Lecture 5: Quantum Mechanics in Periodic Potentials

Tuesday, September 12, 2017

Introduction: Aside from dilute gases, it is rare that solving the Scrhödinger equation for an isolated atom is meaningful. Most often we are faced with describing the behavior of Avagodro's number of atoms, usually in periodic arrangments, or crystals.
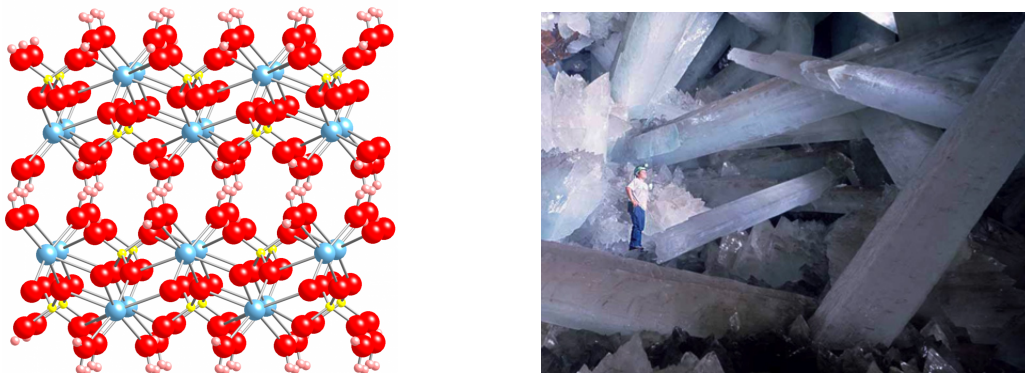

Figure 1: Left: Crystalline structure of Gypsum. Right: Cueva de los Cristales (Cave of Crystals) contains some of the world's largest known natural crystals – translucent beams of gypsum as long as 36 feet (11 meters)[1]

The real space and reciprocal space lattice: In the presence of a potential with translational symmetry, the Eigenfunctions of the Hamiltonian operator $\widehat{H}$ of the Shrödinger equation must also possess translational symmetry, as shown in the figure below:
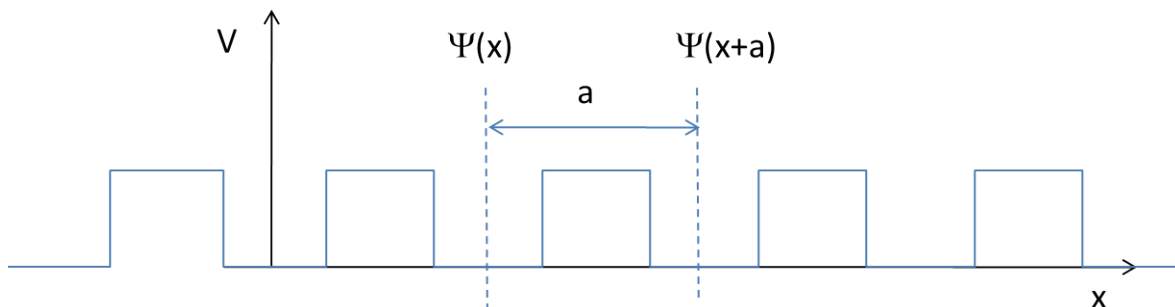

Figure 2: The Eignenfunctions in a periodic one dimensional potential must also possess translational symmetry. The Eigenfunctions $\Psi(x)$ and $\Psi(x + a)$ must be equal within a phase factor, as they sit in equivalent points in the unit cell, designated by region between the two dashed lines in the figure.

[1] http://news.nationalgeographic.com

Bloch postulated that the Eigenstates in a periodic system must satisfy the following equation:

$$\Psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\Psi(\mathbf{r}) \tag{1}$$

The vector $\mathbf{R}$ is called a primitive lattice vector, given by $\mathbf{R} = na\mathbf{a}_1 + mb\mathbf{a}_2 + lc\mathbf{a}_3$, where the set of $\{\mathbf{a_i}\}$ are unit translation vectors which point to equivalent points in the lattice. The above leads us to focus only on a small region defined by symmetry to be the region between the perpendicular bisectors of all lines drawn to equivalent points in an n-dimensional lattice, known as the unit cell (bounded by dotted lines in figures 2 and 3). As will be shown in the following paragraphs, due to the symmetric way that $\mathbf{R}$ and $\mathbf{k}$ appear in (1), we can also define a *reciprocal space* lattice, shown in the rightmost portion of figure 3. The unit cell in reciprocal space is called the 1st Brilloun zone.
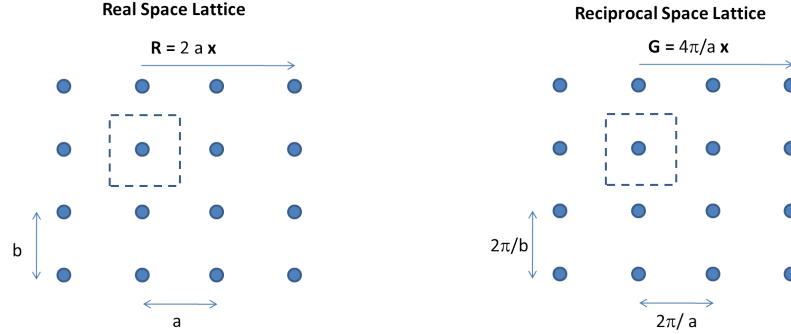

Figure 3: The unit cell (dashed box) in a 2-D rectangular lattice in real space and reciprocal space, with corresponding primitive lattice vectors $\mathbf{R}$ and reciprocal lattice vectors $\mathbf{G}$.

Casting the Schrödinger Equation in a Periodic Potential: Due to the symmetry of the problem, it is advantageous to express $\Psi(\mathbf{r})$ in terms of it's Fourier decomposition, in terms of the spatial frequency $\mathbf{k}$, which is an alternate form of Bloch's Theorem:

$$\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \tag{2}$$

Where $u_{\mathbf{k}}(\mathbf{r})$ is known as the Bloch envelope function and is by definition periodic over one unit cell ($u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$). The above expression guarantees the requirements of equation (1) and translational symmetry if we choose $\mathbf{k}$'s according to the following recipie:

$$\mathbf{k} = 2\pi m/Na\ \hat{\mathbf{k}}\ ,\ -N/2 > m \geq N/2, \text{ where } m \text{ is an integer and } \hat{\mathbf{k}} = \alpha_i\ \mathbf{b}_i$$

where N is the number of periods in the lattice of lattice parameter a, and $\{\mathbf{b}_i\}$ are unit vectors defined below.

Looking at equation (1) we see that adding multiples of $2\pi/a$ to $\mathbf{k}$ will only contribute factors of $e^{i\mathbf{G}\cdot\mathbf{R}} = e^{in2\pi}$ to $\Psi(\mathbf{r})$ in equation (1), thus:

$$\Psi(\mathbf{k} + \mathbf{G}) \text{ and } \Psi(\mathbf{k}) \text{ both satisfy Bloch's Theorem}$$

Thus for every $\mathbf{k}$, there are a number of equivalent $\mathbf{k} + \mathbf{G}$'s, where $\mathbf{G} = n\frac{2\pi}{a}\mathbf{b}_1 + m\frac{2\pi}{b}\mathbf{b}_2 + l\frac{2\pi}{c}\mathbf{b}_3$, and $\{\mathbf{b_i}\}$ are the set of unit vectors which point to equivalent points in reciprocal space. Thus we can imagine an alternative lattice, as plotted in figure 3 for a 2-D square lattice, where all equivalent $\mathbf{k}$-vectors are plotted. Here $\mathbf{G}$, known as a reciprocal lattice vector, translates from one lattice point in reciprocal space to an equivalent point in reciprocal space, to form the so-called *reciprocal lattice*, an n-D lattice in analogy to the real space lattice, as shown in figure 3. Looking at the range of possible $\mathbf{k}$, based on the range of m, we see that unique values of $\mathbf{k}$ satisfy:

$$|\mathbf{k}| \in \left(-\frac{\pi}{a}, \frac{\pi}{a}\right)$$

This range defines the unit cell in reciprocal space and is known as the 1st Brillouin zone, as sketched in figure 3. While Bloch's theorem is unaffected by adding a reciprocal lattice vector $\mathbf{G}$, the Eigenvalue (usually the energy) usually *is* affected, thus $\omega(\mathbf{k}) \neq \omega(\mathbf{k} + \mathbf{G})$. This motivates what is known as the reduced-zone scheme, where we only plot values of $\mathbf{k}$ in the first Brillouin zone, but the values of $\omega(\mathbf{k})$ are not in general periodic in $\mathbf{G}$, as shown in figure 4 below:
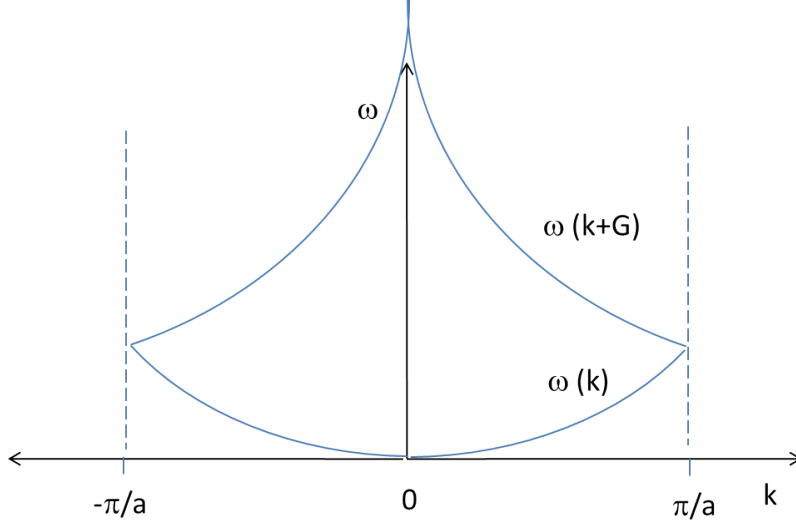
Figure 4: The disperion relation for a free electron plotted in the reduced zone scheme, unique values of $|\mathbf{k}| \in \left(-\frac{\pi}{a}, \frac{\pi}{a}\right)$ define the first Brillouin zone. Note $\omega(\mathbf{k}) \neq \omega(\mathbf{k} + \mathbf{G})$. Here, we have not *solved* for $\omega(\mathbf{k})$, we only show how it will be plotted.

The Central Equation: We have introduced the concept of Bloch functions, which we will see are Eigenfunctions of $\widehat{H}$ in a periodic potential. These Bloch functions are analogous to a Fourier decomposition of the general wavefunction in a solid, they are the so-called normal modes of the system. In a similar way, we will decompose the wavefunction and the 1-D periodic potential of figure 2 in terms of Fourier components:

$$\psi(x) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{ikx} \qquad \text{and} \qquad U(x) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{iGx}$$

Inserting these into the time-independent Schrödinger's equation we arrive at:

$$\frac{\hbar^2}{2m} k^2 \sum_{\mathbf{k}} c_{\mathbf{k}} e^{ikx} + \sum_{\mathbf{G}} \sum_{\mathbf{k}} c_{\mathbf{k}} U_{\mathbf{G}} e^{i(k+G)x} = E \sum_{\mathbf{k}} c_{\mathbf{k}} e^{ikx}$$

since we are summing over all $\mathbf{k}$, we can shift the sum in the second term by $-\mathbf{G}$ and simplify the equation:

$$\sum_{\mathbf{k}} \left\{ (\frac{\hbar^2}{2m} k^2 - E)c_{\mathbf{k}} + \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} U_{\mathbf{G}} \right\} e^{ikx} = 0$$

By the orthogonality of the set of functions $\{e^{ikx}\}$, each term must be identically zero, and we arrive at the central equation of solid state physics:

$$(\lambda_{\mathbf{k}} - E)c_{\mathbf{k}} + \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} U_{\mathbf{G}} = 0$$

where $\lambda_{\mathbf{k}} = \dfrac{\hbar^2 k^2}{2m}$ is the kinetic energy of a free electron with wavevector $\mathbf{k}$.

Solving the Central Equation: We have stated that the time-independent Schrödinger's equation takes the form of an Eigenvalue problem. If the Eigenstates are discrete, this can be expressed in matrix form. For simplicity, let us solve the central equation by assuming only two terms in the sum over $\mathbf{G}$ contribute, namely $\pm\mathbf{G}$. Further, we will solve for a plane wave state with $\mathbf{k} \equiv \mathbf{G}/2$, thus $|\mathbf{k}| = |\mathbf{k} - \mathbf{G}| = |\mathbf{G}/2|$. With these assumptions, we can write out the central equation:

$$(\lambda_{\mathbf{k}} - E)C_{\mathbf{k}} + U_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0$$
$$(\lambda_{\mathbf{k}-\mathbf{G}} - E)C_{\mathbf{k}-\mathbf{G}} + U_{-\mathbf{G}} C_{\mathbf{k}} = 0$$

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Let us write it in the standard Eigenvalue form $\mathbf{A}\mathbf{x} = \lambda\mathbf{x}$:

$$\underbrace{\begin{pmatrix} \lambda_{\mathbf{k}} & U_{\mathbf{G}} \\ U_{-\mathbf{G}} & \lambda_{\mathbf{k-G}} \end{pmatrix}}_{\mathbf{A}} \underbrace{\begin{pmatrix} C_{\mathbf{k}} \\ C_{\mathbf{k-G}} \end{pmatrix}}_{\mathbf{x}} = \underbrace{E}_{\lambda} \underbrace{\begin{pmatrix} C_{\mathbf{k}} \\ C_{\mathbf{k-G}} \end{pmatrix}}_{\mathbf{x}}$$

We can see in this form that the $\lambda_{\mathbf{k}}$ represent the free electron energies, and that the $U_{\mathbf{G}}$'s represent the interaction between the Bloch waves of wavevector $\mathbf{k}$ and $\mathbf{k}-\mathbf{G}$. If $U_{\mathbf{G}} = 0$, then $E = \lambda_{\mathbf{k}}$. With $\mathbf{k} = \mathbf{G}/2$ and $U_G = U_{-G} = U$, this can be written in the form $(\mathbf{A} - \lambda\mathbf{I})\mathbf{x} = 0$:

$$\begin{pmatrix} \lambda - E & U \\ U & \lambda - E \end{pmatrix} \begin{pmatrix} C_{\mathbf{G}/2} \\ C_{-\mathbf{G}/2} \end{pmatrix} = 0$$

Where we used the fact that $\lambda_{\mathbf{G}/2} = \lambda_{-\mathbf{G}/2} \equiv \lambda$. From our knowledge of the Eigenvalue problem, we know that the determinant of the above matrix must be zero, from which we derive the characteristic equation:

$$|\mathbf{A} - \lambda\mathbf{I}| = 0 \longrightarrow (\lambda - E)(\lambda - E) - U^2 = 0 \longrightarrow E = \lambda \pm U$$

The resulting equation says that the degeneracy which appears at $\mathbf{k} = \mathbf{G}/2 = \frac{\pi}{a}$, that is at the Brillouin zone boundary, is lifted by the interaction of the two waves labeled by $\mathbf{k}$ and $\mathbf{k}-\mathbf{G}$ by the interaction potential U, and that the energy splitting is $\Delta E = 2U$. We see in figure 5 that this modifies the energy dispersion relation, by bending the energy levels up or down from the free electron dispersion relation plotted in figure 3. As a result, there is a finite range of energies for which there is no corresponding $\mathbf{k}$-state, this is the so-called "forbidden zone", or "bandgap".
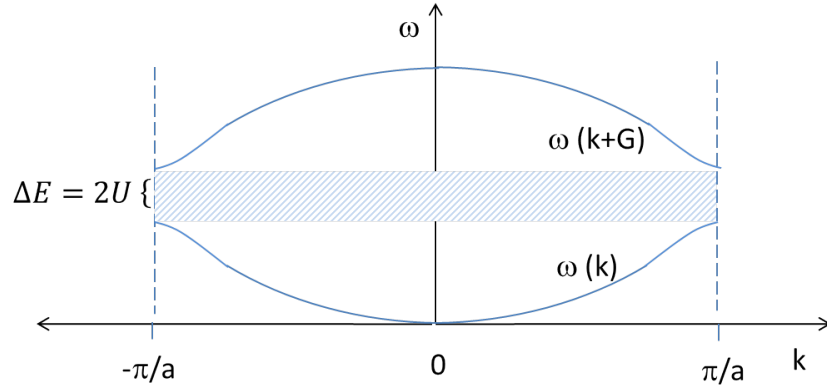

Figure 5: The energy dispersion relation for electrons in a periodic potential, where the interaction of the waves labeled by $\mathbf{k}$ and $\mathbf{k}-\mathbf{G}$, for $\mathbf{k} = \mathbf{G}/2$, splits the energy levels by $\pm U$, leading to a range of energies $\Delta E = 2U$ wherein no state exists – the so-called "bandgap".

In summary, by solving the Schrödinger equation in a periodic potential, we found through Bloch's theorem that the Eigenstates of the Hamiltonian are Bloch waves, and that the Eigenergies and Eigenfunctons are labeled by the wavevector $\mathbf{k}$. We say that $\mathbf{k}$ is "a good quantum number" in a periodic potential, as it serves the role of a label for the quantized states, similar to n in the Bohr model of the Hydrogen atom or the particle in a box problem. Further, we discovered that the free electron energies are modified by the interaction potential $U(\mathbf{r})$, and as a consequence, a range of energies wherein no state exists appears. These so-called "bandgaps" are a fundamental consequence of waves interacting with a periodic potential.

Let us look at another example wherein such a gap appears in the energy spectrum: the vibrational energies in solids.

Lattice vibrations in solids: The vibrations of atoms in a crystal can be cast in the form of an Eigenvalue problem. Further, the Eigenstates of the chain must possess translational symmetry, thus vibrations in a solid can also be described by Bloch states. The energy of these waves will be described by a continuous function of $\mathbf{k}$, a so called *dispersion* relation. As an example, let us derive the dispersion relation for the linear chains shown in figure 6:
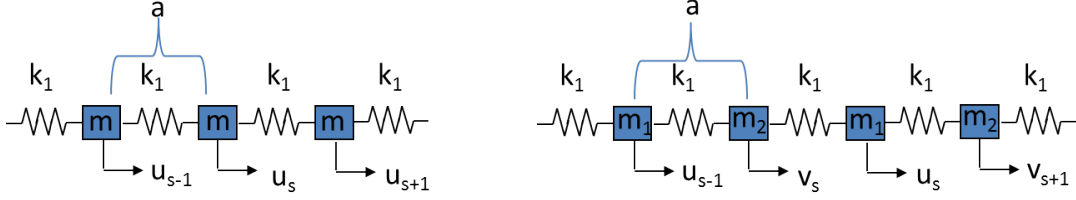

Figure 6: (Left): The infinitessimal displacement of the sth atom of the linear chain of masses m coupled by spring constant k_1, with lattice constant a, represented by the coordinates u_s. (Right) The infinitessimal displacement of the sth atoms of mass m_1 or m_2 in a diatomic chain, are designated by u_s and v_s, respectively. The masses are coupled linearly by springs of spring constant k_1.

If we assume the displacement u_s can be described by a plane wave $u_s = e^{i(ksa-\omega t)}$, we can use Newton's law to write out the equation of motion for the monatomic chain (leftmost chain of identical masses m):

$$F = ma \longrightarrow m\ddot{u}_s = -k_1(u_s - u_{s+1}) - k_1(u_s - u_{s-1}) = k_1(u_{s+1} + u_{s-1} - 2u_s)$$

using $\ddot{u}_s = -\omega^2 u_s$, and substituting the plane wave form for u_s, we have:

$$-m\omega^2 u_s = k_1 u_s(e^{ika} + e^{-ika} - 2) \longrightarrow \omega^2 = \frac{2k_1}{m}(1 - \cos(ka)) \longrightarrow \omega = \sqrt{\frac{4k_1}{m}}|\sin(ka/2)|$$

The result says that the frequency (and thus energy) of vibrations for low wavevector are approximately linear with the wavevector $k = \frac{2\pi}{\lambda}$. Thus very long wavelength vibrations, corresponding to collective displacements of many atoms, have an energy close to zero which varies linearly with k.
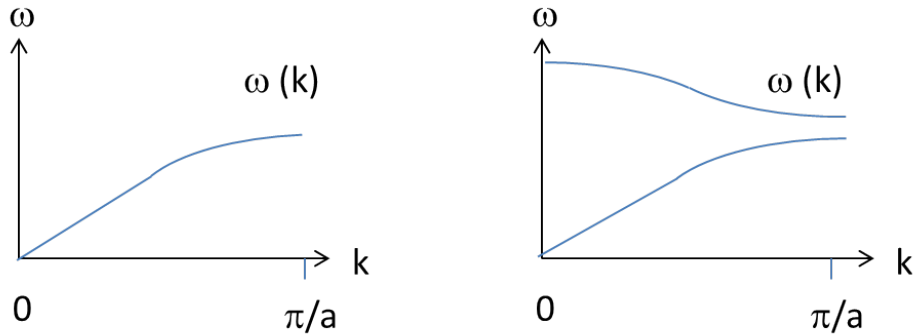

Figure 7: (Left): Dispersion relation for the linear chain of masses m coupled by spring constant k_1, with lattice constant a. (Right): Dispersion relation for the diatomic chain of masses m_1 and m_2, showing upper and lower branches.

The equations for the diatomic chain can be written in a similar way, using the distinct coordinates u_s and v_s to keep track of the different masses, thus we define the vector:

$$\mathbf{x}_s = \begin{pmatrix} u_s \\ v_s \end{pmatrix} e^{i(kas-\omega t)}$$

using $\mathbf{F} = m\mathbf{a}$, one can obtain the system of equations:

$$m_1\ddot{u}_s = k_1(v + v_{s-1} - 2u_s)$$
$$m_2\ddot{v}_s = k_1(u_{s+1} + u_s - 2v_s)$$

We can use the same subsitutions to arrive at a set of coupled equations:

$$-m_1\omega^2 u_s = k_1(1 + e^{-ika})v_s - 2k_1 u_s$$
$$-m_2\omega^2 v_s = k_1(e^{ika} + 1)u_s - 2k_1 v_s$$

If we divide through by $-m$ and define $\omega_i^2 = \frac{k_1}{m_i}$, these equations can be written in the standard Eigenvalue equation form:

$$\underbrace{\begin{pmatrix} 2\omega_1^2 & -\omega_1^2(1 + e^{-ika}) \\ -\omega_2^2(1 + e^{ika}) & 2\omega_2^2 \end{pmatrix}}_{\mathbf{A}} \underbrace{\begin{pmatrix} u_s \\ v_s \end{pmatrix}}_{\mathbf{X}} = \underbrace{\omega^2}_{\lambda} \underbrace{\begin{pmatrix} u_s \\ v_s \end{pmatrix}}_{\mathbf{X}}$$

Computing the determinant $|\mathbf{A} - \lambda\mathbf{I}| = 0$ will yield a quadratic characteristic equation in the eigenvalue ω^2.

This is a general feature of the Eigenvalue problem: an $n \times n$ system yields an nth - order characteristic equation. Because there are two possible roots for every value of k, the corresponding dispersion relation will have two branches, as shown in the rightmost portion of figure 7. This is the energy dispersion relation for vibrations in a solid, the so called "phonon", for a solid with two atoms per unit cell. The upper branch is known as the "optical" branch, because it always has a higher energy, even at $k = 0$, while the lower branch, known as the "acoustic" branch, has very low energy which approaches 0 near $k = 0$. Optical phonons can couple to light at $k = 0$, but have a discrete energy, typically in the range of 30meV. Acoustic phonons have no such threshold, and a continuum of energies starting from $E = 0$.