Lecture 10

Waves in Periodic Potentials

Today:

1. Direct lattice and periodic potential as a convolution of a lattice and a basis.
2. The discrete translation operator: eigenvalues and eigenfunctions.
3. Conserved quantities in systems with discrete translational symmetry.
4. Bloch's theorem.

Questions you should be able to address after today's lecture:

1. How to mathematically represent a crystal
2. What is the definition of an "inverse lattice"?
3. What is the Hamiltonian for a periodic system?
4. What is the definition and eigenvalues/eigenfunctions of the discrete translational operator (DTO)?
5. How is the DTO used to find the energy e-values/e-functions of a system with a periodic potential?
6. What is the conserved number associated with the discrete translational symmetry in a periodic system?

Many materials have crystalline structure and ions are arranged in a periodic lattice. As all the ions in the lattice exert Coulombic potentials on an electron, the overall potential experienced by the electron appears periodic. **The periodicity of the potential defines the electronic and optical properties of the crystalline solids and is consequently "electrons in periodic potentials" is the most important problem of this course.**

I Hamiltonians for periodic potentials:

For simplicity lets consider one-electron Hamiltonian of a crystal - a system with a periodic potential:

$$\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V\left(\vec{r}\right) \rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\left(x\right)$$

where,

$$V\left(\vec{r}+\vec{R}\right) = V\left(\vec{r}\right) \rightarrow V\left(x+na\right) = V\left(x\right)$$

Take a closer look at what makes a potential periodic – the repetition of a basic unit at regular spacings (crystal lattice)!

II Eigenfunctions of infinite crystal: The effect of a periodic potential

Let us define a discrete translation operator: $\hat{T}_a \psi\left(x\right) = \psi\left(x+a\right)$

One can find eigenfunctions for this operator: $\hat{T}_a u\left(x\right) = \lambda u\left(x\right)$

By inspection the eigenfunctions of the discrete translational operator are of the form:

$$\varphi_k\left(x\right) = e^{ikx} f\left(x\right)$$

Where ***f(x)*** is a function that is periodic in ***a*** (***a*** is the lattice period): $f\left(x+a\right) = f\left(x\right)$

Let's verify our hypothesis: $\hat{T}_a \varphi_k\left(x\right) = e^{ik\left(x+a\right)} f\left(x+a\right) = e^{ika}\underbrace{e^{ikx} f\left(x\right)}_{\varphi_k\left(x\right)} = e^{ika}\varphi_k\left(x\right)$

Our objective is to identify the eigenfunctions of the Hamiltonian. We will use the fact that the discrete translational operator $\hat{T}_a$ commutes with the periodic potential Hamiltonian:

$$\left[\hat{T}_a,\hat{H}\right]\psi\left(x\right)=\hat{T}_a\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)\right)\psi\left(x\right)-\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)\right)\hat{T}_a\psi\left(x\right)=$$

$$=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\left(x+a\right)^2}+V\left(x+a\right)\right)\psi\left(x+a\right)-\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)\right)\psi\left(x+a\right)=$$

$$=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)\right)\psi\left(x+a\right)-\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)\right)\psi\left(x+a\right)=0$$

Thus eigenfunctions, which are common to the Hamiltonian and the discrete translation operator can be found of the form:

$$\varphi_k\left(x\right)=e^{ikx}f\left(x\right),\quad f\left(x+a\right)=f\left(x\right)$$

Bloch's Theorem

The eigenfunctions of the one-electron Hamiltonian with a periodic potential:

$\hat{H}=-\frac{\hbar^2}{2m}\vec{\nabla}^2+V\left(\vec{r}\right),\ \ V\left(\vec{r}+\vec{R}\right)=V\left(\vec{r}\right)$, where $\vec{R}$ is the lattice vector, can be written in the form: $\varphi_{n,\vec{k}}\left(\vec{r}\right)=e^{i\vec{k}\cdot\vec{r}}f_{n\vec{k}}\left(\vec{r}\right)$, where $f_{n\vec{k}}\left(\vec{r}\right)$ has the periodicity of the underlying Bravais lattice, $f_{n\vec{k}}\left(\vec{r}+\vec{R}\right)=f_{n\vec{k}}\left(\vec{r}\right)$ for all lattice vectors $\vec{R}$.

Another way of stating Bloch's Theorem is:

The eigenfunctions of the one-electron Hamiltonian with a periodic potential have the form: $\varphi_{n,k}\left(\vec{r}+\vec{R}\right)=e^{i\vec{k}\cdot\vec{R}}\varphi_{n,k}\left(\vec{r}\right)$

Two important comments:

1. The eigenvalues corresponding to the discrete translational operator depend only on ***k*** and not on the particular form of the periodic function.
2. The only distinct eigenvalues correspond to ***k*** in the first Brillouin Zone (BZ).

   For 1D case with the lattice constant ***a***, BZ is $k\in\left[-\frac{\pi}{a},\frac{\pi}{a}\right]$:

   $$\varphi_{n,k}\left(x+a\right)=e^{ika}\varphi_{n,k}\left(x\right)$$

   $$k'=k+\frac{2\pi}{a}n\Rightarrow e^{ik'a}=e^{i\left(k+\frac{2\pi}{a}n\right)a}=e^{ika}e^{i2\pi n}=e^{ika}$$

How do we label our states? What is the conserved quantity in this case?

k is the ***Bloch wave number*** (or wave vector, sometimes called the ***crystal momentum***) and represents a conserved quantity associated with the discrete translation symmetry in the crystal. As we have demonstrated above, crystal momentum is related to the eigenvalue of the discrete translation operator e^{ika}: $\hat{T}_a u_{n,k}(x) = e^{ika}\varphi_{n,k}(x)$.

n is associated with the energy eigenvalues.

We can plot the dispersion relation or a **band diagram**: ***E*** vs. ***k***.

Is the *Crystal momentum* identical to the *Momentum*?
Is the momentum conserved in crystals?

$$\hat{p}\varphi_{n,k}(x) = -i\hbar\frac{\partial}{\partial x}\varphi_{n,k}(x) = -i\hbar\frac{\partial}{\partial x}e^{ikx} f(x) = \hbar k e^{ikx} f(x) + -i\hbar e^{ikx}\frac{\partial}{\partial x} f(x) \neq const \times \varphi_{n,k}(x)$$

$\varphi_{n,k}(x)$ are not eigenfunctions of momentum, this means that momentum operator does not commute with a Hamiltonian – let's check this:

$$\left[\hat{p},\hat{H}\right]\psi(x) = \hat{p}\hat{H}\psi(x) - \hat{H}\hat{p}\psi(x) =$$

$$= -i\hbar\frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x) - \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\left(-i\hbar\frac{\partial}{\partial x}\psi(x)\right) =$$

$$= \frac{i\hbar^3}{2m}\frac{\partial^2}{\partial x^2}\psi(x) - i\hbar V(x)\frac{\partial\psi(x)}{\partial x} - i\hbar\psi(x)\frac{\partial V(x)}{\partial x} - \frac{i\hbar^3}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + i\hbar V(x)\frac{\partial\psi(x)}{\partial x} =$$

$$= -i\hbar\psi(x)\frac{\partial V(x)}{\partial x}$$

$$\left[\hat{p},\hat{H}\right] = -i\hbar\frac{\partial V(x)}{\partial x} \neq 0$$

Then according to the Ehrenfest theorem momentum is NOT conserved in crystals!

k **– Crystal momentum (Bloch wavevector) is conserved and is different from momentum!**

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