TIGHT BINDING MODEL

Lecture 20

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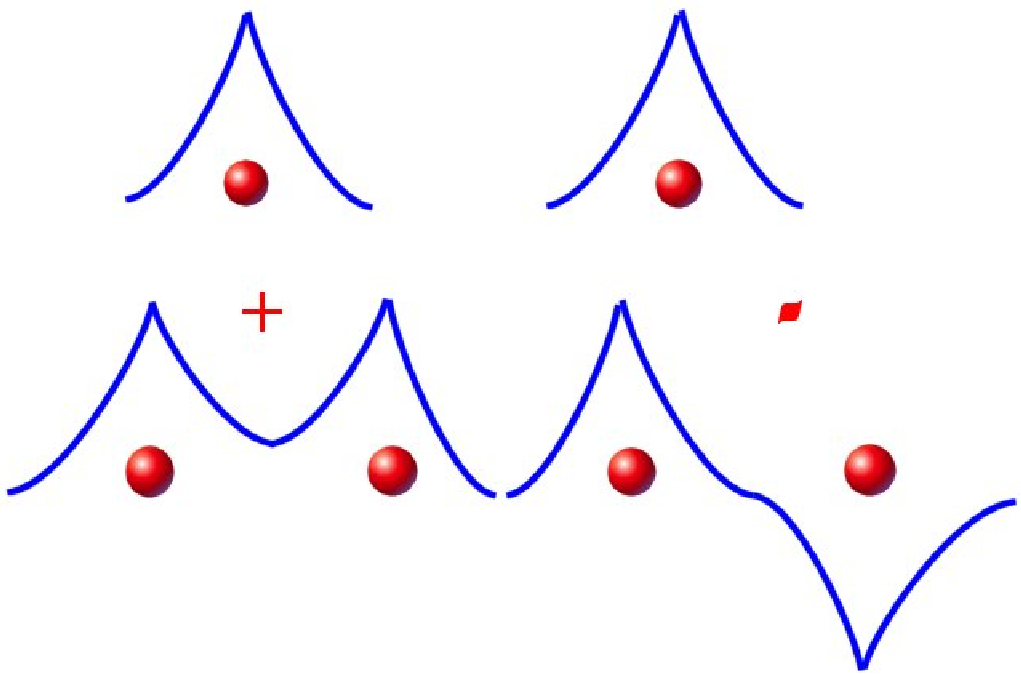
7.6 The tight-binding model

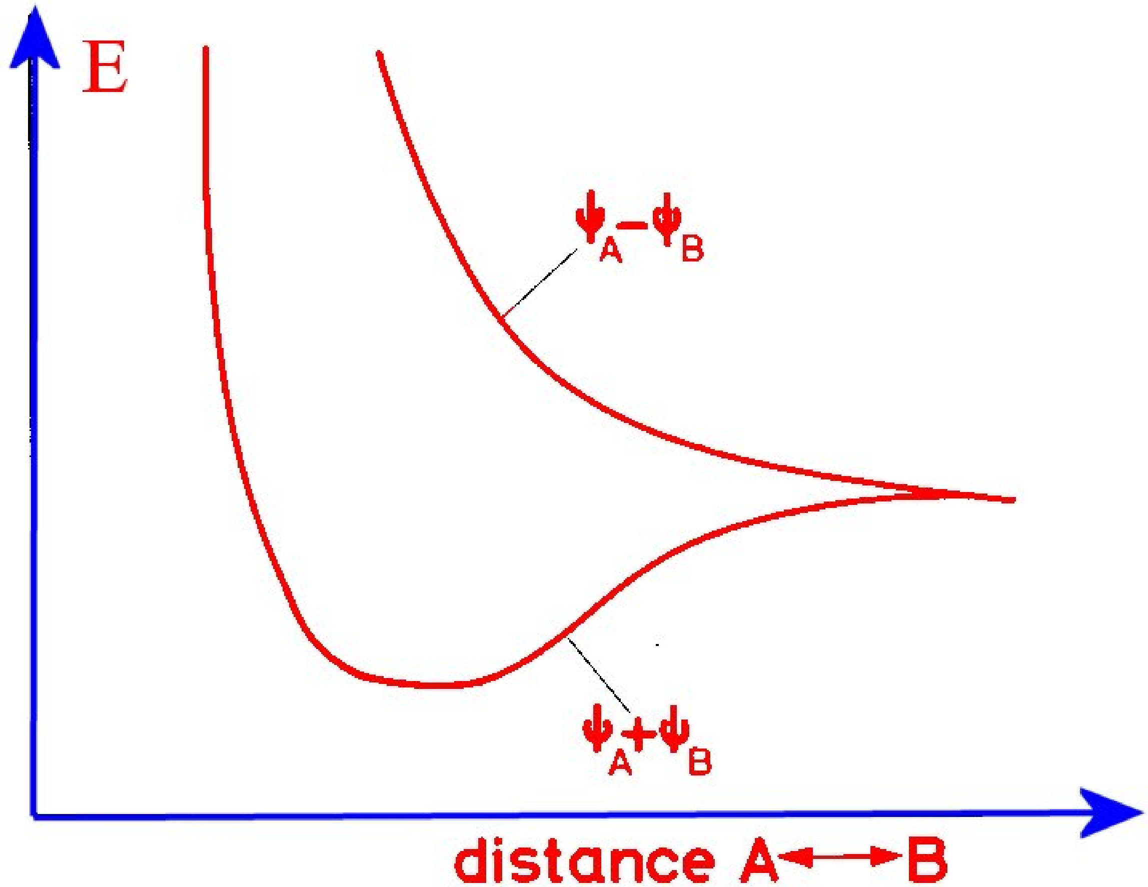
7.6.1 Overview

For materials which are formed from closed-shell atoms or ions, or even covalent solids, the free electron model seems inappropriate. In the tight-binding model, we imagine how the wavefunctions of atoms or ions will interact as we bring them together.

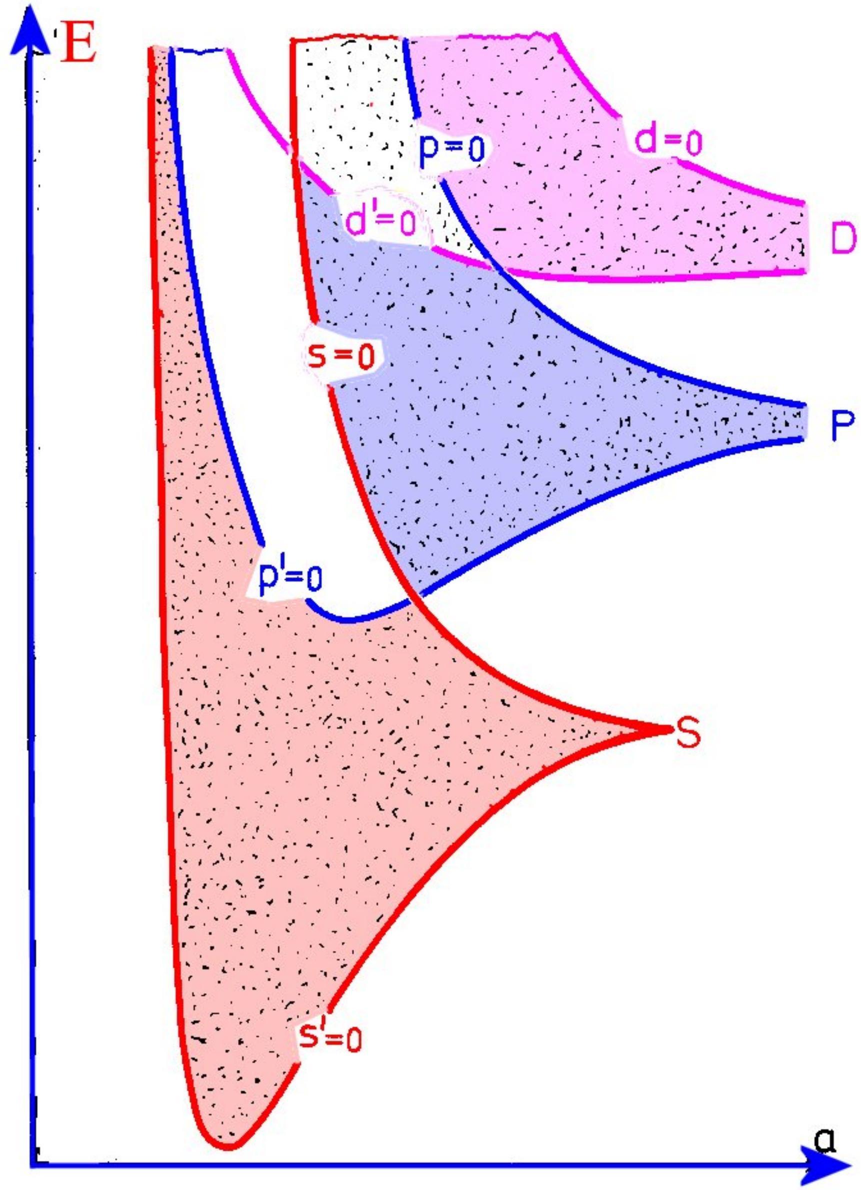
For example, take two hydrogen atoms, A and B, and consider the states $\psi_A \pm \psi_B$.



The symmetric (+) form has more screening charge between the nuclei, and has lower energy.



When more atoms are brought together, the degeneracies are further split - to form bands ranging from fully bonding to fully antibonding. Different orbitals can lead to band overlap.



7.6.2 Tight-binding theory

Consider an element with one atom per unit cell, and suppose that each atom has only one valence orbital, $\phi(\mathrm{r})$. Then we can make a wavefunction of Bloch form by forming

$$\psi_{\mathbf{k}}(\mathbf{r}) = N^{-1/2} \sum_m \exp(i\mathbf{k}.\mathbf{R}_m)\phi(\mathbf{r} - \mathbf{R}_m).$$

Confirm that this is a Bloch function. If T is a translation vector:

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) &= N^{-1/2} \sum_m \exp(i\mathbf{k}.\mathbf{R}_m)\phi(\mathbf{r} - \mathbf{R}_m + \mathbf{T}) \\ &= N^{-1/2} \exp(i\mathbf{k}.\mathbf{T}) \sum_m \exp(i\mathbf{k}.(\mathbf{R}_m - \mathbf{T})\phi(\mathbf{r} - (\mathbf{R}_m - \mathbf{T})) \\ &= \exp(i\mathbf{k}.\mathbf{T})\psi_{\mathbf{k}}(\mathbf{r}) \end{aligned}$$

because if R_m is a lattice vector, so is $\mathrm{R}_m - \mathrm{T}$.

Find the expectation energy of the Hamiltonian:

$$\langle \mathbf{k}|\mathcal{H}|\mathbf{k}\rangle = N^{-1}\sum_m \sum_n \exp(i\mathbf{k}.(\mathbf{R}_n - \mathbf{R}_m))\langle \phi_m|\mathcal{H}|\phi_n\rangle$$

where $\phi_m = \phi(\mathbf{r} - \mathbf{R}_m)$**. Now** $\langle \phi_m|\mathcal{H}|\phi_n\rangle$ **will be large if** n **and** m **are the same atomic site, or nearest neighbours, but will decrease rapidly with separation. Write**

$$\begin{aligned}\langle \phi_n|\mathcal{H}|\phi_n\rangle &= -\alpha,\\ \langle \phi_m|\mathcal{H}|\phi_n\rangle &= -\gamma \text{ if } n \text{ and } m \text{ are nearest neighbours,}\\ \langle \phi_m|\mathcal{H}|\phi_n\rangle &= 0 \text{ otherwise.}\end{aligned}$$

Then

$$E_{\mathbf{k}} = \langle \mathbf{k}|\mathcal{H}|\mathbf{k}\rangle = -\alpha - \gamma\sum_n \exp(i\mathbf{k}.\mathbf{R}_n),$$

where the sum is over nearest neighbours only, and R_n **is a vector joining an atom to its nearest neighbours. For example, in two-dimensional square lattice we have**

$$\{\mathbf{R}_n\} = \{(a,0),(-a,0),(0,a),(0,-a)\}$$

so that if $\mathbf{k} = (k_x, k_y)$

$$E_{\mathbf{k}} = -\alpha - 2\gamma(\cos(k_x a) + \cos(k_y a)).$$

Clearly, as $\cos$ **ranges between** -1 **and** 1 $E_{\mathbf{k}}$ **ranges between** $-\alpha - 4\gamma$ **and** $-\alpha + 4\gamma$**, giving a band width of** 8γ**. Near** $\mathbf{k} = 0$ **we can expand the** $\cos$ **functions as**

$$\cos\theta \approx 1 - \frac{1}{2}\theta^2,$$

so

$$\begin{aligned} E_{\mathbf{k}} &\approx -\alpha - 2\gamma(1 - \frac{1}{2}k_x^2 a^2 + 1 - \frac{1}{2}k_y^2 a^2) \\ &= -\alpha - 4\gamma + \gamma(k_x^2 + k_y^2)a^2 \end{aligned}$$

which is free-electron-like, giving circular constant-energy surfaces near the centre of the Brillouin zone. If both k_x **and** k_y **are close to** π/a**, write**

$$k_x = \frac{\pi}{a} - \delta_x \quad k_y = \frac{\pi}{a} - \delta_y,$$

so that, remembering

$$\cos(a-b) = \cos(a)\cos(b) + \sin(a)\sin(b),$$

we have

$$\begin{aligned} E_{\mathbf{k}} &= -\alpha - 2\gamma(\cos(\pi - \delta_x a) + \cos(\pi - \delta_y a)) \\ &= -\alpha - 2\gamma(\cos(\pi)\cos(\delta_x a) - \sin(\pi)\sin(\delta_x a) \\ &\qquad + \cos(\pi)\cos(\delta_y a) - \sin(\pi)\sin(\delta_y a)) \\ &= -\alpha + 2\gamma(\cos(\delta_x a) + \cos(\delta_y a)) \\ &= -\alpha + 4\gamma - \gamma(\delta_x^2 + \delta_y^2)a^2 \end{aligned}$$

giving circular constant-energy surfaces near the zone corners too. Finally, in the middle of the band

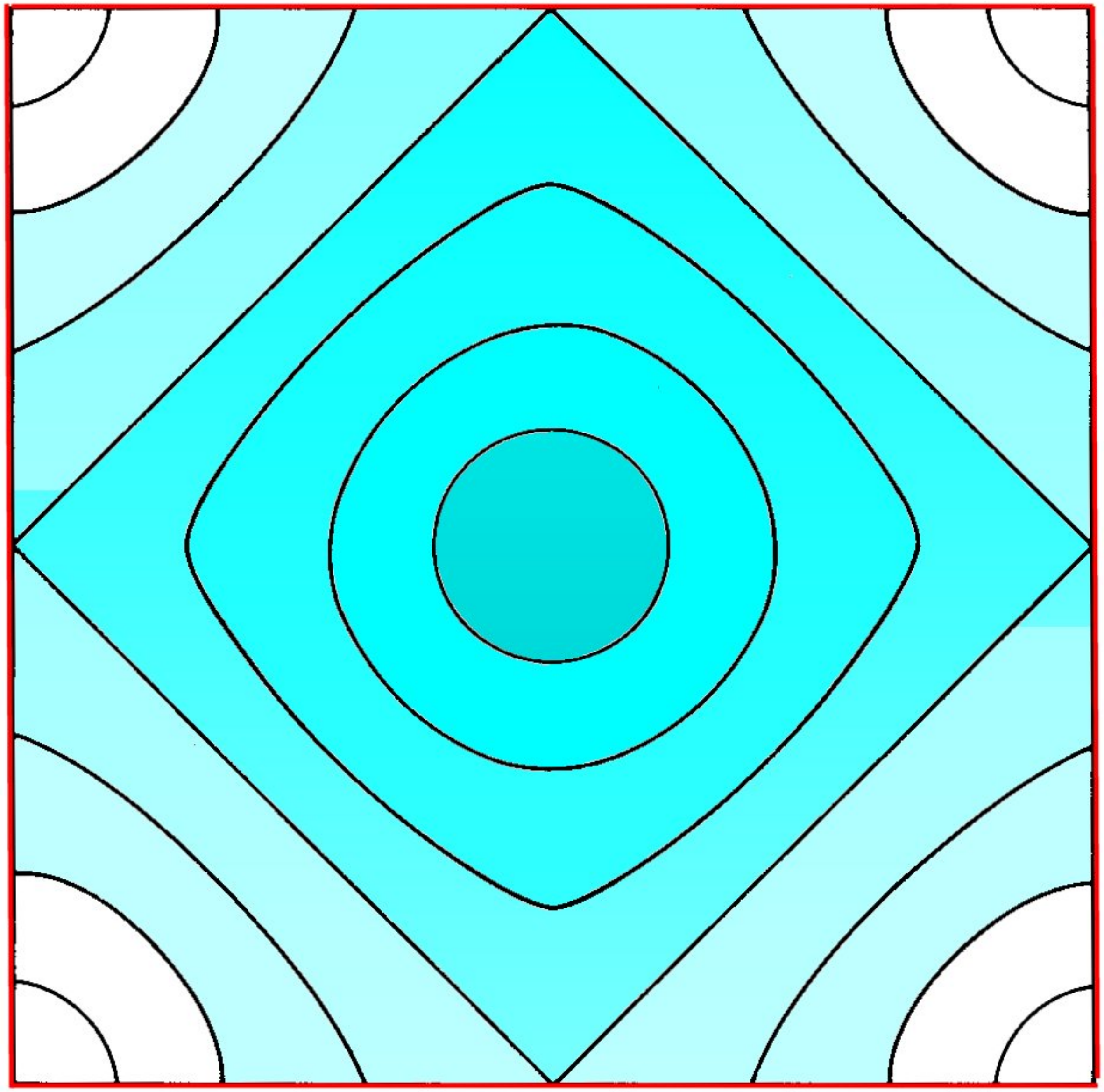
$$\cos(k_x a) + \cos(k_y a) = 0,$$

the solutions to which are of the form

$$k_x a = \pi - k_y a,$$

or straight lines.

Finally, then, we have the constant energy surfaces for this tight-binding model.

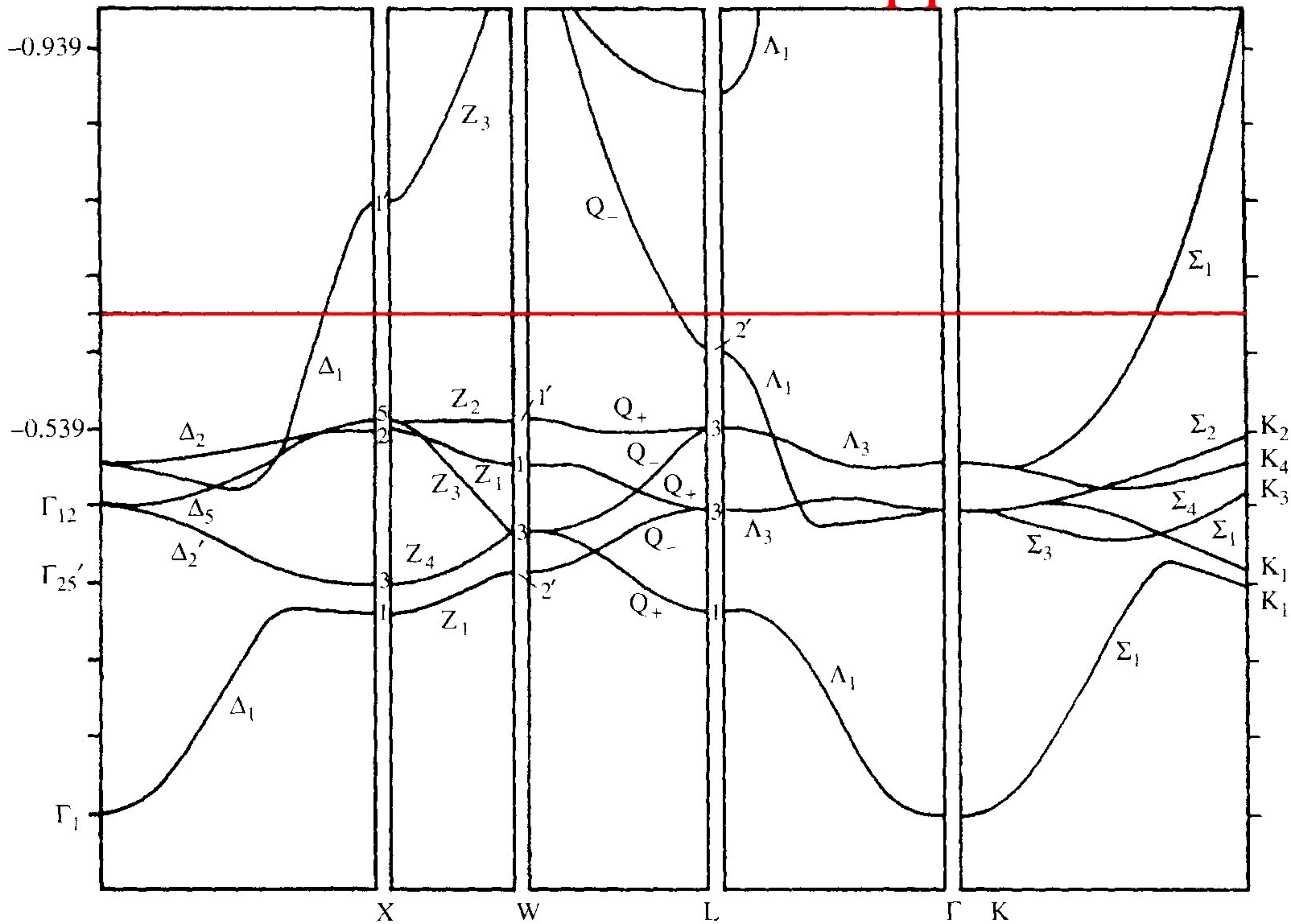


7.6.3 Comments on tight binding theory

- **Note that band width depends on two-centre integrals (γ): for transition metals, this leads to narrow d-bands and wide s-bands.**
- **Near the top and bottom of bands, we have quadratic dependence on k.**

A real band structure.

Copper



-0.939
-0.539
Γ12
Γ25′
Γ1
Δ1
Δ2
Δ5
Δ2′
Z3
Z2
Z1
Z4
Q−
Q+
Λ1
Λ3
Σ1
Σ2
Σ3
Σ4
K2
K4
K3
K1
X
W
L
Γ
K