

Tight-binding approximation

References:

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By N. W. Ashcroft and N. D. Mermin
- 2) The Oxford Solid State Basics
By Steven H. Simon
- 3) Band Theory and Electronic Properties of Solids
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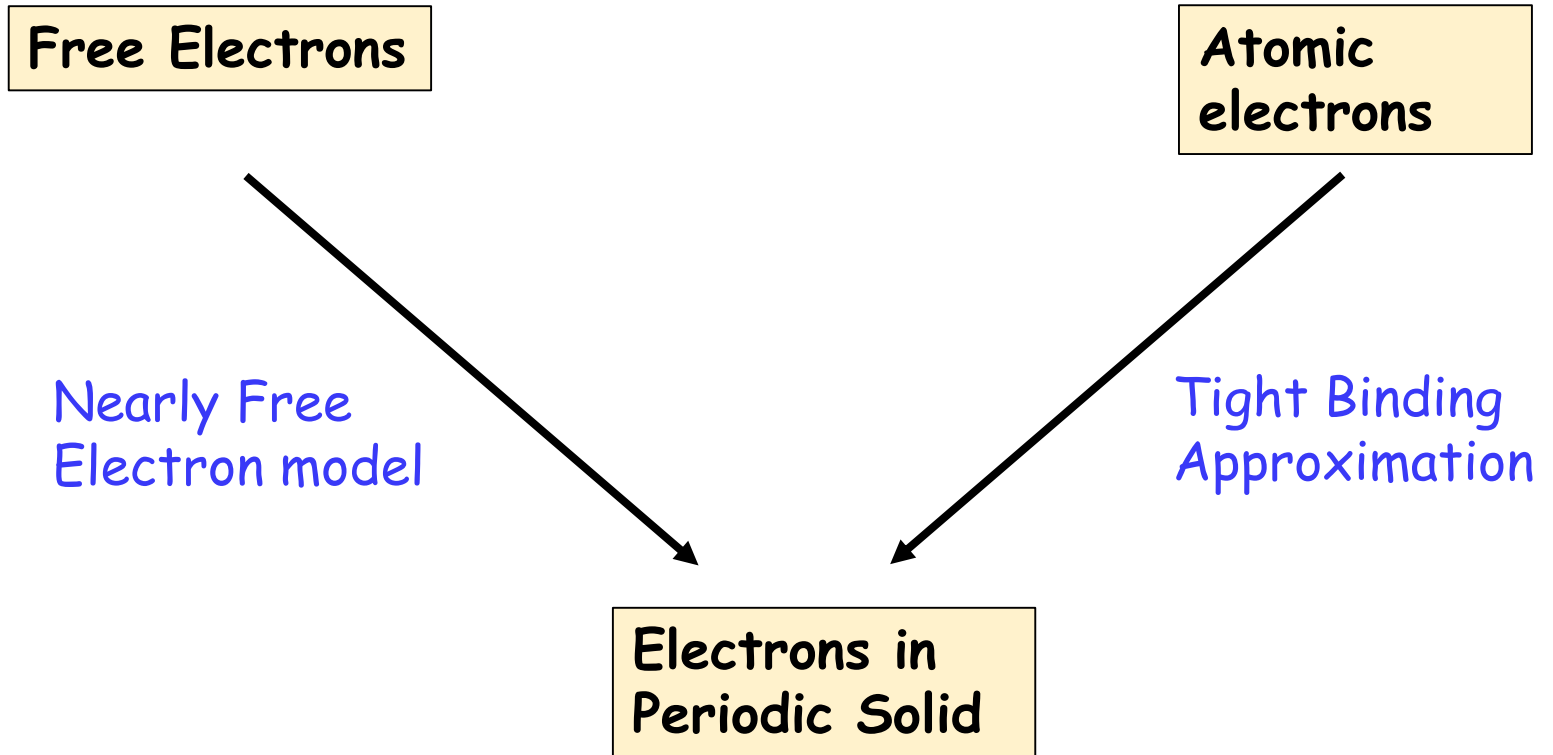
Tight-binding approximation

A group of Na atoms assembled into a body-centered cubic lattice with a lattice constant \sim cm rather than $\sim \text{\AA}$

All electrons would then be in atomic levels localized at lattice sites, bearing no resemblance to the linear combination of a few plane waves described earlier

On gradually shrinking the artificially large lattice constant of Na atoms, at some interatomic spacing (comparable to the spatial extent of its wavefunction), electrons on one atoms will start feeling the presence of the other atoms. Modification of electronic levels thus becomes necessary

The tight-binding approximation deals with the case where the overlap of atomic wave functions is enough to require corrections to the picture of isolated atoms, but not so much as to render the atomic description irrelevant



Crystal Hamiltonian

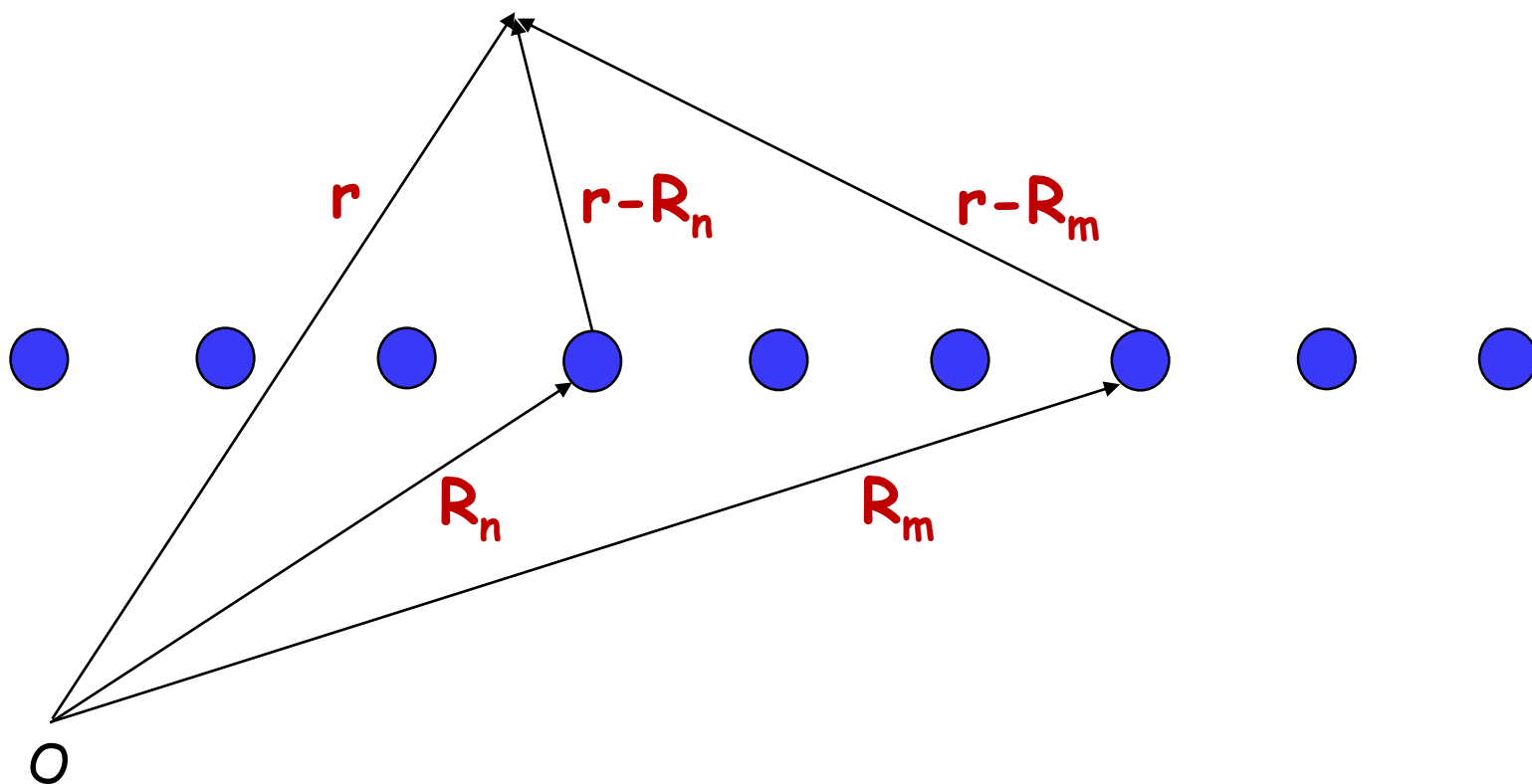
Bound level for H_{at} for an atom at the origin -

$$H_{\text{at}}\psi_n = E_n\psi_n$$

Wave functions $\psi_n(\mathbf{r} - \mathbf{R})$ for all N sites at positions \mathbf{R} in the Bravais lattice

The crystal Hamiltonian is - $H = H_{\text{at}} + \Delta U(\mathbf{r})$

$\Delta U(\mathbf{r})$ - Includes all corrections to the atomic potential required to produce the full periodic crystal potential



Linear combination of localized wave functions

The N linear combinations we require are -

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}'} e^{i\mathbf{k} \cdot \mathbf{R}'} \psi_n(\mathbf{r} - \mathbf{R}')$$

where \mathbf{k} ranges through the N values in the first Brillouin zone

Now

$$\begin{aligned} \psi(\mathbf{r} + \mathbf{R}) &= \sum_{\mathbf{R}'} e^{i\mathbf{k} \cdot \mathbf{R}'} \psi_n(\mathbf{r} + \mathbf{R} - \mathbf{R}') \\ &= e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r}) \end{aligned}$$

Thus, the wavefunctions satisfy the Bloch condition with wavevector \mathbf{k} , while continuing to display the atomic character

The effect of $\Delta U(r)$ - Modification of w.f.

Due to $\Delta U(r)$ the atomic wavefunctions will, however, need modifications from just $\psi_n(\mathbf{r} - \mathbf{R})$

We seek as solutions for the full crystal Schrödinger's equation -

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi(\mathbf{r} - \mathbf{R})$$

One seeks a $\phi(\mathbf{r})$ that can be expanded in a relatively small number of localized atomic wavefunctions -

$$\phi(\mathbf{r}) = \sum_n b_n \psi_n(\mathbf{r})$$

Crystal Schrödinger's equation

The crystal Schrödinger's equation -

$$H\psi(\mathbf{r}) = (H_{\text{at}} + \Delta U(\mathbf{r}))\psi(\mathbf{r}) = \varepsilon(\mathbf{k})\psi(\mathbf{r})$$

Multiplying the above equation by the atomic wavefunction $\psi_m^*(\mathbf{r})$

and using -

$$\int \psi_m^*(\mathbf{r}) H_{\text{at}} \psi(\mathbf{r}) d\mathbf{r} = \int (H_{\text{at}} \psi_m(\mathbf{r}))^* \psi(\mathbf{r}) d\mathbf{r} = E_m \int \psi_m^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r}$$

We get -

$$(\varepsilon(\mathbf{k}) - E_m) \int \psi_m^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = \int \psi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r}$$

The Bloch energies

Using the orthonormality of the wavefunctions -

$$\int \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) d\mathbf{r} = \delta_{nm}$$

The eigenvalue equation that determines the coefficients $b_n(\mathbf{k})$ and the Bloch energies $\varepsilon(\mathbf{k})$ -

$$\begin{aligned} (\varepsilon(\mathbf{k}) - E_m) b_m = & -(\varepsilon(\mathbf{k}) - E_m) \sum_n \left(\sum_{\mathbf{R} \neq 0} \int \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r} - \mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}} d\mathbf{r} \right) b_n \\ & + \sum_n \left(\int \psi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_n(\mathbf{r}) d\mathbf{r} \right) b_n \\ & + \sum_n \left(\sum_{\mathbf{R} \neq 0} \int \psi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_n(\mathbf{r} - \mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}} d\mathbf{r} \right) b_n. \end{aligned}$$

The Bloch energies

The right-hand side contains terms like $\int d\mathbf{r} \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r} - \mathbf{R})$

Or involves terms like $\Delta U(\mathbf{r}) \psi_n(\mathbf{r})$ which are all small.

Thus the product $(\epsilon(\mathbf{k}) - E_m) b_m$ is always small. This is possible if $\epsilon(\mathbf{k}) - E_m$ is small whenever b_m is not and vice versa

Thus, $\epsilon(\mathbf{k})$ must be close to an atomic level, say E_0 , and all the b_m except going with that level and levels degenerate with (or close to) it in energy must be small

$$\epsilon(\mathbf{k}) \approx E_0, \quad b_m \approx 0 \text{ unless } E_m \approx E_0$$

s-band arising from a single atomic s-level

The eigenvalue equation -

$$\varepsilon(\mathbf{k}) = E_s - \frac{\beta + \sum \gamma(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}}}{1 + \sum \alpha(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}}}$$

E_s is the energy of the atomic s-level

$$\beta = - \int d\mathbf{r} \Delta U(\mathbf{r}) |\phi(\mathbf{r})|^2$$

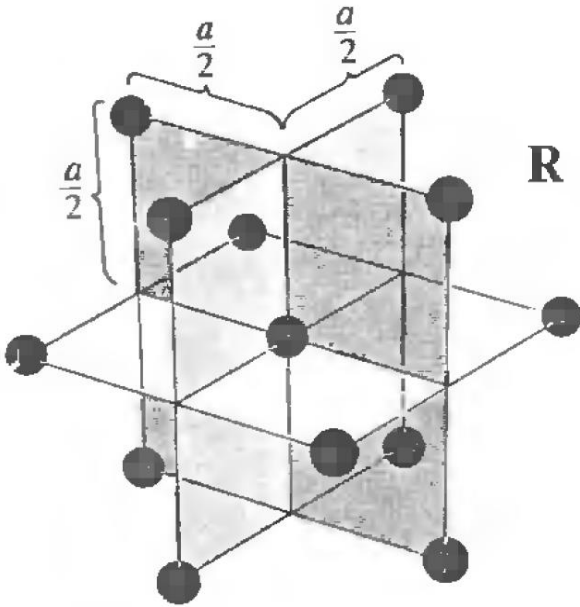
$$\alpha(\mathbf{R}) = \int d\mathbf{r} \phi^*(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R})$$

$$\gamma(\mathbf{R}) = - \int d\mathbf{r} \phi^*(\mathbf{r}) \Delta U(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R})$$

s-band arising from a single atomic s-level

The eigenvalue equation can be simplified to -

$$\varepsilon(\mathbf{k}) = E_s - \beta - \sum_{\text{n.n.}} \gamma(\mathbf{R}) \cos \mathbf{k} \cdot \mathbf{R}$$

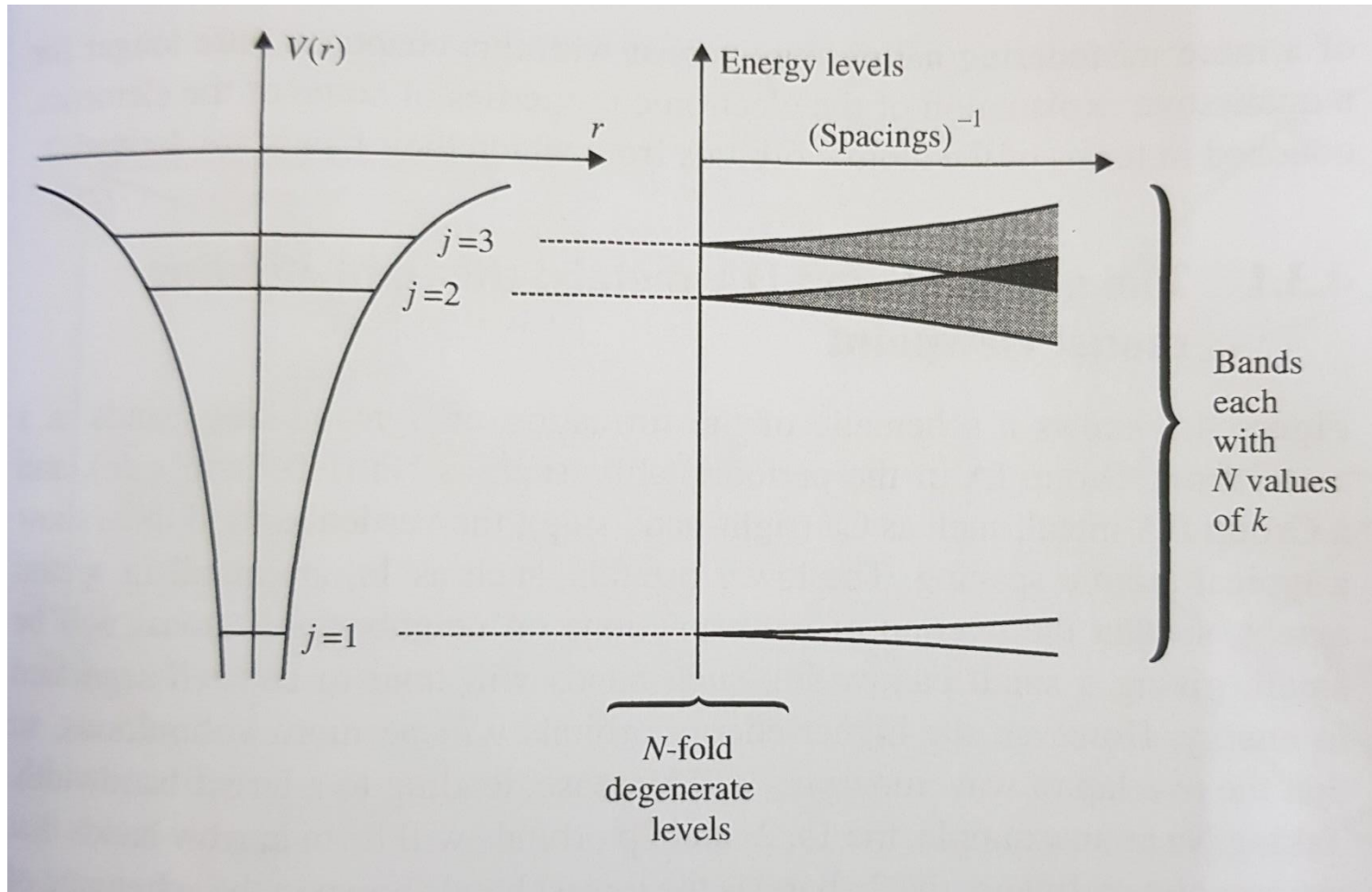


$$\mathbf{R} = \frac{a}{2} (\pm 1, \pm 1, 0), \quad \frac{a}{2} (\pm 1, 0, \pm 1), \quad \frac{a}{2} (0, \pm 1, \pm 1)$$

The 12 nearest neighbors of the origin in a face-centered cubic lattice

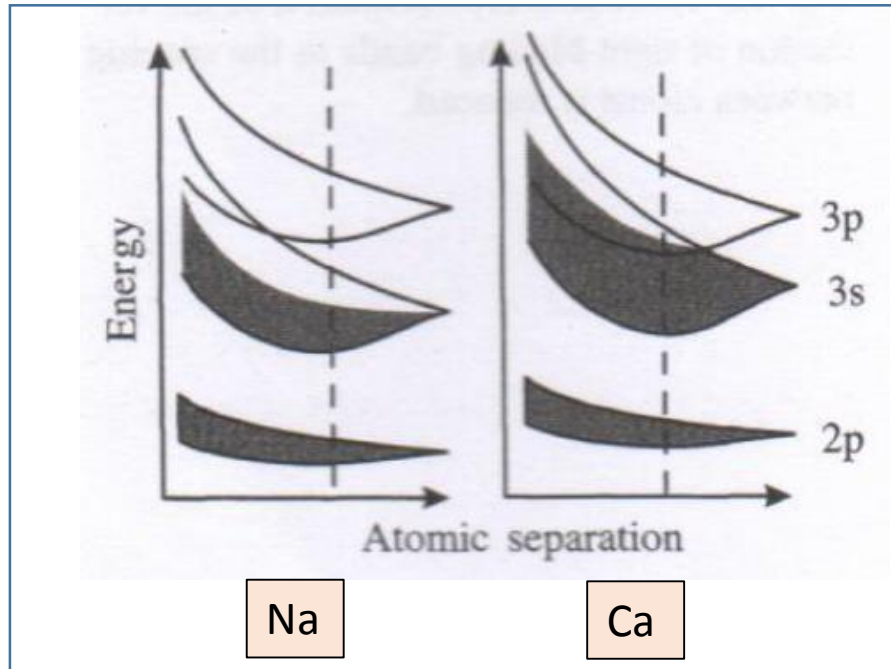
$$\varepsilon(\mathbf{k}) = E_s - \beta - 4\gamma(\cos \tfrac{1}{2}k_x a \cos \tfrac{1}{2}k_y a + \cos \tfrac{1}{2}k_y a \cos \tfrac{1}{2}k_z a + \cos \tfrac{1}{2}k_z a \cos \tfrac{1}{2}k_x a)$$

Bands arising from tight-binding approx.



- N single atoms with j (doubly degenerate) atomic levels have become $2N$ -fold degenerate

Bands arising from tight-binding approx.



- Transfer integrals give a direct measure of the width of a band. Smaller transfer integrals lead to narrow bandwidths (heavy effective mass)
- Taking Na, its 1s, 2s and 2p orbitals will form narrow bands that are completely full up; the 3s band is wider and half-filled (since Na is monovalent, each atom provides one 3s electron, hence Na is metal)
- If the atoms in a certain direction along the crystal structure are far apart, then the bandwidth will be narrow for motion in that direction

General points about bandstructure

Using tight-binding method we get the band dispersion in 1D

$$E(k) = E_0 - 2t \cos(ka)$$

Compare with the band obtained from nearly-free electron model -

- Both bands have qualitatively similar features
- Both bands have minima and maxima (points where $\frac{dE}{dk} = 0$)
- Both bands have the same k-space periodicity
- The tops and bottoms of both bands are approximately parabolic

Thus, both very weak and very strong periodic potentials give rise to qualitatively similar bands. In real solids, the potential strengths will be between the two extremes, and the idea of bands derived from these simple models will apply there too

General points about bandstructure

Bloch functions are not eigenstates of the momentum operator -

$$\begin{aligned}\frac{\hbar}{i}\nabla\psi(\mathbf{r}) &= \frac{\hbar}{i}\nabla e^{i\mathbf{q}\cdot\mathbf{r}}u_{j,\mathbf{q}} \\ &= \hbar\mathbf{q}\psi(\mathbf{r}) + e^{i\mathbf{q}\cdot\mathbf{r}}\frac{\hbar}{i}\nabla u_{j,\mathbf{q}} \\ &\neq \mathbf{p}\psi(\mathbf{r})\end{aligned}$$

The quantity $\hbar\mathbf{k}$ is instead called the crystal momentum

General points about bandstructure

Electrons occupying Bloch states is a superposition of a set of plane waves (a wavepacket)

$$\Psi_{\mathbf{k}}^{\alpha}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{\mathbf{G},\mathbf{k}}^{\alpha} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

It is, thus, possible to use the idea of a group velocity to describe the real space motion of the electron

$$\mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E$$

In optics we use $v = (d\omega/dk)$ for motion of wavepackets

General points about bandstructure

Let an external force f be applied on a 1D band-electron. The force will do work -

$$\delta E = f v \delta t$$

Also from previous discussion $\delta E = \hbar v \delta k$

Equating the above $\hbar \frac{dk}{dt} = f$ In 3D - $\hbar \frac{d\mathbf{k}}{dt} = \mathbf{f}$

The rate of change of velocity $\frac{dv}{dt} = \frac{1}{\hbar} \frac{d^2 E}{dk dt} = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt}$

Substituting from above -

$$\frac{\hbar^2}{\frac{d^2 E}{dk^2}} \frac{dv}{dt} = m^* \frac{dv}{dt} = f$$

Effective mass definition -

$$m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}$$

General points about bandstructure

In general effective mass will be energy dependent

$$m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}$$

Close to the band maximum and minimum where the energy dispersion is usually parabolic we can write (as seen earlier)

$$E(\mathbf{k}) \approx E_0 + \frac{\hbar^2}{2m^*} (\mathbf{k} - \mathbf{k}_0)^2$$

Concept of holes

It is going to be useful to describe a few empty states close to the top of an almost full band using the concept of holes

Consider a band, containing electrons with quantum numbers k_j , velocities v_j and energies $E(k_j)$, where $E = 0$ is at the top of band

For a full band, the values of k should all sum to zero

$$\sum_j \mathbf{k}_j = 0$$

Concept of holes

For a full band, the values of k should all sum to zero

$$\sum_j \mathbf{k}_j = 0$$

We consider removing an electron to create an excitation, which we label a hole

Suppose that the l^{th} electron is removed, the band then requires a net k which we attribute to the presence of a hole.

The hole has $k = k_h$

$$\mathbf{k}_h = \sum_{j \neq l} \mathbf{k}_j = -\mathbf{k}_l$$

Concept of holes

The lower down the band the empty state is, the more excited is the system.

The hole's energy must then take the form-

$$E_h = -E(\mathbf{k}_l)$$

The group velocity associated with the hole is

$$\mathbf{v}_h = \frac{1}{\hbar} \nabla_{\mathbf{k}_h} E_h = \frac{1}{\hbar} \nabla_{-\mathbf{k}_l} (-E(\mathbf{k}_l)) = \mathbf{v}_l$$

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The full band will carry no current $\sum_j (-e) \mathbf{v}_j = 0$

The removal of the p^{th} electron produces a current-

$$\sum_{j \neq l} (-e) \mathbf{v}_j = -(-e) \mathbf{v}_l = (+e) \mathbf{v}_h$$

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Current due to a hole- $(+e) \mathbf{v}_h$

The hole appears to have an associated positive charge
Explains why some metals have positive Hall coefficients !

The effective mass associated with the hole is given by-

$$m_h^* = -m_l^* \quad \text{since} \quad m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}$$