0.1 Bloch waves

Let us consider now a periodic potential in one dimension:

$$V(a+x) = V(x) \tag{1}$$

This potential extends infinitely in both directions, so we can not apply the boundary conditions we would when examining a particle in a box, where the wave function would have to vanish at both sides of the box.

0.2 Shooting

To begin with, let's just simulate a few periods of this function (from $x = 0$ to $x = Na$ where N is some integer). We will be solving the energy eigenvalue equation,

$$\begin{aligned} \hat{H}|\psi\rangle &= E|\psi\rangle & (2) \\ -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) &= E\psi(x) & (3) \end{aligned}$$

You have all turned differential equations like this into finite difference equations before. In fact, this equation looks much like the equation from Balls and springs, with time changed to position. We can integrate this equation to find $\psi(x)$ (given knowledge of the initial conditions for $\psi(0)$ and $\psi(\Delta x)$) by writing this second derivative as a finite difference equation and solving for the "future" value of the wave function, meaning the value $\psi(x+\Delta x)$. Note that in doing this, we will be treating the energy E as a constant.

We can write the second spatial derivative as a finite difference:

$$-\frac{\hbar^2}{2m}\frac{\psi(x+\Delta x) + \psi(x-\Delta x) - 2\psi(x)}{\Delta x^2} = (E - V(x))\psi(x) \tag{4}$$

Solving for $\psi(x+\Delta x)$ gives us

$$\psi(x+\Delta x) = 2\psi(x) - \psi(x-\Delta x) + \frac{2m\Delta x^2}{\hbar^2}(V(x) - E)\psi(x) \tag{5}$$

Because this system is periodic and infinite, you will have no boundary conditions to apply at the right-hand side of your "box"! You can simply start with $\psi(x=0) = 0$. Because it is an unbound system, you also won't have to "aim" to find the energy, since any energy is possible (within a band). (Isn't solid state physics convenient?)

1. Pick a value of a and a periodic potential $V(x)$ such that $V(x+a) = V(x)$. Write a function to evaluate $V(x)$.
2. Write code to solve for $\psi(x)$ for a range 0 to L given the energy eigenvalue E (and of course the potential).
3. Visualize an energy eigenstate, and tweak your potential and energy eigenvalue E such that your energy eigenstate is clearly *not* sinusoidal.

Extra fun Plot dots on your curve at $\psi(a)$, $\psi(2a)$, etc.

0.3 Bloch's theorem

To understand your results, we will use Bloch's theorem. I will review here Bloch's theorem, and how we can use it to treat this periodic system.

Bloch's theorem states that for a periodic system (such as we are examining), the energy eigenstates *may* be written to have the following symmetry:

$$\begin{aligned} H\phi_k &= E_k\phi_k && (6)\\ \phi_k(a+x) &= e^{ika}\phi_k(x) && (7)\end{aligned}$$

In words, this means that when you translate by the distance of a lattice constant, a, the wave function only changes by a fixed phase, which we express using a quantum number k (known as the wave vector). However, Bloch's theorem does not mean that *every energy eigenstate* has this form! Time reversal symmetry guarantees that $E_{-k} = E_k$, which means that every energy eigenstate is degenerate (except at $k = 0$, or at the edge of the Brillouin zone). Thus, when we translate by a lattice constant we may find that the magnitude of the wave function changes, even for an energy eigenstate.

The shooting method that we just implemented enables us to find energy eigenstates. It does require that we have know or guess points ($\psi(0)$ and $\psi(\Delta x)$) as initial conditions. Because there are two degenerate eigenstates, when we guess any two arbitrary initial condidions, we will probably generate some linear combination of ϕ_k and ϕ_{-k}. Due to the nature of the method, we will always generate a linear combination that is purely real, which is in some ways convenient, although it differs greatly from the Bloch form.

You will pick $\psi(0) = 0$ and $\psi(\Delta x) \neq 0$ as your two initial conditions. As would be the case for any linear operator, your choice of the value for $\psi(\Delta x)$ only scales your solution by some constant value. Given these choices (which happen to be the same as you would have used to the particle in a box) and a choice for E, you can integrate to find the wave function $\psi(x)$ for several periods of the potential. As long as your energy is within an allowed band, this will be an energy eigenstate that is some linear combination of ϕ_k and ϕ_{-k}.

$$\psi(x) = A\phi_k(x) + B\phi_{-k}(x) \qquad (8)$$

where A and B are unknown complex constants. We can now apply Bloch's theorem to find a relationship between a few periods.

$$\begin{aligned} \psi(0) &= A\phi_k(0) + B\phi_{-k}(0) && (9)\\ \psi(a) &= A\phi_k(0)e^{ika} + B\phi_{-k}(0)e^{-ika} && (10)\\ \psi(2a) &= A\phi_k(0)e^{2ika} + B\phi_{-k}(0)e^{-2ika} && (11)\end{aligned}$$

Here it pays off that we chose $\psi(0) = 0$, since it means that $A\phi_k(0) = -B\phi_{-k}(0)$, and thus we can simply give each of these two values a name, which I will call C.

$$\begin{aligned} \psi(0) &= 0 && (12)\\ \psi(a) &= Ce^{ika} - Ce^{-ika} && (13)\\ \psi(2a) &= Ce^{2ika} - Ce^{-2ika} && (14)\end{aligned}$$

Now you can see that C must be purely imaginary (since your wave function is purely real). So I will rename it $C = -Di/2$, and reexpress the equation:

$$\begin{aligned} \psi(0) &= 0 \qquad (15) \\ \psi(a) &= D\sin(ka) \qquad (16) \\ \psi(2a) &= D\sin(2ka) \qquad (17) \end{aligned}$$

At this point, we are ready to solve for k, since we have already solved for $\psi(a)$ and $\psi(2a)$ numerically.

$$\begin{aligned} \frac{\sin(2ka)}{\sin(ka)} &= \frac{\psi(2a)}{\psi(a)} \qquad (18) \\ \frac{2\cos(ka)\sin(ka)}{\sin(ka)} &= \frac{\psi(2a)}{\psi(a)} \qquad (19) \\ \cos(ka) &= \frac{\psi(2a)}{2\psi(a)} \qquad (20) \\ k &= \frac{1}{a}\cos^{-1}\left(\frac{\psi(2a)}{2\psi(a)}\right) \qquad (21) \end{aligned}$$

Thus you can solve for the wave vector corresponding to a given energy.

1. Plot an energy eigenstate $\psi(x)$ for your potential. Then plot (on the same plot) dots (plusses, or whatever) at $\psi(0)$, $\psi(a)$, $\psi(2a)$, etc. The dots should lie on top of your curve.

   WARNING : Do **not** say "circle" instead of "dot" when searching for these symbols. All searches for "matplotlib circle" give information for creating geometric shapes.

2. Try a few different energies. Are there any energies that show different behavior? Be sure try energy values that are both larger than the potential energy maximum, as well as energies below the maximum. At the lower energies, your particle will need to tunnel from one well to the next.

   If your wave function grows exponentially (with periodic wiggles), your chosen energy is probably in a band gap or below the ground state energy.

   If your wave function is stubbornly almost sinusoidal, you may need a larger amplitude of potential energy, or you may need to make your lattice constant a larger.

3. Solve for k using the inverse cosine formula (21), and plot $\sin(kx)$ on the same plot as the wave function. It should pass through the points $\psi(nka)$ that you have already plotted.

4. Solve for $\psi(x)$ and k for numerous energies, so that you can construct a band structure plot, which is a plot of E versus k.

Extra fun Plot the wave function at (or as close as you can get to) several symmetry points. $k = 0$ is a wonderful symmetry point, as is the Brillouine zone edge. You will want to do this for several bands.

More fun Try picking some other interesting periodic potential $V(x)$ such that $V(x + a) = V(x)$ for all x. Or perhaps try tweaking the amplitude of the sinusoidal potential.

0.3.1 Energies in the band gap

You will inevitably at some point choose an energy that is within a band gap (or perhaps below the ground state energy). When this happens, your code will still solve for a wave function, but that wave function will be growing exponentially. It may be necessary to plot $\psi(x)$ over many periods to see what is going on. When using the inverse cosine formula, these states may manifest as illegal values, since there will be no solution to the inverse cosine (no angle has a cosine greater than one). You don't want to plot these solutions.

These states in the band gap are truly energy eigenstates, but they are not travelling waves (or linear combinations of travelling waves). Physically, they can manifest as surface states, and in tunneling through a finite layer of crystal. You can understand them if you think of Bloch's theorem from the perspective of a translation operator.

Imagine a translation operator S (named for symmetry) which has the following behavior:

$$S\psi(x) = \psi(x+a) \tag{22}$$

With a bit of work, you can convince yourself that this equation fully defines this translation operator. It is not too hard to prove that for a period system (with period a) the translation operator commutes with the Hamiltonian:

$$[H, S] = 0 \tag{23}$$

This means that the energy eigenstates can be chosen to also be eigenstates of S. Thus we can always write our energy eigenstates such that

$$\psi(x+a) = A\psi(x) \tag{24}$$

Now you may ask what eigenvalues the translation operator might have. The translation operator is a unitary operator, which normally means that its eigenvalues have magnitude 1 (and thus could be written e^{ika}). However, when we consider an infinite system we have the possibility of considering non-normalizable wave functions. As it turns out, if you allow non-normalizable wave functions (e.g exponentially growing functions), the translation operator can have other magnitudes. This is what happens when the energy is not in an "allowed" band. These are "evanescent" waves, which can only physically exist if you place an interface in the system, which allows the waves to be normalized.

0.4 Last day on bloch waves

1. Create a band structure plot.
2. Improve your band structure plot.
3. Visualize $\psi(x)$ for energies at the symmetry points. Ideally you'll end up with at least four plots, with states at the zone center ($k = 0$) and zone edge ($k = \pi/a$) for two different bands.