

# Chapter 7: The Electronic Band Structure of Solids

Bloch & Slater

April 1, 2008

## Contents

<b>1</b>	<b>Symmetry of <math>\psi(\mathbf{r})</math></b>	<b>3</b>
<b>2</b>	<b>The nearly free Electron Approximation.</b>	<b>6</b>
2.1	The Origin of Band Gaps . . . . .	9
<b>3</b>	<b>Tight Binding Approximation</b>	<b>15</b>
<b>4</b>	<b>Photo-Emission Spectroscopy</b>	<b>24</b>

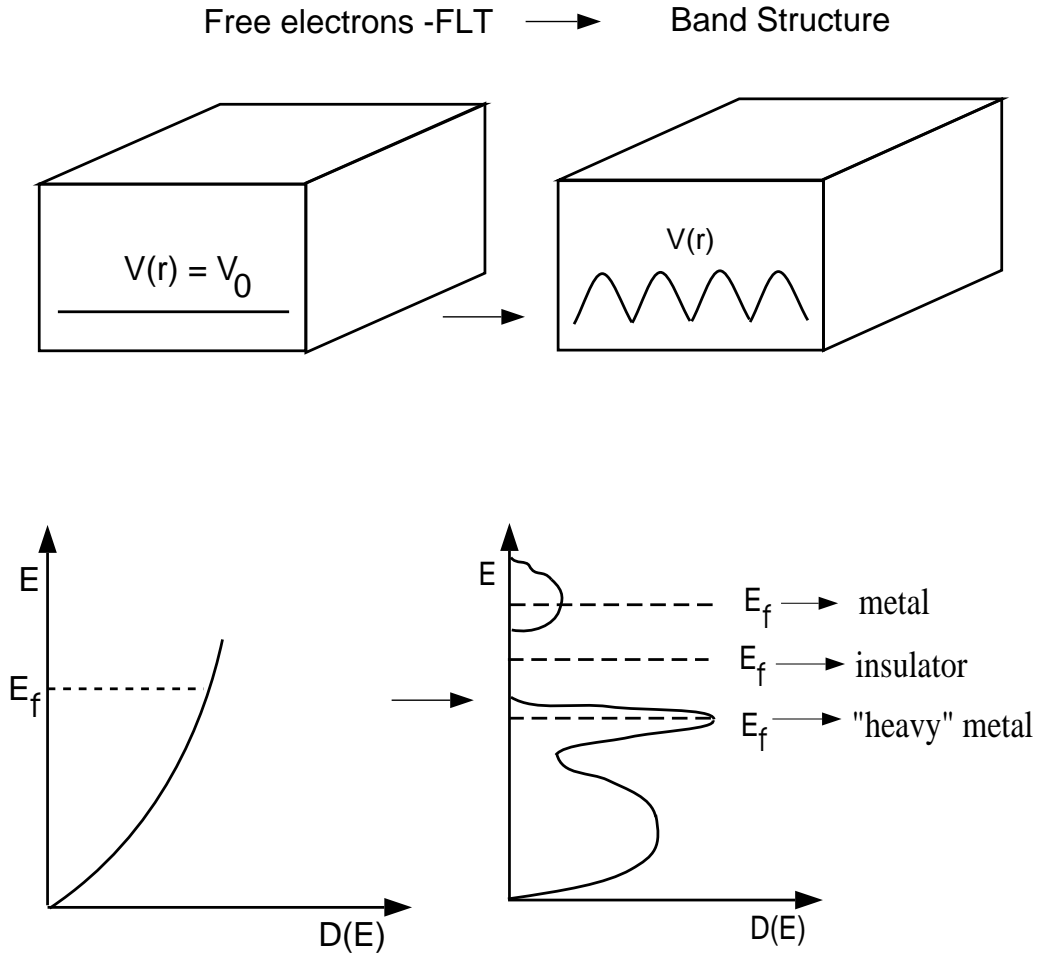


Figure 1: *The additional effects of the lattice potential can have a profound effect on the electronic density of states (RIGHT) compared to the free-electron result (LEFT).*

In the last chapter, we ignored the lattice potential and considered the effects of a small electronic potential  $U$ . In this chapter we will set  $U = 0$ , and consider the effects of the ion potential  $V(\mathbf{r})$ . As shown in Fig. 1, additional effects of the lattice potential can have a profound effect on the electronic density of

states compared to the free-electron result, and depending on the location of the Fermi energy, the resulting system can be a metal, semimetal, an insulator, or a metal with an enhanced electronic mass.

## 1 Symmetry of $\psi(\mathbf{r})$

From the symmetry of the electronic potential  $V(\mathbf{r})$  one may infer some of the properties of the electronic wave functions  $\psi(r)$ .

Due to the translational symmetry of the lattice  $V(r)$  is periodic

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{r}_n), \quad \mathbf{r}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (1)$$

and may then be expanded in a Fourier expansion

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}, \quad \mathbf{G} = h \mathbf{g}_1 + k \mathbf{g}_2 + l \mathbf{g}_3, \quad (2)$$

which, since  $\mathbf{G} \cdot \mathbf{r}_n = 2\pi m$  ( $m \in \mathcal{Z}$ ) guarantees  $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{r}_n)$ . Given this, and letting  $\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}$  the

Schroedinger equation becomes

$$H\psi(\mathbf{r}) = \left[ -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right] \psi = E\psi \quad (3)$$

$$\Rightarrow \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_{\mathbf{k}'\mathbf{G}} C_{\mathbf{k}'} V_{\mathbf{G}} e^{i(\mathbf{k}'+\mathbf{G})\cdot\mathbf{r}} = E \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \mathbf{k}' \rightarrow \mathbf{k}-\mathbf{G} \quad (4)$$

or

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \left\{ \left( \frac{\hbar^2 k^2}{2m} - E \right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} \right\} = 0 \forall \mathbf{r} \quad (5)$$

Since this is true for any  $\mathbf{r}$ , it must be that

$$\left( \frac{\hbar^2 k^2}{2m} - E \right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0, \quad \forall \mathbf{k} \quad (6)$$

Thus the potential acts to couple each  $C_{\mathbf{k}}$  only with its reciprocal space translations  $C_{\mathbf{k}+\mathbf{G}}$  and the problem decouples in to  $N$  independent problems for each  $\mathbf{k}$  in the first BZ. I.e., each of the  $N$  problems has a solution which is a sum over plane waves whos' wave vectors differ only by  $\mathbf{G}$ 's. Thus the eigenvalues may be indexed by  $\mathbf{k}$ .

$$E_{\mathbf{k}} = E(\mathbf{k}), \quad \text{I.e. } \mathbf{k} \text{ is still a good q.n.}! \quad (7)$$

We may now sum over  $\mathbf{G}$  to get  $\psi_{\mathbf{k}}$  with the eigenvector sum

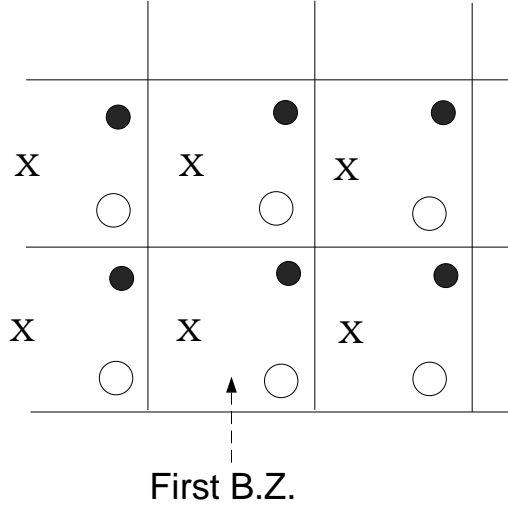


Figure 2: The potential acts to couple each  $C_{\mathbf{k}}$  with its reciprocal space translations  $C_{\mathbf{k}+\mathbf{G}}$  (i.e.  $x \rightarrow x$ ,  $\bullet \rightarrow \bullet$ , and  $\circ \rightarrow \circ$ ) and the problem decouples into  $N$  independent problems for each  $\mathbf{k}$  in the first BZ.

restricted to reciprocal lattice sites  $\mathbf{k}, \mathbf{k} + \mathbf{G}, \dots$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} = \left( \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} \right) e^{i\mathbf{k}\cdot\mathbf{r}} \quad (8)$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = U_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \text{where } U_{\mathbf{k}}(\mathbf{r}) = U_{\mathbf{k}}(\mathbf{r} + \mathbf{r}_n) \quad (9)$$

Note that if  $V(\mathbf{r}) = 0$ ,  $U(\mathbf{r}) = \frac{1}{\sqrt{V}}$ . This result is called *Bloch's Theorem*; i.e., that  $\psi$  may be resolved into a plane wave and a periodic function. Its consequences as follows:

$$\begin{aligned} \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) &= \sum_{\mathbf{G}'} C_{\mathbf{k}+\mathbf{G}-\mathbf{G}'} e^{-i(\mathbf{G}'-\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} = \left( \sum_{\mathbf{G}''} C_{\mathbf{k}-\mathbf{G}''} e^{-i\mathbf{G}''\cdot\mathbf{r}} \right) e^{i\mathbf{k}\cdot\mathbf{r}} \\ &= \psi_{\mathbf{k}}(\mathbf{r}), \quad \text{where } \mathbf{G}'' \equiv \mathbf{G}' - \mathbf{G} \end{aligned} \quad (10)$$

Ie.,  $\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r})$  and as a result

$$H\psi_{\mathbf{k}} = E(\mathbf{k})\psi_{\mathbf{k}} \Rightarrow H\psi_{\mathbf{k}+\mathbf{G}} = E(\mathbf{k} + \mathbf{G})\psi_{\mathbf{k}+\mathbf{G}} \quad (11)$$

$$= H\psi_{\mathbf{k}} = E(\mathbf{k} + \mathbf{G})\psi_{\mathbf{k}+\mathbf{G}} \quad (12)$$

Thus  $E(\mathbf{k} + \mathbf{G}) = E(\mathbf{k})$  :  $E(\mathbf{k})$  is periodic then since both  $\psi_{\mathbf{k}}(\mathbf{r})$  and  $E(\mathbf{k})$  are periodic in reciprocal space, one only needs knowledge of them in the first BZ to know them everywhere.

## 2 The nearly free Electron Approximation.

If the potential is weak,  $V_{\mathbf{G}} \approx 0 \quad \forall \mathbf{G}$ , then we may solve the  $V_{\mathbf{G}} = 0$  problem, subject to our constraints of periodicity, and treat  $V_{\mathbf{G}}$  as a perturbation.

When  $V_{\mathbf{G}} = 0$ , then

$$E(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad \text{free electron} \quad (13)$$

However, we must also have that (if  $V_{\mathbf{G}} \neq 0$ )

$$E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G}) \approx \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \quad (14)$$

Ie., the possible electron states are not restricted to a single parabola, but can be found equally well on paraboli shifted by

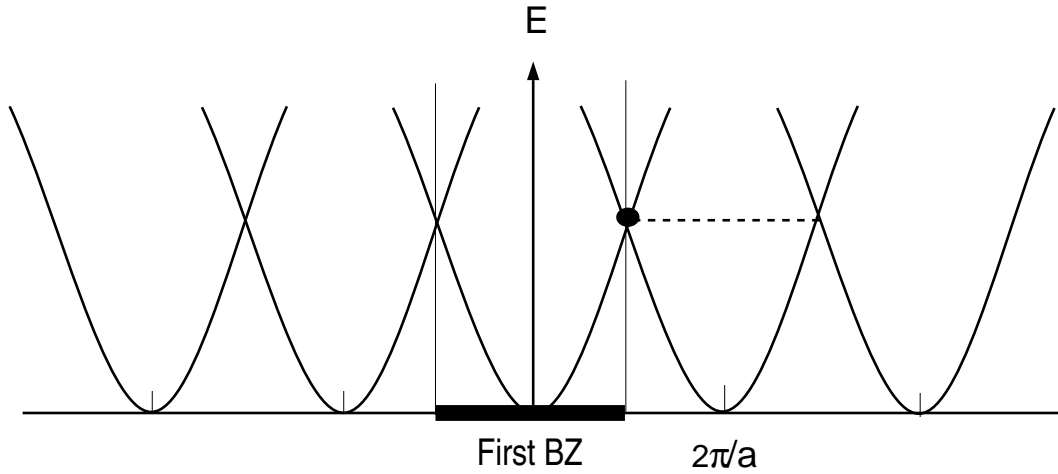


Figure 3: For small  $V_{\mathbf{G}}$ , we may approximate the band structure as composed of  $N$  parabolic bands. Of course, it is sufficient to consider this in the first Brillouin zone, where the parabola centered at finite  $\mathbf{G}$  cross at high energies. To understand the effects of the perturbation  $V_{\mathbf{G}}$  consider this special  $\mathbf{k}$  at the edge of the BZ, where the paraboli cross.

any  $\mathbf{G}$  vector. In 1-d Since  $E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G})$ , it is sufficient to represent this in the first zone only. For example in a 3-D cubic lattice the energy band structure along  $k_x (k_y = k_z = 0)$  is already rather complicated within the first zone. (See Fig.4.)

The effect of  $V_{\mathbf{G}}$  can now be discussed. Let's return to the 1-d problem and consider the edges of the zone where the  $\Phi$ paraboli intersect. (See Fig. 3.) An electron state with  $\mathbf{k} = \frac{\pi}{a}$  will involve *at least* the two  $\mathbf{G}$  values  $G = 0, \frac{2\pi}{a}$ . Of course, the

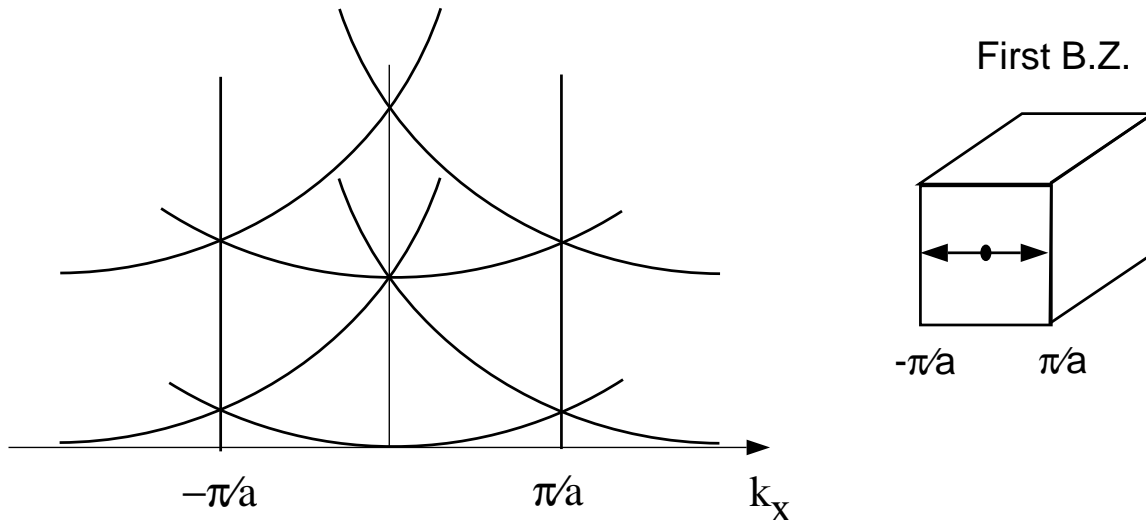


Figure 4: *The situation becomes more complicated in three dimensions since there are many more bands and so they can cross the first zone at lower energies. For example in a 3-D cubic lattice the energy band structure along  $k_x$  ( $k_y = k_z = 0$ ) is already rather complicated within the first zone.*

exact solution must involve all  $\mathbf{G}$  since

$$\left(\frac{\hbar^2 \mathbf{k}^2}{2m} - E_{\mathbf{k}}\right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0 \quad (15)$$

We can generally take  $V_0 = 0$  since this just sets a zero for the potential. Then, those  $\mathbf{G}$  for which  $E_{\mathbf{k}} = E_{\mathbf{k}-\mathbf{G}} \approx \frac{\hbar^2 \mathbf{k}^2}{2m}$  are going to give the largest contribution since

$$C_{\mathbf{k}} = \sum_{\mathbf{G}} V_{\mathbf{G}} \frac{C_{\mathbf{k}-\mathbf{G}}}{\frac{\hbar^2 \mathbf{k}^2}{2m} - E_{\mathbf{k}-\mathbf{G}}} \quad (16)$$

$$C_{\mathbf{k}} \sim V_{\mathbf{G}_1} \frac{C_{\mathbf{k}-\mathbf{G}_1}}{\frac{\hbar^2 \mathbf{k}^2}{2m} - E_{\mathbf{k}-\mathbf{G}_1}} \quad (17)$$



$$C_{\mathbf{k}-\mathbf{G}_1} = \sum_{\mathbf{G}} V_{\mathbf{G}} \frac{C_{\mathbf{k}-\mathbf{G}_1-\mathbf{G}}}{\frac{\hbar^2 \mathbf{k}^2}{2m} - E_{\mathbf{k}-\mathbf{G}-\mathbf{G}_1}} \quad (18)$$

$$C_{\mathbf{k}-\mathbf{G}_1} \sim V_{-\mathbf{G}_1} \frac{C_{\mathbf{k}}}{\frac{\hbar^2 \mathbf{k}^2}{2m} - E_{\mathbf{k}}} \quad (19)$$

Thus to a first approximation, we may neglect the other  $C_{\mathbf{k}-\mathbf{G}}$ , and since  $V_{\mathbf{G}} = V_{-\mathbf{G}}$  (so that  $V(\mathbf{r})$  is real)  $|C_{\mathbf{k}}| \approx |C_{\mathbf{k}-\mathbf{G}_1}| \gg$  other  $C_{\mathbf{k}-\mathbf{G}}$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}} \sim \begin{cases} (e^{iGx/2} + e^{-iGx/2}) \sim \cos \frac{\pi x}{\mathbf{a}} \\ (e^{iGx/2} - e^{-iGx/2}) \sim \sin \frac{\pi x}{\mathbf{a}} \end{cases} \quad (20)$$

The corresponding electron densities are sketched in Fig. 5. Clearly  $\rho_+$  has higher density near the ionic cores, and will be more tightly bound, thus  $E_+ < E_-$ . Thus a gap opens in  $E_k$  near  $k = \frac{G}{2}$ .

## 2.1 The Origin of Band Gaps

Now let's reexamine this gap at  $\mathbf{k} = \mathbf{G}_1/2$  in a quantitative manner. Start with the eigen value equation shifted by  $\mathbf{G}$ .

$$C_{\mathbf{k}-\mathbf{G}} \left( E_{\mathbf{k}} - \frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 \right) = \sum_{\mathbf{G}'} V_{\mathbf{G}'} C_{\mathbf{k}-\mathbf{G}-\mathbf{G}'} = \sum_{\mathbf{G}'} V_{\mathbf{G}'-\mathbf{G}} C_{\mathbf{k}-\mathbf{G}'} \quad (21)$$

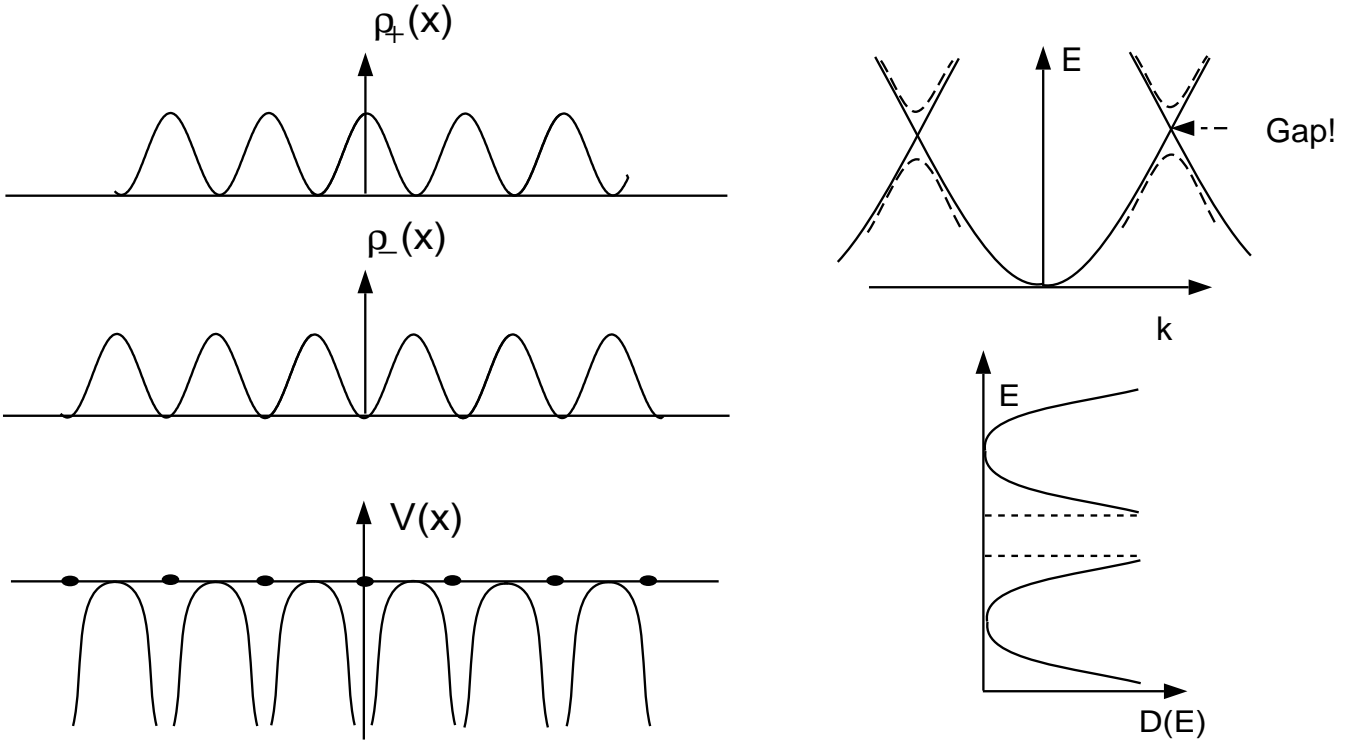


Figure 5:  $\rho_+ \sim \cos^2(\pi x/a)$  has higher density near the ionic cores, and will be more tightly bound, thus  $E_+ < E_-$ . Thus a gap opens in  $E_k$  near  $k = \frac{G}{2}$ .

$$C_{\mathbf{k}-\mathbf{G}} = \frac{\sum_{\mathbf{G}'} V_{\mathbf{G}'-\mathbf{G}} C_{\mathbf{k}-\mathbf{G}'}}{\left(E_{\mathbf{k}} - \frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2\right)} \quad (22)$$

To a first approximation ( $V_{\mathbf{G}} \simeq 0$ ) let's set  $E = \frac{\hbar^2 \mathbf{k}^2}{2m}$  (a free-electron energy) and ignore all but the largest  $C_{\mathbf{k}-\mathbf{G}}$ ; ie., those for which the denominator vanishes.

$$\mathbf{k}^2 = |\mathbf{k} - \mathbf{G}|^2, \quad (23)$$

or in 1-d

$$\mathbf{k}^2 = \left(\mathbf{k} - \frac{2\pi}{\mathbf{a}}\right)^2 \quad \text{or} \quad \mathbf{k} = -\frac{\pi}{\mathbf{a}} \quad (24)$$

This is just the Laue condition, which was shown to be equivalent to the Bragg condition. I.e., the strongest perturbation to the free-electron picture occurs for states with energies at the edge of the first B.Z. Thus the equation above also tells us

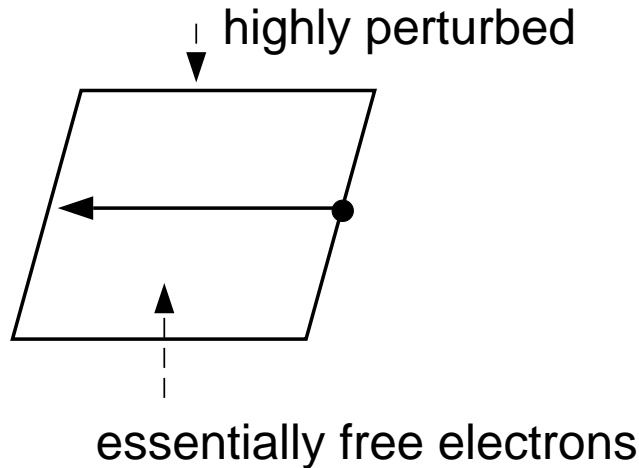


Figure 6: We can satisfy the condition  $E_{\mathbf{k}} \simeq E_{\mathbf{k}-\mathbf{G}}$  only for  $\mathbf{k}$  on the edge of the B.Z.. Here the lattice potential strongly perturbs the electronic states (i.e. more than one  $C_{\mathbf{k}-\mathbf{G}}$  is finite).

that  $C_{\mathbf{k}}$  and  $C_{\mathbf{k}-\mathbf{G}_1}$  are the most important coefficients (if this electronic state was unperturbed, only  $C_{\mathbf{k}}$  would be important). Thus approximately for  $V_{\mathbf{G}} \sim 0, V_0 \equiv 0$  and for  $\mathbf{k}$  near the

zone boundary

$$\mathbf{G} = 0 \quad C_{\mathbf{k}} \left\{ E - \frac{\hbar^2 k^2}{2m} \right\} = V_{\mathbf{G}_1} C_{\mathbf{k}-\mathbf{G}_1} \quad (25)$$

$$\mathbf{G} = \mathbf{G}_1 \quad C_{\mathbf{k}-\mathbf{G}_1} \left\{ E - \frac{\hbar^2 |\mathbf{k} - \mathbf{G}_1|^2}{2m} \right\} = V_{-\mathbf{G}_1} C_{\mathbf{k}}, \quad (26)$$

Again, ignore all other  $C_{\mathbf{G}}$ . This is a secular equation which has a nontrivial solution iff

$$\begin{vmatrix} \left( \frac{\hbar^2 \mathbf{k}^2}{2m} - E \right) & V_{\mathbf{G}_1} \\ V_{-\mathbf{G}_1} & \left( \frac{\hbar^2 |\mathbf{k}-\mathbf{G}_1|^2}{2m} - E \right) \end{vmatrix} = 0 \quad (27)$$

or

$$\begin{vmatrix} E_{\mathbf{k}}^0 - E & V_{\mathbf{G}_1} \\ V_{-\mathbf{G}_1} & E_{\mathbf{k}-\mathbf{G}_1}^0 - E \end{vmatrix} = 0 \quad (28)$$

$$(V_{-\mathbf{G}} = V_{\mathbf{G}}^*, \quad \text{so that } V(\mathbf{r}) \in \mathfrak{R})$$

$$(E_{\mathbf{k}}^0 - E)(E_{\mathbf{k}-\mathbf{G}_1}^0 - E) - |V_{\mathbf{G}_1}|^2 = 0 \quad (29)$$

$$E_{\mathbf{k}}^0 E_{\mathbf{k}-\mathbf{G}_1}^0 - E (E_{\mathbf{k}}^0 + E_{\mathbf{k}-\mathbf{G}_1}^0) + E^2 - |V_{\mathbf{G}_1}|^2 = 0 \quad (30)$$

$$E^{\pm} = \frac{1}{2} (E_{\mathbf{k}-\mathbf{G}_1}^0 + E_{\mathbf{k}}^0) \pm \left\{ \frac{1}{4} (E_{\mathbf{k}-\mathbf{G}_1}^0 - E_{\mathbf{k}}^0)^2 + |V_{\mathbf{G}_1}|^2 \right\}^{\frac{1}{2}} \quad (31)$$

At the zone boundary, where  $E_{\mathbf{k}-\mathbf{G}_1}^0 = E_{\mathbf{k}}^0$ , the gap is

$$\Delta E = E_+ - E_- = 2|V_{\mathbf{G}_1}| \quad (32)$$

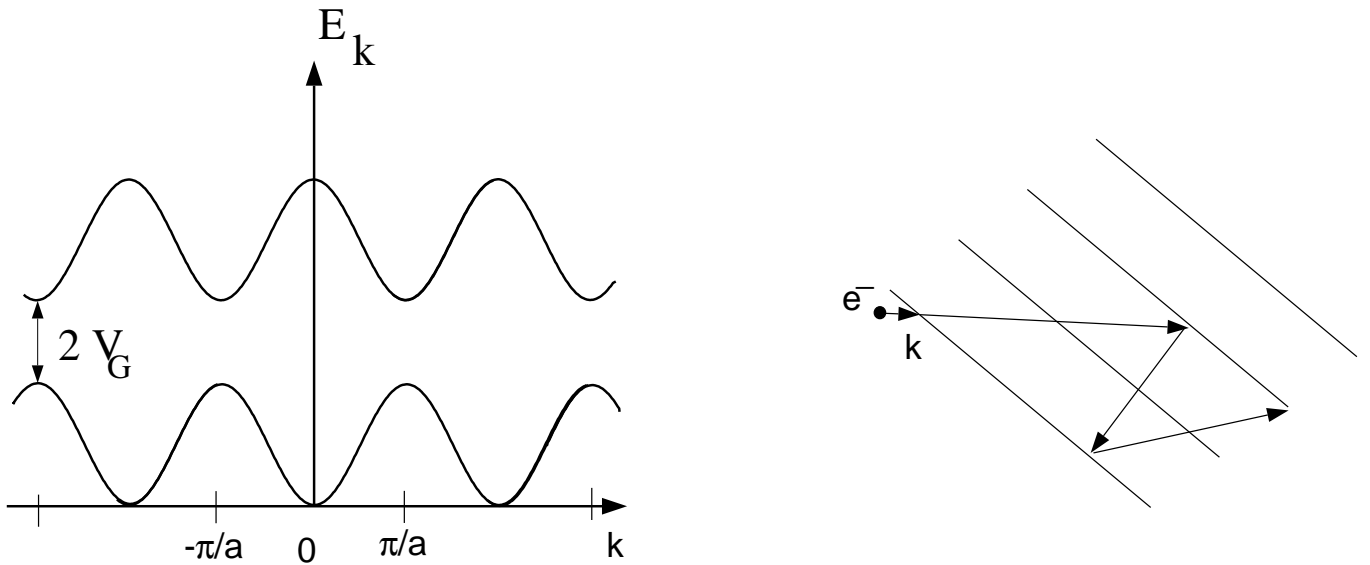


Figure 7:

And the band structure looks something like Fig. 7. Within this approximation, the gap, or forbidden regions in which there are no electronic states arise when the Bragg condition ( $\mathbf{k}_f - \mathbf{k}_0 = \mathbf{G}$ ) is satisfied.

$$|-\mathbf{k}| \approx |\mathbf{k} + \mathbf{G}| \quad (33)$$

The interpretation is clear: the high degree of back scattering for these  $\mathbf{k}$ -values destroys the electronic states.

Thus, by treating the lattice potential as a perturbation to the free electron problem, we see that gaps arise due to enhanced electron-lattice back scattering for  $\mathbf{k}$  near the zone edge. How-

ever, in chapter one, we considered band structure qualitatively and determined that gaps could arise from perturbing about the atomic limit. This in fact, is another natural way of con-

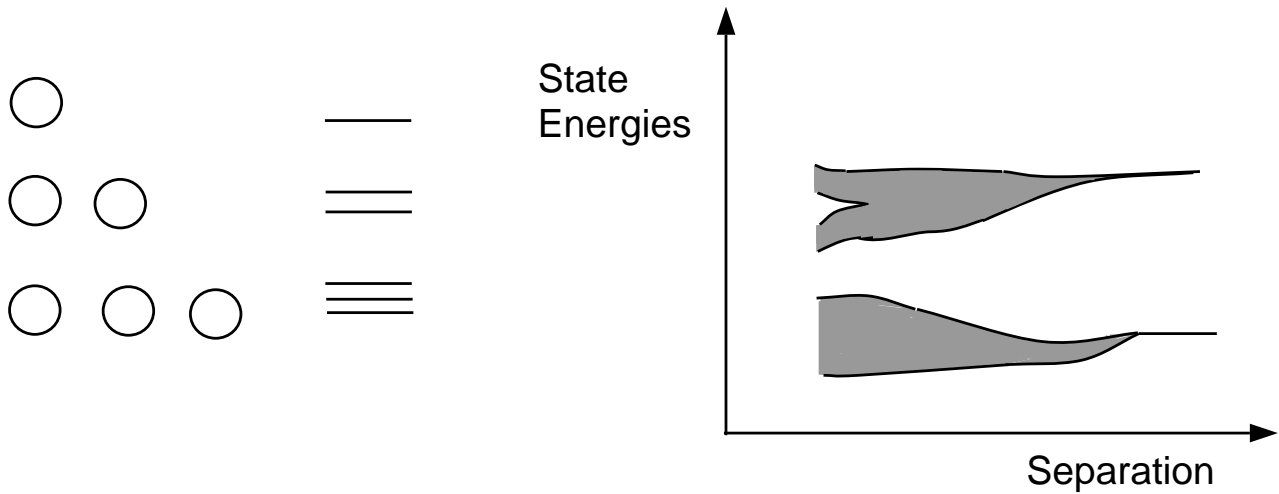


Figure 8: Band gaps in the electronic DOS naturally emerge when perturbing around the atomic limit. As we bring more atoms together (left) or bring the atoms in the lattice closer together (right), bands form from mixing of the orbital states. If the band broadening is small enough, gaps remain between the bands.

structing a band structure theory. It is called the tight-binding approximation.

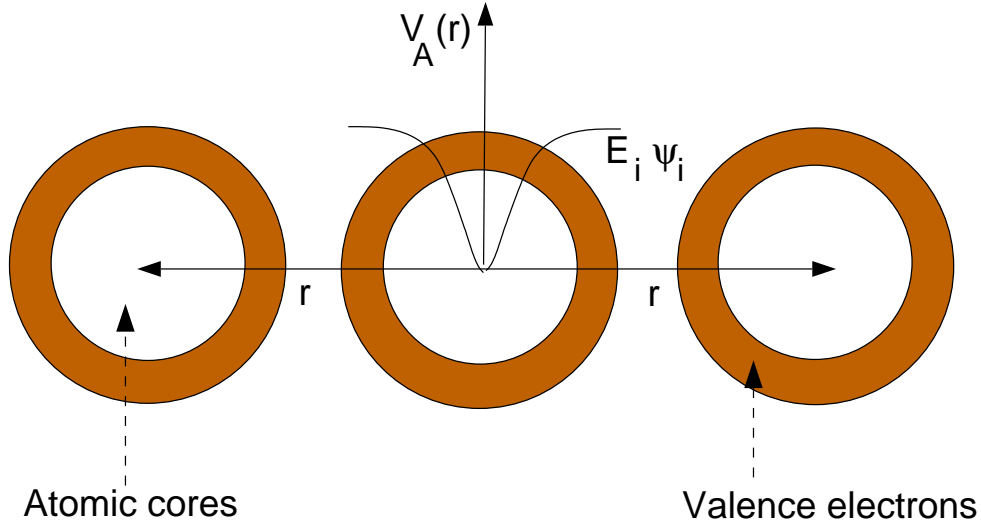


Figure 9: *In the tight-binding approximation, we generally ignore the core electron dynamics and consider only the ionic core potential. For now let's assume that there is only one valence orbital  $\phi_i$  on each atom.*

### 3 Tight Binding Approximation

In the tight-binding approximation, we generally ignore the core electron dynamics and treat consider only the ionic core potential. For now let's assume that there is only one valence orbital  $\phi_i$  on each atom. We will also assume that the atomic problem is solved, and perturb around this solution. The atomic problem has valence eigenstates  $\phi_i$ , and eigen energies  $E_i$ . The unperturbed Schroedinger equation for the  $n$ th atom is

$$H_A(\mathbf{r} - \mathbf{r}_n) \cdot \phi_i(\mathbf{r} - \mathbf{r}_n) = E_i \phi_i(\mathbf{r} - \mathbf{r}_n) \quad (34)$$

There is a weak perturbation  $v(\mathbf{r} - \mathbf{r}_n)$  coming from the atomic potentials of the other atoms  $\mathbf{r}_m \neq \mathbf{r}_n$

$$H = H_A + v = -\frac{\hbar^2 \nabla^2}{2m} + V_A(\mathbf{r} - \mathbf{r}_n) + v(\mathbf{r} - \mathbf{r}_n) \quad (35)$$

$$v(\mathbf{r} - \mathbf{r}_n) = \sum_{\mathbf{m} \neq \mathbf{n}} V_A(\mathbf{r} - \mathbf{r}_m) \quad (36)$$

We now seek solutions of the Schroedinger equation indexed by  $\mathbf{k}$  (Bloch's theorem)

$$H\psi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\Psi_{\mathbf{k}}(\mathbf{r}) \quad (37)$$

$$\Rightarrow \int \psi^* \Rightarrow E(\mathbf{k}) = \frac{\langle \psi_{\mathbf{k}} | H | \psi_{\mathbf{k}} \rangle}{\langle \psi_{\mathbf{k}} | \psi_{\mathbf{k}} \rangle} \quad (38)$$

where

$$\begin{aligned} \langle \psi_{\mathbf{k}} | \psi_{\mathbf{k}} \rangle &\equiv \int d^3\mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) \\ \langle \psi_{\mathbf{k}} | H | \psi_{\mathbf{k}} \rangle &\equiv \int d^3\mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) H \psi_{\mathbf{k}}(\mathbf{r}) \end{aligned} \quad (39)$$

Of course, this problem is almost hopelessly complicated. We cannot solve for  $\psi_{\mathbf{k}}$ . Rather, we will solve for some  $\phi_{\mathbf{k}} \simeq \psi_{\mathbf{k}}$  where the parameters of  $\phi_{\mathbf{k}}$  are determined by minimizing

$$\frac{\langle \phi_{\mathbf{k}} | H | \phi_{\mathbf{k}} \rangle}{\langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}} \rangle} \geq E(\mathbf{k}). \quad (40)$$



This is called the Raleigh-Ritz variational principle.

Consistent with our original motivation, we will approximate  $\psi_{\mathbf{k}}$  with a sum over atomic states.

$$\psi_{\mathbf{k}} \simeq \phi_{\mathbf{k}} = \sum_{\mathbf{n}} a_n \phi_i(\mathbf{r} - \mathbf{r}_{\mathbf{n}}) = \sum_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{r}_{\mathbf{n}}} \phi_i(\mathbf{r} - \mathbf{r}_{\mathbf{n}}) \quad (41)$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \mathbf{U}_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$$

Where  $\phi_{\mathbf{k}}$  must be a Bloch state  $\phi_{\mathbf{k}+\mathbf{G}} = \phi_{\mathbf{k}}$  which dictates our choice  $\mathbf{a}_n = e^{i\mathbf{k}\cdot\mathbf{r}_n}$ . Thus at this level of approximation we have *no free parameters* to vary to minimize  $\langle \phi_{\mathbf{k}} | H | \phi_{\mathbf{k}} \rangle / \langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}} \rangle \approx E(\mathbf{k})$ .

Using  $\phi_{\mathbf{k}}$  as an approximate state the energy denominator  $\langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}} \rangle$ , becomes

$$\langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}} \rangle = \sum_{\mathbf{n}, \mathbf{m}} e^{i\mathbf{k}\cdot(\mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}})} \int d^3\mathbf{r} \phi_i^*(\mathbf{r} - \mathbf{r}_{\mathbf{m}}) \phi_i(\mathbf{r} - \mathbf{r}_{\mathbf{n}}) \quad (42)$$

Let's imagine that the valance orbital of interest,  $\phi_i$ , has an very small overlap with adjacent atoms so that

$$\langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}} \rangle \simeq \sum_{\mathbf{n}} \int d^3\mathbf{r} \phi_i^*(\mathbf{r} - \mathbf{r}_{\mathbf{n}}) \phi_i(\mathbf{r} - \mathbf{r}_{\mathbf{n}}) = N \quad (43)$$

The last identity follows since  $\phi_i$  is normalized.

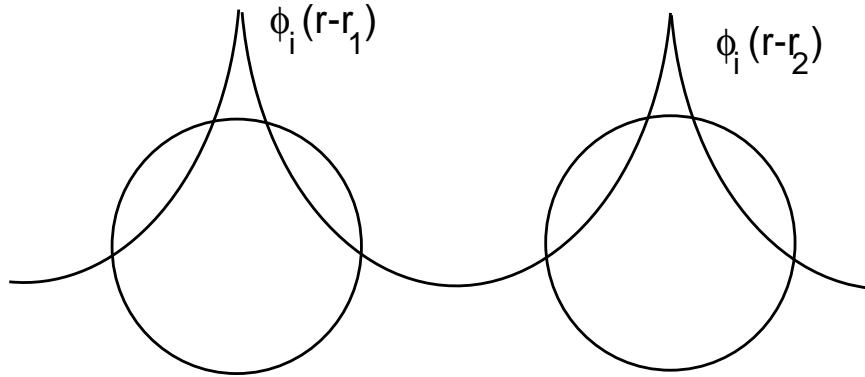


Figure 10: In the tight binding approximation, we assume that the atomic orbitals of adjacent sites have a very small overlap with each other.

The energy for our approximate wave function is then

$$E(\mathbf{k}) \approx \frac{1}{N} \sum_{\mathbf{n}, \mathbf{m}} e^{i\mathbf{k} \cdot (\mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}})} \int d^3\mathbf{r} \phi_i^*(\mathbf{r} - \mathbf{r}_{\mathbf{m}}) \{E_i + v(\mathbf{r} - \mathbf{r}_{\mathbf{n}})\} \phi_i(\mathbf{r} - \mathbf{r}_{\mathbf{n}}). \quad (44)$$

Again, in the first part (involving  $E_i$ ), we may neglect orbital overlap. For the second term, involving  $v(\mathbf{r} - \mathbf{r}_{\mathbf{n}})$ , the overlap should be included, but only to the nearest neighbors of each atom (why?). In the simplest case, where the orbitals  $\phi_i$ , are s-orbitals, then we can use this symmetry to reduce the complexity of the problem to just two more integrals since the hybridization ( $B_i$ ) will be the same in all directions.

$$A_i = - \int \phi_i^*(\mathbf{r} - \mathbf{r}_{\mathbf{n}}) v(\mathbf{r} - \mathbf{r}_{\mathbf{n}}) \phi_i(\mathbf{r} - \mathbf{r}_{\mathbf{n}}) d^3\mathbf{r} \quad \text{ren. } E_i \quad (45)$$

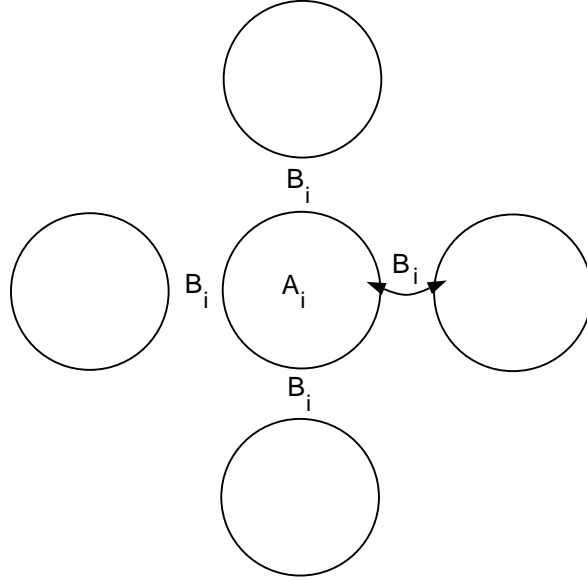


Figure 11: A simple cubic tight binding lattice composed of s-orbitals, with overlap integral  $B_i$ .

$$B_i = - \int \phi_i^*(\mathbf{r} - \mathbf{r}_m) v(\mathbf{r} - \mathbf{r}_n) \phi_i(\mathbf{r} - \mathbf{r}_n) d^3 \mathbf{r} \quad (46)$$

$B_i$  describes the hybridization of adjacent orbitals.

$$A_i; B_i > 0, \quad \text{since } v(\mathbf{r} - \mathbf{r}_n) < 0 \quad (47)$$

Thus

$$E(\mathbf{k}) \simeq E_i - A_i - B_i \sum_{\mathbf{m}} e^{i\mathbf{k}(\mathbf{r}_n - \mathbf{r}_m)} \quad \text{sum over } \mathbf{m} \text{ n.n. to } \mathbf{n} \quad (48)$$

Now, if we have a cubic lattice, then

$$(\mathbf{r}_n - \mathbf{r}_m) = (\pm a, 0, 0)(0, \pm a, 0)(0, 0, \pm a) \quad (49)$$

so

$$E(\mathbf{k}) = E_i - A_i - 2B_i\{\cos k_x a + \cos k_y a + \cos k_z a\} \quad (50)$$

Thus a band centered about  $E_i - A_i$  of width  $12B_i$  is formed. Near the band center, for  $\mathbf{k}$ -vectors near the center of the zone we can expand the cosines  $\cos ka \simeq 1 - \frac{1}{2}(ka)^2 + \dots$  and let  $k^2 = k_x^2 + k_y^2 + k_z^2$ , so that

$$E(k) \simeq E_i - A_i + B_i a^2 k^2 \quad (51)$$

The electrons near the zone center act as if they were free with a renormalized mass.

$$\frac{\hbar^2 k^2}{2m^*} = B_i a^2 k^2, \quad \text{i.e. } \frac{1}{m^*} \propto \text{curvature of band} \quad (52)$$

For this reason, the hybridization term  $B_i$  is often associated with kinetic energy. This makes sense, from its origins of wave function overlap and thus electronic transfer.

The width of the band,  $12 B_i$ , will increase as the electronic overlap increases and the interatomic orbitals (core orbitals or valance f and d orbitals) will tend to form narrow bands with high effective masses (small  $B_i$ ).

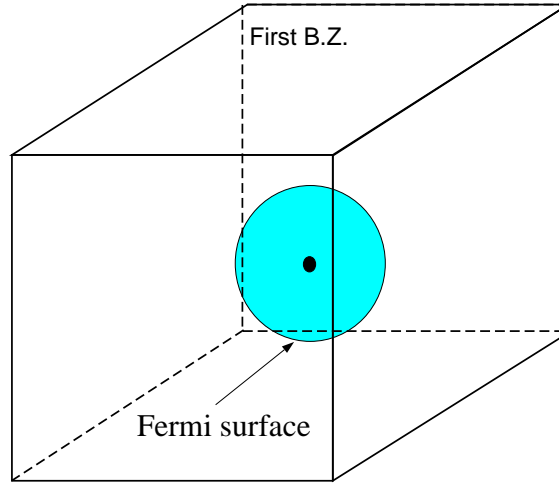


Figure 12: *Electronic states for a cubic lattice near the center of the B.Z. act like free electrons with a renormalized mass. Hence, if the band is partially filled, the Fermi surface will be spherical.*

The bands are filled then by placing two electrons in each band state ( with spins up and down). A metal then forms when the valence band is partially full. I.e., for Na with a  $1s^2 2s^2 2p^6 3s^1$  atomic configuration the 1s, 2s and 2p orbitals evolve into (narrow) filled bands, but the  $3s^1$  band will only be half full, and thus it evolves into a metal. Mg  $1s^2 2s^2 2p^6 3s^2$  also metal since the p and s band overlaps the unfilled d-band. There are exceptions to this rule. Consider C with atomic configuration of  $1s^2 2s^2 2p^2$ . Its valance s and p states form a strong  $sp^3$  hybrid band which is further split into a bonding and anti-

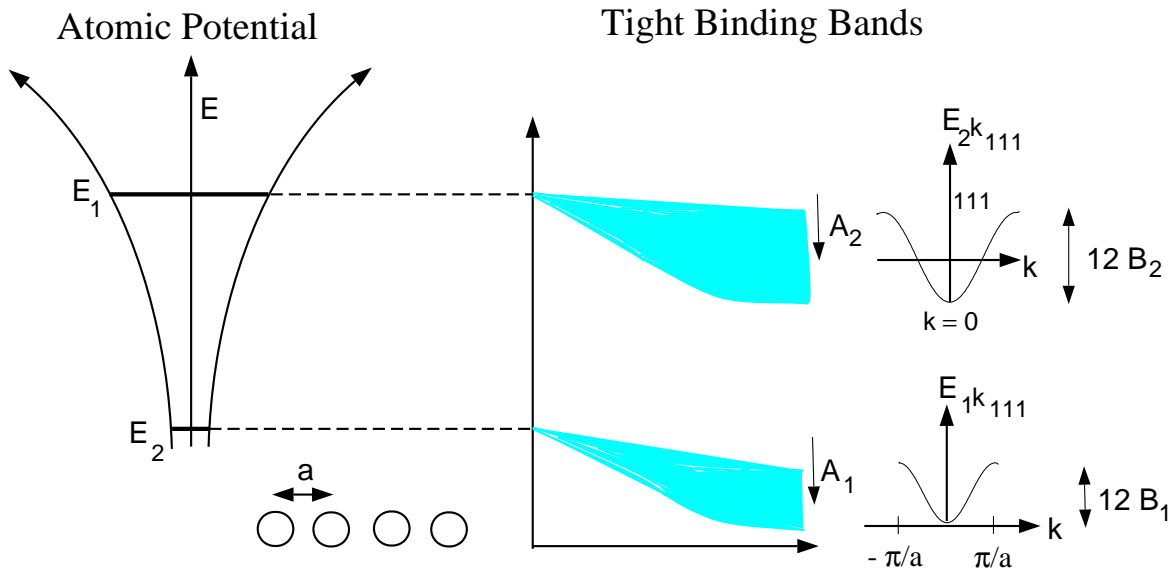


Figure 13: In the tight-binding approximation, band form from overlapping orbitals states (states of the atomic potential). The bandwidth is proportional to the hybridization  $B$  ( $12B$  for a SC lattice). More localized, compact, atomic states tend to form narrower bands.

bonding band. (See Fig.14). Here, the gap is not tied to the periodicity of the lattice, and so an amorphous material of C may also display a gap.

The tight-binding picture can also explain the variety of features seen in the DOS of real materials. For example, in Cu  $(Ar)3d^{10}4s$  the d-orbitals are rather small whereas the valence s-orbitals have a large extent. As a result the s-s hybridization

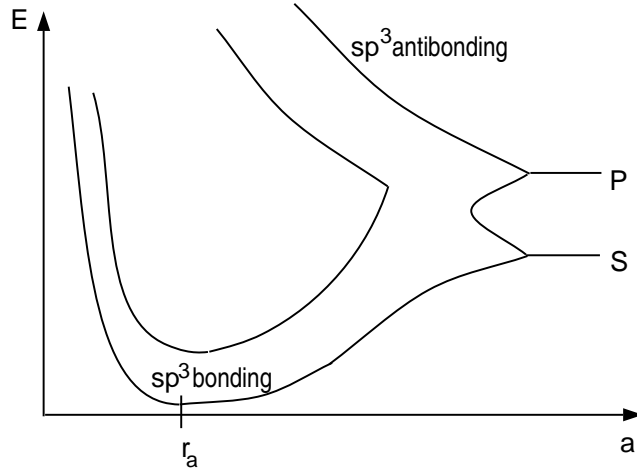


Figure 14: C (diamond) with atomic configuration of  $1s^2 2s^2 2p^2$ . Its valence s and p states form a strong  $sp^3$  hybrid band which is split into a bonding and anti-bonding band.

$B_i^{ss}$ : is strong and the  $B_i^{dd}$  is weak.

$$B_i^{dd} \ll B_i^{ss} \quad (53)$$

In addition the s-d hybridization is inhibited by the opposing symmetry of the s-d orbitals.

$$B_i^{sd} = \int \phi_i^s(\mathbf{r} - \mathbf{r}_1) v(\mathbf{r} - \mathbf{r}_2) \phi_i^d(\mathbf{r} - \mathbf{r}_2) d^3\mathbf{r} \ll B_i^{ss} \quad (54)$$

where  $\phi_i^s$  is essentially even and  $\phi_i^d$  is essentially odd. So  $B_i^{sd} \ll B_i^{ss}$ . Thus, to a first approximation the s-orbitals will form a very wide band of mostly s-character and the d-orbitals will form a very narrow band of mostly d-character. Since both the

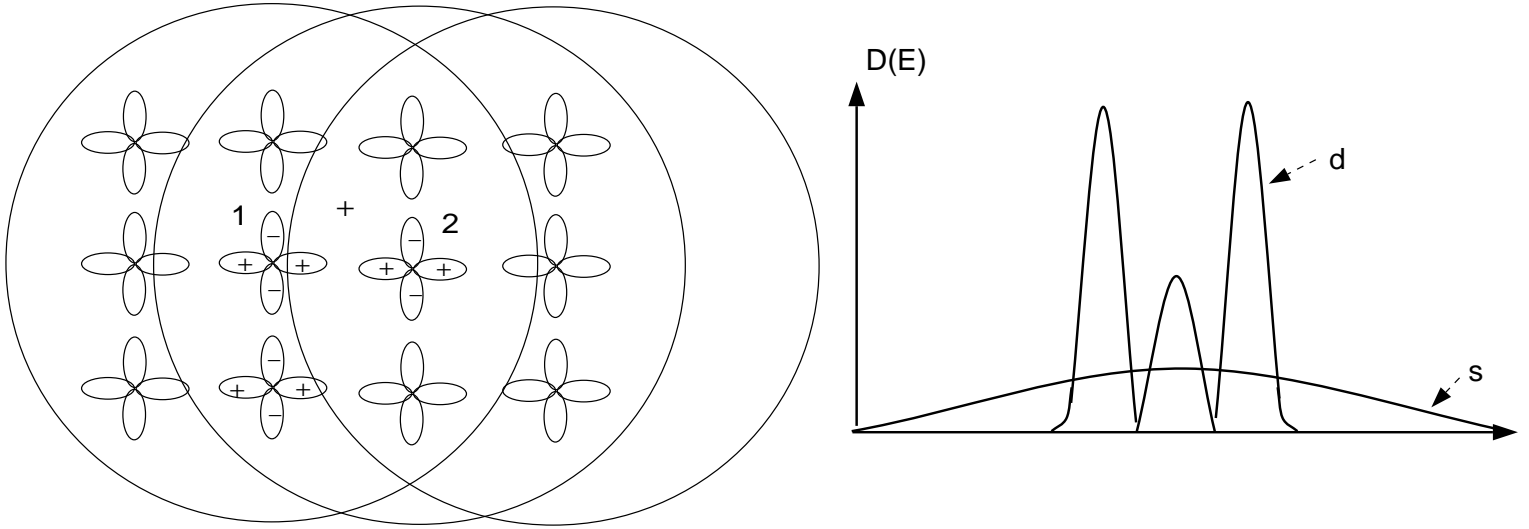


Figure 15: Schematic DOS of Cu  $3d^{10}4s^1$ . The narrow d-band feature is split due to crystal fields.

s and d bands are valance, they will overlap leading to a DOS with both d and s features superimposed.

## 4 Photo-Emission Spectroscopy

The electronic density of electronic states (especially for occupied states), and to a less extent band structure, are very important for illuminating the interesting physics of materials. As we saw in Chap. 6, an enhanced DOS at the Fermi surface indicates an enhanced electronic mass, and if  $D(E_F) = 0$ , we have an insulator (semiconductor). The effective electronic



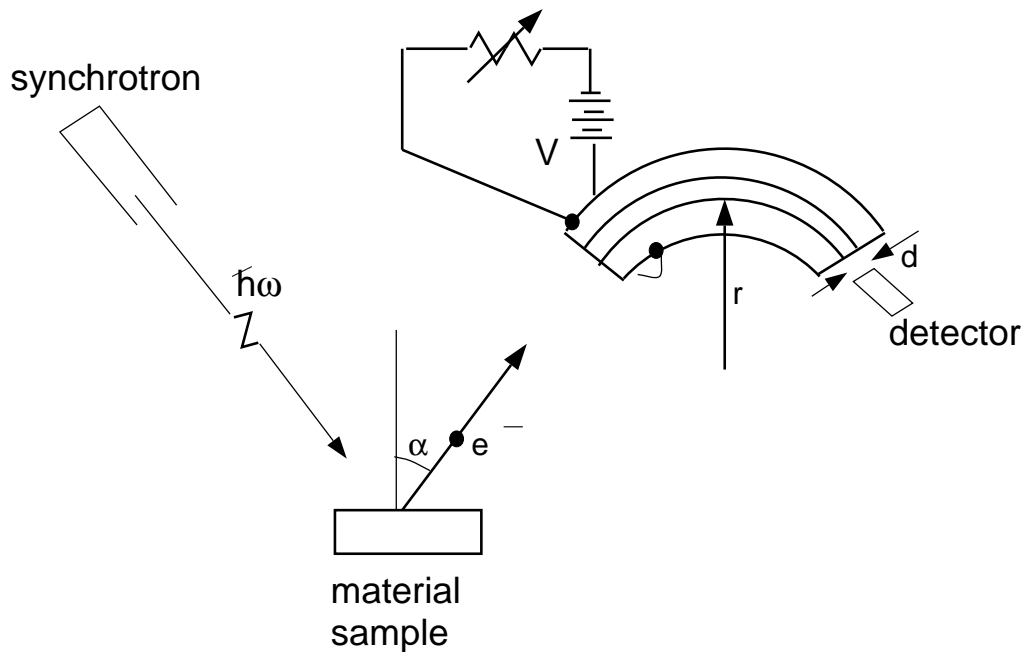


Figure 16: **XPS Experiment:** *By varying the voltage one may select the kinetic energy of the electrons reaching the counting detector.*

mass also varies inversely with the curvature of the bands. The density of states away from the Fermi surface can allow us to predict the properties of the material upon doping, or it can yield information about core-level states. Thus it is important to be able to measure  $D(E)$ . This may be done by x-ray photoemission (XPS), UPS or PS in general. The band dispersion  $E(\mathbf{k})$  may also be measured using angle-resolved photoemission (ARPES) where angle between the incident radiation and the

detector is also measured.

The basic idea is that a photon (usually an x-ray) is used to knock an electron out of the system (See figure 17.) Of

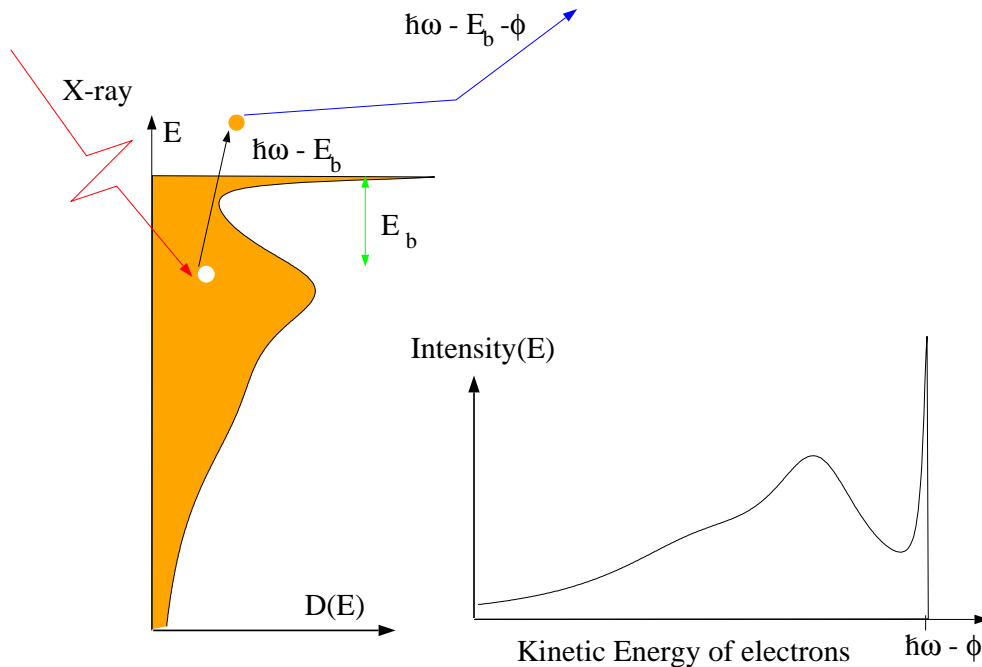


Figure 17: Let the binding energy be defined so that  $E_b > 0$ ,  $\phi =$  work function, then the detected electron intensity  $I(E_{kin} - \hbar\omega - \phi) \propto D(-E_b)f(-E_b)$

course, in order for an electron at an energy of  $E_b$  below the Fermi surface to escape the material, the incident photon must have an energy which exceeds  $E_b$  and the work function  $\phi$  of the material. If  $\hbar\omega > \phi$ , then the emitted electrons will have a distribution of kinetic energies  $E_{kin}$ , extending from zero to

$\hbar\omega - \phi$ . From Fermi's golden rule, we know that the probability per unit time of an electron being ejected is proportional to the density of occupied electronic states times the probability (Fermi function) that the electronic state is occupied

$$\begin{aligned}
 I(E_{kin}) &= \frac{1}{\tau(E_{kin})} \propto D(-E_b)f(-E_b) \\
 &\propto D(E_{kin} + \phi - \hbar\omega)f(E_{kin} + \phi - \hbar\omega) \quad (55)
 \end{aligned}$$

Thus if we measure the energy and number of ejected particles, then we know  $D(-E_b)$ .

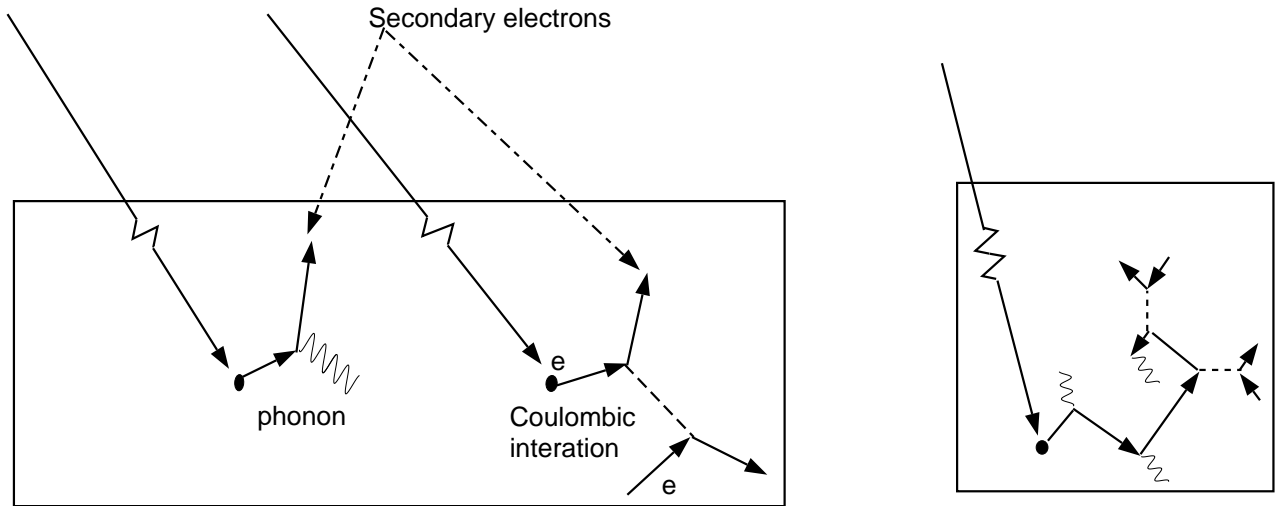


Figure 18: Left: Origin of the background in  $I(E_{kin})$ . Right: Electrons excited deep within the bulk scatter so often that they rarely escape. Thus, most of the signal  $I$  originates at the surface, which must be clean and representative of the bulk.

There are several problems with this procedure. First some

of the photon excited particles will scatter off phonons and electronic excitations within the material. Since these processes can occur over a very wide range of energies, they will produce a broad featureless background in  $N(E_{\mathbf{k}})$ . Second, due to these

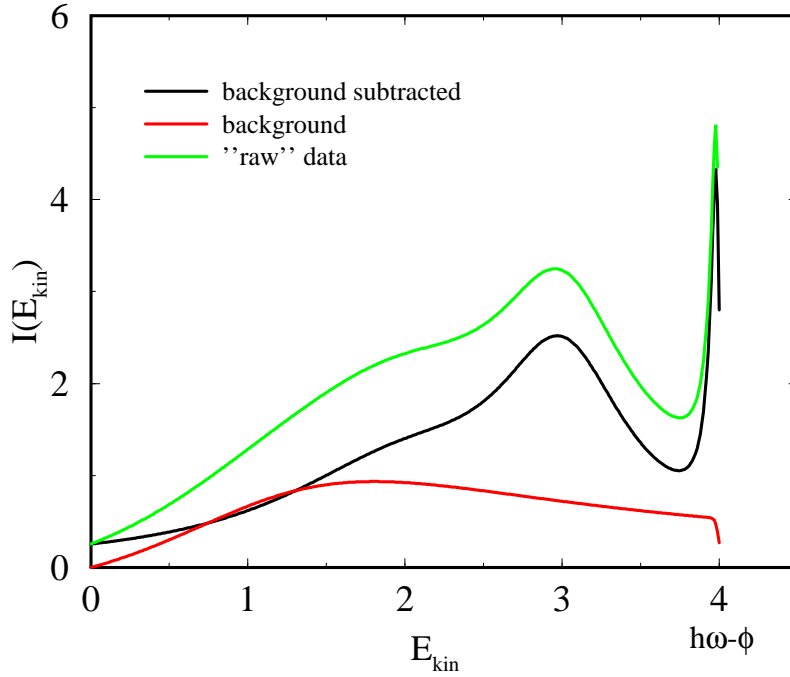


Figure 19: *In Photoemission, we measure the rate of ejected electrons as a function of their kinetic energy. The raw data contains a background. Once this is subtracted off, the subtracted data is proportional to the electronic density of states convolved with a Fermi function  $I(E_{kin}) \propto D(E_{kin} + \phi - \hbar\omega)f(E_{kin} + \phi - \hbar\omega)$ .*

secondary scattering processes, it is very unlikely that an electron which is excited deep within the bulk, will ever escape from

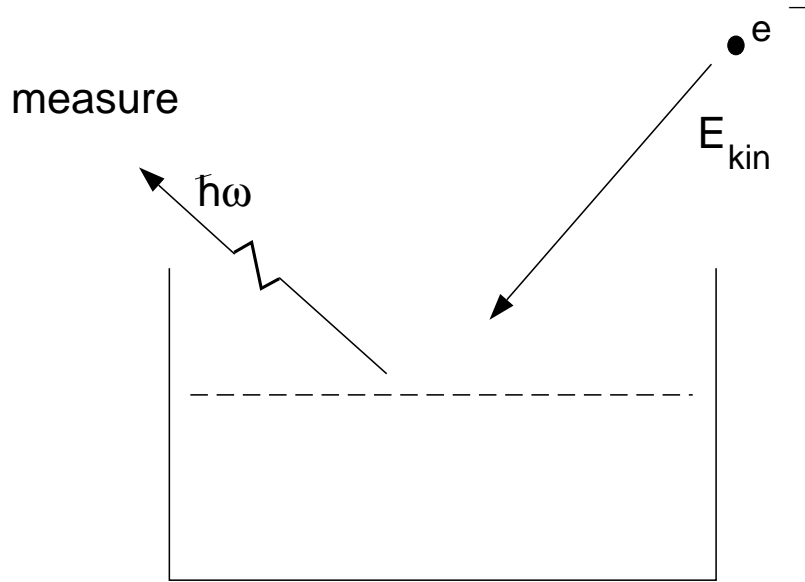


Figure 20: **BIS**  $E_{kin} = \hbar\omega - E_b - \phi$ ,  $E_b = \hbar\omega - E_{kin} - \phi$

the material. Thus, we only learn about  $D(E)$  near the surface of the material. Therefore it is important for this surface to be “clean” so that it is representative of the bulk. For this reason these experiments are often carried out in ultra-high vacuum conditions.

We can also learn about the electronic states  $D(E)$  above the Fermi surface,  $E > F_F$ , using *Inverse Photoemission*. Here, an electron beam is focussed on the surface and the outgoing flux of photons are measured.