LECTURE # 19

Note Title 2/25/2009

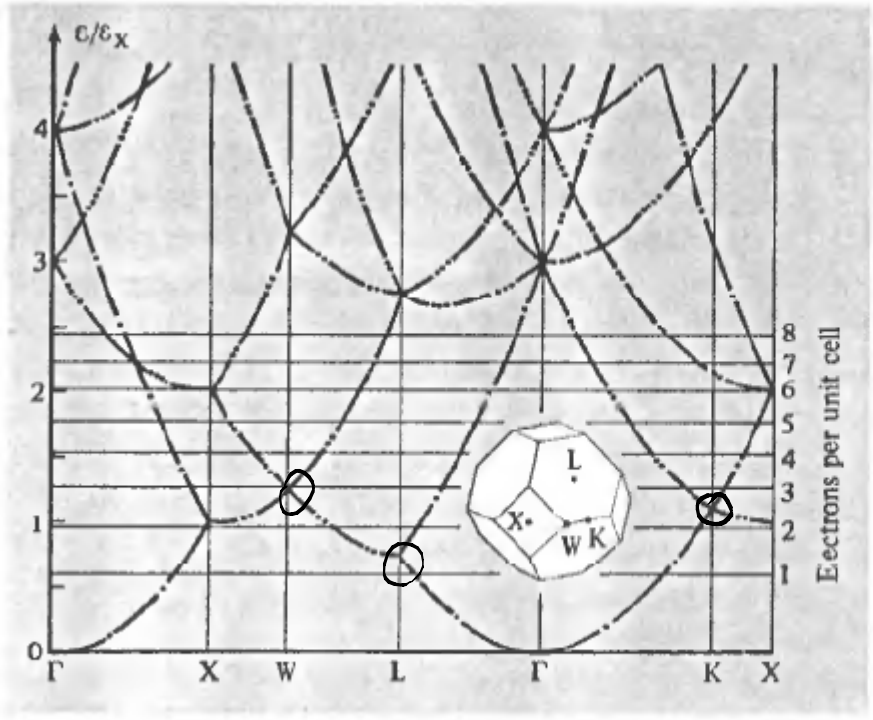


Figure 9.5
Free electron energy levels for an fcc Bravais lattice. The energies are plotted along lines in the first Brillouin zone joining the points $\Gamma(\mathbf{k} = 0)$, K, L, W, and X. ε_x is the energy at point X ($[\hbar^2/2m][2\pi/a]^2$). The horizontal lines give Fermi energies for the indicated numbers of electrons per primitive cell. The number of dots on a curve specifies the number of degenerate free electron levels represented by the curve. (From F. Herman, in *An Atomistic Approach to the Nature and Properties of Materials*, J. A. Pask, ed., Wiley, New York, 1967.)

FCC

FREE ELECTRON BANDS

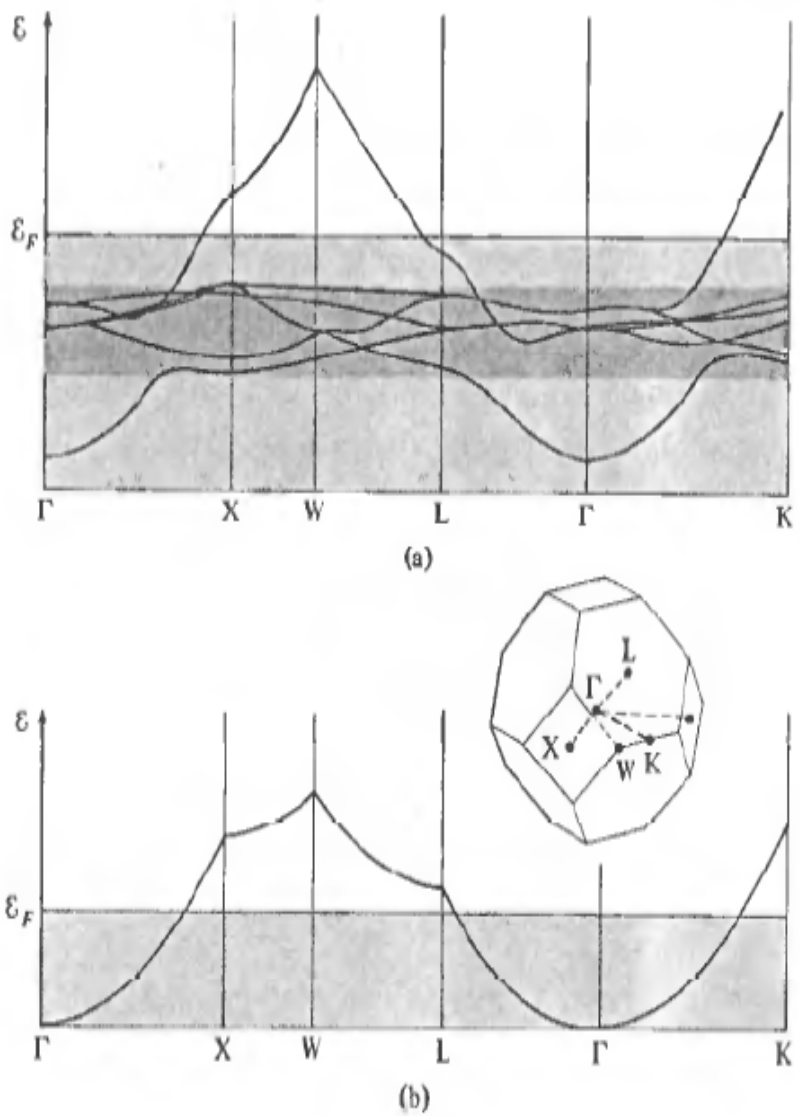


Figure 15.4
(a) Calculated energy bands in copper. (After G. A. Burdick, *Phys. Rev.* **129**, 138 (1963).) The ε vs. k curves are shown along several lines in the interior and on the surface of the first zone. (The point Γ is at the center of the zone.) The d-bands occupy the darkest region of the figure, whose width is about 3.5 eV. (b) The lowest-lying free electron energies along the same lines as in (a). (The energy scales in (a) and (b) are not the same.)

Cu

$[Ar]\ 3d^{10}\ 4s^1$

FCC CRYSTAL

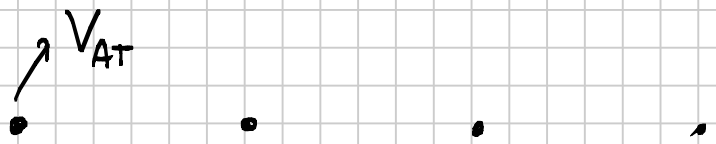
4 d-type

$\ell = \pm 2, \pm 1, 0$

T1 T1 T2 T2 T1 T2

HYBRIDIZATION (MIXING OF d-s ORBITAL CHARACTER)

TIGHT - BINDING APPROACH



SCHRÖ FOR 1 e IN V_{AT}

ε_m $\varphi_m(r)$

$$V(\vec{r}) = \sum_R V_{AT}(r-R)$$

BLOCH FUNCTIONS

$$\psi_{Km} = \sum_R e^{i\vec{K}\cdot\vec{R}}\, \varphi_m(r-R)$$

m INDEX FOR THE ATOMIC ORBITAL

↳ NEEDED FOR ψ_{Km} IN ORDER TO SATISFY BLOCH THEOREM:

$$\psi_{Km}(\vec{r}+\vec{R}) = e^{i\vec{K}\cdot\vec{R}}\, \psi_{Km}(\vec{r})$$

LCAO LINEAR COMBINATION OF ATOMIC ORBITALS

$$\Psi_K(\vec{r}) = \sum_m b_m \, \Psi_{Km}(\vec{r})$$

$m \rightarrow$ DIFFERENT ATOMIC ORBITAL

Ψ_m BASIS 6-DIMENSIONAL

$\Psi_s, \Psi_{d_1}, \Psi_{d_2}, \Psi_{d_3}, \Psi_{d_4}, \Psi_{d_5}$

$$H\Psi_K = E(k)\,\Psi_K \qquad (1)$$

IN ORDER TO FIND COEFFICIENTS b_m

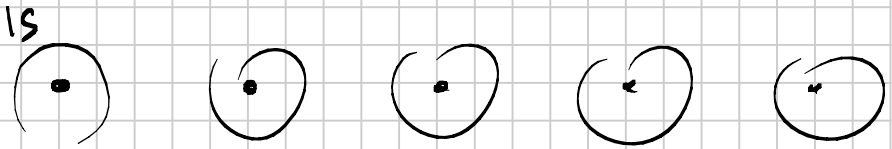
I NEED TO DIAGONALIZE (1)

e.g. 6×6 MATRIX

$$\text{DET} \left\| \langle \Psi_{mK} | H | \Psi_{m'K} \rangle - E(k) \langle \Psi_{mK} | \Psi_{m'K} \rangle \right\| = 0$$

$= 0$

CONSIDER THE CASE 1 ORBITAL / SITE



$\varphi_{1s}(\vec{r})$

BLOCH FUNCTION

$$\psi_{ks}(\vec{r}) = \sum_R e^{i\vec{k}\cdot\vec{R}} \varphi_s(r-R)$$

$$\langle \psi_{ks} | H | \psi_{ks} \rangle - E(k) \langle \psi_{ks} | \psi_{ks} \rangle = 0$$

$$H = T + \sum_R V_{AT}(\vec{r}-\vec{R})$$

$$\langle \psi_{ks} | H | \psi_{ks} \rangle = \leftarrow$$

$$\int d^3r \sum_{R\,R'} \varphi_s(r-R) \left[T + \sum_{R''} V_{AT}(r-R'') \right] \varphi_s(r-R') e^{i\vec{k}\cdot(R-R')}$$

FIX $R' = 0$ AND MULTIPLY ENERGY BY TOTAL # OF SITES

DIFFERENT TERMS APPEAR:

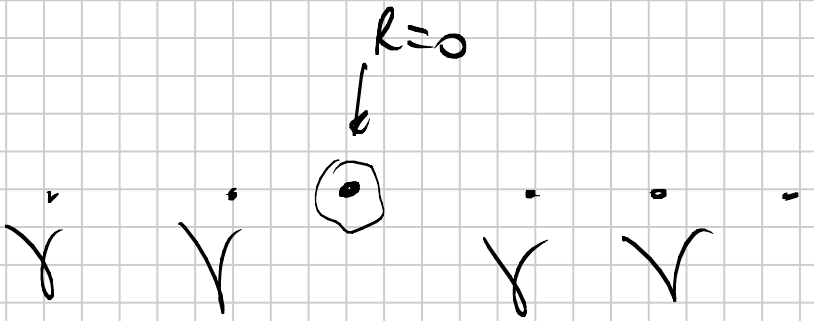
① $R' = 0$ $\quad R = 0$ $\quad R'' = 0$

$$\int d^3r \; \varphi_{1s}(r) \left[T + V_{AT}(r) \right] \varphi_{1s}(r) \rightarrow \varepsilon_{1s}$$

ON SITE CONTRIBUTION TO THE ENERGY

② $R' = R = 0$

$R'' \neq 0$



$$\int d^3r \; \varphi_{1s}(r) \sum_{R'' \neq 0} V_{AT}(r - R'') \varphi_{1s}(r)$$

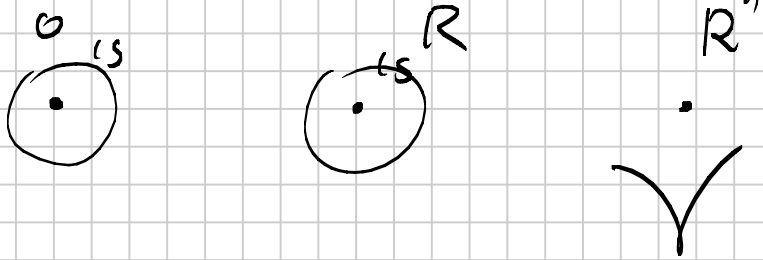
CRYSTAL FIELD TERM

DOES NOT DEPEND ON K, CONSTANT SHIFT

③

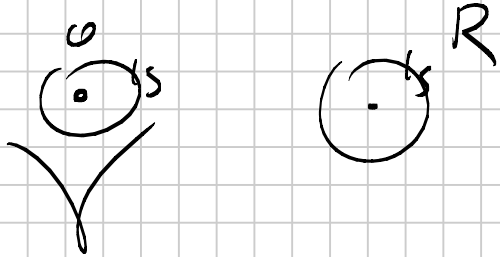
$$\int d^3r \; \varphi_{1s}(r-R) \sum_{R''} V_{AT}(r-R'') \; \varphi_{1s}(r) \; e^{i\vec{K}\cdot\vec{R}} = \begin{cases} R'=0 \\ R\neq 0 \end{cases}$$

HOPPING INTEGRALS



FURTHER APPROXIMATIONS

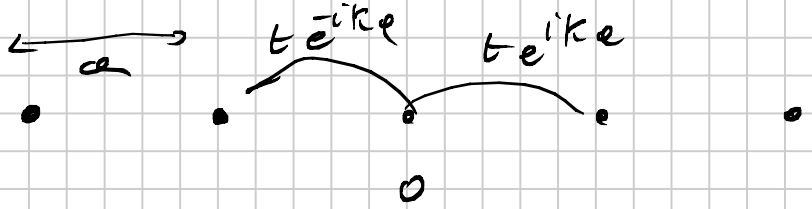
④ 2 CENTERS R'' AT R OR AT 0



⑤ $\sum_R \rightarrow \sum$ FIRST NEIGHBORS

⑥ $\int \varphi_{1s}(r)\, \varphi_{1s}(r-\vec{R})\, d^3r$ OVERLAP INTEGRALS

$\sim \delta_{0,R}$



φ_{1s} ε_{1s}

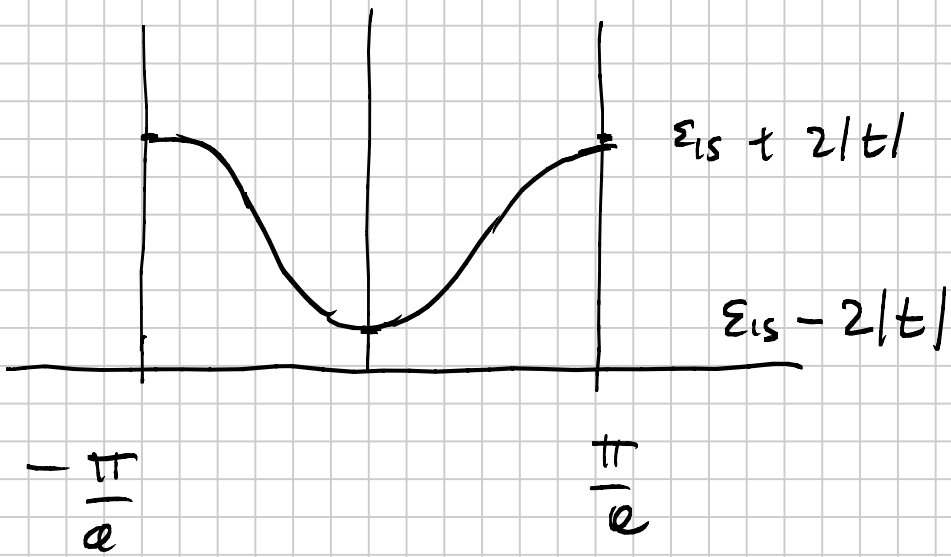
$$\varepsilon_{1s} + te^{ika} + te^{-ika} = \varepsilon(k)$$

$$t = \int d^3r\, \varphi_{1s}(r)\, V_{AT}(r)\, \varphi_{1s}(r-a)$$

↗ FIRST NEIGHBOR

$$\varepsilon_k = \varepsilon_{1s} + 2t\cos ka$$

$t < 0$



Ch 9

SKIP HIGH ORDER BZ

TIGHT BINDING

Chapt 10