The Central Equation
by Dr. Colton, Physics 581 (last updated: Fall 2020)

This is the Central Equation:

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

It's a set of equations, one for each $\mathbf{k}$, which basically represent a Fourier transform of the Schroedinger equation.

- The $\mathbf{G}$ vectors are the reciprocal lattice vectors, or RLVs for short.
- The $U_{\mathbf{G}}$ terms are the Fourier components of the potential energy, $U(\mathbf{r})$. Remember from Chapter 2 that the 3D Fourier transform of a periodic function results in a summation over the reciprocal lattice vectors, $U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$.
- The $C_{\mathbf{k}}$ terms are the expansion coefficients of the wave function ψ written as a Fourier series of plane waves, $\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$.
- $\lambda_k = \frac{\hbar^2 k^2}{2m}$ represents the free particle energy corresponding to a given momentum k.

Here's a recipe for how to use the Central Equation to solve for allowed energies, given a periodic potential energy function $U(\mathbf{r})$.

1) Decide on an appropriate level in which to truncate the summation over the RLVs; in the example below we use 14 $\mathbf{G}$ values.
2) Calculate the Fourier coefficients of U, the $U_{\mathbf{G}}$ values, for the $\mathbf{G}$'s decided on in step 1.
3) Pick a particular $\mathbf{k}$ value you're interested in.
4) Figure out which other $\mathbf{k}$ values are connected to your particular $\mathbf{k}$ via your chosen set of $\mathbf{G}$'s. The ones that couple to $\mathbf{k}$ are $\mathbf{k} - \mathbf{G}_1$, $\mathbf{k} - \mathbf{G}_2$, etc. Those form a set of $\mathbf{k}$ values. Similarly $C_{\mathbf{k}}$, $C_{\mathbf{k}-\mathbf{G}_1}$, $C_{\mathbf{k}-\mathbf{G}_2}$, etc., form a set of expansion coefficients you'll be working with.
5) Write down the Central Equation for each of the $\mathbf{k}$'s in your set: your $\mathbf{k}$ plus each of the connected $\mathbf{k}$'s. There will be a lot of $C_{\mathbf{k}}$-type expansion coefficients in the equations, some of which are $C_{\mathbf{k}}$ for your particular $\mathbf{k}$ of interest; others of which are coefficients for different $\mathbf{k}$'s.
6) Throw out all of the $C_{\mathbf{k}}$'s that go beyond your chosen set of $\mathbf{k}$ values. You'll be left with, say, five equations and five unknowns (the number depends on your choice in step 2). The unknowns are the $C_{\mathbf{k}}$ coefficients for your particular $\mathbf{k}$ and for all of the connected $\mathbf{k}$'s which remain.
7) Set up an eigenvalue-style matrix equation which you can use to solve for the energies, e.g. five different E values which are the energies for the first five bands at your chosen $\mathbf{k}$.

Compare this to how you might calculate the Madelung constant for an arbitrary crystal type: you would set up an infinite summation, but then cut it off at a certain point in real space and say that further distances don't matter. Here we are cutting off an infinite summation at a certain point in *reciprocal* space, and are saying that further spatial frequencies don't matter.

How to use that recipe is best shown via an example. This particular example is an actual final exam question from when I took this class, and very likely uses more terms in the summation than I would ever require you to keep.

Example: Apply the Central Equation to GaAs to solve for the energies at $k = (0,0,0)$. Only use RLVs with magnitude $|G| \leq \frac{4\pi}{a}$. Work out the equations to the level that you could solve for the energies were you to be given the $U(x)$ function.

The problem says to consider all of the **G**'s with $|G| \leq \frac{4\pi}{a}$. To figure those out, I need to consider the lattice type. GaAs has an fcc lattice, so I'll look up the primitive RLVs in chapter 2:

$$\mathbf{b}_1 = \frac{2\pi}{a}(-1,1,1)$$
$$\mathbf{b}_2 = \frac{2\pi}{a}(1,-1,1)$$
$$\mathbf{b}_3 = \frac{2\pi}{a}(1,1,-1)$$

A general RLV is given by a linear combination of the primitive RLVs:

$$\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

I'm labeling the RLVs with hkl subscripts so we can tell them apart. Plugging in the primitive RLV formulas, we have:

$$\mathbf{G}_{hkl} = h\frac{2\pi}{a}(-1,1,1) + k\frac{2\pi}{a}(1,-1,1) + l\frac{2\pi}{a}(1,1,-1)$$
$$\mathbf{G}_{hkl} = \frac{2\pi}{a}(-h+k+l, h-k+l, h+k-l)$$

With a little bit of experimenting, I can tell that there are 14 **G**'s which have magnitude $\leq \frac{4\pi}{a}$. Using the notation that a negative sign is indicated by a bar over a number, they are:

$$G_{100} = \frac{2\pi}{a}(-1+0+0, 1-0+0, 1+0-0) = \frac{2\pi}{a}(-1,1,1)$$
$$G_{010} = \frac{2\pi}{a}(0+1+0, 0-1+0, 0+1-0) = \frac{2\pi}{a}(1,-1,1)$$
$$G_{001} = \frac{2\pi}{a}(0+0+1, 0-0+1, 0+0-1) = \frac{2\pi}{a}(1,1,-1)$$
$$G_{\bar{1}00} = \frac{2\pi}{a}(1+0+0, -1-0+0, -1+0-0) = \frac{2\pi}{a}(1,-1,-1)$$
$$G_{0\bar{1}0} = \frac{2\pi}{a}(0-1+0, 0+1+0, 0-1-0) = \frac{2\pi}{a}(-1,1,-1)$$

(skipping some work now)

$$G_{00\bar{1}} = \frac{2\pi}{a}(-1,-1,1)$$
$$G_{111} = \frac{2\pi}{a}(1,1,1)$$
$$G_{\overline{111}} = \frac{2\pi}{a}(-1,-1,-1)$$
$$G_{011} = \frac{2\pi}{a}(2,0,0)$$
$$G_{101} = \frac{2\pi}{a}(0,2,0)$$

$$G_{110} = \frac{2\pi}{a}(0,0,2)$$
$$G_{0\bar{1}\bar{1}} = \frac{2\pi}{a}(-2,0,0)$$
$$G_{\bar{1}0\bar{1}} = \frac{2\pi}{a}(0,-2,0)$$
$$G_{\bar{1}\bar{1}0} = \frac{2\pi}{a}(0,0,-2)$$

The first eight have magnitudes of $\frac{2\pi}{a}\sqrt{3}$. The other six have magnitudes of $\frac{4\pi}{a}$.

Another, possibly better, way of thinking about these 14 **G** values is that they are the 14 points on the bcc lattice which is reciprocal to the GaAs fcc lattice, which points are closest to the origin: the eight centered atoms of the eight cubes surrounding the origin, plus the six closest points along the $\pm x, \pm y, \pm z$ directions. All other RLVs have magnitudes larger than the specified cutoff.

Step 2
We aren't given the details of $U(\mathbf{r})$ so we can't calculate the Fourier coefficients, $U_{\mathbf{G}}$. We'll just assume that we could do that if we had the details. I will index the Fourier coefficients with hkl like I'm doing for the **G** vectors, and will refer to them as U_{100}, U_{010}, etc.

Step 3:
The specified **k** value is $(0,0,0)$.

Step 4:
The set of **k** values is obtained doing the operation $(0,0,0) - \mathbf{G}$ for each of the 14 **G** values (plus keeping $(0,0,0)$ itself). They are summarized in the right hand column of this table, with the left hand column values indicating which **G** vector gave rise to the **k** value via the $\mathbf{k} - \mathbf{G}$ operation.

G	Set of k's obtained from $(0,0,0) - \mathbf{G}$
n/a	$(0,0,0)$
G_{100}	$\frac{2\pi}{a}(1,-1,-1)$
G_{010}	$\frac{2\pi}{a}(-1,1,-1)$
G_{001}	$\frac{2\pi}{a}(-1,-1,1)$
$G_{\bar{1}00}$	$\frac{2\pi}{a}(-1,1,1)$

G	
$G_{0\bar{1}0}$	$\frac{2\pi}{a}(1,-1,1)$
$G_{00\bar{1}}$	$\frac{2\pi}{a}(1,1,-1)$
G_{111}	$\frac{2\pi}{a}(-1,-1,-1)$
$G_{\bar{1}\bar{1}\bar{1}}$	$\frac{2\pi}{a}(1,1,1)$
G_{011}	$\frac{2\pi}{a}(-2,0,0)$

G	
G_{101}	$\frac{2\pi}{a}(0,-2,0)$
G_{110}	$\frac{2\pi}{a}(0,0,-2)$
$G_{0\bar{1}\bar{1}}$	$\frac{2\pi}{a}(2,0,0)$
$G_{\bar{1}0\bar{1}}$	$\frac{2\pi}{a}(0,2,0)$
$G_{\bar{1}\bar{1}0}$	$\frac{2\pi}{a}(0,0,2)$

The set of expansion coefficients can be written as $C_{(0,0,0)}, C_{\frac{2\pi}{a}(1,-1,-1)}, C_{\frac{2\pi}{a}(-1,1,-1)}$, etc.

Step 5:
Here's the Central Equation again:
$$(\lambda_k - E)C_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0$$

Notice that there are actually only two different values of λ_k for our situation: the first k value in the set has $\lambda_k = 0$, then the next eight all have $\lambda_k = \frac{\hbar^2}{2m}\frac{12\pi^2}{a^2}$, which I will call λ_1, and the final six all have $\lambda_k = \frac{\hbar^2}{2m}\frac{16\pi^2}{a^2}$, which I will call λ_2.

I now need to write out 15 equations! One equation for each of the **k** values in my set.

For $k = (0,0,0)$:

$$(0 - E)C_{(0,0,0)} + U_{100}C_{\frac{2\pi}{a}(1,-1,-1)} + U_{010}C_{\frac{2\pi}{a}(-1,1,-1)} + [12 \text{ more terms}] = 0$$

$$-EC_{(0,0,0)} + U_{100}C_{\frac{2\pi}{a}(1,-1,-1)} + U_{010}C_{\frac{2\pi}{a}(-1,1,-1)} + [12 \text{ more terms}] = 0$$

For $k = \frac{2\pi}{a}(1,-1,-1)$:

$$(\lambda_1 - E)C_{\frac{2\pi}{a}(1,-1,-1)} + U_{100}C_{\underbrace{\frac{2\pi}{a}(1,-1,-1)-\frac{2\pi}{a}(-1,1,1)}_{\frac{2\pi}{a}(2,-2,-2)}} + U_{010}C_{\underbrace{\frac{2\pi}{a}(1,-1,-1)-\frac{2\pi}{a}(1,-1,1)}_{\frac{2\pi}{a}(0,0,-2)}} + [12 \text{ more terms}] = 0$$

$$(\lambda_1 - E)C_{\frac{2\pi}{a}(1,-1,-1)} + U_{100}C_{\frac{2\pi}{a}(2,-2,0)} + U_{010}C_{\frac{2\pi}{a}(0,0,-2)} + [12 \text{ more terms}] = 0$$

For $k = \frac{2\pi}{a}(-1,1,-1)$:

$$(\lambda_1 - E)C_{\frac{2\pi}{a}(-1,1,-1)} + U_{100}C_{\underbrace{\frac{2\pi}{a}(-1,1,-1)-\frac{2\pi}{a}(-1,1,1)}_{\frac{2\pi}{a}(0,0,-2)}} + U_{010}C_{\underbrace{\frac{2\pi}{a}(-1,1,-1)-\frac{2\pi}{a}(1,-1,1)}_{\frac{2\pi}{a}(-2.2.-2)}} + [12 \text{ more terms}] = 0$$

$$(\lambda_1 - E)C_{\frac{2\pi}{a}(-1,1,-1)} + U_{100}C_{\frac{2\pi}{a}(0,0,-2)} + U_{010}C_{\frac{2\pi}{a}(-2.2.-2)} + [12 \text{ more terms}] = 0$$

[Plus 12 more equations, the last six of which have λ_2's in them.]

<u>Step 6</u>:
Throw out all of the terms that have coefficients corresponding to **k**'s outside of our set. For example, the second equation contains $C_{\frac{2\pi}{a}(2,-2,0)}$ and the third equation has $C_{\frac{2\pi}{a}(-2.2.-2)}$.

The 15 equations become

$$-EC_{(0,0,0)} + U_{100}C_{\frac{2\pi}{a}(1,-1,-1)} + U_{010}C_{\frac{2\pi}{a}(-1,1,-1)} + \cdots = 0$$

$$(\lambda_1 - E)C_{\frac{2\pi}{a}(1,-1,-1)} + U_{010}C_{\frac{2\pi}{a}(0,0,-2)} + \cdots = 0$$

$$(\lambda_1 - E)C_{\frac{2\pi}{a}(-1,1,-1)} + U_{100}C_{\frac{2\pi}{a}(0,0,-2)} + \cdots = 0$$

[Plus 12 more equations, the last six of which have λ_2's in them.]

There are now 15 equations and only 15 unknowns.

<u>Step 7</u>:
The set of equations can be written as a matrix equation as:

$$\begin{pmatrix} -E & U_{100} & U_{010} & \cdots & U_{\overline{1}\overline{1}0} \\ \cdots & \lambda_1 - E & & & \\ & & \lambda_1 - E & & \\ & & & \cdots & \\ \cdots & & & \cdots & \lambda_2 - E \end{pmatrix} \begin{pmatrix} C_{(0,0,0)} \\ C_{\frac{2\pi}{a}(1,-1,-1)} \\ C_{\frac{2\pi}{a}(-1,1,-1)} \\ \cdots \\ C_{\frac{2\pi}{a}(0,0,2)} \end{pmatrix} = 0$$

For brevity I'll refrain from writing down very many matrix elements, but the on-diagonal elements of the matrix end up being the $\lambda_k - E$ values where lambda is the energy for the matching C_k of the row. The (i,j) off-diagonal elements end up being the U_G Fourier components where $\mathbf{G}$ is the reciprocal lattice vector connecting the ith $\mathbf{k}$-value in your set to the jth $\mathbf{k}$-value.

You can solve for the allowed energies by setting the determinant of the matrix equal to 0. Or you can use an eigenvalue solver by noticing that the allowed energies are the eigenvalues of this matrix:

$$\begin{pmatrix} 0 & U_{100} & U_{010} & \cdots & U_{\overline{1}\overline{1}0} \\ \cdots & \lambda_1 & & & \\ & & \lambda_1 & & \\ & & & \cdots & \\ \cdots & & & \cdots & \lambda_2 \end{pmatrix}$$

The eigenvectors are vectors comprised of the $C_\mathbf{k}$ coefficients, that tell you how the wave functions at those particular energy states are made up of plane waves. A large coefficient for $C_{\frac{2\pi}{a}(1,-1,-1)}$, for

example, means that particular energy state has a lot of $e^{i\frac{2\pi}{a}(1,-1,-1)\cdot\mathbf{r}}$ character to it.