

## Physics 211B : Problem Set #0

These problems provide a cross section of the sort of exercises I would have assigned had I taught 211A. Please take a look at all the problems, and turn in problems 1, 4, 6, 8, 9, 11, 13, 15, 17, and 18.

[1] Determine the bulk modulus  $\kappa = -V \frac{\partial p}{\partial V}$  of NaCl, using the facts that the Madelung constant for the NaCl lattice is  $A = 1.748$  and the lattice constant is  $a = 5.64 \text{ \AA}$ . Start by writing the total energy as

$$E(d) = N \left\{ -A \frac{e^2}{d} + C d^{-p} \right\},$$

where  $d$  is the nearest neighbor Na-Cl separation and  $C$  and  $p$  are constants. The first term is the Coulomb energy, and the second term describes a phenomenological short-ranged repulsion. The quantity  $p$  may be taken to be  $p = 12$  for a Lennard-Jones potential. Minimizing  $E$  with respect to  $d$  will then determine  $C$  in terms of other constants and  $d_0$ , the equilibrium Na-Cl separation at  $T = 0$ .

[2] In analogy to the  $sp^3$  hybridization of carbon in the diamond structure, discuss the possibility of planar  $sp^2$  carbon hybridization. Provide expressions for the wavefunctions for an orthonormal set of three  $sp^2$ -hybridized orbitals, and sketch qualitatively their density distributions in the plane.

[3] The benzene molecule  $C_6H_6$  consists of a ring of carbon atoms each bound to a hydrogen atom. Benzene is a planar molecule, and the  $2s$  orbitals hybridize with the  $2p$  orbitals as described in problem [2]. Each of the  $sp^2$  orbitals forms what is called a  $\sigma$ -bond with the two neighboring C and one neighboring H atoms. The remaining  $p_z$  electrons participate in the so-called  $\pi$ -bonds. One electron per carbon atom participates in the  $\pi$ -bonding.

(a) If we neglect interactions, then a simple model for the  $\pi$ -orbitals is given by the tight-binding Hamiltonian

$$\mathcal{H}_0 = -t \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^N \left\{ |j, \sigma\rangle \langle j+1, \sigma| + |j+1, \sigma\rangle \langle j, \sigma| \right\},$$

where  $|j, \sigma\rangle = |j + N, \sigma\rangle$  and  $N = 6$  for benzene. The quantity  $t > 0$  is called the *hopping integral*. Find the ground state wavefunction and the ground state energy. Show how the physics of the ground state depends on the parity of  $N$  modulo 4. Is the ground state ever degenerate? Start by showing that the eigenstates of  $\mathcal{H}_0$  are all of the form

$$|k, \sigma\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{ikj} |j, \sigma\rangle,$$

where  $e^{ikN} = 1$ . Then find the eigenvalues  $\varepsilon(k)$ .

(b) For  $N = 4m + 2$  the ground state of  $\mathcal{H}_0$  is a nondegenerate spin singlet. What is the dimension of the subspace of spin singlet wavefunctions? How many spin singlet states are there for benzene ( $N = 6$ )?

(c) For  $N = 4m + 2$  one can also construct the so-called Kekulé states by writing

$$|\psi_A\rangle = \left( \frac{|\uparrow_1 \downarrow_2\rangle - |\downarrow_1 \uparrow_2\rangle}{\sqrt{2}} \right) \otimes \left( \frac{|\uparrow_3 \downarrow_4\rangle - |\downarrow_3 \uparrow_4\rangle}{\sqrt{2}} \right) \otimes \dots \otimes \left( \frac{|\uparrow_{N-1} \downarrow_N\rangle - |\downarrow_{N-1} \uparrow_N\rangle}{\sqrt{2}} \right).$$

Such a structure consists of alternating single and double bonds (recall that the  $\sigma$ -orbitals already contribute one single bond between each neighboring pair of sites). Compare and contrast this state with the ground state of  $\mathcal{H}_0$  found in part (a). Note that there is a state  $|\psi_B\rangle$  where the bond pattern is shifted by one link. Both these states are favored by a strong local on-site repulsion term,

$$\mathcal{H}_1 = U \sum_j n_{j\uparrow} n_{j\downarrow}$$

when  $U$  is large. The Hamiltonian  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$  is known as the *Hubbard model*.

[4] A  $C_{60}$  molecule consists of 60 carbon atoms arranged in the shape of a soccer ball. Each site is threefold coordinated (*i.e.* it has three neighbors), and there are a total of 32 faces, with 12 pentagons and 20 hexagons. It may be useful to have an actual soccer ball available for this problem!

(a) Note that unlike benzene, where all the bonds are equivalent by sixfold rotational symmetry, in  $C_{60}$  there are two inequivalent sets of bonds: those shared by pentagons and hexagons, and those shared between hexagons. What does this suggest?

(b) Fun with math: Let  $F$  denote the number of faces,  $V$  the number of vertices, and  $E$  the number of edges of an arbitrary planar graph. Prove that  $F - E + V = 1$ . This is known as Euler's theorem.

(c) On the sphere, one has  $F - E + V = 2$ , since the area 'outside' the graph on a plane counts as another face when the plane is compactified to a sphere by identifying all the points at infinity. The fullerenes are a family of spheroidal carbon molecules where every carbon atom is threefold coordinated. Assuming only pentagonal and hexagonal faces, prove that every fullerene molecule contains precisely 12 pentagons. What is the smallest fullerene possible?

[5] The honeycomb structure is a triangular lattice with a two-element basis. Write down a set of two primitive triangular lattice vectors and a set of basis vectors for the honeycomb lattice. Assume the nearest neighbor separation is  $a$ .

[6] For each of the following structures, indicate whether or not it is a Bravais lattice. If it is, find a set of three smallest primitive direct lattice vectors. If it is not, identify the underlying Bravais lattice, and find the primitive smallest direct lattice vectors as well as the smallest possible basis.

(i) Base-centered cubic (simple cubic with additional points in the centers of each horizontal face).

(ii) Side-centered cubic (simple cubic with additional points in the centers of each of the vertical faces but not the horizontal faces).

(iii) Edge-centered cubic (simple cubic with additional points at the midpoints of all nearest-neighbor links).

[7] Prove that the volume of the primitive cell of a Bravais lattice in  $d$  dimensions is

$$\Omega = |\epsilon_{j_1 j_2 \dots j_d} a_1^{j_1} a_2^{j_2} \dots a_d^{j_d}|,$$

where  $\{\mathbf{a}_j\}$  with  $j = 1, \dots, d$  are primitive reciprocal lattice vectors.

[8] Prove that any reciprocal lattice vector  $\mathbf{G}$  is an integral multiple of the shortest reciprocal lattice vector parallel to  $\mathbf{G}$ .

[9] Prove that it is impossible for any Bravais lattice to have an axis of five-fold symmetry.

[10] Show that, under the most general conditions, the elastic tensor  $c_{\alpha\mu\beta\nu}$  for a three-dimensional solid has 21 independent components.

[11] At low temperatures elemental argon crystallizes into an FCC structure. The binding is due to van der Waals forces and the interatomic potential may be modeled by the Lennard-Jones formula,

$$V(\mathbf{r}) = 4\epsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right\},$$

with  $\epsilon = 10.5 \text{ meV}$  and  $\sigma = 3.4 \text{ \AA}$ . Neglecting all but nearest neighbor forces, calculate the phonon dispersion in the (110) direction and sketch your results. Compute the acoustic phonon velocities in meters per second.

[12] A one-dimensional lattice consists of alternating masses  $M$  and  $m$ . The equilibrium distance between nearest neighbors is  $\frac{1}{2}a$ , *i.e.* the unit cell length is  $a$ . The potential energy is given by

$$\Phi = \frac{1}{2}K \sum_{j=-\infty}^{\infty} \left\{ (u_{j,1} - u_{j,2})^2 + (u_{j,2} - u_{j+1,1})^2 \right\},$$

where  $u_{j,s}$  is the displacement of the  $s^{\text{th}}$  basis atom ( $s = 1, 2$ ) in the  $j^{\text{th}}$  unit cell. Calculate the phonon spectrum and sketch your result. What is the acoustic phonon velocity? Show that for  $m = M$  the spectrum coincides with that for a chain of equal masses.

[13] A linear chain of identical atoms is described by the potential energy function

$$\Phi = \frac{1}{2} \sum_{j=-\infty}^{\infty} \sum_{j'=-\infty}^{\infty} K(j-j') (u_j - u_{j'})^2,$$

where  $K(m) = K(-m)$  depends only on the relative distance. Find the phonon dispersion and examine its long wavelength limit. Show that if  $K(m) \propto |m|^{-p}$  for large separations  $m$  then the long-wavelength dispersion in the vicinity of the zone center  $k = 0$  is linear in the crystal momentum  $k$  if  $p > 3$  but for  $1 < p < 3$  one has  $\omega(k) \propto k^{(p-1)/2}$ .

[14] Consider a crystal of elemental silver (Ag).

(a) Obtain an expression in terms of the phonon spectrum and the temperature, for the mean square displacement  $\langle \mathbf{u}^2(\mathbf{R}) \rangle$  of an Ag atom from its equilibrium position.

(b) Look up the mass, elastic constants, and melting temperature  $T_M$  of Ag and estimate  $\langle \mathbf{u}^2(\mathbf{R}) \rangle$  at  $T = 0$  and  $T = T_M$ .

[15] Consider a one-dimensional square well potential

$$v(x) = -V_0 \Theta\left(\frac{1}{2}b - |x|\right) .$$

An electron propagates in the crystalline lattice potential

$$V(x) = \sum_{j=-\infty}^{\infty} v(x - ja) ,$$

where  $a > b$ . Obtain the equation which determines the band structure  $E_n(k)$ , solve numerically, and plot your results.

[16] Use the tight-binding method to evaluate the band structure for the two-dimensional periodic potential

$$V(x, y) = V_0 \cos(2\pi x/a) + V_0 \cos(2\pi y/a) .$$

Work only with the lowest band, and include only nearest-neighbor hopping terms. Assume that the individual atomic orbitals are harmonic oscillator ground state wavefunctions whose width is determined by the curvature of  $V(\mathbf{r})$  at its minima.

[17] Find the dependence of the density of states  $g(E)$  on the energy  $E$  in the vicinity of  $E = E_c$  for the following cases:

(a) Parabolic minimum:

$$E(\mathbf{k}) = E_c + \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 k_z^2}{2m_z}$$

(b) Saddle point:

$$E(\mathbf{k}) = E_c + \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} - \frac{\hbar^2 k_z^2}{2m_z}$$

[18] Two thought experiments on band structures and Fermi surfaces:

(a) Consider a crystalline solid with an odd number of electrons per unit cell. Argue on the basis of band structure considerations that it should be a metal, *i.e.* that it should have a finite density of states at the Fermi energy. (In fact this conclusion is only valid if the electrons are noninteracting. Interacting electrons can localize and form what is known as a *Mott insulator*.)

(b) Consider a crystalline solid with an even number of electrons per unit cell. In the absence of interactions, should such a material be a metal or an insulator? Show that both situations are possible, depending on the position of the Fermi level and the band structure. Provide some sketches to illustrate your conclusions.