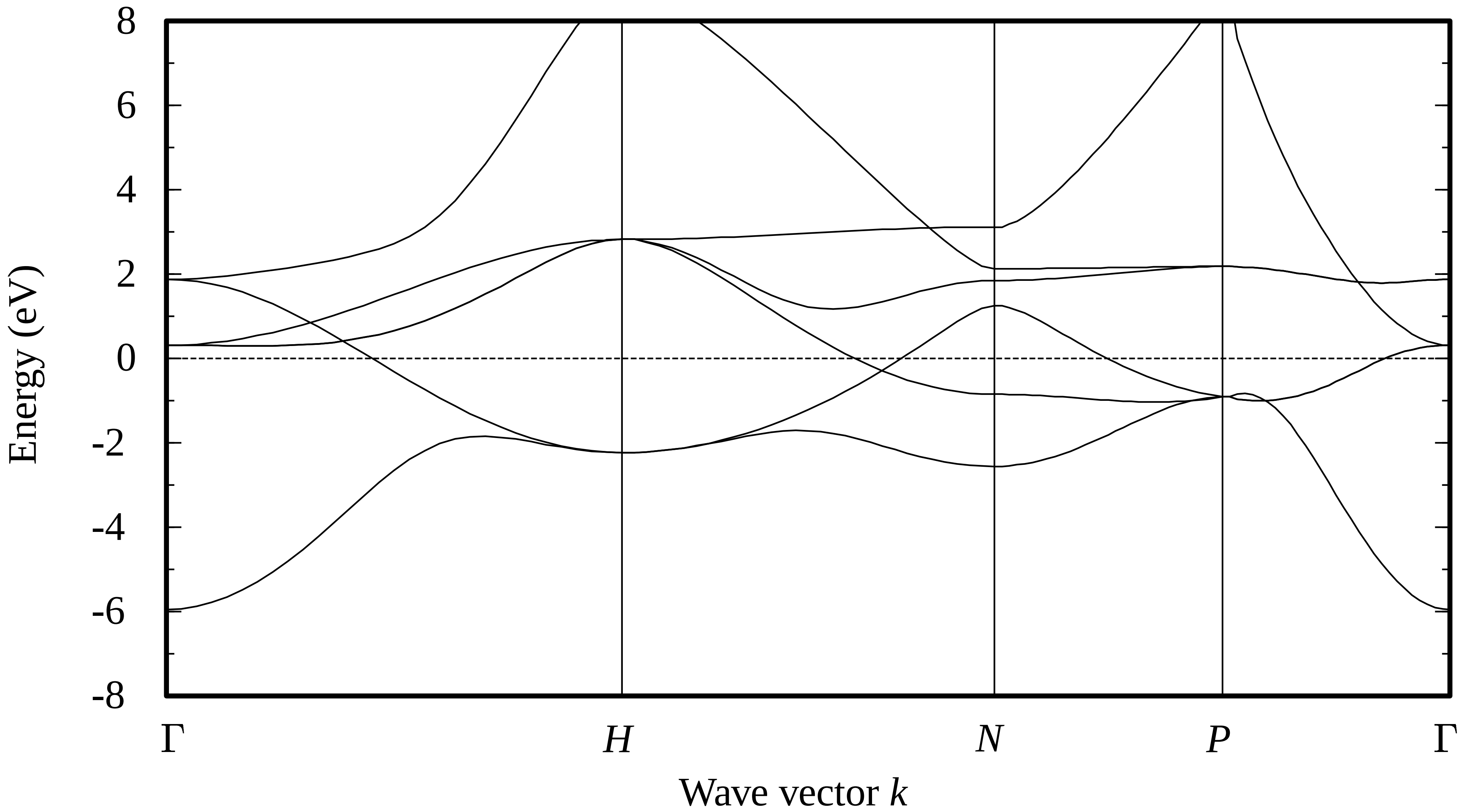
Band Structure Calculations



Pseudopotentials

Question: How could it ever be true that electrons in a metal think they are moving freely in an empty box?

Pseudopotentials give conceptual answer.

- ☞ Restrict attention to single unit cell.
- ☞ Let $|\vec{k}\rangle$ denote plane waves $e^{i\vec{k}\cdot\vec{r}}$.
- ☞ Let $|\psi_c\rangle$ denote core states.

$$|\vec{k}_{\rm ps}\rangle = |\vec{k}\rangle - \sum_c |\psi_c\rangle\langle\psi_c|\vec{k}\rangle, \tag{L1}$$

$$\hat{U}|\vec{k}_{\rm ps}\rangle = \hat{U}|\vec{k}\rangle - \sum_c \hat{U}\langle\psi_c|\vec{k}\rangle|\psi_c\rangle. \tag{L2}$$

$$\begin{aligned}(\hat{\mathcal{H}} - \mathcal{E})|\vec{k}_{\rm ps}\rangle &= \left(\frac{\hat{P}^2}{2m} + \hat{U} - \mathcal{E}\right)|\vec{k}_{\rm ps}\rangle \quad \text{(L3)} \\ &= \; ?\end{aligned}$$

Pseudopotentials

$$? \quad = \quad \left(\frac{\hat{P}^2}{2m} + \hat{U}_{\rm ps} - \mathcal{E}\right)|\vec{k}\rangle = (\hat{\mathcal{H}}_{\rm ps} - \mathcal{E})|\vec{k}\rangle, \tag{L6}$$

$$\hat{U}_{\rm ps} = \hat{U} - \sum_c (\mathcal{E}_c - \mathcal{E})|\psi_c\rangle\langle\psi_c|. \tag{L7}$$

$$(\hat{\mathcal{H}} - \mathcal{E})|\vec{k}_{\rm ps}\rangle = (\hat{\mathcal{H}}_{\rm ps} - \mathcal{E})|\vec{k}\rangle. \tag{L8}$$

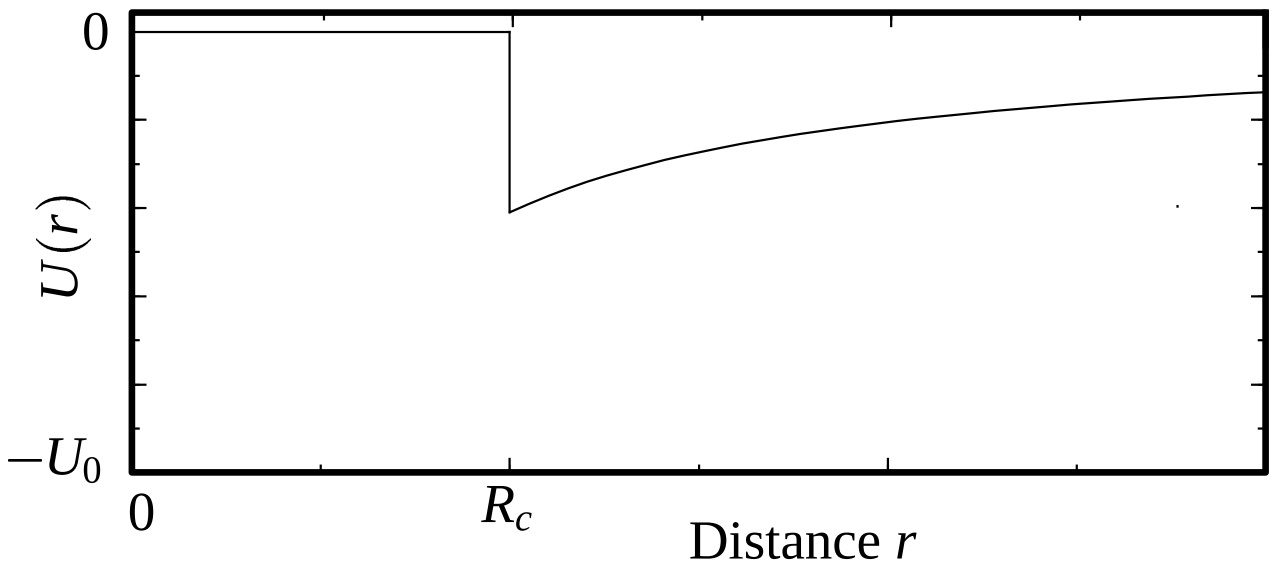


Figure 1: The Ashcroft empty core pseudopotential is zero up to a critical radius R_c, and it equals a screened Coulomb potential $-U_0 \exp[-r/d]/r$ thereafter.

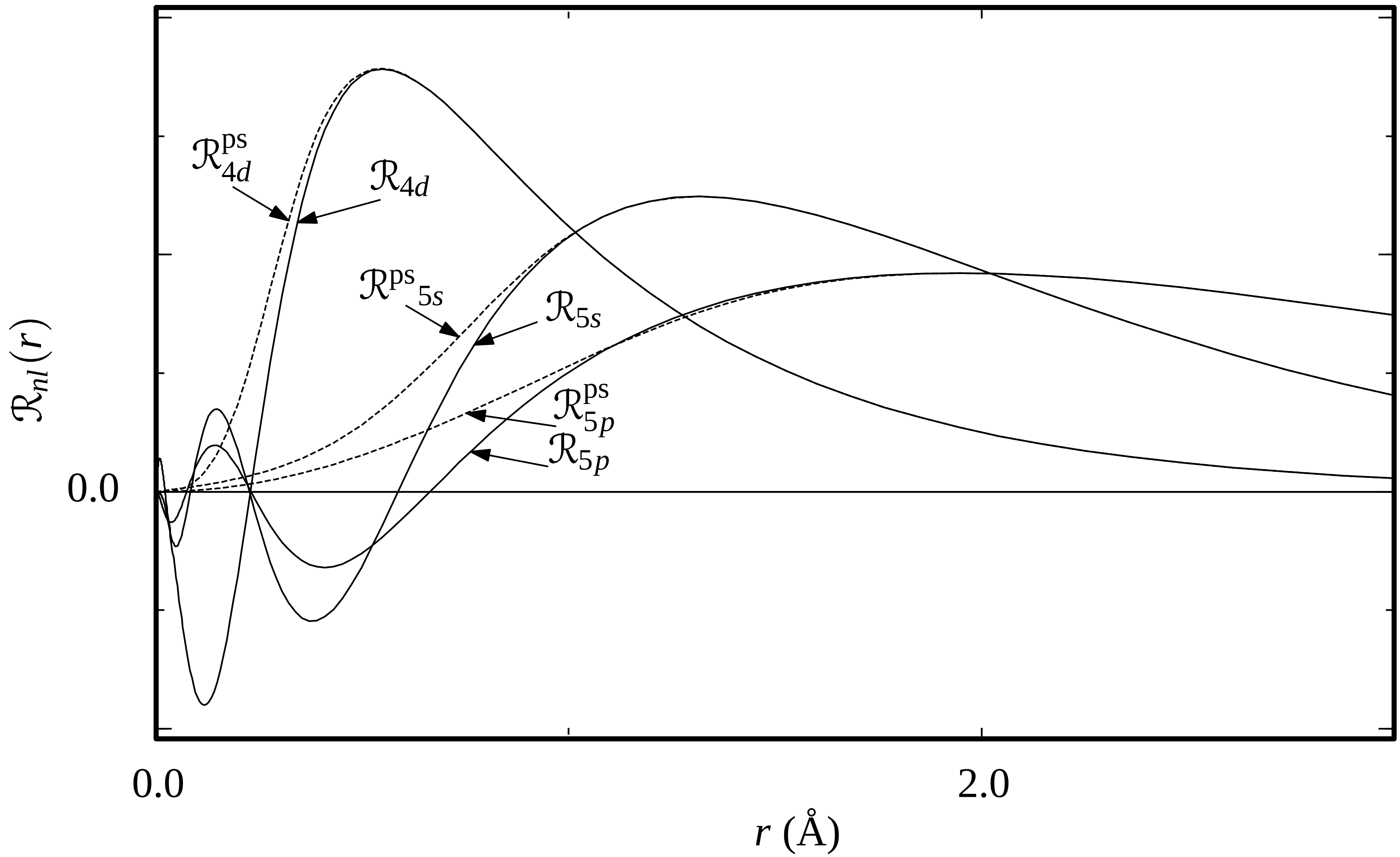


Figure 2: Real and pseudo wave functions for the 5s, 5p, and 4d levels of silver. The 5p level is not much occupied in the ground state of silver, but it can be included in the pseudopotential nevertheless.

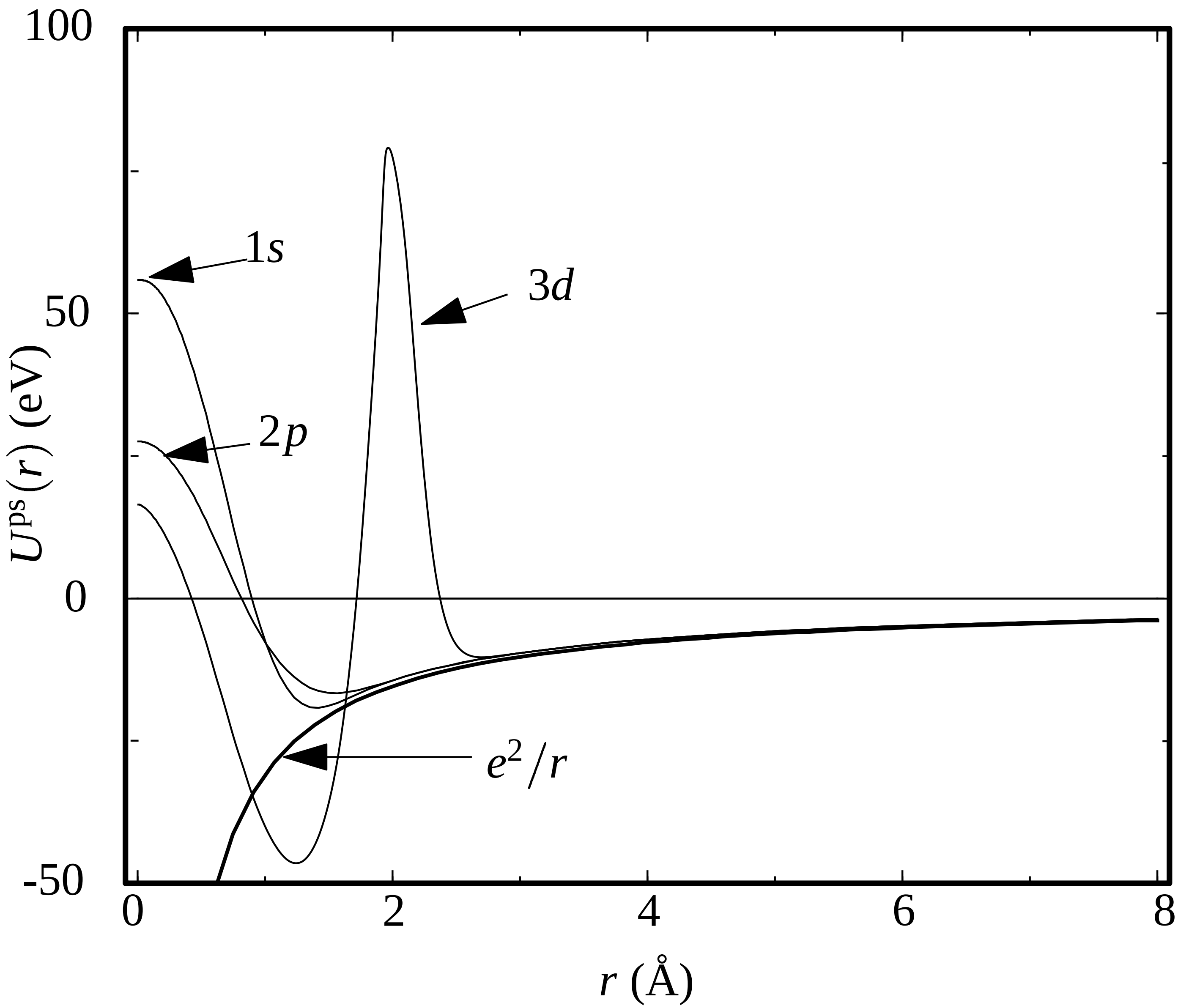


Figure 3: Pseudopotentials for the 5s, 5p, and 4d states of silver.

Electron density $n(\vec{r}) = \sum |\psi_i(\vec{r})|^2$ is spherically symmetrical in vicinity of nucleus

Equation for radial functions is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{l(l+1)}{r^2}\right]\mathcal{R}_{nl} + \left[\int \frac{e^2 n(r')}{|\vec{r}-\vec{r}'|}d\vec{r}' - \frac{e^2 Z}{r} + \frac{\delta \mathcal{E}_{xc}}{\delta n} - \mathcal{E}_{nl}\right]\mathcal{R}_{nl}(r) = 0. \quad \text{(L9)}$$

$$U_l^{\text{ps}}(r) = \frac{\hbar^2}{2m}\left[\frac{1}{r\mathcal{R}_{nl}^{\text{ps}}}\frac{\partial^2 r\mathcal{R}_{nl}^{\text{ps}}}{\partial r^2} - \frac{l(l+1)}{r^2}\right] - \left[\int \frac{e^2 n^{\text{ps}}(r')}{|\vec{r}-\vec{r}'|}d\vec{r}' + \frac{\delta \mathcal{E}_{xc}}{\delta n^{\text{ps}}} - \mathcal{E}_{nl}\right]. \quad \text{(L10)}$$

$$\psi(\vec{r}) = \sum_{lm} Y_{lm}(\theta,\phi)\psi_{lm}(r); \;\; \psi_{lm}(r) = \int d\theta d\phi \sin\theta Y_{lm}^*(\theta,\phi)\psi(\vec{r}), \quad \text{(L11)}$$

$$U^{\rm ps} = \frac{4\pi Z e^2}{q^2+\kappa^2}. \tag{L12}$$

Result from later work....

$$\frac{1}{\Omega} U^{\rm ps}(q=0) = -\frac{2}{3}\mathcal{E}_F. \tag{L13}$$

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R},l} b_l e^{i\vec{k}\cdot\vec{R}} a_l^{\text{at}}(\vec{r}-\vec{R}), \tag{L14}$$

$$\langle\psi|\hat{\mathcal{H}} - \mathcal{E}|\psi\rangle. \tag{L15}$$

$$\langle\psi|\mathcal{E}|\psi\rangle = \mathcal{E}\sum_{\vec{R}\vec{R}'}\int d\vec{r}a^{\text{at}}(\vec{r}-\vec{R})a^{\text{at}}(\vec{r}-\vec{R}')\frac{e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}{N}b^2 \tag{L16}$$

$$= b^2\mathcal{E}(1+\sum_{\vec{\delta}}\alpha e^{i\vec{k}\cdot\vec{\delta}}) \tag{L17}$$

and

$$\alpha = \int d\vec{r}\, a^{\text{at}}(\vec{r})a^{\text{at}}(\vec{r}+\vec{\delta}). \tag{L18}$$

$$\langle\psi|\hat{\mathcal{H}}|\psi\rangle = \sum_{\vec{R}\vec{R}'}\int d\vec{r}a^{\text{at}}(\vec{r}-\vec{R})[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})]a^{\text{at}}(\vec{r}-\vec{R}')\frac{e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}{N}b^2 \tag{L19}$$

$$= \sum_{\vec{R}\vec{R}'} \int d\vec{r} a^{\mathrm{at}}(\vec{r}-\vec{R}) \left\{ \begin{array}{ll} & [-\frac{\hbar^2}{2m}\nabla^2 + U^{\mathrm{at}}(\vec{r}-\vec{R}')]a^{\mathrm{at}}(\vec{r}-\vec{R}') \\ + & [U(\vec{r}) - U^{\mathrm{at}}(\vec{r}-\vec{R}')]a^{\mathrm{at}}(\vec{r}-\vec{R}') \end{array} \right\} \frac{e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}{N} b^2 \quad \text{(L20)}$$

$$= \int d\vec{r} \sum_{\vec{R}\vec{R}'} \mathcal{E}^{\mathrm{at}} \frac{a^{\mathrm{at}}(\vec{r}-\vec{R}) a^{\mathrm{at}}(\vec{r}-\vec{R}')}{N} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} b^2$$

$$+ \int d\vec{r} \sum_{\vec{R}\vec{R}'} a^{\mathrm{at}}(\vec{r}-\vec{R})[U(\vec{r}) - U^{\mathrm{at}}(\vec{r}-\vec{R}')]a^{\mathrm{at}}(\vec{r}-\vec{R}') \frac{e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}{N} b^2. \quad \text{(L21)}$$

$$\mathcal{E}(1 + \sum_{\vec{\delta}} \alpha e^{i\vec{k}\cdot\vec{\delta}}) = \mathcal{E}^{\mathrm{at}} \sum_{\vec{\delta}} \alpha e^{i\vec{k}\cdot\vec{\delta}} + U + (\mathfrak{t} - \alpha\mathcal{E}^{\mathrm{at}}) \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}, \quad \text{(L22)}$$

where

$$U = \mathcal{E}^{\mathrm{at}} + \int d\vec{r} a^{\mathrm{at}}(\vec{r})[U(\vec{r}) - U^{\mathrm{at}}(\vec{r})]a^{\mathrm{at}}(\vec{r}) \quad \text{(L23)}$$

and

$$\mathfrak{t} = \alpha\mathcal{E}^{\mathrm{at}} + \int d\vec{r} a^{\mathrm{at}}(\vec{r})[U(\vec{r}) - U^{\mathrm{at}}(\vec{r}+\vec{\delta})]a^{\mathrm{at}}(\vec{r}+\vec{\delta}). \quad \text{(L24)}$$

$$\mathcal{E} = U + \mathfrak{t} \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}. \tag{L25}$$

$$\vec{K} = l_1\vec{b}_1 + l_2\vec{b}_2 + l_3\vec{b}_3 \tag{L26}$$

$$\sum_{i=1}^{N} \lambda_i^r \hat{e}_i(\hat{e}_i \cdot \vec{a}_1). \tag{L27}$$

$$\hat{\mathcal{H}} = \frac{\hat{P}^2}{2m} + U(\hat{R}). \tag{L28}$$

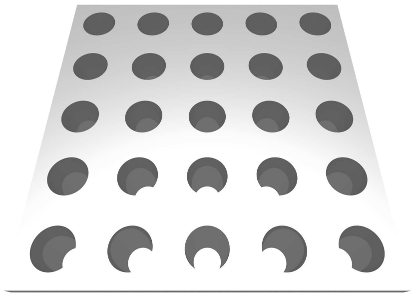
$\hbar^2 K_{\text{max}}^2/2m = \mathcal{E}_{\text{max}}$

$$\hat{\mathcal{H}}\psi = \sum_{\vec{K}'} \left\{ \left[\mathcal{E}^0_{\vec{k}+\vec{K}'} - \mathcal{E}_{\text{max}} \right] \delta_{\vec{K}\vec{K}'} + U_{\vec{K}-\vec{K}'} \right\} \psi_{n\vec{k}}(\vec{K}'), \tag{L29}$$

$$1 + \hat{\mathcal{H}}\, dt/\hbar. \tag{L30}$$

$$\psi_{n+1} = (1 + \hat{\mathcal{H}} dt/\hbar)\psi_n \Rightarrow \frac{\psi_{n+1} - \psi_n}{dt} = \frac{1}{\hbar}\hat{\mathcal{H}}\psi_n, \tag{L31}$$

Linear Augmented Plane Waves (LAPW)



$$\phi_{\mathcal{E}\vec{k}} = e^{i\vec{k}\cdot\vec{r}}$$

$$-\frac{1}{2m}\hbar^2\nabla^2\phi_{\mathcal{E}\vec{k}} + U(r)\phi_{\mathcal{E}\vec{k}} = \mathcal{E}\phi_{\mathcal{E}\vec{k}}$$

$$\psi_{\mathcal{E}} = Y_{lm}\mathcal{R}_{l\mathcal{E}}(r), \tag{L32}$$

$$\frac{-\hbar^2}{2mr^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\mathcal{R}_{l\mathcal{E}}(r) + [U(r) + \frac{\hbar^2 l(l+1)}{2mr^2}]\mathcal{R}_{l\mathcal{E}}(r) = \mathcal{E}\mathcal{R}_{l\mathcal{E}}(r). \tag{L33}$$

$$\phi_{\mathcal{E}\vec{k}} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} A_{lm}Y_{lm}(\hat{r})\mathcal{R}_{l\mathcal{E}}(r), \tag{L34}$$

Linear Augmented Plane Waves (LAPW)

$$e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) Y^*_{lm}(\hat{k}) Y_{lm}(\hat{r}). \tag{L35}$$

$$\phi_{\mathcal{E}\vec{k}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{i^l j_l(kR_h) Y^*_{lm}(\hat{k})}{\mathcal{R}_{l\mathcal{E}}(R_h)} Y_{lm}(\hat{r}) \mathcal{R}_{l\mathcal{E}}(r). \tag{L36}$$

$$\psi_{\vec{k}} = \sum_{\vec{K}} b_{\vec{k}+\vec{K}} \phi_{\mathcal{E},\vec{k}+\vec{K}}. \tag{L37}$$

$$\langle \psi | \hat{\mathcal{H}} - \mathcal{E} | \psi \rangle, \tag{L38}$$

$$0 = \sum_{\vec{K}} \langle \phi_{\mathcal{E}\vec{q}} | \hat{\mathcal{H}} - \mathcal{E} | \phi_{\mathcal{E}\vec{q}+\vec{K}} \rangle b_{\vec{q}+\vec{K}}, \tag{L39}$$

where

$$\langle \phi_{\mathcal{E}\vec{q}} | \hat{\mathcal{H}} - \mathcal{E} | \phi_{\mathcal{E}\vec{q}'} \rangle = \left(\frac{\hbar^2 \vec{q}\cdot\vec{q}'}{2m} - \mathcal{E}\right) \Omega \delta_{\vec{q},\vec{q}'} + \mathcal{U}_{\vec{q},\vec{q}'} \tag{L40}$$

$$\mathcal{U}_{\vec{q},\vec{q}'} = 4\pi R_h^2 \left\{ \begin{array}{ll} - & \left(\frac{\hbar^2 \vec{q}\cdot\vec{q}'}{2m} - \mathcal{E}\right) \frac{j_1(|\vec{q}-\vec{q}'|R_h)}{|\vec{q}-\vec{q}'|} \\ + & \sum_{l=0}^{\infty} \frac{\hbar^2}{2m}(2l+1)P_l(\hat{q}\cdot\hat{q}')\, j_l(qR_h)\, j_l(q'R_h) \frac{\mathcal{R}'_{l\mathcal{E}}(R_h)}{\mathcal{R}_{l\mathcal{E}}(R_h)} \end{array} \right\}. \qquad \text{(L41)}$$

$$\chi_{lm}(\mathcal{E},r) = \begin{cases} i^l Y_l^m(\hat{r})[\mathcal{R}_{l\mathcal{E}}(r) + (\frac{r}{R_h})^l p_{l\mathcal{E}}] & \text{for } r < R_h \\ i^l Y_l^m(\hat{r})(\frac{R_h}{r})^{l+1} & \text{for } r > R_h. \end{cases} \tag{L42}$$

$$\begin{aligned} \mathcal{R}_{l\mathcal{E}}(R_h) + p_{l\mathcal{E}} &= 1 \\ \mathcal{R}'_{l\mathcal{E}}(R_h) + l\frac{p_{l\mathcal{E}}}{R_h} &= -\frac{l+1}{R_h}. \end{aligned} \tag{L43}$$

$$p_{l\mathcal{E}} = \frac{-(l+1)/R_h - \left.\frac{\partial \mathcal{R}_{l\mathcal{E}}}{\partial r}\right|_{R_h}}{l/R_h - \left.\frac{\partial \mathcal{R}_{l\mathcal{E}}}{\partial r}\right|_{R_h}} = \frac{\mathcal{D}_l(\mathcal{E}) + l + 1}{\mathcal{D}_l(\mathcal{E}) - l} \tag{L44a}$$

with

$$\mathcal{D}_l(\mathcal{E}) = \frac{R_h}{\mathcal{R}_{l\mathcal{E}}(R_h)} \left.\frac{\partial \mathcal{R}_{l\mathcal{E}}}{\partial r}\right|_{R_h}. \tag{L44b}$$

$$\psi(\vec{r}) = \sum_{lm} B_{lm}^{n\vec{k}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \chi_{lm}(\mathcal{E}, \vec{r} - \vec{R}) \tag{L45}$$

$$0 = \sum_{lm} B^{n\vec{k}}_{lm} \left[p_{l\varepsilon} i^l Y^m_l(\hat{r}) \left(\frac{r}{R_h}\right)^l + \sum_{\vec{R}\neq 0} i^l Y^m_l\left(\widehat{\vec{r}-\vec{R}}\right)\left(\frac{R_h}{|\vec{r}-\vec{R}|}\right)^{l+1} e^{i\vec{k}\cdot\vec{R}} \right]. \tag{L46}$$

$$\sum_{\vec{R}\neq 0} i^l Y^m_l(\widehat{\vec{r}-\vec{R}})\left(\frac{R_h}{|\vec{r}-\vec{R}|}\right)^{l+1} e^{i\vec{k}\cdot\vec{R}} = -\sum_{l'm'} \frac{\mathcal{S}^{\vec{k}}_{ll'mm'}}{2(2l'+1)}\left(\frac{r}{R_h}\right)^{l'} i^{l'} Y^{m'}_{l'}(\hat{r}). \tag{L47}$$

$$0 = \sum_{lm} B^{n\vec{k}}_{lm} \left[p_{l\varepsilon} i^l Y^m_l(\hat{r}) \left(\frac{r}{R_h}\right)^l - \sum_{l'm'} \frac{\mathcal{S}^{\vec{k}}_{ll'mm'}}{2(2l'+1)}\left(\frac{r}{R_h}\right)^{l'} i^{l'} Y^{m'}_{l'}(\hat{r}) \right] \tag{L48}$$

$$\Rightarrow 0 = \sum_{lml'm'} B^{n\vec{k}}_{lm} \left[p_{l\varepsilon}\delta_{ll'}\delta_{mm'} - \frac{\mathcal{S}^{\vec{k}}_{ll'mm'}}{2(2l'+1)} \right] \left(\frac{r}{R_h}\right)^{l'} i^{l'} Y^{m'}_{l'}(\hat{r}). \tag{L49}$$

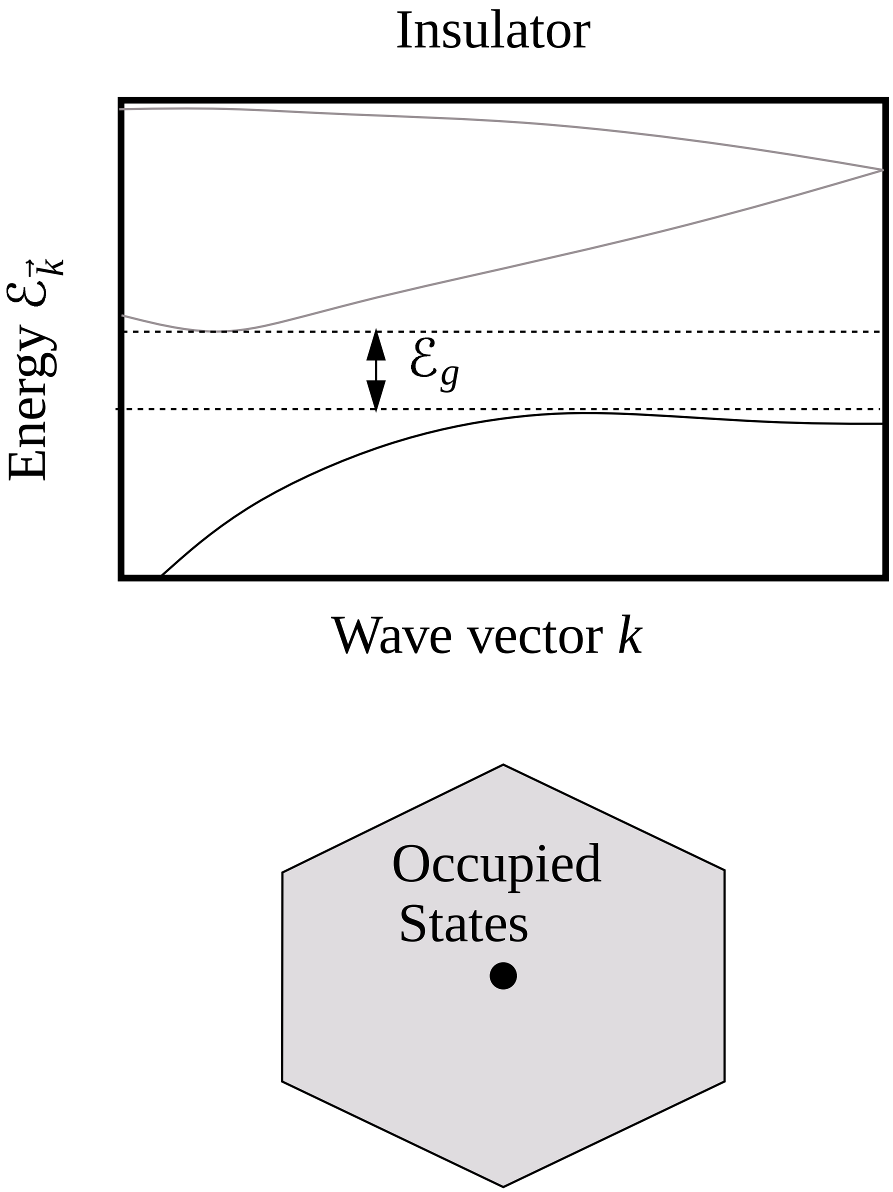
$$0 = \sum_{lm} \left[2(2l+1) p_{l\varepsilon}\delta_{ll'}\delta_{mm'} - \mathcal{S}^{\vec{k}}_{ll'mm'} \right] B^{n\vec{k}}_{lm}. \tag{L50}$$

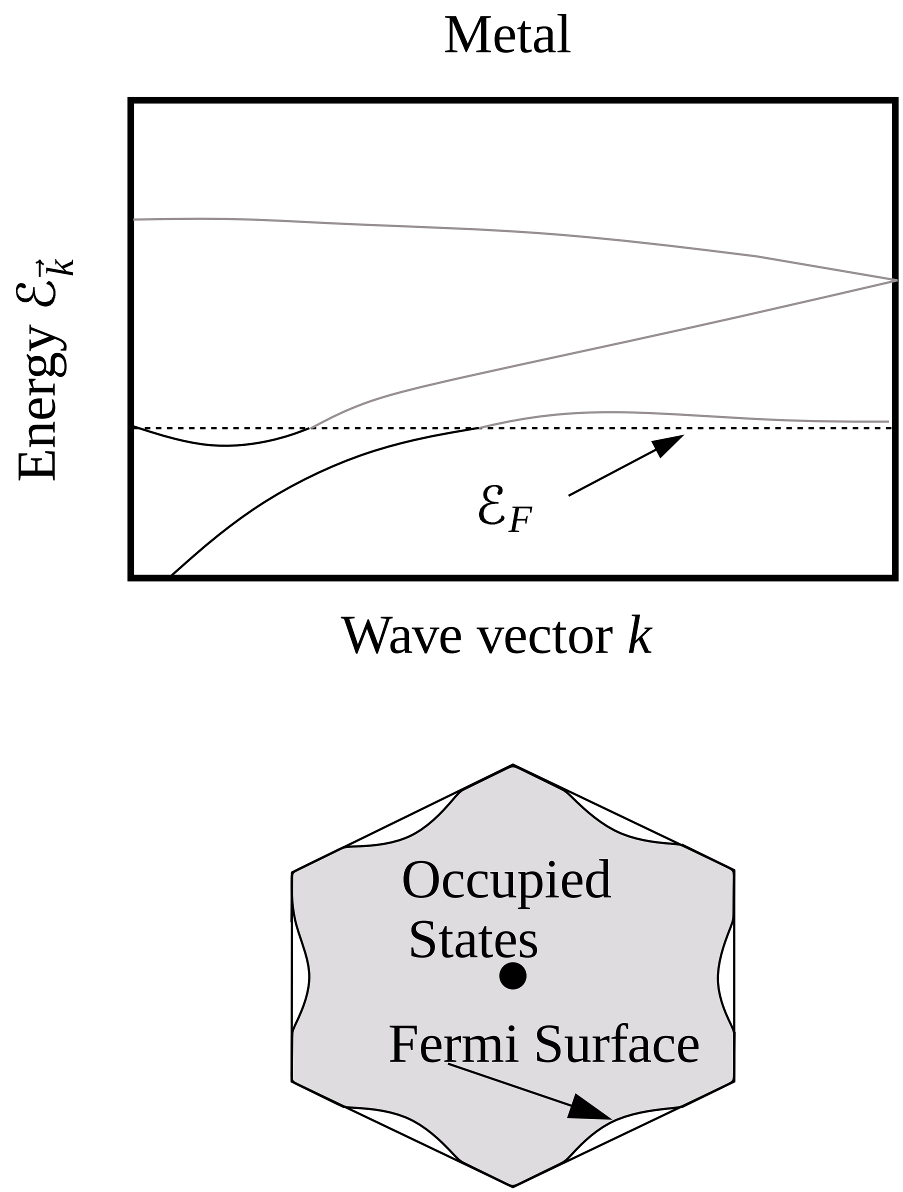
Definition of Metals, Insulators, and Semiconductors

Wilson's theory:

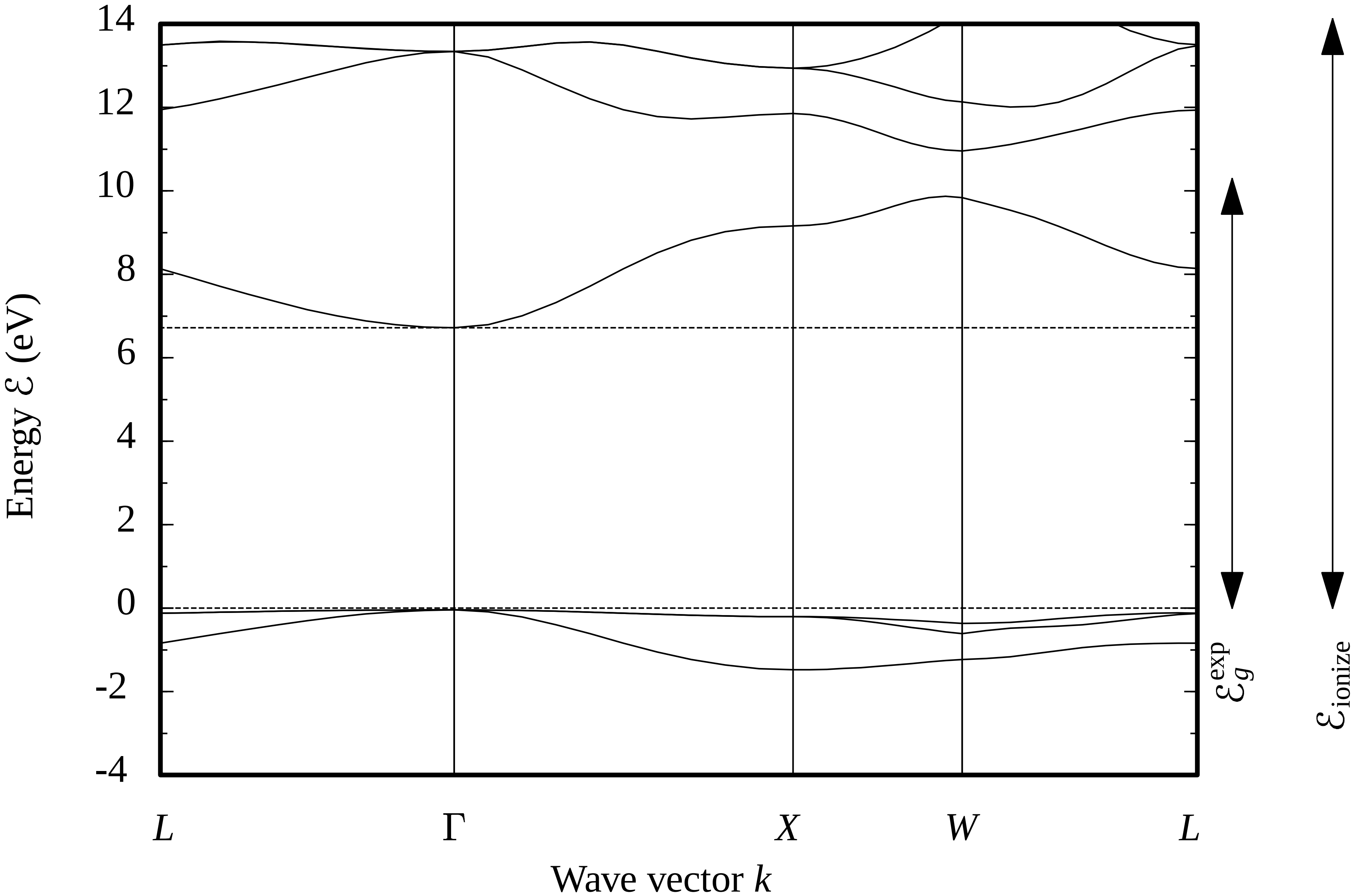
- ☞ Insulator: All bands are either full or empty.
- ☞ Metal: At least one band is partially occupied.
- ☞ Semiconductor: Insulator where energy gap is less than around 1 eV.
- ☞ Semimetal: Metal with very small population of conduction electrons.

Definition of Metals, Insulators, and Semiconductors



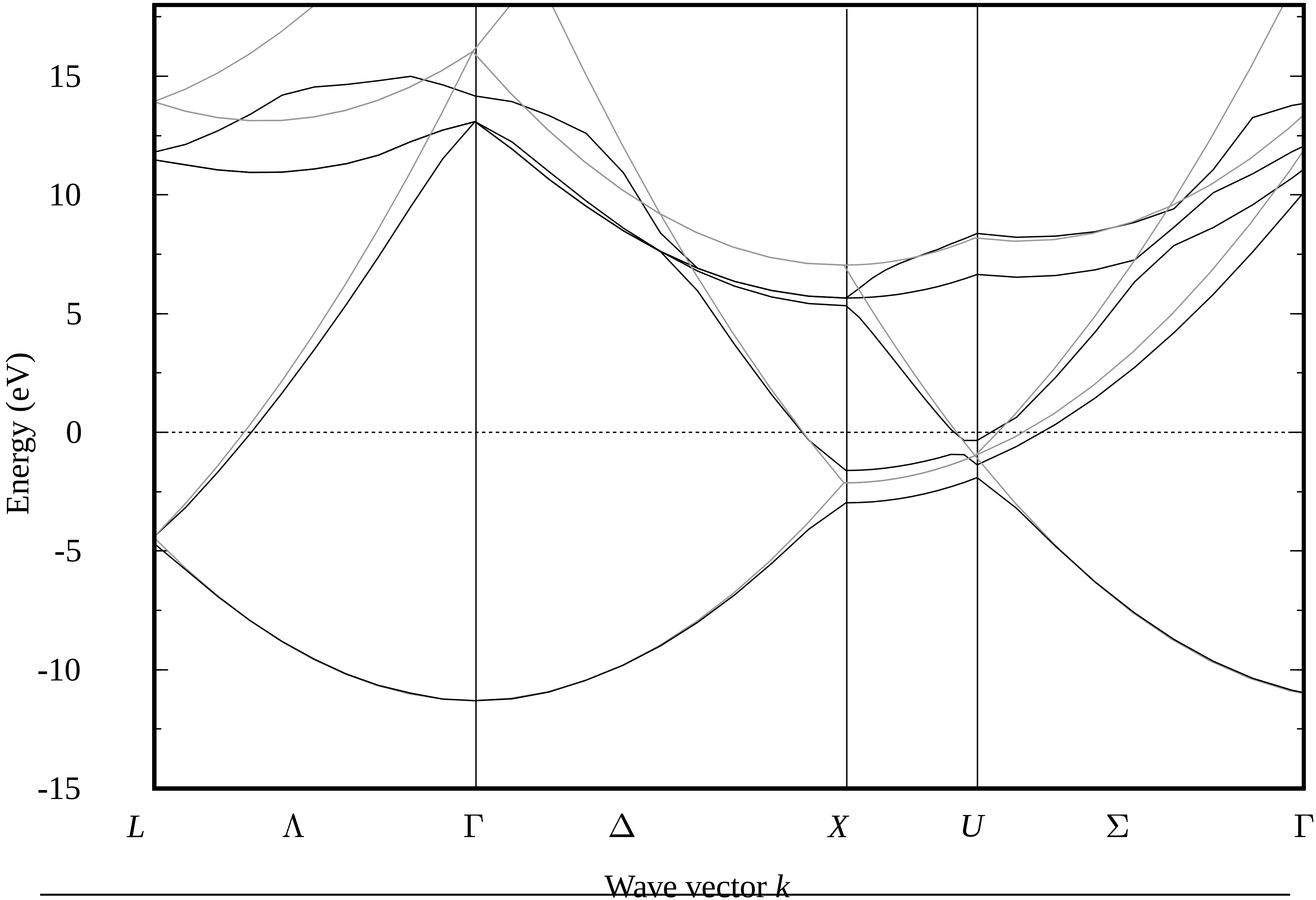


Noble Gases

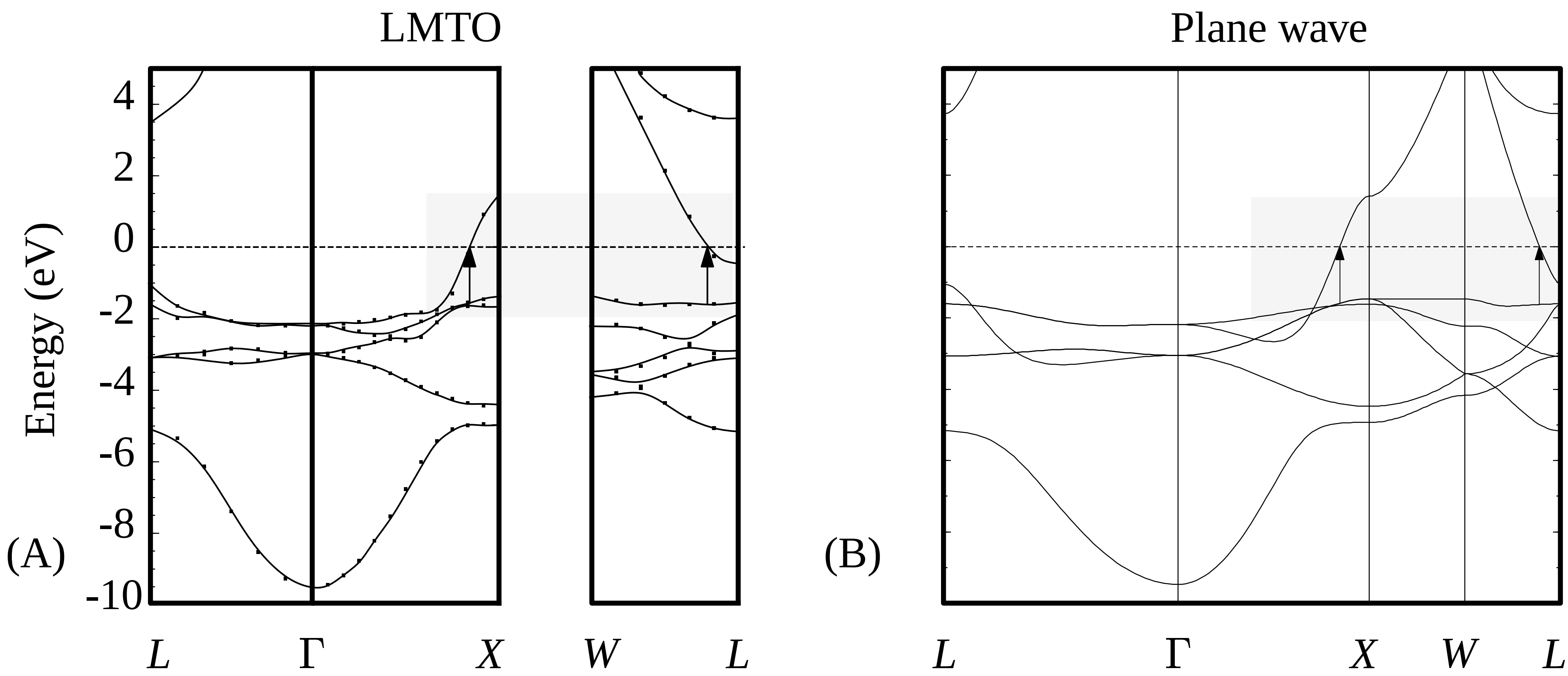


14
12
10
8
6
4
2
0
-2
-4
Energy $\mathcal{E}$ (eV)
L
Γ
X
W
L
Wave vector k
$\mathcal{E}_g^{\text{exp}}$
$\mathcal{E}_{\text{ionize}}$

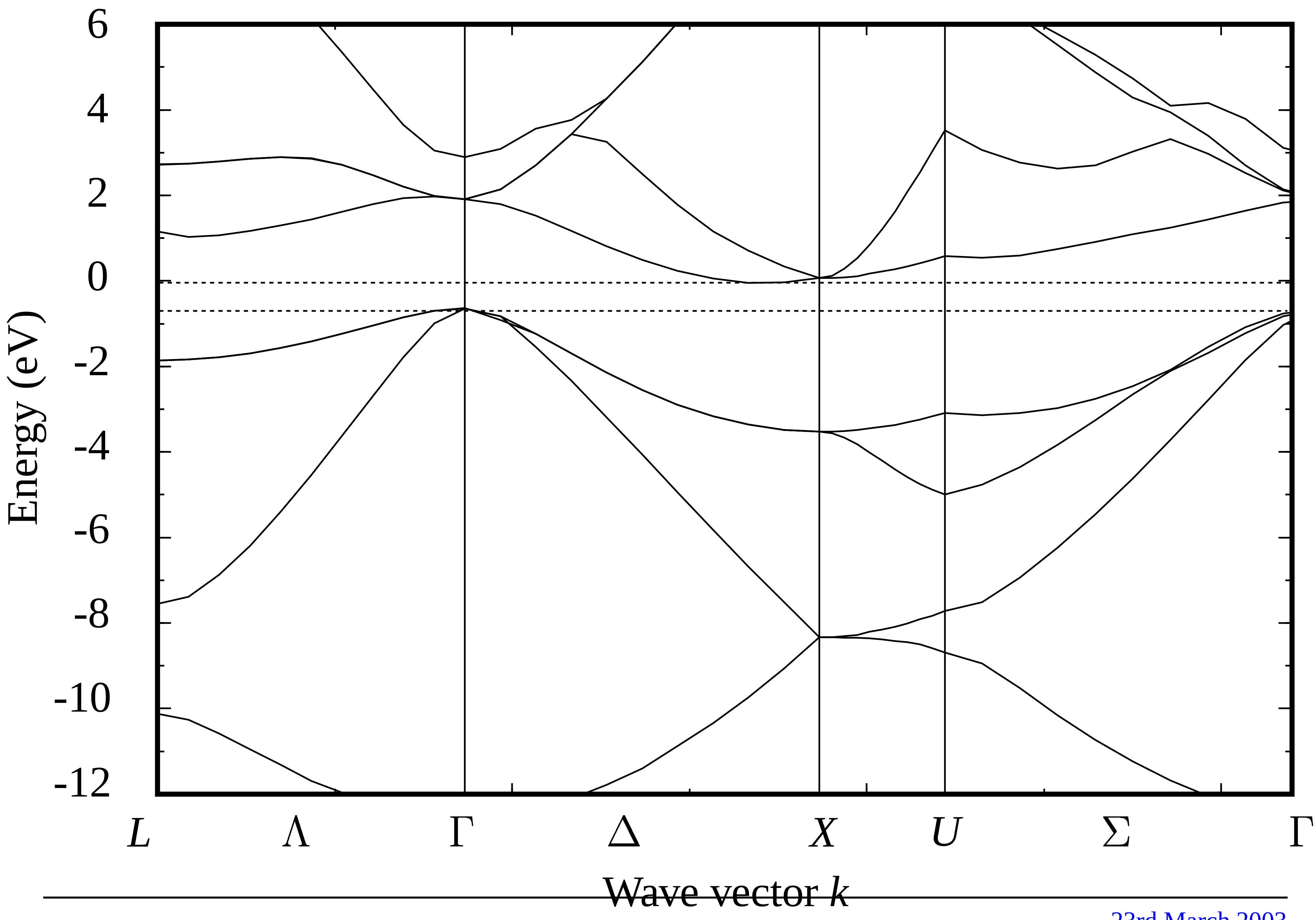
Nearly Free Electron Metals



Nearly Free Electron Metals



Semiconductors



Transition Metals