



Keble College - Hilary 2012
Section VI: Condensed matter physics
Tutorial 3 - Bonding, phonons and expansion

Please leave your work in the Clarendon laboratory's 'J' pigeon hole by 5pm on Monday of 5th week.
Suggested reading: Hook & Hall 2, 4.3; Kittel 3, 4; Ashcroft/Mermin 19, 20, 22.

1 Chemical bonding

Understanding exactly why neutral atoms form materials is a formidable task. As a first simplification one normally makes the Born-Oppenheimer approximation (the same one as you would have come across in molecular physics) whereby the N nuclei, whose positions are given by $\mathbf{R}_1, \dots, \mathbf{R}_N$, feel a potential $V_{\text{BO}}(\mathbf{R}_1, \dots, \mathbf{R}_N)$ that is the energy of system if the positions of the nuclei were fixed. There are two main contributions to V_{BO} . First, the repulsive internuclear interaction. Second, the energy of the electrons moving in the Coulomb potential of the nuclei. For materials to form, the second contribution must overcome the first, so that V_{BO} is lower for nuclei that are separated by finite rather than infinite distances. We now survey and classify different possible ways in which the electronic energies are reduced such that this is possible.

1. *Summary* — Qualitatively describe the four main types of chemical bonds, including the combinations of types of atoms expected to form each bond (make reference to location on the periodic table) and some of the properties of materials utilising each bond.
2. *Van der Waals bonding* — It is possible for electrons to reduce their combined energy while still orbiting their original atoms. For example, solids comprising noble gas atoms are principally held together by van der Waals forces. Explain why the attractive force between two noble gas atoms is proportional to $1/R^7$ where R is the distance between two atoms.

Delocalisation should reduce the kinetic energy of electrons (for the same reason that the energy of a particle is proportional to the inverse square of the size of a box containing it), and this underlies both covalent and metallic bonding. However, it is difficult to quantify the energy reduction due to delocalisation. To get a feel for the effect, we now study a toy model that captures the essence of covalent bonding and is also analytically solvable. Several (gross) approximations will be made: (i) We will work within an ansatz for the electronic state, the so-called linear combination of atomic orbitals. This can be very accurate if a large number of orbitals are considered, however we will only consider one; (ii) We will ignore interactions between the electrons; (iii) We will consider the nuclei to be far enough apart that their orbitals barely overlap; (iv) We will only consider two nuclei.

3. *Covalent bonding* — Consider two identical nuclei fixed at positions \mathbf{R}_1 and \mathbf{R}_2 , sharing non-interacting electrons. The single electron Hamiltonian is

$$\mathcal{H}_{\text{se}} = \frac{p^2}{2m} + V_1 + V_2,$$

where V_i represents the Coulomb potential $V(\mathbf{r} - \mathbf{R}_i)$ due to the i -th nucleus.

We wish to find the eigenvectors and eigenvalues of this Hamiltonian. To make things simpler we will instead find the closest approximation to the eigenvectors, and their eigenvalues, within

an ansatz. To define this ansatz, let $|i\rangle$ be the lowest energy single electron eigenstate for a Hamiltonian of an electron and nucleus i in isolation, i.e.

$$\left[\frac{p^2}{2m} + V_i \right] |i\rangle = \epsilon|i\rangle.$$

Our ansatz is then a superposition of the $|i\rangle$ states, $|\Phi\rangle = \sum_i \phi_i |i\rangle$.

Assuming that the $|i\rangle$ have a small overlap (true when the nuclei are well separated), one can show (we will do this in the class) that within this ansatz the eigenstates of \mathcal{H}_{se} are given by the eigenvectors of the *effective Schrödinger equation*,

$$H\phi = E\phi.$$

Here H is a matrix with elements $H_{ij} = \langle i|\mathcal{H}_{\text{se}}|j\rangle$, and ϕ is a vector with elements ϕ_i .

(a) Using the nomenclature

$$\begin{aligned} V_c &= \langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle, \\ t &= -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle, \end{aligned}$$

explicitly construct the 2×2 matrix H . Show that its two eigenvalues are

$$E = \epsilon + V_c \pm |t|.$$

The eigenstate with the lower (higher) energy is called the bonding (anti-bonding) state. The total energy of the system is the sum of the nuclear repulsion and the energies of the occupied single electron eigenstates.

- (b) Argue that if the nuclei are well separated then in a neutral molecule the energy term V_c in each occupied orbital will approximately cancel the repulsive potential between the nuclei. Why will this not be true when the nuclei get very close?
- (c) Which molecular orbitals will be occupied for hydrogen in this model? What about helium? In each case, calculate the total energy $V_{\text{BO}}(\mathbf{R}_1, \mathbf{R}_2)$ and compare to energy when $|\mathbf{R}_1 - \mathbf{R}_2| \rightarrow \infty$. Use this to justify the different bonding properties of the two elements.

We will extend this treatment from two atoms to many atoms in the next tutorial, covering metallic bonding. However, instead of understanding bonding, our focus will then be on the form of the single-electron eigenstates and energies. We will not look into any quantitative models of ionic or hydrogen bonding, but you should be able to describe these qualitatively.

2 Normal modes and phonons

For crystalline solids, the potential in which the nuclei move V_{BO} has a minimum when the nuclei form a lattice. To keep things simple we will firstly restrict ourselves to a 1D crystal and then qualitatively generalise this to higher dimensions. Secondly we will focus on the case when the potential can be split into terms corresponding to each pair of nuclei $V_{\text{BO}}(X_1, \dots, X_N) = \sum_{i,j} V_{ij}(X_i - X_j)$ — this is not always justified, but you can imagine it to be the case if only van der Waals forces are present, for example. Thirdly, we will specialise to the case where only nearest-neighbour interactions are important. All the right qualitative behaviour is observed in this special case, adding more realism just changes the numbers a bit (you can check this, for example, by including next-nearest-neighbour interactions).

Given these approximation, we then only need to take into account the potentials between each pair of neighbouring atoms i and j , which for small displacements from their equilibrium separation X_0^{ij} can always be written

$$V_{ij}(X_i - X_j) = \frac{\kappa_2^{ij}}{2}(X_i - X_j - X_0^{ij})^2 - \frac{\kappa_3^{ij}}{3!}(X_i - X_j - X_0^{ij})^3 + \mathcal{O}(X_i - X_j - X_0^{ij})^4.$$

For typical potentials $\kappa_3^{ij} > 0$ (for example, a Lennard-Jones potential – see Wikipedia for details!) So long as the displacements of atoms are small we only need to take into account the first term in the expansion; this is called the harmonic approximation and it leads to normal modes and their quantum excitations called phonons, which will be the topic of the next five questions. For larger displacements we might also need to take into account the second term in the expansion; phenomena arising due to this type of term are called anharmonic effects and we will look at the example of thermal expansion in Qu. 9.

4. Use the harmonic approximation with spring constant κ and consider a 1D crystal with N identical atoms of mass m whose motion is restricted to one dimension. Denote the lattice spacing with a and use periodic boundary conditions.

- (a) Show that the Newtonian equations of motion may be written in matrix form

$$\ddot{\mathbf{x}} = -\mathbf{M}\mathbf{x},$$

where $\mathbf{x} = (x_1, x_2, \dots, x_N)^T$ is a vector giving the displacements of the atoms from their equilibrium positions, and the dynamical matrix is

$$\mathbf{M} = \frac{\kappa}{m} \begin{pmatrix} 2 & -1 & 0 & \cdots & 0 & 0 & -1 \\ -1 & 2 & -1 & \cdots & 0 & 0 & 0 \\ 0 & -1 & 2 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 2 & -1 & 0 \\ 0 & 0 & 0 & \cdots & -1 & 2 & -1 \\ -1 & 0 & 0 & \cdots & 0 & -1 & 2 \end{pmatrix}.$$

- (b) Now consider some unitary matrix \mathbf{U} , which diagonalises \mathbf{M} , such that $\mathbf{U}^\dagger \mathbf{M} \mathbf{U} = \mathbf{D}$, where \mathbf{D} is a diagonal matrix with non-negative diagonal elements ω_n^2 . Show that the equations of motion may then be rewritten in terms of N independent harmonic oscillators as

$$\ddot{\mathbf{x}}' = -\mathbf{D}\mathbf{x}',$$

where $\mathbf{x}' = \mathbf{U}^\dagger \mathbf{x}$ and $\mathbf{x}' = (x'_1, x'_2, \dots, x'_N)^T$.

- (c) Further, show that this equation has the solution $x'_n = A_n e^{i\omega_n t} + B_n e^{-i\omega_n t}$, and therefore $x_n = \sum_m U_{nm} [A_m e^{i\omega_m t} + B_m e^{-i\omega_m t}]$.

- (d) To obtain the solution for the displacements x_n , we therefore need to know U_{nm} and ω_n^2 . From second year linear algebra we might remember that the n -th column $\mathbf{u}_n = (U_{1n}, U_{2n}, \dots, U_{Nn})^T$ of \mathbf{U} and diagonal element ω_n^2 are the n -th eigenvector and eigenvalue of \mathbf{M} . Finding U_{nm} and ω_n^2 thus reduces to solving the eigenvalue equation

$$\mathbf{M}\mathbf{u}_n = \omega_n^2\mathbf{u}_n.$$

Solving this eigenvalue equation is simplified by the fact that \mathbf{M} has translational symmetry, and can be done in the following way. Start by considering some translation matrix \mathbf{T}_n , which shifts the elements of a vector down by n . Show that \mathbf{M} commutes with this translational matrix $[\mathbf{T}_n, \mathbf{M}] = 0$ and that translational matrices commute with each other $[\mathbf{T}_n, \mathbf{T}_m] = 0$.

- (e) This implies the translational matrices and \mathbf{M} all share the same eigenvectors. Writing this for a specific translational operator

$$\mathbf{T}_n\mathbf{u}_m = c_{nm}\mathbf{u}_m.$$

Using the additive properties of translations (or the group properties of translational matrices under multiplication), we have that $\mathbf{T}_n = (\mathbf{T}_1)^n$ and $\mathbf{T}_N = \mathbb{1}$. Show that this implies $c_{nm} = (c_{1m})^n$ and $c_{Nm} = 1$, and argue that together this means we must be able to write $c_{nm} = e^{ik_m a n}$ where k_m is defined only up to translation by an amount $2\pi/a$, and satisfies $e^{ik_m a N} = 1$.

- (f) Show then that $U_{nm} = e^{ik_m a(n-n')}U_{n'm}$. This is Bloch's theorem for discrete systems, and is equivalent to $U_{nm} = e^{ik_m a n}w_{nm}$, where $\mathbf{w}_n = (w_{1n}, w_{2n}, \dots, w_{Nn})^T$ is invariant under all translational matrices commuting with \mathbf{M} . In this case, since all translational matrices commute with \mathbf{M} , \mathbf{w}_n is uniform, i.e. $w_{nm} = w_{n'm}$.
- (g) We are now in a position to solve the problem. Use what we have done to show that $x_n = N^{-1/2} \sum_m e^{ik_m a n} [A_m e^{i\omega_m t} + B_m e^{-i\omega_m t}]$, and thus solutions are linear superpositions of solutions of the form $x_n \propto e^{i(k_m n \pm \omega_m t)}$.
- (h) Use that $\mathbf{M} = (\kappa/m) [2\mathbf{T}_0 - \mathbf{T}_1 - \mathbf{T}_{-1}]$ to show that $\omega_n^2 = (\kappa/m) \sin^2(k_n a/2)$.

The previous question was quite a long winded way of finding the solutions to the equations of motion. However, it allowed us to fully justify the ansatz $x_n \propto e^{i(k_m n \pm \omega_m t)}$ and allowed wavevectors k_n used in other approaches. It also introduced many essential concepts and the mathematics underlying them. For instance, we found that the equations of motion describe decoupled simple harmonic motion in some transformed set of normal coordinates. Independent harmonic oscillators therefore represent the basic collective excitations of the atomic motional degrees of freedom. We also derived Bloch's theorem, which we will see again when we find the single-electron states for periodic potentials. Bloch's theorem tells us that eigenstates of an operator with translational symmetry must be plane waves modulated by some state with the same translational symmetry as the operator. Finally, we got to see the origins of the crystal momentum $\hbar k_n$. It is merely related to the eigenvalue associated with a discrete translation, in the same way that real momenta are related to the eigenvalues associated with continuous translations. This tells us why we use the name crystal momentum instead of momentum when our system has discrete rather than continuous translational symmetry.

This approach could also be used in more complicated situations, e.g. when there are alternating types of atoms. In that case, not all translational matrices will commute with the dynamical matrices; \mathbf{T}_n commutes with \mathbf{M} iff n is even. Therefore the periodic vector will not be uniform but alternating $\mathbf{w}_n = (C_n, D_n, C_n, \dots, D_n)^T$. Bloch's theorem then tells us that solutions will be of the form

$$x_n \propto e^{i(k_m n \pm \omega_m t)} \begin{cases} C_m & \text{for odd } n \\ D_m & \text{for even } n \end{cases},$$

justifying the ansatz you will use in Qu. 7.

Next, we consider the implications of treating atomic oscillations quantum mechanically, which will lead to the concept of a phonon.

5. The Hamiltonian for the system considered in Qu. 4 is

$$\mathcal{H} = \sum_n \left[\frac{p_j^2}{2m} + \frac{\kappa^2}{2} (x_{n+1} - x_n - a)^2 \right] = \sum_n \left[\frac{p_n^2}{2m} + \frac{\kappa^2}{2} (x_{n+1} - x_n)^2 \right] + \frac{N\kappa^2 a^2}{2},$$

where the sum is over all sites $n = 1, \dots, N$.

From our Newtonian treatment, we know the Hamiltonian should be simplified under a coordinate transformation of the type

$$x_n = N^{-1/2} \sum_k e^{-ikan} x'_k,$$

where the sum is over the N values $k = \frac{2\pi}{Na}, \frac{4\pi}{Na}, \dots, \frac{2\pi}{a}$. If the position is transformed according to a Fourier transform then the momentum should undergo an inverse Fourier transform

$$p_n = N^{-1/2} \sum_k e^{ikan} p'_k.$$

Using this transformation, the system decouples into independent harmonic oscillators

$$\mathcal{H} = \sum_k \left(\frac{p'_{-k} p'_k}{2m} + \frac{m\omega_k^2 x'_{-k} x'_k}{2} \right),$$

where $\omega_k^2 = (\kappa/m) \sin^2(ka/2)$. The enthusiastic student might want to confirm this using the identity $\sum_n \exp(i(k+q)an) = N\delta_{k,q}$.

So far, all we have done is the same transformation we saw in the Newtonian framework, but now in the Hamiltonian framework which can be applied to a quantum as well as classical system. We now specify to the quantum case and use second year quantum mechanics to find the energy spectrum of the decoupled harmonic oscillators.

- (a) Use that $[x'_k, p'_q] = i\hbar\delta_{k,q}$ follows from $[x_m, p_n] = i\hbar\delta_{m,n}$, and that $x'_k = x'_{-k}$ and $p'_k = p'_{-k}$ follows from the Hermiticity of x_n and p_n . Defining the operator a_k by

$$a_k = \left(\frac{m\omega_k}{2\hbar}\right)^{1/2} \left(x'_k + \frac{i}{m\omega_k} p'_k\right),$$

show that the Hamiltonian simplifies to the form

$$\mathcal{H} = \sum_k \hbar\omega_k (a_k^\dagger a_k + 1/2).$$

- (b) We have now quantised the decoupled oscillators. What is the energy spectrum? Explain what each of the new operators means physically. Referring to your answer, or otherwise, explain what a phonon is.

What we have done in the previous two questions is really important. We have shown that for atoms with harmonic coupling, there is some linear transformation into a set of normal coordinates independently undergoing harmonic motion. In the quantum regime, the excitation of any motion must be quantised. For a normal coordinate, this quantisation is particularly simple because it is of the form of a harmonic oscillator; the allowed quantised energies of each mode are linear increments of $\hbar\omega_k$. The quantised excitations of normal modes then have an elegant interpretation. If the quantum state for one of the normal modes is in the n -th excited state then we say there are n phonons in that mode, each contributing an energy $\hbar\omega_k$. This interpretation can be extended, a_k^\dagger (a_k) can be thought of as creation (annihilation) operators for a phonon in mode k , and we find that phonons must then be bosons since $[a_k, a_k^\dagger] = 1$.

This is general, and is not specific to the case of identical equally spaced atoms in one dimension. For any periodic arrangement of atoms with harmonic coupling, there will be some linear transformation into a set of normal coordinates independently undergoing harmonic motion with frequency ω_k , which can be found classically via an ansatz provided by Bloch's theorem. The quantised excitations of these modes will be phonons with energies $\hbar\omega_k$. So next we will find ω_k for both a uniform and non-uniform set of atoms, using classical Newtonian mechanics, as would be asked of you in an exam. We will now also be able to understand the significance of this for the quantum description of the atoms, and why we use the ansatz and allowed wavevectors we do.

6. (a) State the equations governing the motion of the longitudinal atomic displacements. State the appropriate ansatz for solving these equations, assuming BvK boundary conditions. Which wavevectors are permitted by these conditions?
- (b) Show that the mode with wavevector k has the same pattern of mass displacements as the mode with wavevector $k + 2\pi/a$, and so the two solutions are identical. Hence show that all independent modes can be represented by wavenumbers in the first Brillouin zone $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$.
- (c) Derive and sketch the dispersion relation for longitudinal vibrations of the chain. Show that there are N independent modes in total.
- (d) Derive the phase and group velocities and sketch them as a function of k . Calculate the sound velocity v_s . Show that the the sound velocity is also given by $v_s = 1/\sqrt{\beta_c\rho}$ where ρ and β_c are the chain density and compressibility, respectively.
7. Now consider a diatomic chain of alternating masses m_1 and m_2 , with $m_1 < m_2$ and a unit cell size of a , i.e. adjacent masses have an equilibrium separation of $a/2$. Assume the effective spring constant κ between masses is the same for all neighbours, and there are N masses in total.

- (a) and (b) Repeat parts (a) and (b) of the previous question.
- (c) Derive and sketch both branches of the dispersion relation for longitudinal vibrations of the chain, explaining the process what is meant by *optical* and *acoustic* modes. How is the motion different between the two in the limit $k \rightarrow 0$? Show that there are N independent modes in total.
- (d) State the number of optical and acoustic modes in d -dimensional system with s atoms per unit cell, and give reasons why this is the case.
8. Relate the treatments of Dulong and Petit, Einstein and Debye for the heat capacity to the description of atomic vibrations in terms of phonons. In your answer, refer to the number and type of phonon modes, and both high and low temperature predictions of heat capacity.

3 Thermal expansion

We have extensively studied the properties of atoms whose coupling can be approximated by harmonic forces, which is usually a decent approximation and explains many properties of solids. However, the symmetry of a harmonic potential means that exciting the atoms is as likely to decrease the separation between them as it is to increase it. Therefore thermal expansion requires anharmonic effects to explain it. As a simple example, we again focus on just two atoms and consider only the lowest order anharmonic term in 1D.

9. In the two atom case and for small energies we can expand the interatomic potential about its minimum x_0 up to third order as

$$V(x - x_0) = \frac{\kappa}{2}(x - x_0)^2 - \frac{\kappa_3}{3!}(x - x_0)^3 + \mathcal{O}(x - x_0)^4,$$

where x is the separation of the two atoms and $\kappa_3 > 0$.

- (a) By expanding the Boltzmann factor as

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

evaluate the classical expectation of x

$$\langle x \rangle = \frac{\int dx x e^{-\beta V(x-x_0)}}{\int dx e^{-\beta V(x-x_0)}}.$$

to the lowest order in κ_3 . When is the expansion likely to be valid? Show, further assuming $k_B T \ll \kappa x_0^2$, that the coefficient of thermal expansion is given by $\alpha = \frac{1}{x_0} \frac{d\langle x \rangle}{dT} = \frac{1}{x_0} \frac{\kappa_3 \kappa}{2\kappa^2}$.

- (b) Quantum mechanically, we can treat the cubic term as a perturbation to a harmonic oscillator. If we do this, we obtain for the expectation value of x in the n -th eigenstate

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

with energies $E_n = \hbar \omega_0 (n + 1/2) + \mathcal{O}(\kappa_3)$, and $\omega_0 = \sqrt{\kappa/m}$. Show that

$$\langle x \rangle = \frac{\sum_n \langle n|x|n \rangle \exp(-\beta E_n)}{\sum_n \exp(-\beta E_n)} \approx x_0 + \frac{\langle E \rangle_{\text{harm}} \kappa_3}{2\kappa^2},$$

where $\langle E \rangle_{\text{harm}}$ is the average energy of a quantum harmonic oscillator of frequency ω_0 at temperature T . Evaluate the coefficient of thermal expansion (solutions to Qu. 7 in the first tutorial might help) and compare to the classical limit.

(c) How good is this model at explaining the thermal expansion of a 1D chain of atoms?

In this tutorial we have looked in depth at how electrons stick atoms together to form solids. Considering only harmonic coupling between atoms, we showed that the periodicity of atoms leads to their collective vibrations being labelled by some crystal momentum $\hbar\mathbf{k}$. These collective vibrations are just harmonic motion with frequencies $\omega_{\mathbf{k}}$ in some set of normal coordinates, and the elementary quantum excitations of these modes are bosonic, called phonons and have energies $\hbar\omega_{\mathbf{k}}$. We found the modes were uniquely labelled by \mathbf{k} in some primitive cell of the reciprocal lattice and for multiple dimensions and non-trivial basis there are multiple modes for each wavevector \mathbf{k} (the reduced zone interpretation), such that the total number of modes equals to the number of original degrees of freedom dN . Beyond this, removing the harmonic approximation is needed to explain some things, e.g. thermal expansivity.