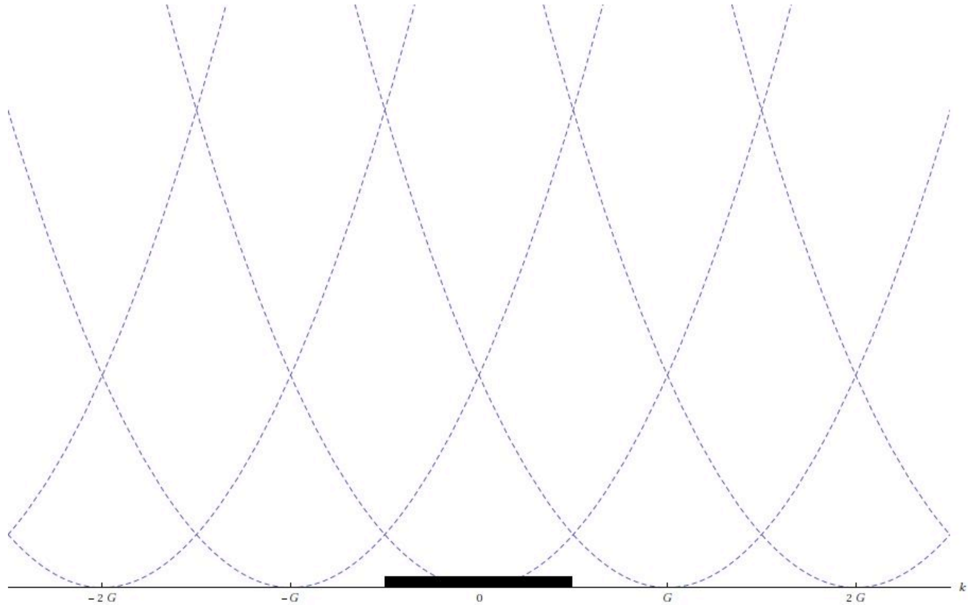
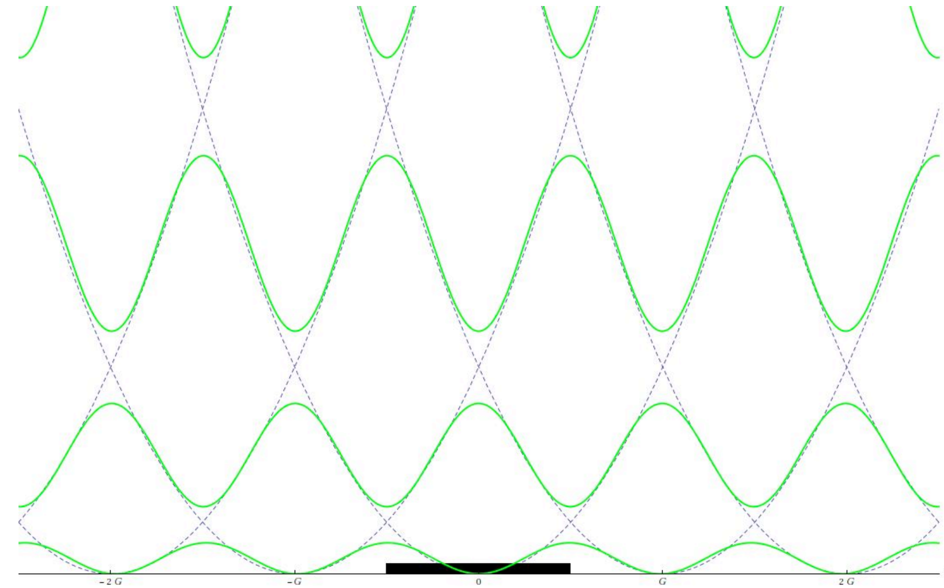

−2 G
−G
0
G
2 G
k


−2 G
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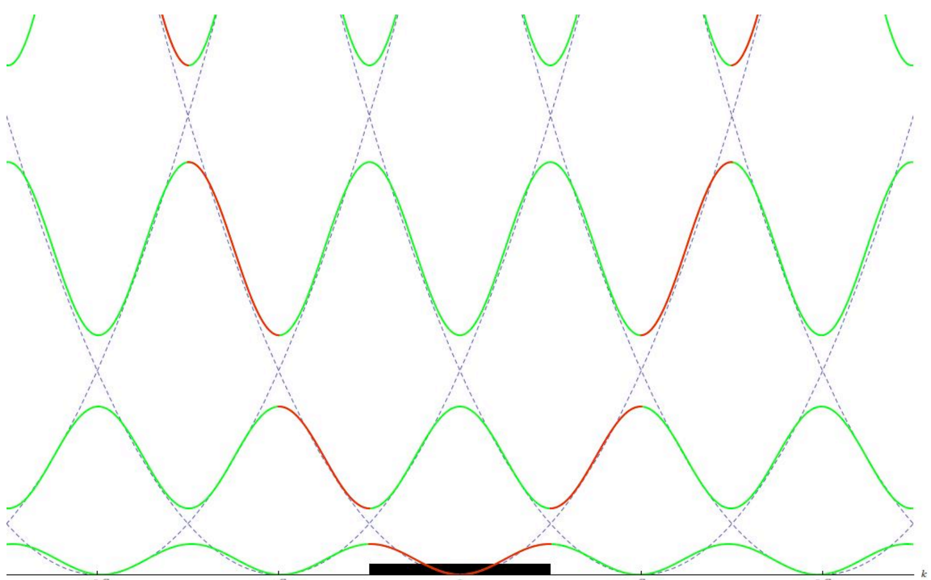
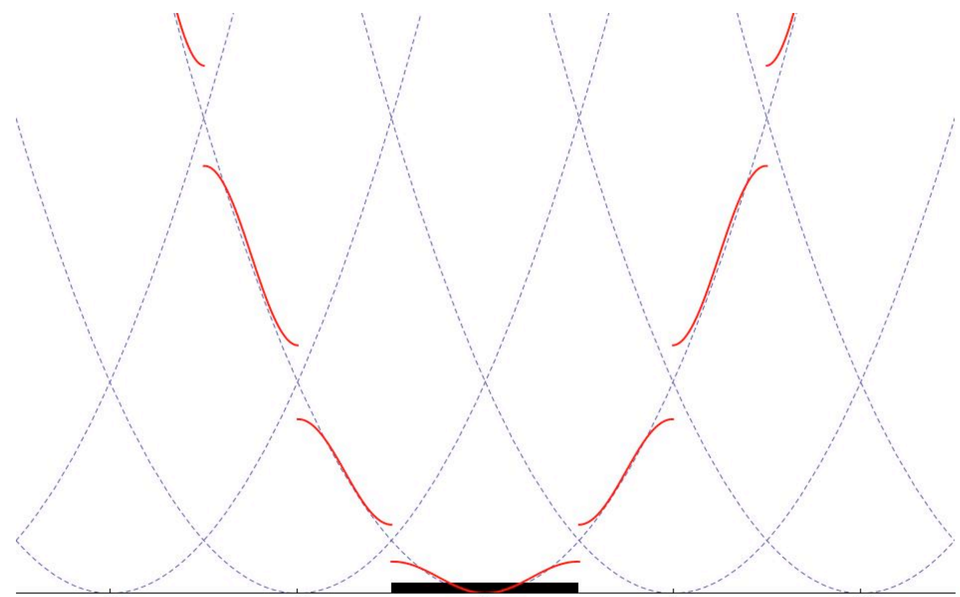

−2 G
−G
0
G
2 G
k


−2 G
−G
0
G
2 G
k

The Origin of Band Gaps

Now let's reexamine this gap at k = $G_1/2$ by considering the eigenvalue equation shifted by G

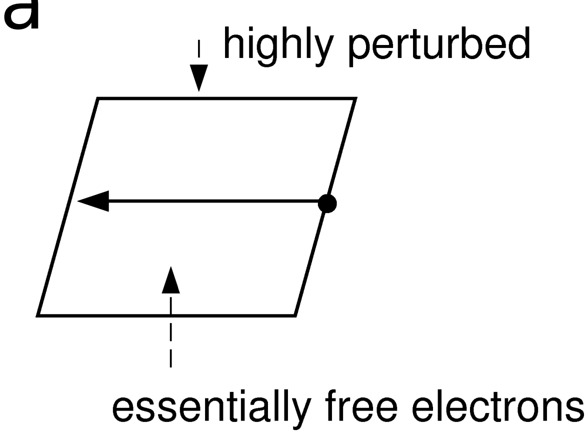
$$C_{\mathsf{k}-\mathsf{G}}\left(E_{\mathsf{k}}-\frac{\hbar^2}{2m}|\mathsf{k}-\mathsf{G}|^2\right)=\sum_{\mathsf{G}'}V_{\mathsf{G}'}C_{\mathsf{k}-\mathsf{G}-\mathsf{G}'}=\sum_{\mathsf{G}'}V_{\mathsf{G}'-\mathsf{G}}C_{\mathsf{k}-\mathsf{G}'}$$

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

To a first approximation *($V_G \simeq 0$)* $E=\frac{\hbar^2\mathsf{k}^2}{2m}$

$$\mathsf{k}^2=|\mathsf{k}-\mathsf{G}|^2 \qquad \text{1-D:}\quad \mathsf{k}^2=(\mathsf{k}-\frac{2\pi}{\mathsf{a}})^2 \qquad or\quad \mathsf{k}=-\frac{\pi}{\mathsf{a}}$$

$E_k \simeq E_{k-G}$ only for k on the edge of the B.Z.



$V_G \sim 0$, $V_0 \equiv 0$ and for ***k*** near the zone boundary

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

$$G = \mathbf{G}_1 \qquad C_{\mathbf{k}-\mathbf{G}_1}\left\{E - \frac{\hbar^2 |\mathbf{k} - \mathbf{G}_1|^2}{2m}\right\} = V_{-\mathbf{G}_1} C_{\mathbf{k}}$$

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

$$\begin{vmatrix} E^0_{\mathbf{k}} - E & V_{\mathbf{G}_1} \\ V_{-\mathbf{G}_1} & E^0_{\mathbf{k}-\mathbf{G}_1} - E \end{vmatrix} = 0$$

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

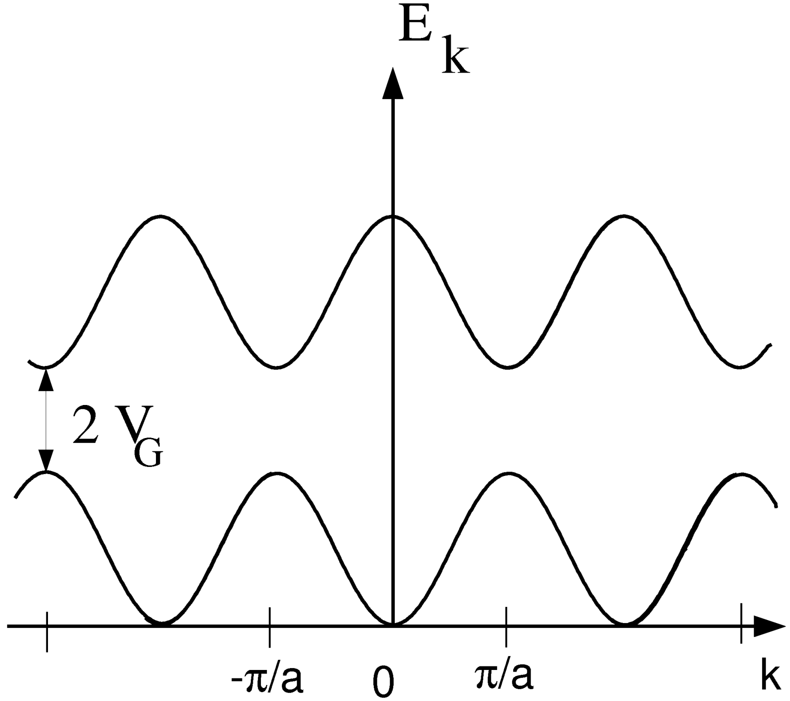
$$(E^0_{\mathbf{k}} - E)(E^0_{\mathbf{k}-\mathbf{G}_1} - E) - |V_{\mathbf{G}_1}|^2 = 0$$

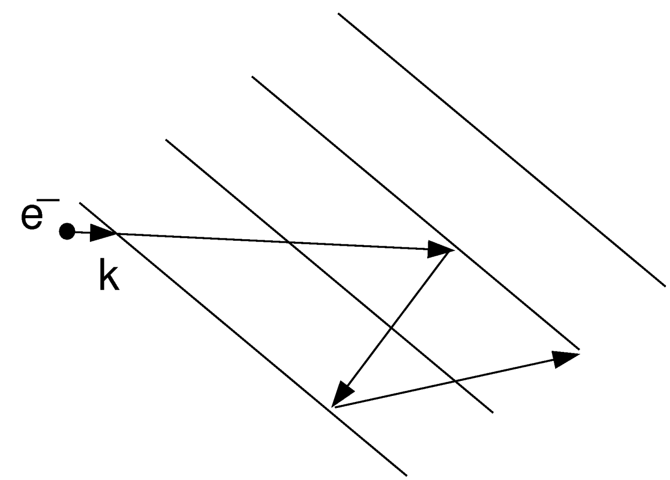
$$E^0_{\mathsf{k}} E^0_{\mathsf{k}-\mathsf{G}_1} - E\left(E^0_{\mathsf{k}} + E^0_{\mathsf{k}-\mathsf{G}_1}\right) + E^2 - |V_{\mathsf{G}_1}|^2 = 0$$

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

At the zone boundary, where $E_{k-G1} = E_k$, the gap is

$$\Delta E = E_+ - E_- = 2|V_{\mathsf{G}_1}|$$

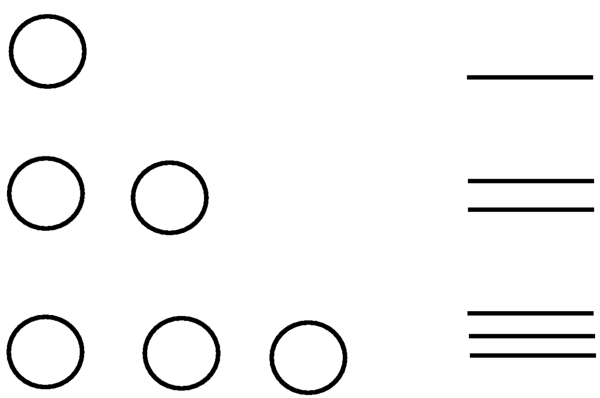


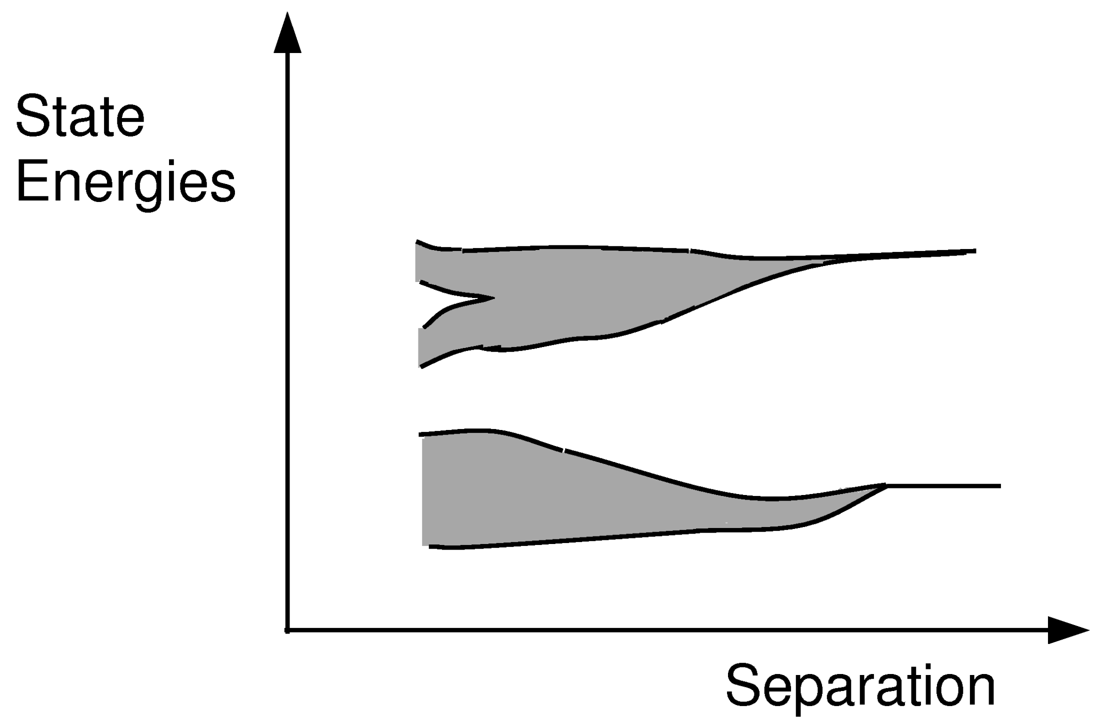


Bragg condition *($k_f - k_0 = G$)* is satisfied

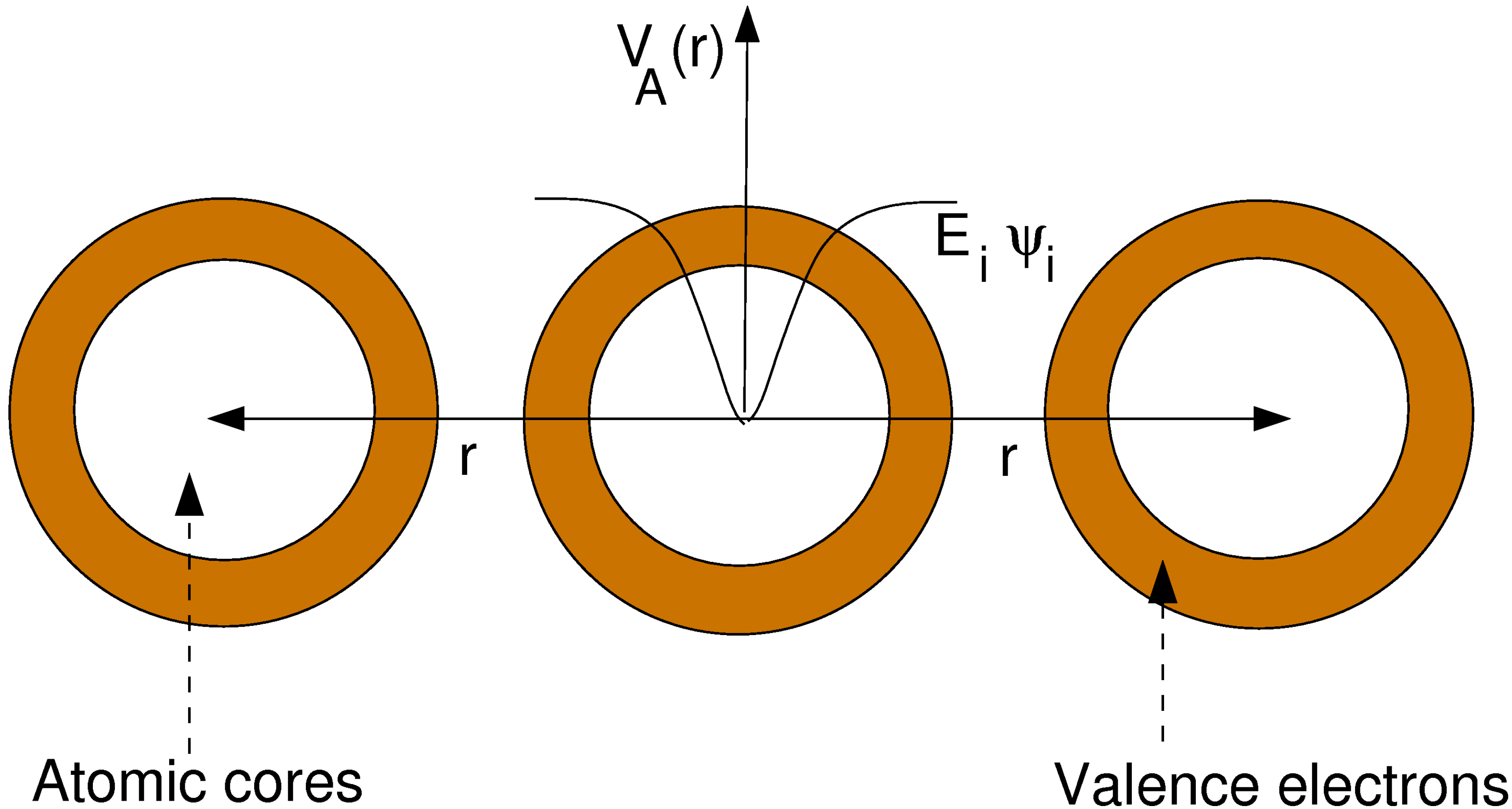
$$|-\mathsf{k}| \approx |\mathsf{k} + \mathsf{G}|$$

Band gaps in the electronic DOS





Tight Binding Approximation



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

There is a weak perturbation $v(r - r_n)$ coming from the atomic potentials of the other atoms $r_m \neq r_n$

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

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

We now seek solutions of the Schroedinger equation $H\psi_{\mathsf{k}}(\mathsf{r}) = E(\mathsf{k})\Psi_{\mathsf{k}}(\mathsf{r})$ indexed by ***k*** (Bloch's theorem)

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

$$\langle \psi_{\mathsf{k}} | \psi_{\mathsf{k}} \rangle \equiv \int d^3\mathsf{r}\, \psi^*_{\mathsf{k}}(\mathsf{r}) \psi_{\mathsf{k}}(\mathsf{r})$$

$$\langle \psi_{\mathsf{k}} | H | \psi_{\mathsf{k}} \rangle \equiv \int d^3\mathsf{r}\, \psi^*_{\mathsf{k}}(\mathsf{r}) H \psi_{\mathsf{k}}(\mathsf{r})$$

$$\frac{\langle \phi_{\mathsf{k}} | H | \phi_{\mathsf{k}} \rangle}{\langle \phi_{\mathsf{k}} | \phi_{\mathsf{k}} \rangle} \geq E(\mathsf{k})$$ → Raleigh-Ritz variational principle

We will approximate ψ_k with a sum over atomic states.

$$\psi_{\mathsf{k}} \simeq \phi_{\mathsf{k}} = \sum_n a_n \phi_i(\mathsf{r} - \mathsf{r}_n) = \sum_n e^{i\mathsf{k}\cdot\mathsf{r}_n} \phi_i(\mathsf{r} - \mathsf{r}_n)$$

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

ϕ_k must be a Bloch state $\phi_{k+G}=\phi_k$ which dictates our choice $\boldsymbol{a}_n = e^{ik\cdot rn}$. *Using* ϕ_k *as an approximate state the energy denominator* $<\phi_k|\phi_k>$, becomes

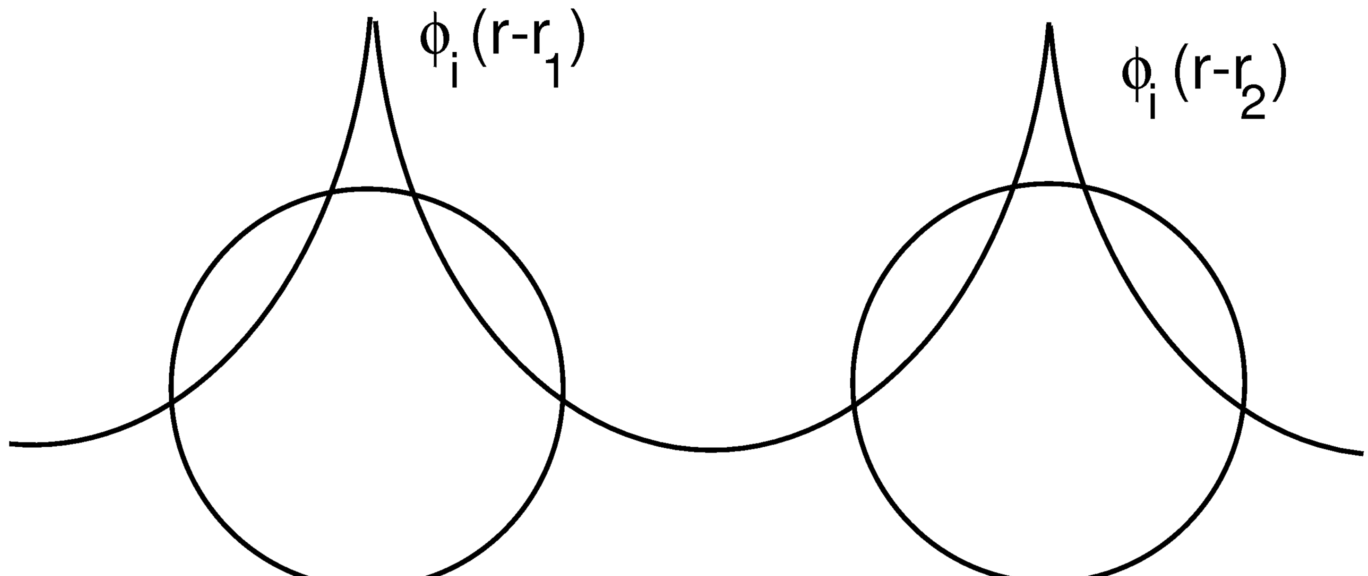
$$\langle \phi_{\mathsf{k}} | \phi_{\mathsf{k}} \rangle = \sum_{n,m} e^{i\mathsf{k}\cdot(\mathsf{r}_n - \mathsf{r}_m)} \int d^3\mathsf{r} \phi_i^*(\mathsf{r} - \mathsf{r}_m) \phi_i(\mathsf{r} - \mathsf{r}_n)$$

We take the valance orbital of interest, ϕ_i , has a very small overlap with adjacent atoms so that

$$\langle \phi_{\mathsf{k}} | \phi_{\mathsf{k}} \rangle \simeq \sum_n \int d^3 \mathsf{r} \phi_i^*(\mathsf{r} - \mathsf{r}_n) \phi_i(\mathsf{r} - \mathsf{r}_n) = N$$

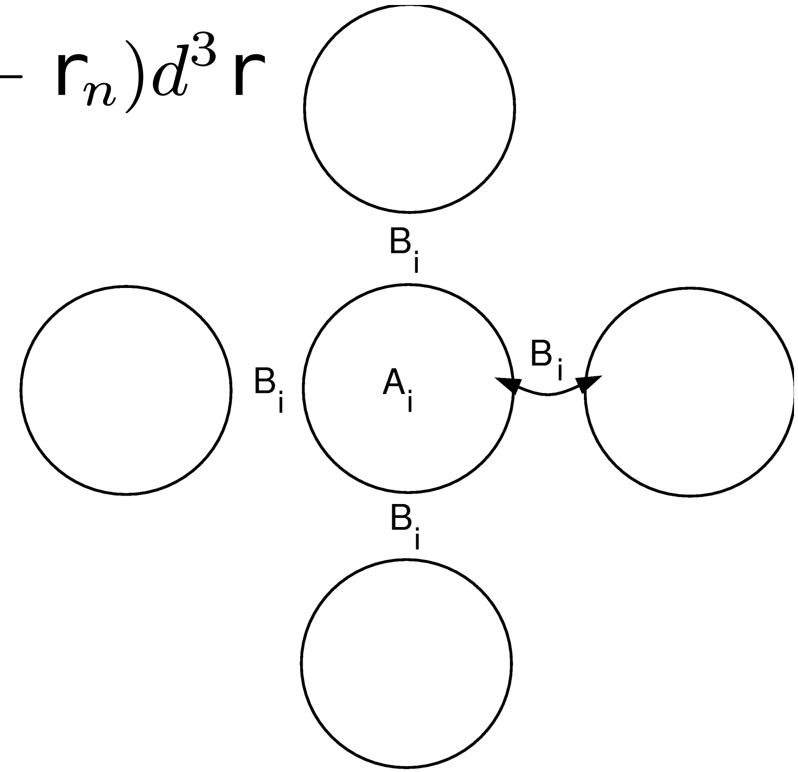
The energy for our approximate wave function is

$$E(\mathsf{k}) \approx \frac{1}{N} \sum_{n,m} e^{i\mathsf{k}\cdot(\mathsf{r}_n - \mathsf{r}_m)} \int d^3 \mathsf{r} \phi_i^*(\mathsf{r} - \mathsf{r}_m) \{E_i + v(\mathsf{r} - \mathsf{r}_n)\} \phi_i(\mathsf{r} - \mathsf{r}_n)$$



$$A_i = -\int \phi_i^*(\mathsf{r} - \mathsf{r}_n) v(\mathsf{r} - \mathsf{r}_n) \phi_i(\mathsf{r} - \mathsf{r}_n) d^3\mathsf{r} \qquad \text{ren. } E_i$$

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



A_i, $B_i > 0$, since $v(r - r_n) < 0$

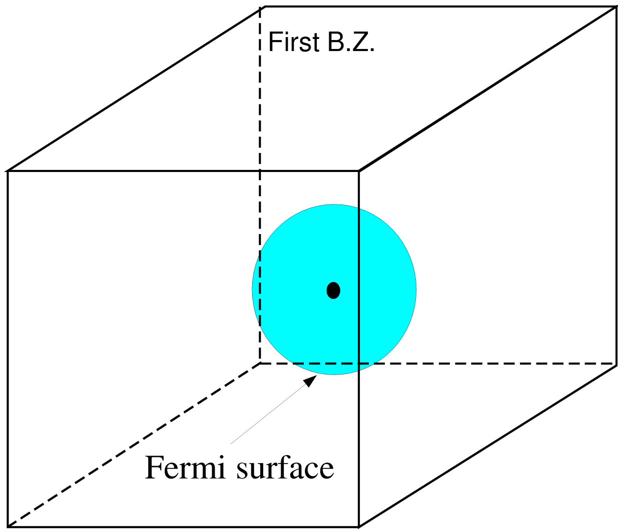
$$E(\mathsf{k}) \simeq E_i - A_i - B_i \sum_m e^{i\mathsf{k}(\mathsf{r}_n - \mathsf{r}_m)} \qquad \text{sum over } m \text{ n.n. to } n$$

Consider a cubic lattice: $(\mathbf{r}_n - \mathbf{r}_m) = (\pm a, 0, 0)(0, \pm a, 0)(0, 0, \pm a)$

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

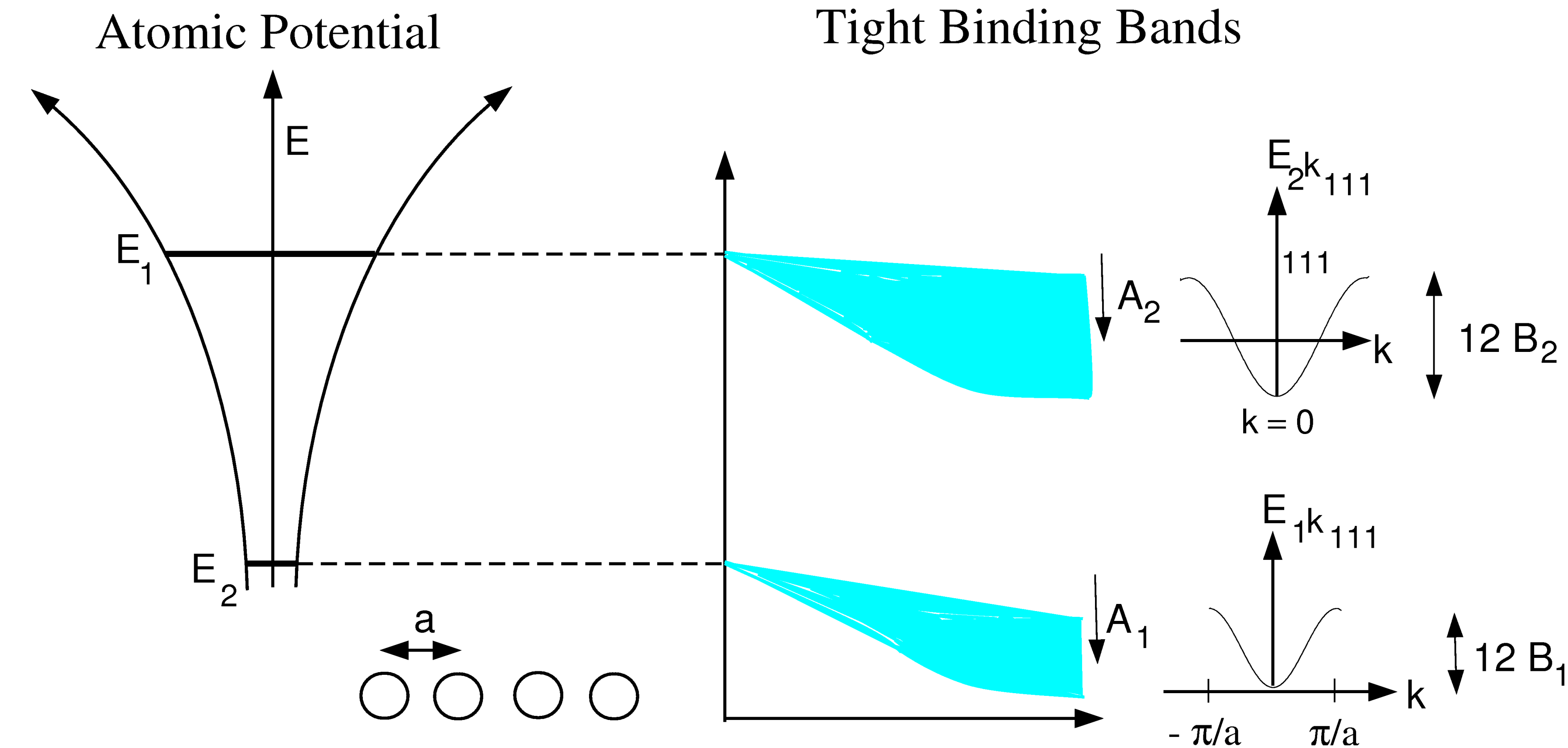
Expand the cosines *cos ka ≃ 1 − 1/2 (ka)*^{2} + · · · and let $k^2 = k_x^2 + k_y^2 + k_z^2$, so that

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

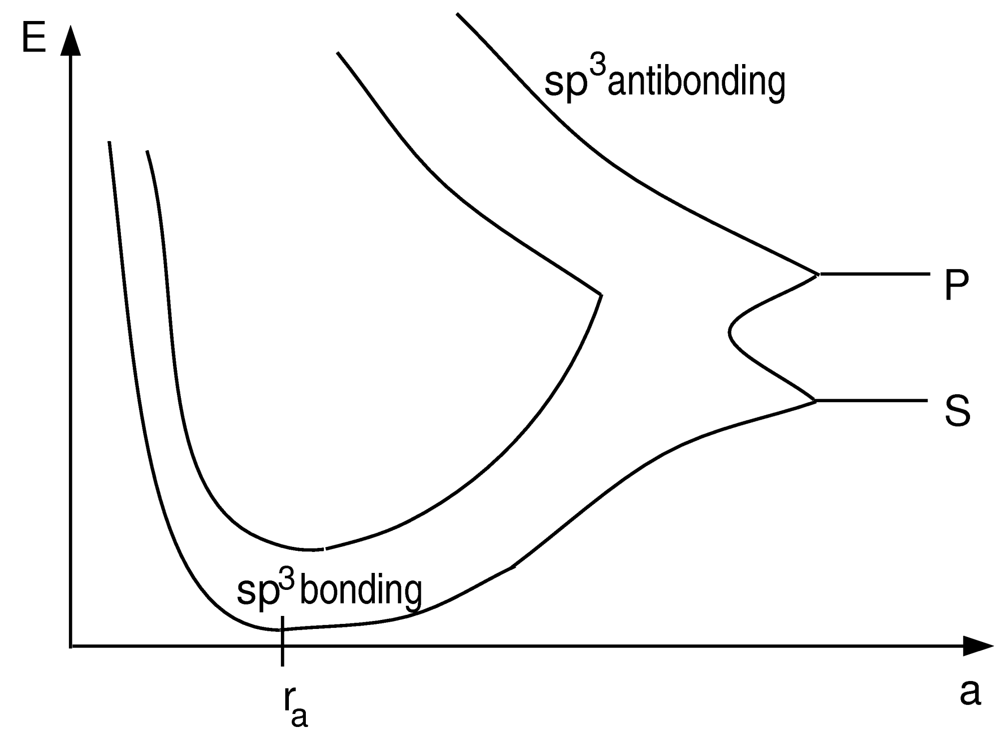


The electrons near the zone center act as if they were free with a renormalized mass.

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



C (diamond) with atomic configuration of $1s^2\ 2s^2\ 2p^2$



Example: *Cu 3d¹⁰4s* - the d-orbitals are rather small whereas the valence s-orbitals have a large extent . As a result the s-s hybridization B_i^{ss} is strong and the B_i^{dd} is weak: $B_i^{dd} \ll B_i^{ss}$

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