assume the lattice is extended infinitely in all directions). Assume that each mass is attached to each of its 6 neighbors by equal springs of equal length. Find the first Brillouin zone. Calculate the dispersion curve $\omega(\mathbf{k})$.

A.3.4. **Tight Binding in 2d**



Consider a rectangular lattice in 2 dimensions with lattice constants a_1 in the horizontal direction and a_2 in the vertical direction. Describe the first Brillioun zone for this lattice.

Now imagine a tight binding model where there is one orbital at each lattice site, and where the hopping matrix element is $\langle n|H|m\rangle = t_1$ if sites n and m are neighbors in the horizontal direction and is $= t_2$ if n and m are neighbors in the vertical direction. Calculate the dispersion relation for this tight binding model. What does the dispersion relation look like near the bottom of the band?

A.3.5. **Diatomic Tight Binding Model: Peierls disortion**

Consider a chain made up of all the same type of atom, but in such a way that the spacing between atoms alternated as long-short-long-short as follows

$$-A = A - A = A - A = A-$$

In a tight binding model, the shorter bonds (marked with $=$) will have hopping matrix element $t_{short} = t(1+\epsilon)$ whereas the longer bonds marked with $-$ have hopping matrix element $t_{long} = t(1-\epsilon)$. Calculate the tight-binding energy spectrum of this chain. (The onsite energy ϵ is the same on every atom). Expand your result to linear order in ϵ. Suppose the lower band is filled and the upper band is empty (what is the valence of each atom in this case?). Calculate the total ground state energy of the filled lower band, and show it decreases linearly with increasing ϵ.

Now consider a chain of equally spaced identical A atoms connected together with identical springs with spring constant κ. Show that making a distortion whereby every other spacing is shorter by δx costs energy proportional to $(\delta x)^2$. Conclude that for a chain with the valence discussed above, a distortion of this sort will occur spontaneously. This is known as a Peierls distortion.

More problems associated with Problem Set 4

A.4.1. p-n junction

[Note: Presumably p-n junction is not supposed to be on the syllabus, but for years it was a standard question.]

Explain the origin of the depletion layer in an abrupt p-n junction and discuss how the junction causes rectifcation to occur. Stating your assumptions, show that the total width w of the depletion layer of a p-n junction is:

$$w = w_n + w_p$$

where

$$w_n = \left(\frac{2\epsilon_r \epsilon_0 N_A \phi_0}{e N_D (N_A + N_D)} \right)^{1/2}$$

and a similar expression for w_p Here ϵ_r is the relative permittivity and N_A and N_D are the acceptor and donor densities per unit volume, while ϕ_0 is the difference in potential across the p-n junction with no applied voltage. Calculate the total depletion charge and infer how this changes when an additional voltage, V ,is applied.

What is the differential capacitance of the diode and why might it be useful to use a diode as a capacitor in an electronic circuit?

More problems associated with Problem Set 5

A.5.1. **Spin J Paramagnet**

Given the hamiltonian for a system of noninteracting spin-J atoms

$$\mathcal{H} = -\tilde{g}\mu_B \mathbf{B} \cdot \mathbf{J}$$

Determine the magnetization as a function of B and T. Show that the susceptibility is given by

$$\chi = \frac{\rho \mu_0 (\tilde{g}\mu_B)^2}{3} \frac{J(J+1)}{k_B T}$$

where ρ is the density of spins.

A.5.2. **Correction to Mean Field**

Consider the spin-1/2 Ising Ferromagnet on a cubic lattice in d dimensions. When we consider mean field theory, we treat exactly a single spin σ_i and the $z = 2d$ neighbors on each side will be considered to have an average spin $\rightarrow \langle\sigma\rangle$. The critical temperature you calculate should be $k_b T_c = Jz/4$.

To improve on mean field theory, we can instead treat a block of two connected spins σ_i and $\sigma_{i'}$ where the neighbors outside of this block are assumed to have the average spin $\rightarrow \langle\sigma\rangle$. Each of the spins in the block has $2d-1$ such averaged neighbors. Use this improved mean field theory to write a new equation for the critical temperature (it will be a transcendental equation). Is this improved estimate of the critical temperature higher or lower than that calculated in the more simple mean-field model?