Materials & Solid State Physics Notes

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1.1 Pauli Exclusion Principle

1.2 Condensation

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2 Interacting Electrons and Nuclei

The starting point for solving for the dynamics and properties of a system of electrons and nuclei is the Hamiltonian:

$$\begin{aligned} H = &\frac{-\hbar^2}{2m_e}\sum_i^n \nabla_i^2 - \sum_I^N \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{i\neq j}^n \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \\ &+ \frac{1}{2}\sum_{I\neq J}^N \frac{Z_I Z_J e^2}{|\boldsymbol{r}_I - \boldsymbol{r}_J|} - \sum_{i,I}^{n,N} \frac{Z_I e^2}{|\boldsymbol{r}_I - \boldsymbol{r}_i|}. \end{aligned} \tag{1}$$

The goal is to then solve the many-body Schrodinger equation for this Hamiltonian:

$$i\hbar\frac{\partial\Psi(\{r_i\},t)}{\partial t} = \hat{H}\Psi(\{r_i\},t). \tag{2}$$

We now define the density operator, which reduces solving the Schrodinger equation for each of the individual N particles to solving it for just a three-dimensional density. First defining a density:

$$\hat{n}(\boldsymbol{r}) = \sum_i^N \delta(\boldsymbol{r} - \boldsymbol{r}_i), \tag{3}$$

telling us that the density of a particle is sharply defined at a single point $\boldsymbol{r}_i$, we compute the number density of a many-body system by computing the expectation value of the number density operator:

$$\begin{aligned} n(\boldsymbol{r}) &= \langle\Psi|\hat{n}(\boldsymbol{r})|\Psi\rangle \\ &= \int \Psi^* d^3r_1 \dots d^3r_N \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \int \Psi d^3r_1 \dots d^3r_N \\ &= \int \Psi^* d^3r_1 \dots d^3r_N \sum_i^N \int \Psi\delta(\boldsymbol{r} - \boldsymbol{r}_i) d^3r_1 \dots d^3r_N \\ &= N\int |\Psi|^2 d^3r_1 \dots d^3r_N \end{aligned} \tag{4}$$

3 Crystals

3.1 Lattice Structure

Crystals are solids with a periodic nature. Their periodic nature allows for a simple description of crystals, since the information necessary to describe it is only the set of repeating atoms, called a unit cell, and the translational symmetry of the unit cell, or how the unit cell spans the full material. The smallest possible unit cell, called the *primitive unit cell*, is described by primitive lattice vectors $\boldsymbol{a}_i$. These primitive lattice vectors span the full material under the translation vectors

$$\boldsymbol{R}(n_1, n_2, n_3) = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3 \tag{5}$$

where n_i are integers that describe the number of translations of the primitive unit vector $\boldsymbol{a}_i$ are needed to span the full material in the direction of $\boldsymbol{a}_i$.

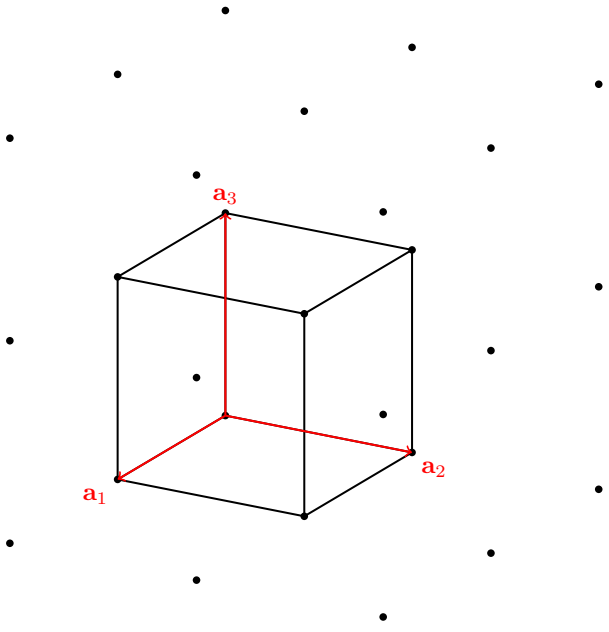

Figure 1: Primitive unit cell of a simple cubic lattice.

The number of translations in each direction N_i, or cells, needed to span the whole crystal determines its volume

$$\Omega_{\text{crystal}} = (N_1 \times N_2 \times N_3)\Omega_{\text{cell}}. \tag{6}$$

3.2 Bloch's Theorem

Before solving the Schrodinger equation for a periodic potential, we first define the translation operator

$$\begin{aligned}\hat{T}_{\boldsymbol{R}}\psi(\boldsymbol{r}) &= \psi(\boldsymbol{r}+\boldsymbol{R}) \\ &= \psi(\boldsymbol{r}+n_1\boldsymbol{a}_1+n_2\boldsymbol{a}_2+n_3\boldsymbol{a}_3) \\ &\equiv \psi(\boldsymbol{r}+\boldsymbol{A}\cdot\boldsymbol{n})\end{aligned} \tag{7}$$

where $\boldsymbol{R}$ is the translation vector defined in Eq (5) and we have made the following vector simplifications:

$$\boldsymbol{A} = \begin{pmatrix}\boldsymbol{a}_1 \\ \boldsymbol{a}_2 \\ \boldsymbol{a}_3\end{pmatrix} \quad \& \quad \boldsymbol{n} = \begin{pmatrix}n_1 \\ n_2 \\ n_3\end{pmatrix}. \tag{8}$$

The translation operator thus takes a state ψ at a position $\boldsymbol{r}$ and moves the state by some translation $\boldsymbol{R}$ in the crystal.

We can now see how the translation operator acts on the Hamiltonian of a periodic potential:

$$\begin{aligned}\hat{T}_{\boldsymbol{R}}\hat{H} &= \hat{T}_{\boldsymbol{R}}\left(\frac{\hat{p}^2}{2m}+\hat{V}(\boldsymbol{r})\right) \\ &= \frac{\hat{p}^2}{2m}+\hat{V}(\boldsymbol{r}+\boldsymbol{R}) \\ &\equiv \frac{\hat{p^2}}{2m}+\hat{V}(\boldsymbol{r}) = \hat{H},\end{aligned} \tag{9}$$

where we used the fact that the potential of a periodic crystal is invariant under translations $\boldsymbol{R}$. We have thus shown that the translation operator commutes with the Hamiltonian that features a periodic potential;

$$[\hat{T}_{\boldsymbol{R}}, \hat{H}] = 0, \tag{10}$$

so we know that the translation operator and Hamiltonian of a periodic potential have simultaneous eigenvectors.

We will first look for the eigenvalues of the translation operator:

$$\hat{T}_{\boldsymbol{R}}\psi(\boldsymbol{r}) = \lambda_{\boldsymbol{R}}\psi(\boldsymbol{r}). \tag{11}$$

Given that $\hat{T}_{\boldsymbol{R}}$ is an additive operator:

$$\hat{T}_{\boldsymbol{R}_1}\hat{T}_{\boldsymbol{R}_2}\psi(\boldsymbol{r}) = \psi(\boldsymbol{r}+\boldsymbol{R}_1+\boldsymbol{R}_2) \equiv \hat{T}_{\boldsymbol{R}_1+\boldsymbol{R}_2}, \tag{12}$$

this tells us that its eigenvalues must be additive as well:

$$\begin{aligned} &\lambda_{\boldsymbol{R}_1}\lambda_{\boldsymbol{R}_2}\psi(\boldsymbol{r}) = \lambda_{\boldsymbol{R}_1+\boldsymbol{R}_2}\psi(\boldsymbol{r}) \\ &\implies \lambda_{\boldsymbol{R}_1}\lambda_{\boldsymbol{R}_2} = \lambda_{\boldsymbol{R}_1+\boldsymbol{R}_2} \end{aligned} \tag{13}$$

A function that satisfies this property is the exponential function, so we first express the eigenvectors of the translation operator as:

$$\lambda_{\boldsymbol{R}} = e^{s\boldsymbol{A}\cdot\boldsymbol{n}} \tag{14}$$

where $s \in \mathbb{C}$.

Now using the normalization of the wavefunction within a volume Ω_{cell} determine s:

$$\begin{aligned} 1 &= \int_\Omega |\psi(\boldsymbol{r})|^2 d^3r \equiv \int_\Omega |\hat{T}_{\boldsymbol{R}}\psi(\boldsymbol{r})|^2 d^3r \\ &= |\lambda_{\boldsymbol{R}}|^2 \int_\Omega |\psi(\boldsymbol{r})|^2 d^3r \\ &\implies |\lambda_{\boldsymbol{R}}|^2 = |e^{s\boldsymbol{A}\cdot\boldsymbol{n}}|^2 = 1 \implies s = ik \end{aligned} \tag{15}$$

where k is some real number to be determined.

Using Eq. (11), we have shown that

$$\hat{T}_{\boldsymbol{R}}\psi(\boldsymbol{r}) = e^{ik\boldsymbol{A}\cdot\boldsymbol{n}}\psi(\boldsymbol{r}) \tag{16}$$

Since the translation operator and the periodic Hamiltonian share eigenvectors, we have demonstrated that the shared eigenvectors should include the plane waves from the translation operator we have just derived and the eigenvalues of the Hamiltonian itself, which we are commonly denoted as $u(\boldsymbol{r})$. Then for solving the Schrodinger equation

$$\hat{H}\psi_n(\boldsymbol{r}) = E_n\psi_n(\boldsymbol{r}), \tag{17}$$

we have that

$$\psi_n(\boldsymbol{r}) = e^{ik\boldsymbol{A}\cdot\boldsymbol{n}}u_n(\boldsymbol{r}), \tag{18}$$

which is called **Bloch's theorem**. The $u(\boldsymbol{r})$ functions, called Bloch functions, have the same periodicity as the lattice.

Bloch's theorem is very important in determining the energy level structure of a crystalline material, since it tells us that the whole material shares the same spectrum as one of the cells.

3.3 Reciprocal Space

Since a quantity $f(\boldsymbol{r})$, such as number density, is periodic in a crystalline material:

$$\hat{T}_{\boldsymbol{R}} f(\boldsymbol{r}) = n(\boldsymbol{r} + \boldsymbol{R}) = f(\boldsymbol{r}), \tag{19}$$

it can be represented by Fourier transforms in terms of Fourier components at wavevectors $\boldsymbol{k}$. Assuming a finitude of the crystal volume, this imposes the usual boundary conditions that

$$\boldsymbol{k} \cdot \boldsymbol{a}_i = \frac{2\pi n}{N_i} \tag{20}$$

where $n \in \mathbb{N}$. This allows us to represent one of these periodic quantities as

$$f(\boldsymbol{k}) = \frac{1}{\Omega} \int_{\Omega} f(\boldsymbol{r}) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} d^3 r \tag{21}$$

Applying the translation operator:

$$\begin{aligned} \hat{T}_{\boldsymbol{K}} f(\boldsymbol{k}) &= \frac{1}{\Omega} \int_{\Omega} \hat{T}_{\boldsymbol{R}} \left(f(\boldsymbol{r}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \right) d^3 r \\ &= \frac{1}{\Omega} \int_{\Omega} f(\boldsymbol{r}) \hat{T}_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} d^3 r \\ &= \frac{1}{\Omega} \int_{\Omega} f(\boldsymbol{r}) e^{i\boldsymbol{k}\cdot(\boldsymbol{r}+\boldsymbol{R})} d^3 r \end{aligned} \tag{22}$$

3.4 Brillouin Zone

4 Band Theory

4.1 Band Structure Basics

(follow derivation given in Griffiths)

4.2 Nearly Free Electron

4.3 Tight Binding

4.4 Band Gaps

4.5 Gamma band plots

Note: in trying to determine the energy bands of a crystalline material, the Bloch theorem is used to state that the energy bands inside of the Brillouin Zone are all that is needed, since the energy levels are eigenvalues of the Hamiltonian within the unit cell.

4.6 Flat Bands

5 Lattice Vibrations

5.1 Phonons

5.2 Dispersion

5.3 Electron-Phonon Coupling

6 Density Functional Theory

6.1 Energy above Hull