1 Periodic potentials in one dimension

For obvious reasons, the problem of a particle moving in a periodic potential is ubiquitous in the theory of solids. Consider the simplest periodic potential in one dimension

\[ V(x) = -V_0 \cos \left( \frac{2\pi x}{a} \right). \]

Let’s treat the effect of the potential as a perturbation acting on the plane wave states (in solid state courses, you’ll see this called *nearly free electron theory*). In order to deal with discrete indices, we make the whole system periodic with period \( L = Na \), so that the free particle eigenstates are

\[ \psi_{k_n}^{(0)} = \frac{1}{\sqrt{L}} e^{ik_n x}, \quad k_n = \frac{2\pi n}{L}, n = 0, \pm 1, \ldots \]

Naive first order perturbation theory gives us

\[ E_k^{(1)} = \langle \psi_k^{(0)} | V | \psi_k^{(0)} \rangle = \frac{1}{L} \int_0^L dx e^{-ikx} V(x) e^{ikx} = 0 \]

\[ |\psi_k^{(1)}\rangle = \sum_{n \neq kL/2\pi} \sqrt{\frac{E_k^{(0)} - E_{k_n}^{(0)}}{E_k^{(0)}}} |\psi_{k_n}^{(0)}\rangle, \quad E_k^{(0)} = \frac{\hbar^2 k^2}{2m} \]

Now the matrix elements \( \langle \psi_{k_n}^{(0)} | V | \psi_k^{(0)} \rangle \) in the numerator of Eq. (2) are non-zero only if \( |k_n - k| = 2\pi/a \), in which case they are \(-V_0/2\). On the other hand the denominator is non-zero unless \( E_k^{(0)} = E_{k_n}^{(0)} \), so that \(|k| = |k_n|\). So we see that there is a problem for \( k = \pm \pi/a \).

We know that the solution is to use degenerate perturbation theory, diagonalizing the perturbation in the subspace of degenerate states spanned by \( |\psi_{\pm \pi/a}\rangle \). In this subspace the perturbation takes the form

\[ \langle \psi_{\pm \pi/a}^{(0)} | V | \psi_{\pm \pi/a}^{(0)} \rangle \xrightarrow{\text{Diagonalize}} \begin{pmatrix} 0 & -V_0/2 \\ -V_0/2 & 0 \end{pmatrix} \]

Giving a pair of eigenvalues \( \pm V_0/2 \). Thus we conclude

\[ E_{|k|=\pi/a}^{(\pm)} = \frac{\hbar^2 \pi^2}{2ma^2} \pm V_0/2. \]
Figure 1: Dispersions relations $E^{(\pm)}(k)$ from degenerate perturbation theory along with the unperturbed eigenvalues.

Of course, as we approach the points $k = \pm \pi/a$ the denominators in the nonvanishing terms in Eq. (2) become large, so it makes sense to treat those nearby $k$ values in the same way. In the $2 \times 2$ subspace spanned by $k$ and $k - 2\pi/a$, we then have the matrix elements of the total Hamiltonian

$$
\begin{pmatrix}
\varepsilon_k & -V_0/2 \\
-V_0/2 & \varepsilon_{k-2\pi/a}
\end{pmatrix},
$$

with eigenvalues ($\Delta k = k - \pi/a$)

$$
E^{(\pm)}_k = \frac{\hbar^2\pi^2}{2ma^2} + \frac{\hbar^2\Delta k^2}{2m} \pm \sqrt{\left(\frac{\hbar^2\Delta k\pi}{ma}\right)^2 + \left(\frac{V_0^2}{2}\right)^2} \quad (3)
$$

The eigenvalues are sketched in Fig. [1]. A few comments are worth making at this point:

- What kind of approximation is this? $|\psi_k\rangle$ also has non-zero matrix element with $|\psi_{k+2\pi/a}\rangle$, and this in turn with $|\psi_{k+4\pi/a}\rangle$, (and likewise in the other direction). By considering the energy denominators with which such states would appear in perturbation theory, we see missing terms are of order $ma^2V_0/\hbar^2$.

- A general periodic potential only couples states with momenta differing by integer multiples of $2\pi/a$, so one can always write the eigenstates as

$$
\psi_k(x) = \sum_{n=-\infty}^{+\infty} a_n(k)e^{i(kx+2\pi nx/a)} = e^{ikx}\varphi_k(x) \quad (4)
$$

where $\varphi_k(x) = \varphi(x+a)$ is a periodic function. The result is called Bloch’s theorem (or Floquet’s theorem by the mathematicians). Although we label the solution by $k$, this is no longer the momentum. Instead of allowing this (pseudo-)momentum to range over $-\infty < k < \infty$, it is more convenient to restrict its values to $-\pi/a < k < \pi/a$ (the first Brillouin zone), and additionally use a discrete index to label the energy eigenbasis in the space spanned by the plane waves $|\psi_{k+2\pi n/a}\rangle$ for $-\infty < n < \infty$.
The result is a band structure, of which Fig. [1] is an example, with the two lowest bands shown. Bands are usually separated by bandgaps, the energy of closest approach. In our example the bandgaps for the higher bands arise from higher orders of perturbation theory.

- There are energy eigenfunctions in the band gaps – we just have to take $\Delta k$ in Eq. (3) to be imaginary i.e. exponentially growing or decaying solutions. This perspective is more often encountered when dealing with time-dependent problems of the form

$$\ddot{x} + \omega_0^2 (1 + \epsilon \cos \Omega t) = 0,$$

(Mathieu equation) which describes an oscillator in an oscillating quadratic potential. Translating the above results into this language shows that such an oscillator becomes unstable when its resonant frequency $\omega_0$ is close to $\Omega/2$ (which makes sense if you think about it).

2 Triangular lattice

This treatment can be generalized to higher dimensions, and we turn now to the particularly interesting example of the triangular lattice. Such a lattice can be formed by the minima of the potential

$$V_{\text{Triang.}}(r) = -V_0 \sum_{i=1}^{3} \cos k_i \cdot r$$

(5)

with $r = (z, x)$ (for reasons that will become clear shortly) and with the three vectors
Figure 3: The shaded triangle shows the Brillouin zone in \( k \)-space. The three red \( K \) points are coupled together by the perturbation, as are the three blue points (which correspond \( K \) points in the neighboring Brillouin zones)

(chosen so that the resulting lattice has constant \( a \))

\[
\begin{align*}
\mathbf{k}_1 &= \frac{4\pi}{\sqrt{3}a} (0, 1) \\
\mathbf{k}_2 &= \frac{4\pi}{\sqrt{3}a} \left( \sqrt{3}/2, 1/2 \right) \\
\mathbf{k}_3 &= \frac{4\pi}{\sqrt{3}a} \left( -\sqrt{3}/2, 1/2 \right)
\end{align*}
\]

\( V_{\text{Triang.}} \) is shown in Fig. 2. Let’s treat \( V_{\text{Triang.}} \) using degenerate perturbation theory. After some thought we can identify three degenerate states that are coupled by the perturbation, with momenta

\[
\begin{align*}
\mathbf{K}_1 &= \frac{2\pi}{\sqrt{3}a} (1, 0) \\
\mathbf{K}_2 &= \frac{2\pi}{\sqrt{3}a} \left( -1/2, \sqrt{3}/2 \right) \\
\mathbf{K}_3 &= \frac{2\pi}{\sqrt{3}a} \left( -1/2, -\sqrt{3}/2 \right)
\end{align*}
\]

and similarly for the three states related to these by rotation through 60°, see Fig. 3. In the basis of the plane waves \( e^{i\mathbf{K}_i \cdot \mathbf{r}} \) the matrix elements of \( V_{\text{Triang.}}(\mathbf{r}) \) are

\[
\begin{pmatrix}
0 & -V_0/2 & -V_0/2 \\
-V_0/2 & 0 & -V_0/2 \\
-V_0/2 & -V_0/2 & 0
\end{pmatrix},
\]

(6)
which has eigenvalues \(-V_0, V_0/2, V_0/2\): the degeneracy is not lifted by the lattice potential! In other words, two of the bands touch at the \(K\)-points.

Now we consider moving away from the \(K\)-points, just as we moved away from \(\pm \pi/a\) in the 1D case. If we consider the three states \(K_i + \Delta k\) coupled by the lattice potential, the kinetic energies of the three are no longer equal, and this tends to lift the remaining degeneracy. This turns out to be a linear effect, so we consider the expansion

\[
\begin{pmatrix}
E^{(0)}_{K_1 + \Delta k} - E^{(0)}_{K_1} \\
0 \\
E^{(0)}_{K_2 + \Delta k} - E^{(0)}_{K_2} \\
0 \\
E^{(0)}_{K_3 + \Delta k} - E^{(0)}_{K_3} \\
0
\end{pmatrix}
\sim \frac{\hbar^2}{m}
\begin{pmatrix}
K_1 \cdot \Delta k & 0 & 0 \\
0 & K_2 \cdot \Delta k & 0 \\
0 & 0 & K_3 \cdot \Delta k
\end{pmatrix}
\]

(9)

as a perturbation acting in the two dimensional degenerate subspace. The eigenvalue \(-V_0\) of Eq. (8) has eigenvector \((1, 1, 1)/\sqrt{3}\), while the degenerate subspace is spanned by the vectors with entries adding to zero. We pick the following basis

\[
\kappa_+ = \sqrt{\frac{2}{3}}(1, -1/2, -1/2) \quad \kappa_- = (0, -1/\sqrt{2}, 1/\sqrt{2})
\]

(10)

[remember these are not vectors in \(k\)-space, but in the subspace spanned by the plane waves \(e^{iK_i \cdot r}\)] If the kinetic energy matrix Eq. (9) is written \((\hbar^2/m) (\Sigma z \Delta k_z + \Sigma x \Delta k_x)\) with

\[
\Sigma_i = \text{diag} ((K_1)_i, (K_2)_i, (K_3)_i), \quad i = z, x
\]

then one can show that the action of \(\Sigma_i\) in the subspace spanned by \(\kappa_\pm\) is just (proportional to) that of the corresponding Pauli matrices

\[
\Sigma_z \kappa_\pm = \pm \frac{\pi}{\sqrt{3a}} \kappa_\pm
\]

\[
\Sigma_x \kappa_\pm = \frac{\pi}{\sqrt{3a}} \kappa_\mp
\]

(11)

[be careful here – the matrices \(\Sigma_i\) of course commute in the three dimensional space: it is only their projection into the degenerate subspace spanned by \(\kappa_\pm\) that is non-trivial]

The overall conclusion is that in the bands that touch at the \(K\)-points the kinetic energy operator Eq. (9) has the form

\[
\frac{\hbar^2}{2} \frac{\pi}{\sqrt{3a}} (\sigma_z \Delta k_z + \sigma_x \Delta k_x)
\]

(12)

so that just away from these points the bands have the structure \(E_\pm(\Delta k) = \pm \frac{\hbar^2}{2} \frac{\pi}{\sqrt{3a}} |\Delta k|\).

Eq. (12) has the form of a general symmetric 2 \(\times\) 2 matrix. In fact it is just the momentum space version of a Dirac equation. Let’s write the real space wavefunction for \(k\) near one of the \(K\) points as

\[
\psi_k(r) = \psi_+(r) \left( \sum_{i=1}^{3} (\kappa_+)_i e^{iK_i \cdot r} \right) + \psi_-(r) \left( \sum_{i=1}^{3} (\kappa_-)_i e^{iK_i \cdot r} \right)
\]

\[
= \psi_+(r) \varphi_+(r) + \psi_-(r) \varphi_-(r),
\]

(13)
where we identify $\varphi_{\pm}(r)$ with the periodic Bloch functions for the two touching bands (c.f. Eq. (4)). The doublet $\Psi = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}$ then satisfies two-dimensional (massless) Dirac equation

$$-i (\sigma_z \partial_z + \sigma_x \partial_x) \Psi = E \psi$$

- Note that there are three sublattices in the triangular lattice (see Fig. 4): removing the A sites leaves behind a honeycomb lattice.

Although these lattices are two-dimensional, they have real physical incarnations. A particularly popular material in current research is graphene, which consists of a single layer of the graphite structure of Carbon, see Fig. 5. Recent experiments on the electronic properties of these two-dimensional structures have revealed striking evidence for the Dirac spectrum. A more detailed calculation of the band structure is shown in Fig. 6: the Dirac cones are clearly visible. While the structure away from the cones is complicated, the position of the $K$-points is fixed by the lattice symmetry.

- What would happen if we destroyed or reduced the symmetry of the problem, for instance by stretching the lattice slightly in one direction? Is there still a point of degeneracy where the two bands touch? At least for small deformations this must be true: the effect of this deformation will be to introduce some additional $2 \times 2$ symmetric matrix into the band Hamiltonian. Obviously this may be compensated by a shift in $\Delta k$, so that the $K$-point moves. This is an example of the Wigner-von Neumann theorem: for a real symmetric Hamiltonian a degeneracy may generically be found by tuning two parameters (in this case the two components of the momentum). Contrast this situation with the 1D case, where a bandgap is the generic situation because we only have one parameter to vary. Note that for general hermitian Hamiltonians (that would result from breaking time-reversal symmetry) we would need to vary three parameters (c.f. problem 6, problem set 3).
Figure 5: Honeycomb graphene layers of carbon atoms stacked to form graphite.

Figure 6: Band structure of graphene showing the Dirac ($\kappa$) points arranged in a hexagon.
Some of the unusual properties arising from the Dirac cones are connected with the phase acquired by a particle whose momentum encircles one of the $K$-points. This can occur due to motion in a perpendicular magnetic field, for example. Using the result of problem 6, problem set 3, we see that this phase is just $\pm \pi$, and this enters into the semiclassical quantization rule for the particle’s energy.