UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

H4.SMR/994-8

SPRING COLLEGES IN
COMPUTATIONAL PHYSICS

19 May - 27 June 1997

ELECTRONS IN SOLIDS - I

A. MOOKERJEE
S.N. Bose National Centre
for Basic Sciences
Salt Lake, 700 091 Calcutta
INDIA

ELECTRONS IN SOLIDS - I

Abhijit Mookerjee

S.N. Bose National Centre for Basic Sciences,

Salt lake City, Calcutta 700091, India.

International Centre for Theoretical Physics

Trieste, Italy

ELECTRONS IN SOLIDS - I

Definitions and Concepts

Lattice translation vectors : three mutually linearly independent vectors λ_i. i=1.2.3 essentially define the lattice structure.

Lattice points : The set of vectors $\{r_L = \sum n_i \lambda_i\}$ where L = $\{n_1, n_2, n_3\}$ with the n-s being integers, defines the lattice points.

Primitive lattice translation operators : The operators $\mathbf{T}_i$ defined by $\mathbf{T}_i \psi(\underline{r}) = \psi(\underline{r} + \lambda_i)$ are called the primitive lattice translation operators.

Unit Cell : An enclosed volume C which when translated by all possible lattice translations fully cover the entire lattice space. is called a unit cell. Unit cells with the minimum possible volume are called primitive unit cells. A primitive unit cell associated with a lattice point such that any point in it is nearer to to this point than any other lattice point is called a **Wigner- Seitz cell**

Reciprocal Lattice : If we define a set of lattice translation vectors from a given lattice translation vector of a lattice by :

$$\hat{\lambda}_1 = 2\pi \frac{\lambda_2 \times \lambda_3}{[\lambda_1 \lambda_2 \lambda_3]}$$

$$\hat{\backslash}_2 = 2\pi \frac{\backslash_3 \times \backslash_1}{[\backslash_1 \backslash_2 \backslash_3]}$$

$$\hat{\backslash}_3 = 2\pi \frac{\backslash_1 \times \backslash_2}{[\backslash_1 \backslash_2 \backslash_3]}$$

Then the set of vectors $\{\underline{G}_M = \sum m_i \, \hat{\backslash}_i\}$ defines the reciprocal lattice.

$$\underline{G}_M.\underline{r}L = 2\pi \, N \quad \text{N is an integer}$$

and.

$$\exp\left(\imath \, \underline{G}_M.\underline{r}_L\right) = 1$$

Corollary : Any function V($\underline{r}$) which has lattice periodicity. i.e. $V(\underline{r}) = V(\underline{r} + r_L)$ can be expanded as a Fourier series in terms of the reciprocal lattice vectors alone.

$$V(\underline{r}) = \sum_{\underline{G}} V(\underline{G}) \, \exp\left(\imath \underline{G}.\underline{r}\right)$$

Brilluoin Zone : is the Wigner-Seitz cell of the reciprocal lattice.

The Bloch Theorem

In a crystalline solid the potential has lattice periodicity :

$$\mathbf{T}_{\backslash} V(\underline{r}) \; = \; V(\underline{r} \, + \, \backslash) \; = \; V(\underline{r})$$

Since the kinetic energy is a periodic function (being a second derivative), the entire hamiltonian also has lattice periodicity.

$$\mathbf{T}_{\backslash} H(\underline{r})\psi(r) \; = \; H(\underline{r} \, + \, \backslash)\psi(\underline{r} \, + \, \backslash) \; = \; H(\underline{r})\mathbf{T}_{\backslash}\psi(\underline{r})$$

It follows from above that the Lattice translation operators and the hamiltonian commute.

$$[H \; \mathbf{T}_{\backslash}] \; = \; 0$$

Therefore these operators must have common eigenfunctions. The wavefunction, which is an eigenfunction of the hamiltonian is also an eigenfunction of the lattice translation vectors.

$$\mathbf{T}_{\backslash}\psi(\underline{r}) \; = \; \lambda_{\backslash}\psi(\underline{r})$$

But,

$$\mathbf{T}_{\backslash} \, \mathbf{T}_{\backslash'} \; = \; \mathbf{T}_{\backslash + \backslash'} \; = \; \mathbf{T}_{\backslash'} \, \mathbf{T}_{\backslash}$$

This implies.

$$\lambda_{\chi}\,\lambda_{\chi'} \;=\; \lambda_{\chi\,+\,\chi'} \;=\; \lambda_{\chi'}\,\lambda_{\chi}$$

But we also have :

$$\int d^3\underline{r}|\mathbf{T}_{\chi}\psi(\underline{r})|^2 \;=\; \int d^3\underline{r}|\psi(\underline{r})|^2$$

So :

$$|\lambda_{\chi}|^2 \;=\; 1$$

The functional form of λ_{χ} is now fully determined by the above :

$$\lambda_{\chi} \;=\; \exp\left(\imath\,\underline{k}.\underline{r}\right)$$

In other words :

$$\psi(\underline{r} \;+\; \chi) \;=\; \exp\left(\imath\,\underline{k}.\underline{r}\right)\psi(\underline{r})$$

The above can also be expressed as follows :

$$\psi_{\underline{k}}(\underline{r}) \;=\; \exp\left(i\underline{k}.\underline{r}\right) U_{\underline{k}}(\underline{r})$$

with

$$U_{\underline{k}}(\underline{r} + \lambda) \;=\; U_{\underline{k}}(\underline{r})$$

This is the theorem of Bloch.

NEARLY FREE ELECTRONS

The Bloch Theorem states that the wavefunction in a crystalline solid looks like a free electron part modulated by a lattice periodic function. Thus since both the potential V($\underline{r}$) and the wavefunction modulator U($\underline{r}$) are lattice periodic we can write :

$$\begin{aligned} V(\underline{r}) &= \sum_{\underline{G}'} V(\underline{G}') \exp\left(i\underline{G}'.\underline{r}\right) \\ U(\underline{r}) &= \sum_{\underline{G}} B(\underline{G}) \exp\left(i\underline{G}.\underline{r}\right) \end{aligned}$$

If we put this into the Schödinger equation we obtain (in atomic units where h=1,m=1 and energy is in rydbergs) :

$$\sum_{\underline{G}} B_{\underline{G}} \left\{ E - (\underline{k} + \underline{G})^2/2 \right\} \exp(\imath \underline{G}.\underline{r}) - \sum_{\underline{G}} \sum_{\underline{G}'} B_{\underline{G}} V(\underline{k}') \exp(\imath(\underline{G} + \underline{G}').\underline{r}) = 0 \tag{1}$$

This is the Schrödinger equation written in a plane wave basis.

Since the functions $\exp(\imath \underline{G}.\underline{r})$ form an orthogonal set :

$$\sum_{\underline{G}'} B_{\underline{G}'} \left\{ (E - E_0(\underline{k} + \underline{G}))\, \delta_{\underline{GG'}} - V(\underline{G} - \underline{G}') \right\} = 0$$

These sets of equations have a solution if

$$\det ||(E - E_0(\underline{k} + \underline{G}))\delta_{\underline{GG'}} - V(\underline{G} - \underline{G}')|| = 0$$

This is the **Secular Equation**

Let us now consider the reciprocal space near the Γ point at $\underline{G}=0$. Suppose that the periodic potential is small.

$$B_0 \simeq 1. \quad B_{\underline{G}} \simeq \epsilon \;\; \underline{G} \neq 0. \quad V(\underline{G}) = \epsilon$$

From equation (1) keeping only terms of order ϵ we get :

$$\begin{aligned} B_0(E - k^2/2) \;+\; \sum_{\underline{G}\neq 0} B_{\underline{G}}(E - (\underline{k} \;+\; \underline{G})^2/2)\exp(\imath \underline{G}.\underline{r}) \\ - \sum_{\underline{G}} B_0 V_{\underline{G}} \exp(\imath \underline{G}.\underline{r}) \;&=\; 0 \end{aligned}$$

From this we have :

$$\begin{aligned} E \;&=\; E_0(k) \;=\; k^2/2 \\ B_{\underline{G}} \;&=\; (B_0 V(\underline{G}))/(E_0(\underline{k}) - E_0(\underline{k}+\underline{G})) \end{aligned} \tag{3}$$

In the above equation (1) if we go upto second order and from the double sum in the last term choose the term in which $\underline{G} \;=\; \underline{G}'$ then we get the second order correction to energy :

$$E \;=\; E_0(\underline{k}) \;+\; \sum_{\underline{G}} \frac{|V(\underline{G})|^2}{E_0(\underline{k}) - E_0(\underline{k}+\underline{G})}$$

This treatment breaks down when we have a degeneracy and $E_0(\underline{k}) = E_0(\underline{k} \;+\; \underline{G})$. This happens if :

$$2\,\underline{k}.\underline{G} \; + \; |\underline{k}|^2$$

This occurs when $\underline{k}$ lies on a Brillouin zone surface. Now we have.

$$B_0 \simeq 1, \;\; B_{\underline{G}_1} \simeq 1, \;\; E_1 \;\; = \;\; (\underline{k} \; + \; \underline{G}_1)^2/2$$

Again, going back to (1) and keeping terms of the order 1, we obtain :

$$B_0(E - E_0(k)) \; + \; B_1(E - E_1)\exp\left(\imath\underline{G}_1.\underline{r}\right) \; - \; B_1V_1 - B_0V_1\exp\left(\imath\underline{G}_1.\underline{r}\right) \;\; = \;\; 0$$

Again, using the orthogonality of the basis,

$$\begin{aligned} B_0(E - E_0) - B_1V_1 \;\; &= \;\; 0 \\ -B_0V_1 + B_1(E - E_1) \;\; &= \;\; 0 \end{aligned}$$

These equations have a solution if :

$$(E - E_0)(E - E_1) \;\; = \;\; |V_1|^2$$

At the Brilluoin zone boundary E_0=E_1 and we have the solutions :

$$E = E_0(\underline{k}) \pm |V_1|^2$$

The degeneracy at the Brilluoin zone is lifted by the periodic potential. There is a gap of the order of $|V_1|^2$ at the boundary.