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## 3.23 Electrical, Optical, and Magnetic Properties of Materials

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## 3.23 midterm exam. Solutions

Nicola Marzari & Nicolas Poilvert

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### 1 Question 1 [20 points]

Define and explain the following concepts, and for each of them explain their relevance with an example.

a) **Commuting operators:**

One says that the set  $\{\hat{A}, \hat{B}, \dots\}$  form a set of commuting operators, when we have the following property:  $\hat{A}\hat{B} = \hat{B}\hat{A}$  etc... When those operators are hermitian, we have a special result that says that we can find a basis constituted by common eigenvectors of those commuting hermitian operators. This property has been used in class to classify the eigenfunctions for the hydrogen atom. In this case, we have that  $\{\hat{H}, \hat{L}^2, \hat{L}_z\}$  form a set of commuting hermitian operators.

b) **Acoustic and optical phonons:**

Phonons are the elementary vibrational excitations of the crystal in a periodic solid. We can always distinguish between two types of excitations. The ones for which the energy (or the frequency) of the phonon goes to zero when the wavevector goes to zero (or the wavelength to infinity), and the ones for which even when the wavevector goes to zero the energy of the phonon is finite. The former ones are called *acoustic* phonons when the latter ones are called *optical* phonons. Another feature for acoustic phonons is the fact that the energy dispersion  $\omega(\vec{k})$  goes to zero linearly with the wavevector  $\omega(\vec{k}) \approx (c_x k_x + c_y k_y + c_z k_z)$ . The coefficients in this asymptotic behavior are nothing but the speed of sound in x, y and z directions. Phonons are key contributors to the heat capacity of solids.

c) **Time-dependant Schrödinger equation:**

The TDSE is the fundamental equation of quantum mechanics (in the non-relativistic limit) from which someone can, *in principle*, find all the informations concerning a system. It is the equivalent of Newton's second law in classical dynamics. The TDSE has been used in homework to find the time evolution of the electron's spin in an NMR experiment for example.

d) **Hartree's equations:**

Hartree's equations were obtained in the first attempt to deal with the complexity of the many-body Schrodinger equation. Those equations can be found

by substituting the many-body wavefunction by a product of single-particle wavefunctions in the variational principle. The physics hidden behind those equations is the following: one wants to describe the assembly of interacting electrons as a collection of independent particles interacting with the average electric field generated by the other particles. This description can be substantially improved by introducing the Pauli exclusion principle and writing the many-body wavefunction as a Slater determinant.

## 2 Question 2 [50 points]: One dimensional metals and Peierls distortions

This correction contains more than one needs in order to get the maximum grade. But it is intended to make you understand better the material.

a) The direct space primitive vector is nothing but:  $\vec{a}_1 = a\vec{e}_x$ . The reciprocal space primitive vector  $\vec{b}_1$  is such that  $\vec{b}_1 \cdot \vec{a}_1 = 2\pi$ . So a good choice for  $\vec{b}_1$  is  $\vec{b}_1 = \frac{2\pi}{a}\vec{e}_x$ . Inside the unit cell we have a single atom so we can choose to put this atom at the origin of the coordinates, such that the basis vector be  $\vec{r}_1 = \vec{0}$ .

b) With the conventions taken in question a), we see that atomic's equilibrium positions are given by:  $\vec{R} = n_1\vec{a}_1 = R\vec{e}_x$ . In this question we consider the periodic one dimensional crystal in the limit where the lattice spacing is **huge**. In this limit, we can already say the each atom will be surrounded by only one valence electron, and moreover the energy of each electron will be simply the energy of the  $\phi_s$  orbital:  $\epsilon_s$ . If N is the total number of unit cells in the crystal, then the correctly normalized Bloch functions will be:

$$\Phi_k(x) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \phi_s(x - R)$$

In this sum,  $\vec{k} = k_1\vec{b}_1$  is a vector in the first Brillouin Zone, meaning that  $k_1$  varies between  $-\frac{1}{2}$  and  $\frac{1}{2}$  (such that its norm varies between  $-\frac{\pi}{a}$  and  $\frac{\pi}{a}$ ). We have the following result when one translates this wavefunction by a lattice vector  $\vec{R}_0$ :

$$\Phi_k(x + R_0) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \phi_s(x + R_0 - R) = \frac{e^{i\vec{k}\vec{R}_0}}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}(\vec{R} - \vec{R}_0)} \phi_s(x - (R - R_0))$$

Now if we look at the right hand side of the above equation, we see that the mathematical expression is the same as in the case of the Bloch function, except that we sum over  $\vec{R} - \vec{R}_0$  instead of just  $\vec{R}$ . Summing over  $\vec{R}$  or summing over  $\vec{R} - \vec{R}_0$  is just a way of saying which of the unit cell in the crystal is the "origin", but because of the Born-Von Karman boundary conditions, all the unit cells are equivalent and so summing over  $\vec{R}$  or summing over  $\vec{R} - \vec{R}_0$  is exactly equivalent! We then end up with the identity:

$$\Phi_k(x + R_0) = e^{i\vec{k}\vec{R}_0} \Phi_k(x)$$

which is nothing but Bloch's theorem. So indeed the "Bloch sum" satisfies Bloch's theorem.

c) In question b), we were considering a one dimensional crystal with a huge lattice spacing. In this limit each atom in the solid is surrounded by one valence electron and the energy for this electron is just  $\epsilon_s$ . So the band diagram shows a straight line of energy  $\epsilon_s$  as in figure 1.

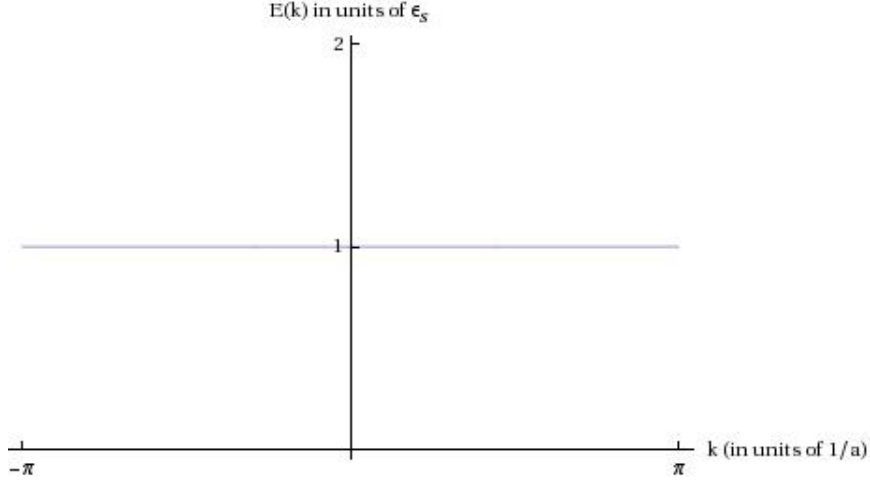


Figure 1: Band diagram when the atoms are far apart from each other. The lattice spacing is huge here such that no overlap between nearest neighbours is possible. The band dispersion is flat over the entire first Brillouin Zone.

The Born-Von Karman boundary conditions imposes a quantization condition for the wavevector  $\vec{k}$ . Indeed we see that if  $\Phi_k(x + Na) = \Phi_k(x)$ , then using Bloch's theorem, we arrive at:  $e^{i2\pi kN} = 1$  ( $\vec{k} = k\vec{b}_1$ ). So we see that  $kN$  must be an integer. But since  $k$  must lie inside the first Brillouin Zone (here between  $-\frac{1}{2}$  and  $\frac{1}{2}$ ), we can conclude that:  $k = \frac{n}{N}$  with  $n$  varying between  $-N/2$  and  $N/2$ . What it changes on the band diagram is just the density of points, but not the value of the band dispersion. For  $N = 10$ , the band diagram becomes a regular array of 10 points at energy  $\epsilon_s$  like the one shown on figure 2. For  $N \approx 10^{23}$ , the density of points is so big that the plot looks basically like figure 1.

d) We now shrink the lattice parameter such that a nearest neighbour overlap is possible. In this case, we can write down the hamiltonian as  $\hat{H} = \hat{H}_{at} + \Delta\hat{U}$ . We want the Bloch function to be an eigenstate of  $\hat{H}$ , so we must have  $\hat{H}\Phi_k(x) = E_s(k)\Phi_k(x)$ . If one multiplies both sides of this equation by  $\Phi_k^*(x)$  and integrate over  $x$ , one ends up with:

$$E_s(k) = \frac{\int \Phi_k^*(x)\hat{H}\Phi_k(x)dx}{\int \Phi_k^*(x)\Phi_k(x)dx}$$

where one integrates over **a unit cell**. Now if one plugs in the expressions for  $\Phi_k(x)$  and  $\hat{H} = \hat{H}_{at} + \Delta\hat{U}$  and defines the following integrals:

- $\beta = -\int \phi_s^*(x)\Delta\hat{U}\phi_s(x)dx$
- $\gamma = -\int \phi_s^*(x)\Delta\hat{U}\phi_s(x - R)dx$  where  $R$  is a nearest neighbour of the atom centered at the origin

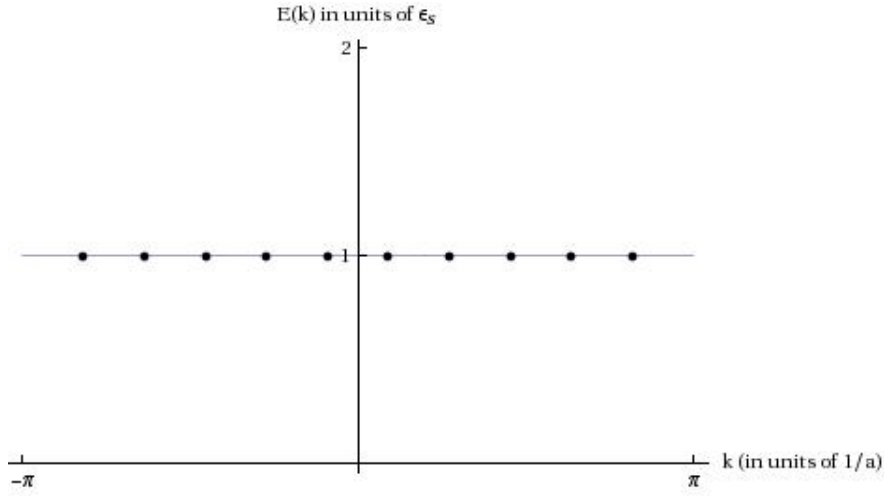


Figure 2: Band diagram when atoms are far apart from each other and with a super-periodicity of 10 unit cells for the wavefunction.

- $\alpha = \int \phi_s^*(x)\phi_s(x-R)$  where  $R$  is a nearest neighbour of the atom centered at the origin

then one ends up with the following expression for  $E_s(k)$ :

$$E_s(k) = \frac{\epsilon_s - \beta - \gamma \sum_{R \text{ NN}} e^{ikR}}{1 + \alpha \sum_{R \text{ NN}} e^{ikR}}$$

The symbol  $R \text{ NN}$  means that the sum is carried out over all the  $R$ 's that are nearest neighbours to the atom centered at the origin. If we consider the basis  $\{\phi_s(x-R)\}_R$  to be orthonormal, then  $\alpha = 0$  and the simplified expression is:

$$E_s(k) = \epsilon_s - \beta - 2\gamma \cos(ka) \text{ where } k \text{ varies between } -\frac{\pi}{a} \text{ and } \frac{\pi}{a}$$

A plot of the band diagram is given on figure 3. To obtain this plot i took  $\beta = 0.2\epsilon_s$  and  $\gamma = 0.2\epsilon_s$ .

e) The general expression for the density of states of a 1D system with an energy dispersion  $E_s(k)$  is the following:

$$D(E) = 2 \frac{L}{2\pi} \int_{FBZ} \delta(E - E_s(k)) dk$$

This formula takes into account the spin degeneracy (the factor 2 in front). The Dirac delta function will be non-zero only when  $E = E_s(k)$ . We will at this point use a well-known formula for the Dirac delta function:

$$\int \delta(f(k)) dk = \sum_{k_0} \frac{1}{\left| \frac{df(k)}{dk} \right|_{(k=k_0)}}$$

In this formula  $k_0$  are **all the points** in the interval of integration that are such that:  $f(k_0) = 0$ . Using this formula in our problem, we find with  $f(k) = E - E_s(k)$  that:

$$D(E) = 2 \frac{L}{2\pi} \sum_{k_0} \frac{1}{\left| -\frac{dE_s(k)}{dk} \right|_{(k=k_0)}}$$

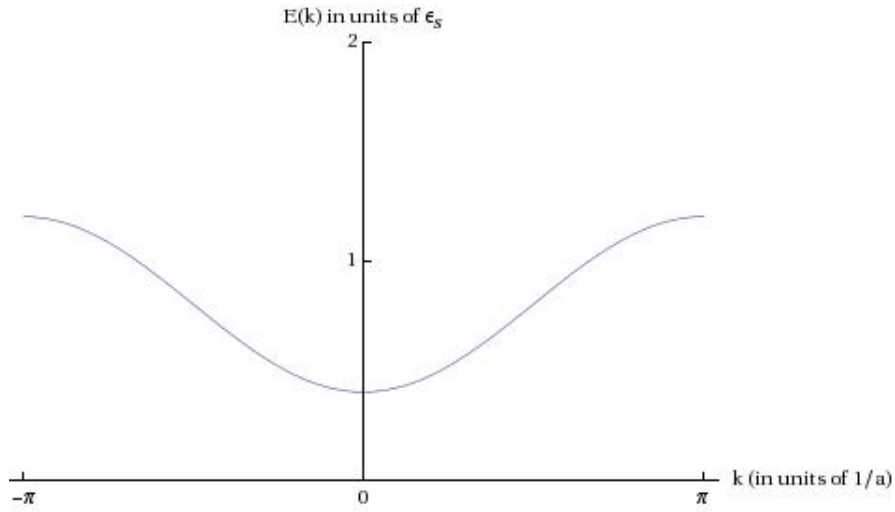


Figure 3: Band diagram when the overlap between atoms is reduced to nearest neighbour interactions.

We can easily see that there are only two (symmetric) points in the First Brillouin Zone (FBZ) that are such that  $E = E_s(k_0)$ . Those points are given by:  $E = \epsilon_s - \beta - 2\gamma \cos(k_0 a)$ . The first derivative of  $E_s(k)$  is given by  $2a\gamma \sin(ka)$  and we also know that  $|\sin(\cos(x))| = \sqrt{1 - x^2}$ , such that the final result is:

$$D(E) = \frac{L}{\pi\gamma a} \frac{1}{\sqrt{1 - \left(\frac{E - \epsilon_s + \beta}{2\gamma}\right)^2}}$$

A plot of the density of states in reduced units is shown on figure 4.

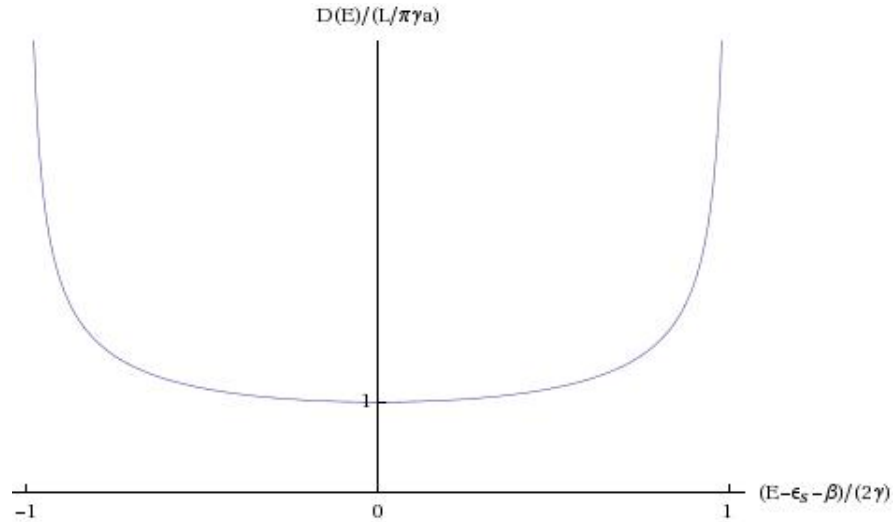


Figure 4: Density of states for this 1d crystal in a tight-binding nearest neighbour description.

Given that we have **one valence electron per unit cell** so N valence

electrons in total, and that a band can accommodate  $2N$  electrons in total, we see that the band is half-filled and so this system should be metallic. Given the symmetry of the band dispersion with respect to the middle value  $\epsilon_s - \beta$ , we see that the Fermi energy is given by  $E_F = \epsilon_s - \beta$ .

f) In question e), we calculated the total density of states of the system and the Fermi energy. So we can calculate the total energy of the system! Indeed since  $D(E)dE$  is the total number of quantum states of the system with an energy  $E$ , then the energy of all those states is just  $E * D(E)dE$ . If we sum this number over all the occupied interval of energy (from the bottom of the band  $E = \epsilon - \beta - 2\gamma$  up to the Fermi energy  $E = E_F = \epsilon_s - \beta$ ), we see that we obtain the total energy of the system:

$$\varepsilon = \int_{\epsilon_s - \beta - 2\gamma}^{\epsilon_s - \beta} ED(E)dE$$

Using the expression for  $D(E)$  and changing the variable in the integral to  $x = \frac{E - \epsilon_s + \beta}{2\gamma}$ , we arrive at:

$$\varepsilon = \frac{2L}{\pi a} \left\{ 2\gamma \int_{-1}^0 \frac{x dx}{\sqrt{1-x^2}} + (\epsilon_s - \beta) \int_{-1}^0 \frac{dx}{\sqrt{1-x^2}} \right\}$$

The two integrals are classic ones:  $\int_{-1}^0 \frac{x dx}{\sqrt{1-x^2}} = -1$  and  $\int_{-1}^0 \frac{dx}{\sqrt{1-x^2}} = \frac{\pi}{2}$ , so the final answer is the following:

$$\varepsilon = \frac{L}{a} (\epsilon_s - \beta - \frac{4}{\pi} \gamma) = N(\epsilon_s - \beta - \frac{4}{\pi} \gamma)$$

**Remark:** In solid state physics, we define the **cohesive energy** as the energy per atom of the solid, or the energy per unit cell of solid. If we use the answer above, one sees that the cohesive energy of this one dimensional solid is  $\varepsilon_{coh} = \epsilon_s - \beta - \frac{4}{\pi} \gamma$ .

g) If one uses a unit cell twice as big then the number of atom per unit cell is now 2. The new real space primitive vector is  $2a\vec{e}_x$  and the new reciprocal space primitive vector is  $\frac{2\pi}{2a}\vec{e}_x$ . So the new first Brillouin zone is twice as small as the one we used up to now. Using our nearest neighbour tight-binding model, we see that the band dispersion obtained in question d) has to be folded back into the new first Brillouin Zone. The result of this operation is shown on figure 5.

h) If we had been using a free electron gas model, the physics of the problem wouldn't have changed. The only difference is the analytic form of the band dispersion  $E_s(k) = \frac{\hbar^2 k^2}{2m}$  that one needs to fold back into the new first Brillouin Zone.

i) If one distorts the structure by displacing one of the atoms in the unit cell containing two atoms, then the unit cell containing two atoms becomes the smallest possible unit cell that can describe the distorted crystal. The description of the system using a two atom unit cell is not redundant any more as it was before in the completely symmetric structure of questions a) to h)! Using a free electron gas model, the two bands can be obtained by diagonalizing the "master equation":

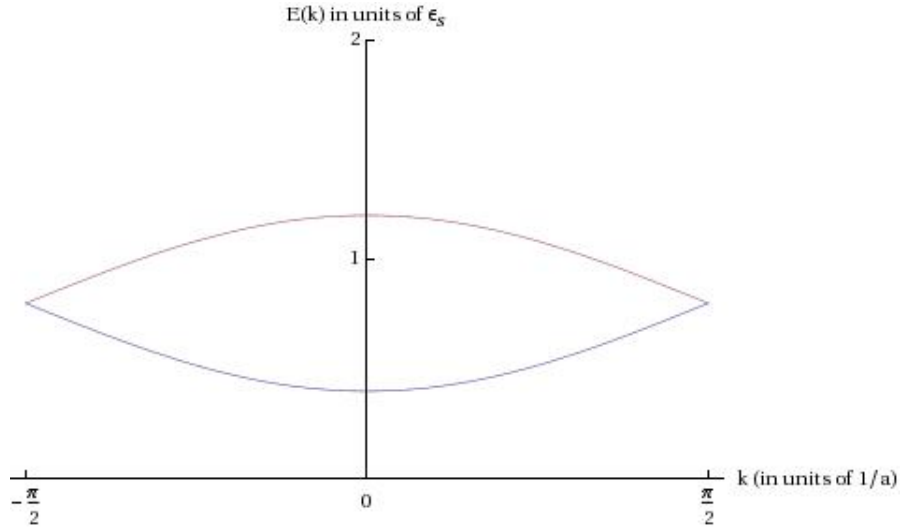


Figure 5: Band diagram obtained by folding the band diagram of question d) back into the new first Brillouin Zone. The crystal is described by a unit cell twice as big as before.

$$\begin{pmatrix} \ddots & & & & & & \\ V_{-g} & \frac{\hbar^2(k+g)^2}{2m} - E & V_g & \cdots & & & \\ \cdots & V_{-g} & \frac{\hbar^2 k^2}{2m} - E & V_g & \cdots & & \\ & \cdots & V_{-g} & \frac{\hbar^2(k-g)^2}{2m} - E & V_g & \cdots & \\ & & & & \ddots & & \end{pmatrix} \begin{pmatrix} \vdots \\ c_{k+g} \\ c_k \\ c_{k-g} \\ \vdots \end{pmatrix} = 0$$

where  $g = \frac{2\pi}{2a} = \frac{\pi}{a}$  is the smallest possible  $\vec{G}$  vector in reciprocal space and  $V_{ng}$  are the Fourier coefficients of the perturbing potential. We see on the master equation that the dominant component of the perturbing potential is  $V_g = V_{-g}$ . This equality is true because we can choose the origin of the coordinate system such that the perturbing potential is an even (and of course real) function. If the potential is really weak we can only keep  $V_g$  and forget about all the other  $V_{ng}$ 's. Far from the Brillouin Zone boundaries, the band dispersion is really close to the case of a free electron for which all the  $V_{ng}$  are zero. Only close the Brillouin Zone boundaries the band structure will look different. Indeed if we focus on  $k \approx \frac{\pi}{2a}$ , we see that the two kinetic energy terms  $\frac{\hbar^2 k^2}{2m}$  and  $\frac{\hbar^2(k-g)^2}{2m}$  are almost equal in magnitude. Given that all the other kinetic energy terms are quite different in magnitude from those two, we can simplify the "master equation" and only consider a  $2 \times 2$  matrix equation:

$$\begin{pmatrix} \frac{\hbar^2 k^2}{2m} - E & V_g \\ V_{-g} & \frac{\hbar^2(k-g)^2}{2m} - E \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-g} \end{pmatrix} = 0$$

The eigenvalues corresponding to the two band dispersions around  $k \approx \frac{\pi}{2a}$  are then straightforwardly given by:

$$E_{\pm}(k) = \frac{1}{2} \left\{ E(k) + E(k-g) \pm \sqrt{(E(k) - E(k-g))^2 + (2V_g)^2} \right\}$$



where  $E(k) = \frac{\hbar^2 k^2}{2m}$ . So we see that there is a gap at  $k = \frac{\pi}{2a}$ , given by the difference of the two band dispersions which is just  $2|V_g|$ . We conclude that around the Brillouin Zone boundary, two bands that are degenerate in the free electron gas model will be separated by a weak perturbing periodic potential.

j) With what we saw in question i) and in question g), we can see that when one goes from a one atom per unit cell description in a perfect solid to a two atom per unit cell description in a distorted solid, we have changed the nature of the solid. Indeed in the one atom per unit cell, the band was half-filled and the solid was a metal. In the case of the distorted solid where the unit cell is twice as big, there are two bands, but each of them can accommodate only  $2 * \frac{N}{2}$  (=spin degeneracy \* number of unit cells of length  $2a$  in the solid). So we conclude since we have one valence electron per atom, that the first band is completely filled. But since the two bands are separated by a gap calculated in question i), we see that the system is now an insulator! Moreover we see that because of the gap opening at the Brillouin Zone boundary, the energy states around  $k = \frac{\pi}{2a}$  (and symmetrically around  $k = -\frac{\pi}{2a}$ ) have been lowered in energy. So the conclusion is that the total energy of the system by going from a perfect structure to a distorted structure has decreased. It is then energetically favorable for a one dimensional metallic crystal to distort itself and create a unit cell twice as big in order to become an insulator: This spontaneous transition is called a **Peierls instability** and it has been observed experimentally on polymeric chains.

### 3 Question 3 [30 points]: The ammonia maser

This exercise should be easy to answer because it requires a minimum knowledge of quantum mechanics and the quantum mechanical postulates.

Ask questions if something is not clear.

a) The  $|R\rangle$  and  $|L\rangle$  states are *a priori* not **eigenstates** of the hamiltonian. So off-diagonal matrix elements like  $\langle L|\hat{H}|R\rangle$  and  $\langle R|\hat{H}|L\rangle$  are not zero in general. As a consequence the hamiltonian matrix expressed in the  $\{|R\rangle, |L\rangle\}$  basis is not diagonal in general. Another way to see this is to realize that since we have some tunneling probability to go from state  $|R\rangle$  to state  $|L\rangle$  (that is why the molecule spends some time in the  $|R\rangle$  state and some time in the  $|L\rangle$  state), those states cannot be eigenstates of the hamiltonian.

b) In agreement with the result of question a), the hamiltonian matrix expressed in the  $\{|R\rangle, |L\rangle\}$  basis is:

$$\begin{pmatrix} \langle L|\hat{H}|L\rangle & \langle L|\hat{H}|R\rangle \\ \langle R|\hat{H}|L\rangle & \langle R|\hat{H}|R\rangle \end{pmatrix} = \begin{pmatrix} E_0 & V \\ V & E_0 \end{pmatrix}$$

Since the basis  $\{|R\rangle, |L\rangle\}$  is orthonormal (it is stated in the text!), the eigenvalues are easily obtained by setting the determinant of the following matrix to zero:

$$\begin{pmatrix} E_0 - E & V \\ V & E_0 - E \end{pmatrix}$$

which gives us:

$$E_{\pm} = E_0 \pm V$$

Let us calculate the eigenvector corresponding to the eigenvalue  $E_- = E_0 - V$ . To do this we go back to the Schrodinger equation in matrix form and inject the expression for the eigenvalue  $E$ .

$$\begin{pmatrix} E_0 - E & V \\ V & E_0 - E \end{pmatrix} \begin{pmatrix} c_1^- \\ c_2^- \end{pmatrix} = 0$$

Simplifying the matrix system gives us:

$$\begin{pmatrix} V & V \\ V & V \end{pmatrix} \begin{pmatrix} c_1^- \\ c_2^- \end{pmatrix} = 0$$

and we find that  $c_2^- = -c_1^-$ . So the eigenvector looks like:  $|v_-\rangle = c_1^- (|L\rangle - |R\rangle)$  (Do not forget that the hamiltonian matrix and the eigenvectors are expressed in the  $\{|R\rangle, |L\rangle\}$  basis!). In order to find  $c_1^-$ , we impose the following normalization condition:  $\langle v_- | v_- \rangle = 1$ . the expression for  $\langle v_- |$  is nothing but  $\langle v_- | = (c_1^-)^* (\langle L| - \langle R|)$ . So when one calculates  $\langle v_- | v_- \rangle$  and uses the orthonormality of the  $\{|R\rangle, |L\rangle\}$  basis, one finds the following result for  $|c_-|$ :

$$|c_-| = \frac{1}{2}$$

So a perfectly suitable choice for  $|v_-\rangle$  is  $|v_-\rangle = \frac{1}{\sqrt{2}}(|L\rangle - |R\rangle)$ . If one does the same calculation for the second eigenvector, one finds:

$$|v_+\rangle = \frac{1}{\sqrt{2}}(|L\rangle + |R\rangle)$$

c) In question b), one found the eigenvalues and eigenvectors of the hamiltonian. We found an expression for  $|v_-\rangle$  and  $|v_+\rangle$  in the  $\{|R\rangle, |L\rangle\}$  basis. Now we want to express  $|L\rangle$  in the  $\{|v_-\rangle, |v_+\rangle\}$  basis. We see with no effort that  $|v_-\rangle + |v_+\rangle = \frac{2}{\sqrt{2}} |L\rangle = \sqrt{2} |L\rangle$ . So in the end  $|L\rangle$  is just:

$$|L\rangle = \frac{1}{\sqrt{2}}(|v_-\rangle + |v_+\rangle)$$

At  $t = 0$ , the text says that the quantum state of the system is  $|\psi(t = 0)\rangle = |L\rangle = \frac{1}{\sqrt{2}}(|v_-\rangle + |v_+\rangle)$ . In order to find the time evolution of the system, all we have to do is to multiply each of the coefficients in the expansion of  $|\psi(t = 0)\rangle$  in the basis of the eigenvectors of  $\hat{H}$  by the corresponding phase factor  $e^{-i\frac{E_{\pm}t}{\hbar}}$ . So the quantum state of the system at time t is just:

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}(e^{-i\frac{E_-t}{\hbar}} |v_-\rangle + e^{-i\frac{E_+t}{\hbar}} |v_+\rangle)$$

d) The probability to find the system in the quantum state  $|L\rangle$  at time t is obtained by applying one of the quantum mechanics postulate:

$$P(t) = |\langle L | \psi(t) \rangle|^2$$

Using the expression for  $|\psi(t)\rangle$  obtained in question c), we find this probability:

$$P(t) = \frac{1}{4} |e^{-i\frac{E_-t}{\hbar}} + e^{-i\frac{E_+t}{\hbar}}|^2 =$$

Simplifying the expression gives us:

$$P(t) = \cos^2\left(\frac{E_+ - E_-}{2\hbar}t\right)$$

The molecule is then oscillating between the two configurations  $|L\rangle$  and  $|R\rangle$  with a frequency  $\omega_0 = \frac{E_+ - E_-}{\hbar}$ .