

Welcome to CHE 384T: Computational Methods in Materials Science

Electronic structure and DFT preliminaries

LeSar Ch. 4; App. F



The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

Announcements

Due Nov 4, 11:59pm: project proposal;

Proposal guidelines

Nov 8: peer review day for project proposals

Due Nov 15, 11:59pm: project progress report: ~ 1 page , may include

- What you are on track to accomplish
- On-going challenges/questions

8:30am

Due Dec 2, 9am: Report and Presentation

Final Report Rubric

- ~5 pages (including figures/tables)
- 12 or 11 point font, single-space
- Example report

~ 10

~8 min

Final Project Presentation (~12 min per presentation; 10 min presentation, 2 min Q&A)

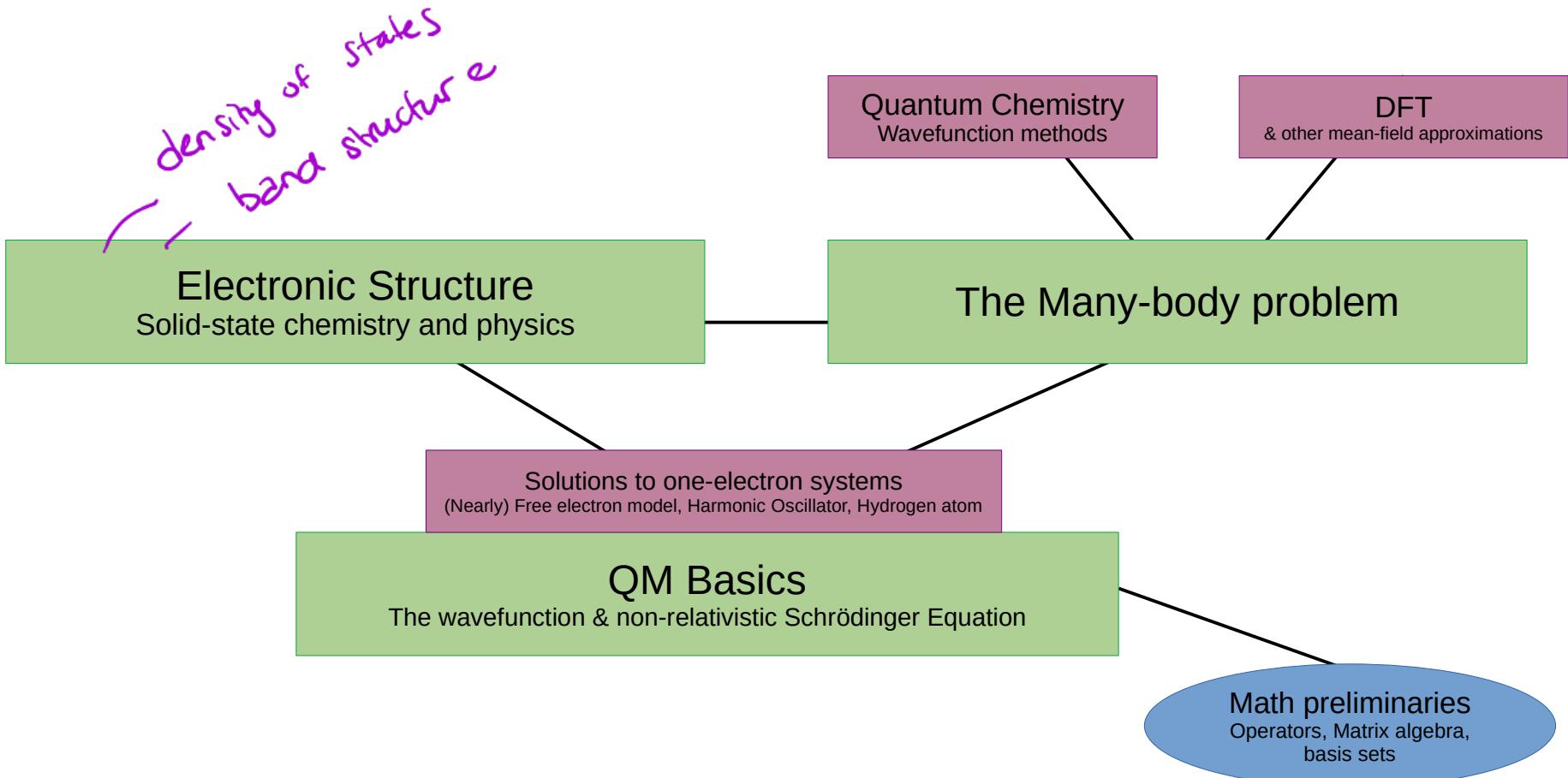
In-class starting Dec 2

Awards for audience favorite

(considering topic, implementation, use of computation and methods learned in class)

OH 11/13
CPE 4.450
10am

Road map



Lecture Outline

What is electronic structure?

Part 1: Density of States

- Molecular orbital theory
- Classification of electronic structure
- Connection to materials properties
 - electrical conductivity and optical absorption
- Free electron model
 - Derivation and interpretation

Fermi-Dirac statistics and the Fermi level
Application to the free electron model

$D(E)$

Part 2: electronic band structure (of solids)

$\epsilon(k)$

Crystallography:
Bloch's theorem
Reciprocal space
Brillouin zone

Free electron model and dispersion
BZ folding
Band gap- from perturbation theory

Example band structures

Variational principle

Matrix formulation of QM

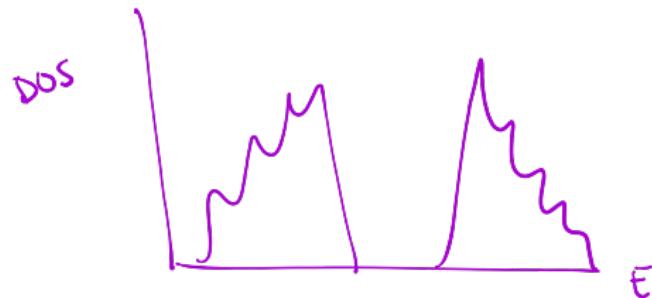
Basis sets- Gaussian and plane waves

Energy cutoff and k-point integration

Irreducible Brillouin zone and symmetry

What is electronic structure?

Part 1: Introduction to the Density of States



→ count #
electronic states
 w_i at E and $E + dE$

Some physical intuition: Molecular Orbital theory

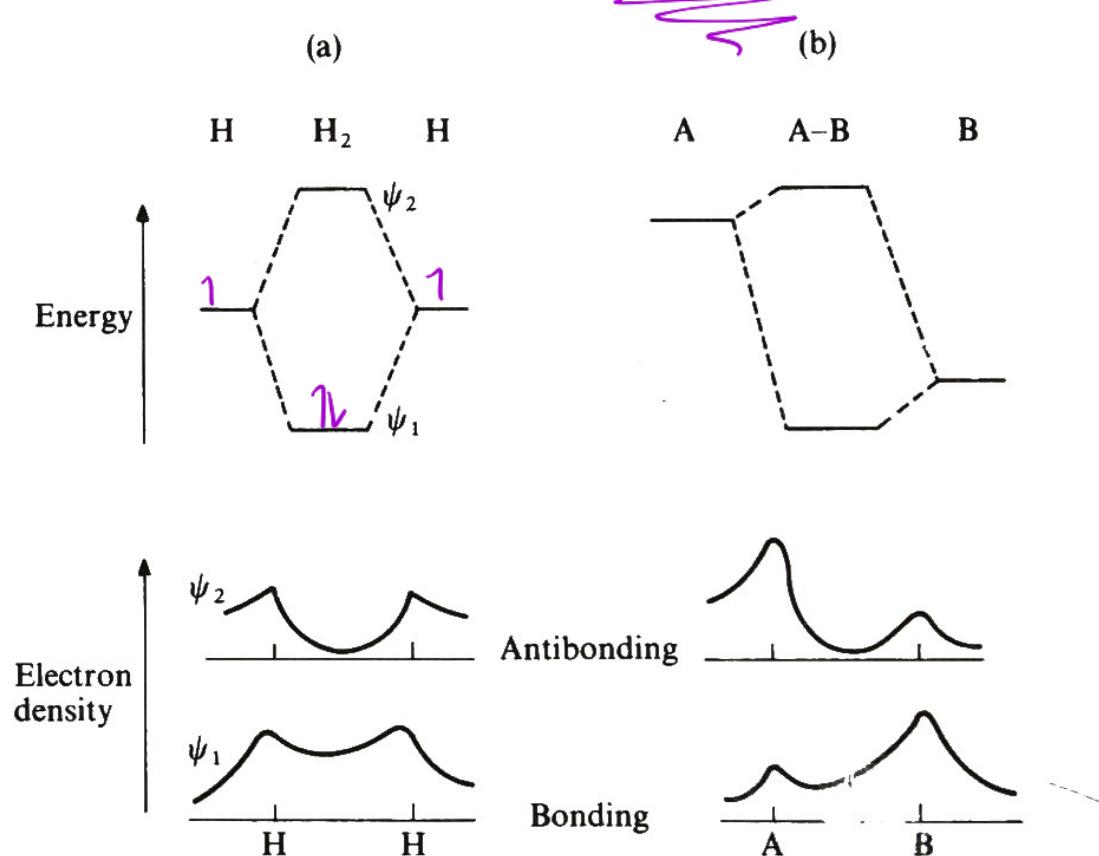
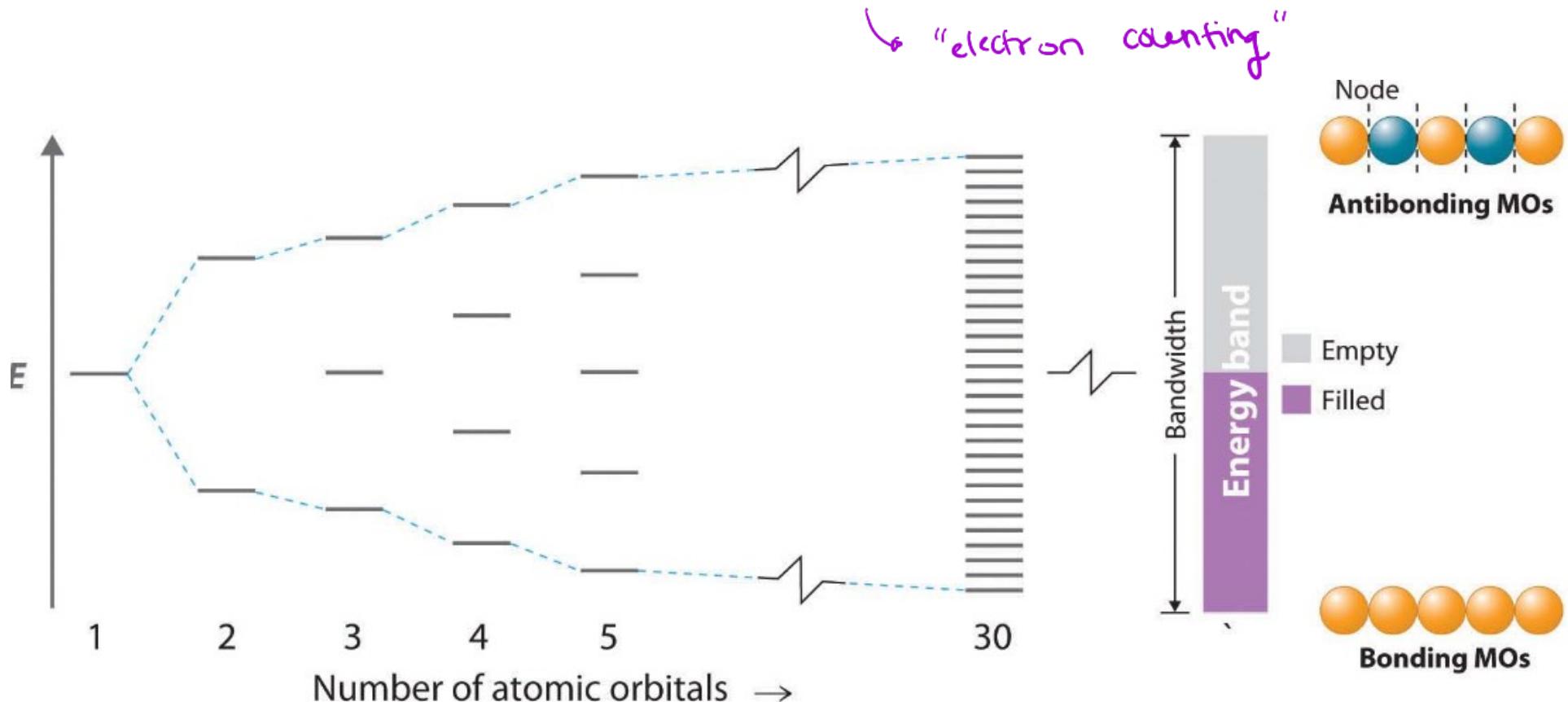


Fig. 1.6 Electron distributions and energies of molecular orbitals in (a) H_2 , and (b) a heteronuclear molecule AB.

Some physical intuition: forming energy bands in solid



Some physical intuition: forming energy bands in solid

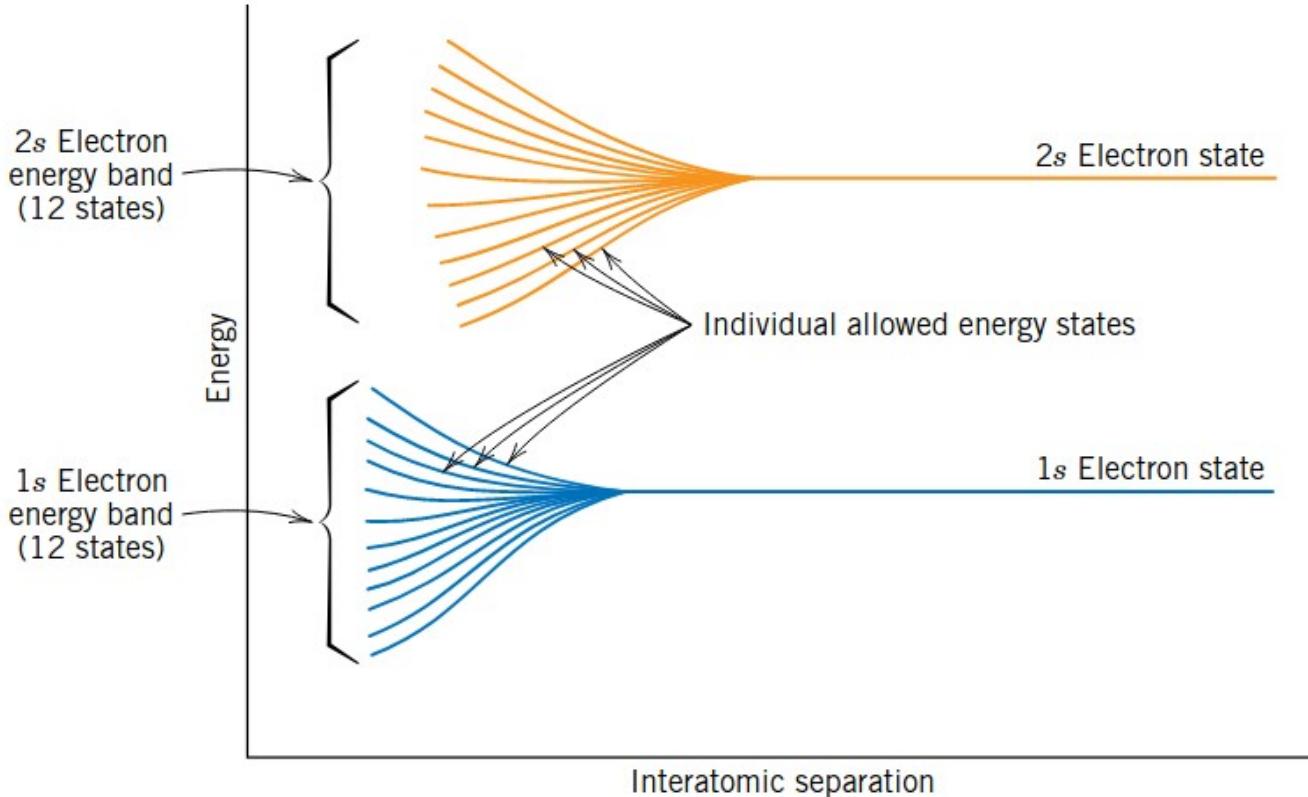


Figure 18.2 Schematic plot of electron energy versus interatomic separation for an aggregate of 12 atoms ($N = 12$). Upon close approach, each of the 1s and 2s atomic states splits to form an electron energy band consisting of 12 states.

Some physical intuition: forming energy bands in solid

Pauli's exclusion principle
Aufbau principle

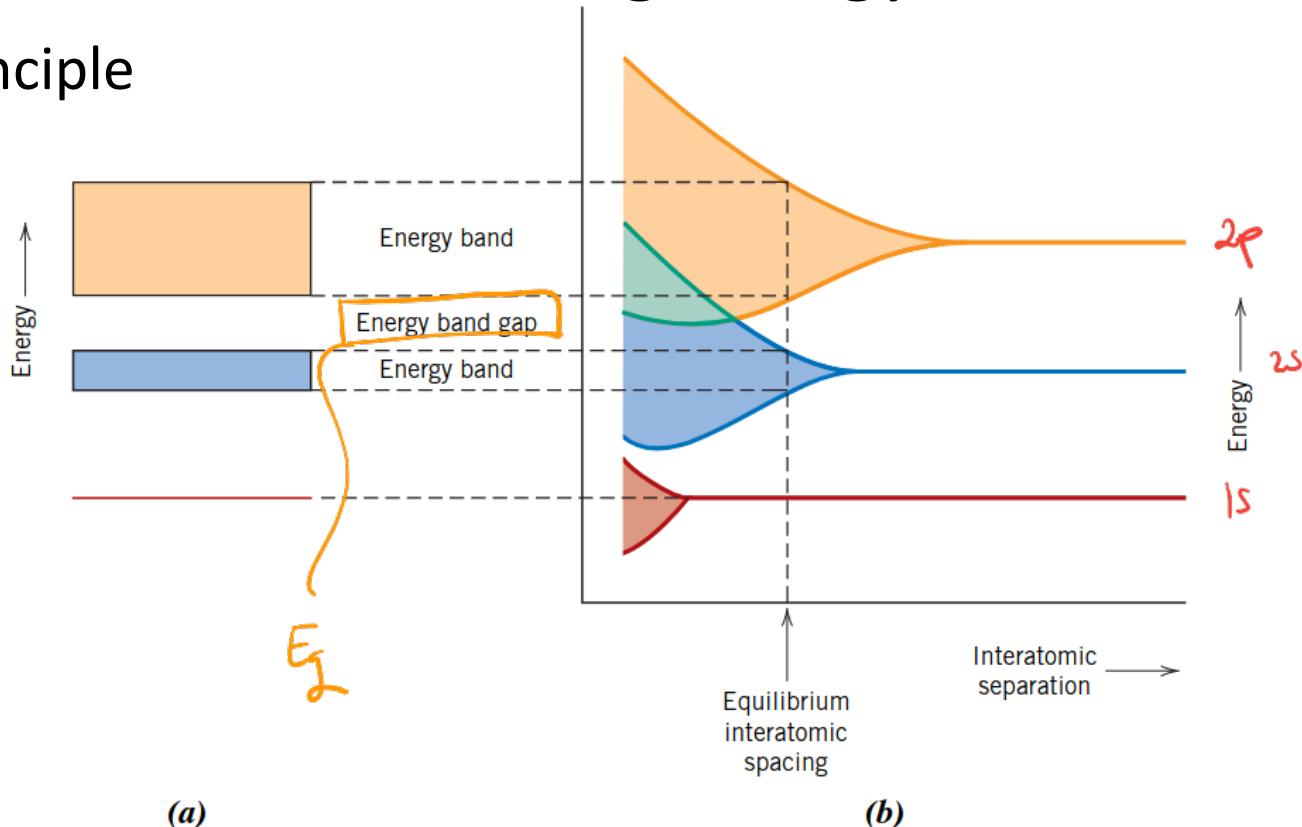
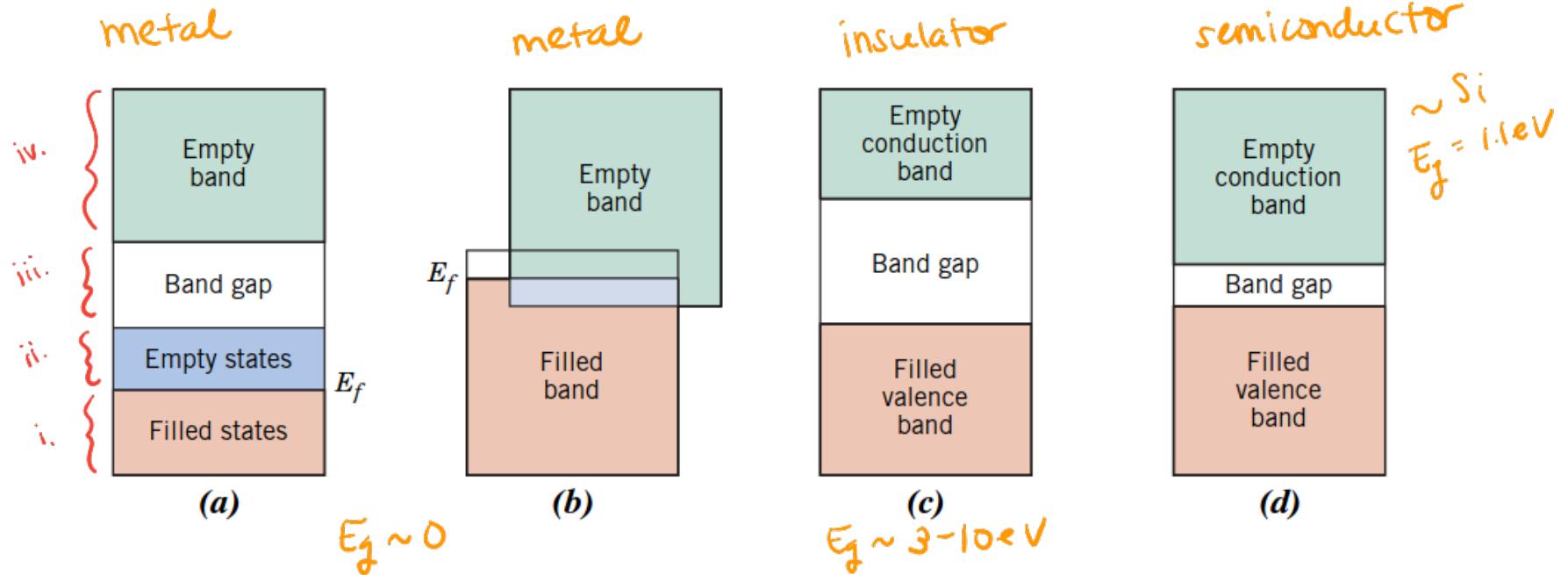


Figure 18.3 (a) The conventional representation of the electron energy band structure for a solid material at the equilibrium interatomic separation. (b) Electron energy versus interatomic separation for an aggregate of atoms, illustrating how the energy band structure at the equilibrium separation in (a) is generated.

(From Z. D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd edition. Copyright © 1987 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

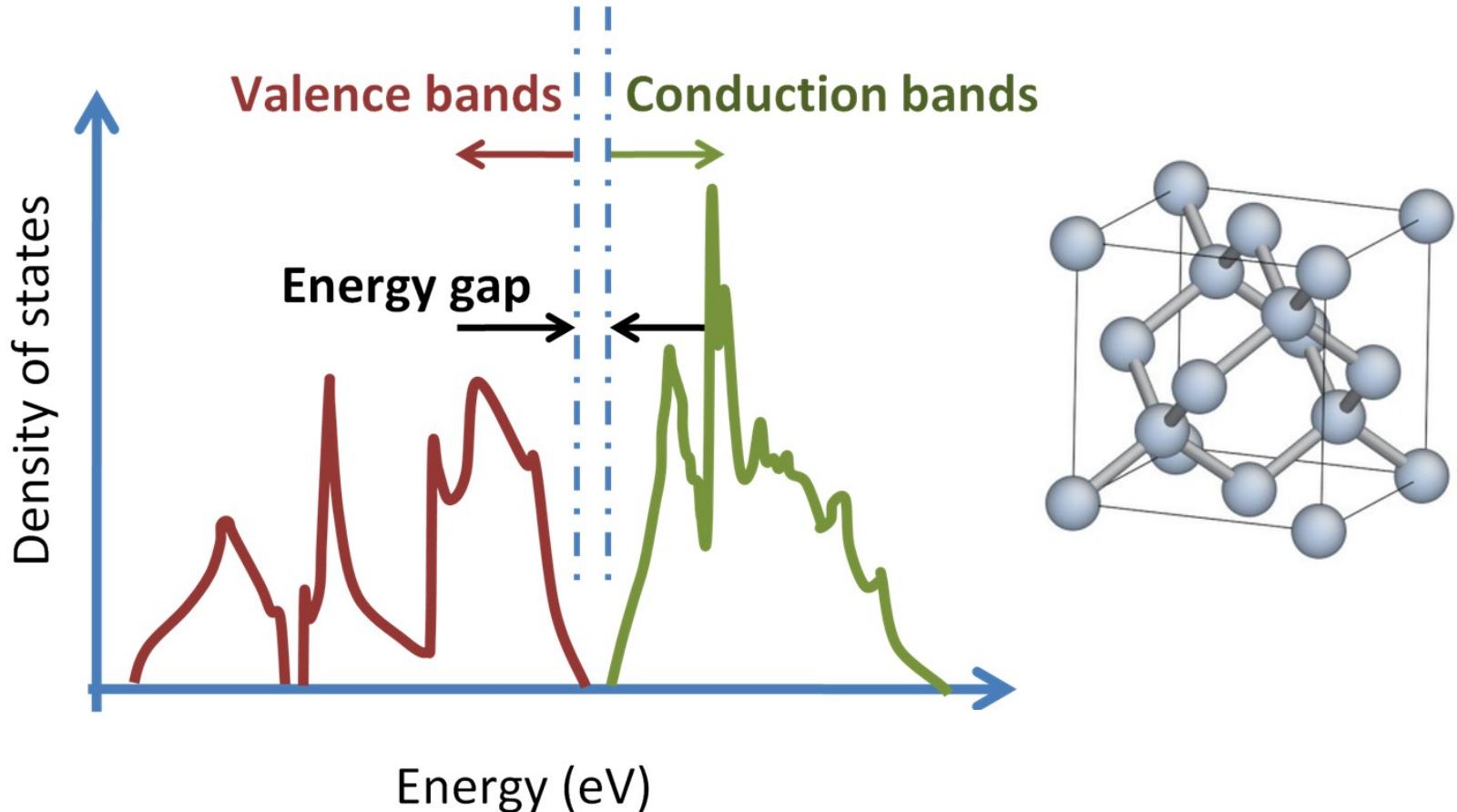
The electronic band gap



Where are the allowed electronic transitions?

Which schematic corresponds to a metal, semiconductor, insulator?

Density of States of Silicon



DOS: Free electron model (3D)

$$1D: E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

$$3D: E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

TABLE 11-2
Quantum States and Energy Levels for Free Electrons

Quantum States			Energy Level ($\hbar^2/8mL^2$)	Number of Quantum States	Number of Electron Homes
n_x	n_y	n_z			
1	1	1	3	1	2
2	1	1	6		
1	2	1	6	→ 3	6
1	1	2	6		
2	2	1	9		
2	1	2	9	3	6
1	2	2	9		
3	1	1			
1	3	1	11	3	6
1	1	3			
2	2	2	12	1	2
1	2	3	14		
1	3	2	14		
2	1	3	14	6	12
2	3	1	14		
3	1	2	14		
3	2	1	14		

ground state →
1st excited state {

In 3D, energetically degenerate quantum states emerge

DOS: Free electron model (3D)

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z \in \mathbb{Z}^+$$

$$D(E) = \frac{1}{V} \frac{dN}{dE}$$

↗ # electronic states
 ↙ b_L E and $E+dE$

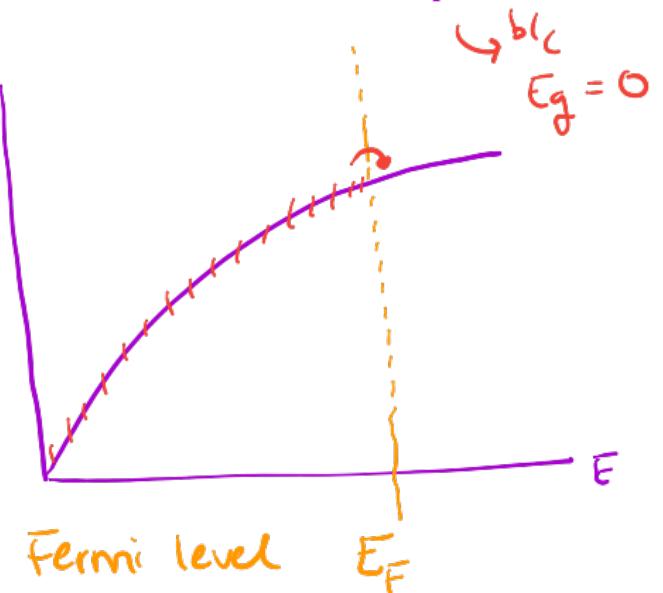
$$D(E) = 2 \cdot \frac{\pi}{6} \left(\frac{2m}{\hbar^2 \pi^2} \right)^{3/2} \cdot \frac{3}{2} E^{1/2}$$

↓ spin degeneracy

\sqrt{E}

$D(E)$

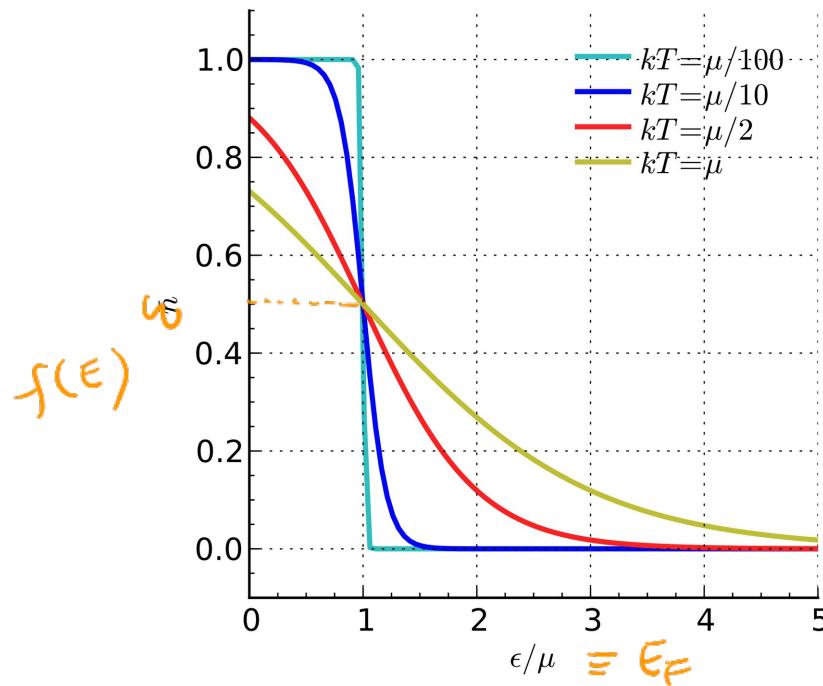
free-electron model
is a metal



Fermi-Dirac distribution

Fermi-Dirac distribution: describes occupation statistics of electronic states

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$$



Fermi level

$$f(E = E_F) = \frac{1}{2}$$

$$T \rightarrow 0 \quad f(E)$$

$$\begin{aligned} E > E_F &\rightarrow 0 \\ E < E_F &\rightarrow 1 \end{aligned}$$

DOS: Free electron model (3D)

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z \in \mathbb{Z}^+$$

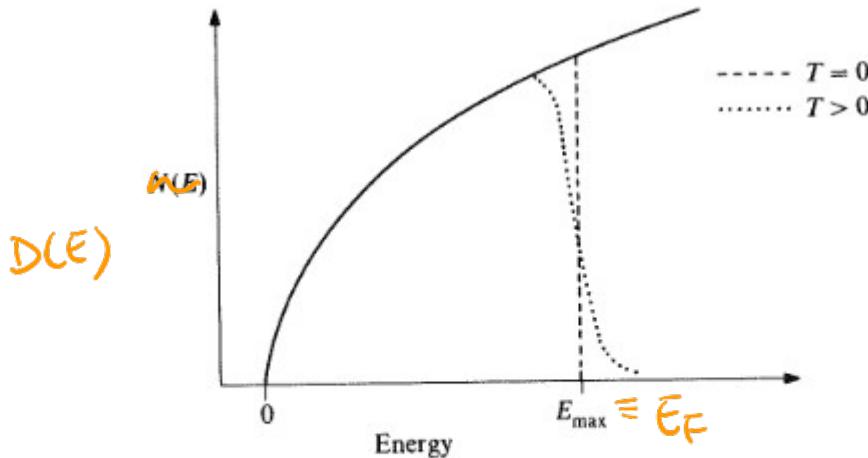


Fig. 3.10 Density of states in the free electron model. The Fermi–Dirac functions showing the occupancies of levels at absolute zero and at some higher temperature are indicated.

Filling up to E_{\max} (E_F)

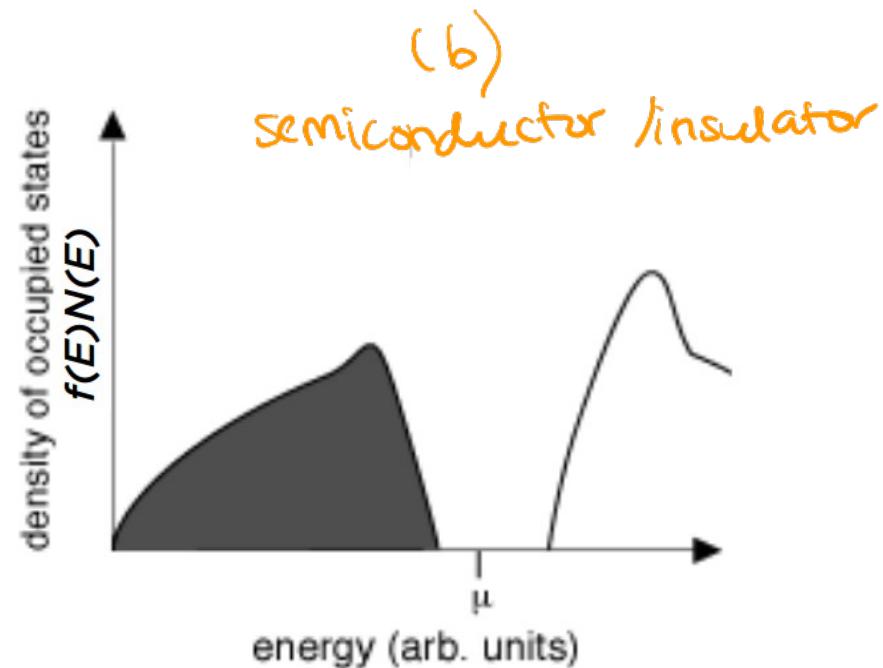
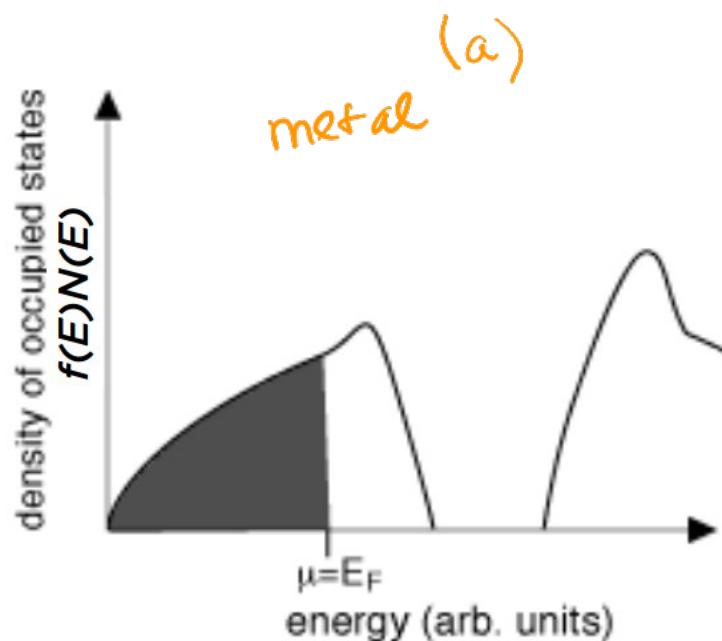
Free-electron model →

Photoelectron or X-ray spectroscopy →

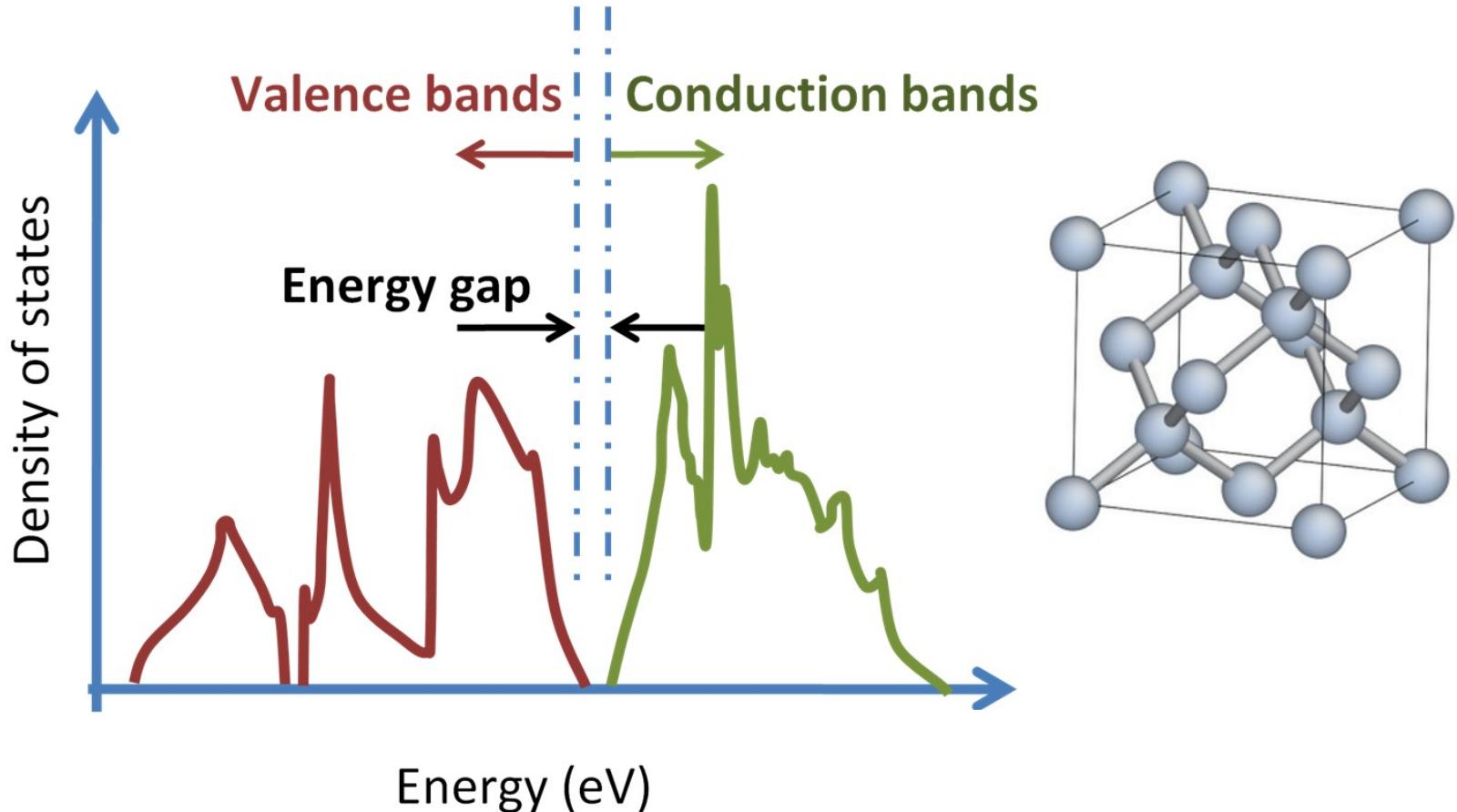
E_{\max} (eV)	Na	Mg	Al
Calculated	3.2	7.2	12.8
Experimental	2.8	7.6	11.8

P.A. Cox. *Intro to Electronic Structure and Chemistry of Solids.*
Ch. 3

Density of States (of solid)



Density of States of Silicon



Heuristic origins of electrical conductivity

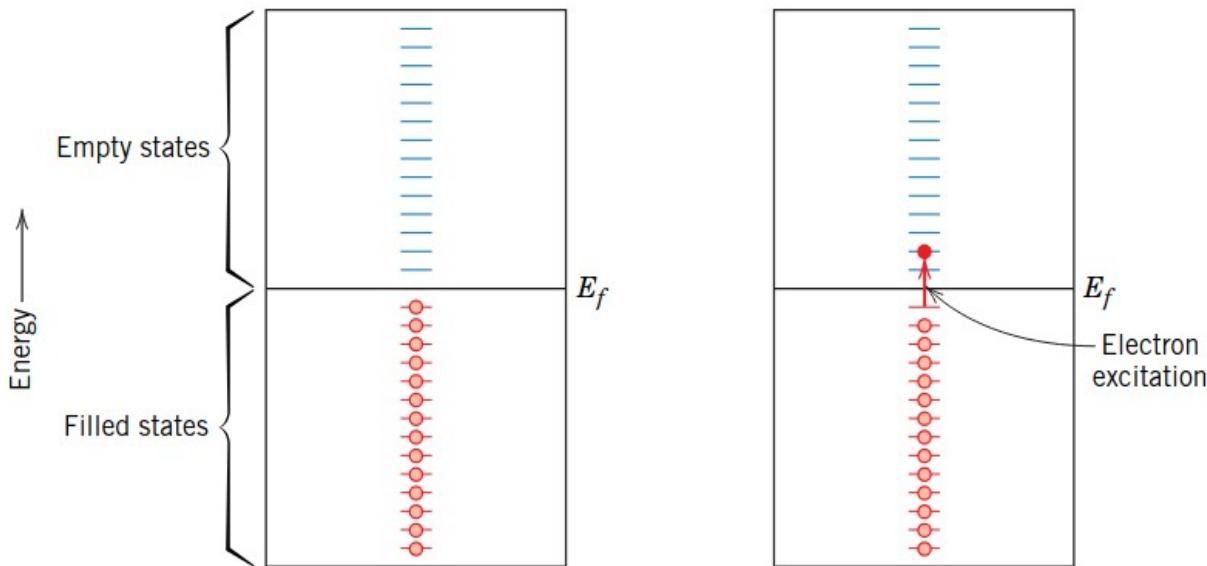
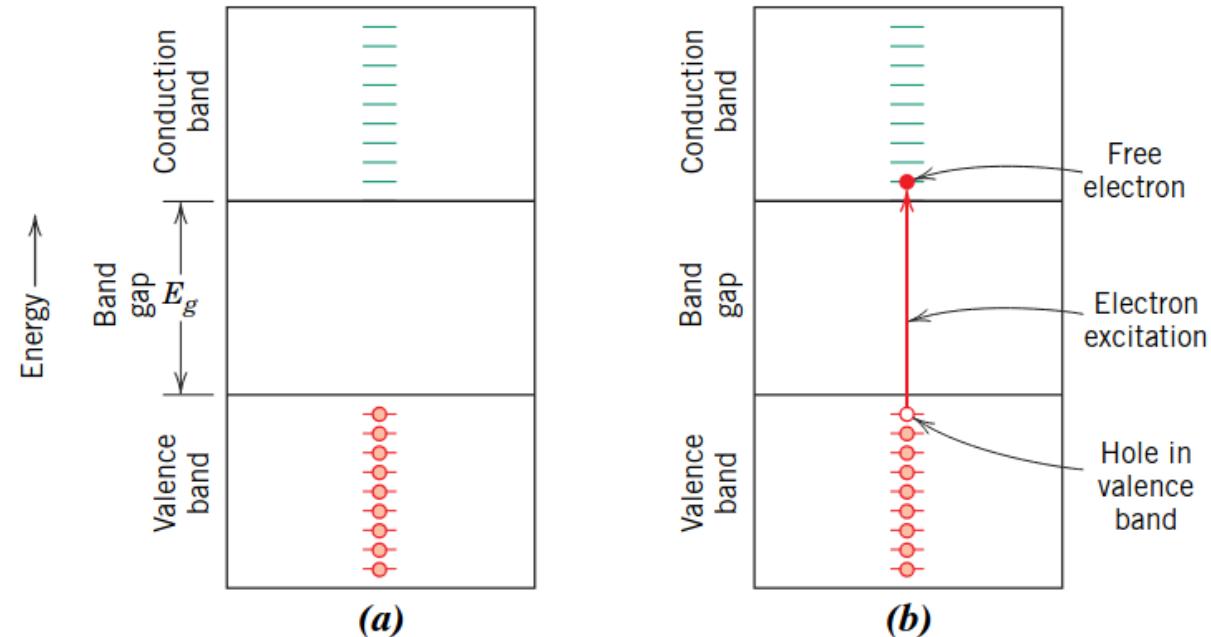


Figure 18.5 For a metal, occupancy of electron states (a) before and (b) after an electron excitation.

Heuristic origins of electrical conductivity

Figure 18.6 For an insulator or semiconductor, occupancy of electron states (a) before and (b) after an electron excitation from the valence band into the conduction band, in which both a free electron and a hole are generated.



Heuristic origins of optical absorption

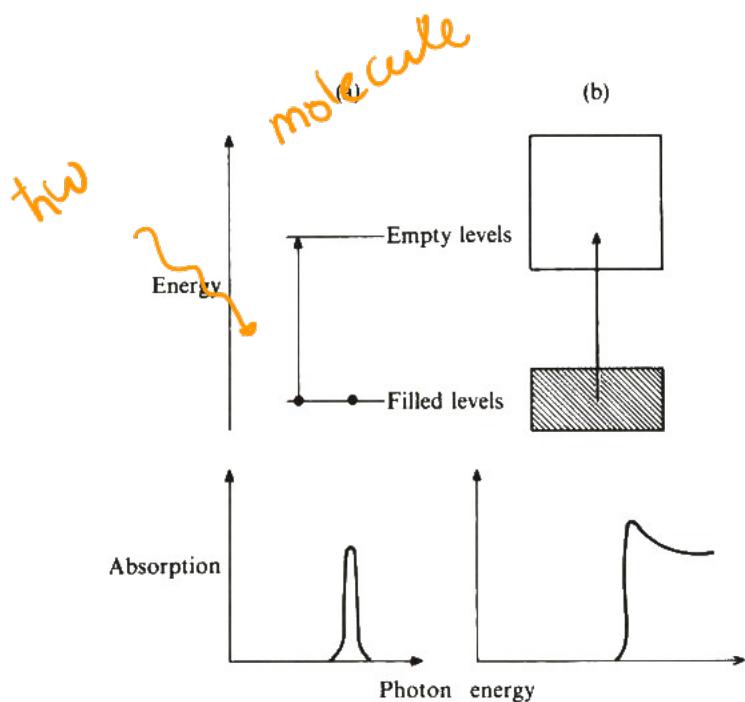
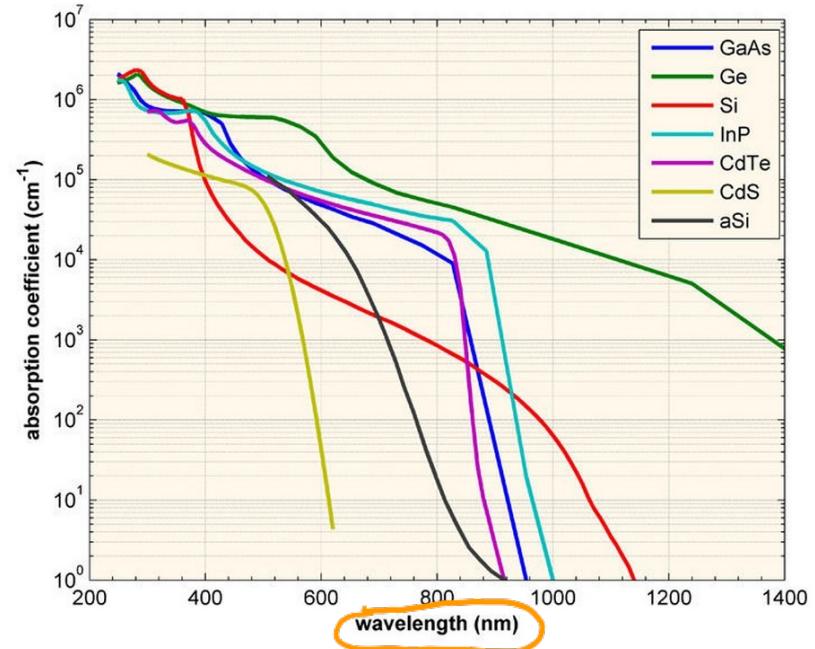


Fig. 1.9 Spectroscopic transition between the top filled and bottom empty levels in (a) an atom or molecule, and (b) a non-metallic solid.

Absorption spectrum of common solar PV materials



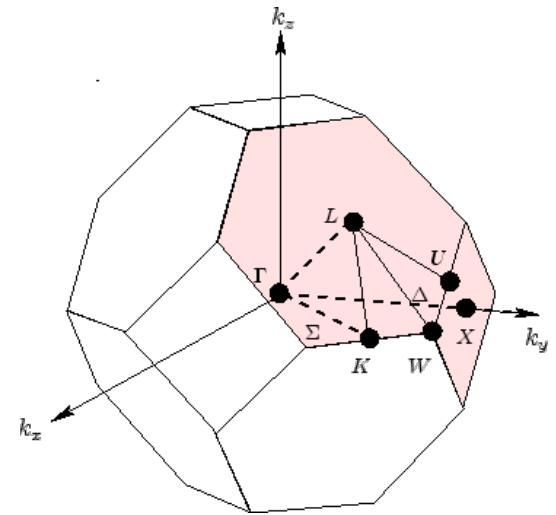
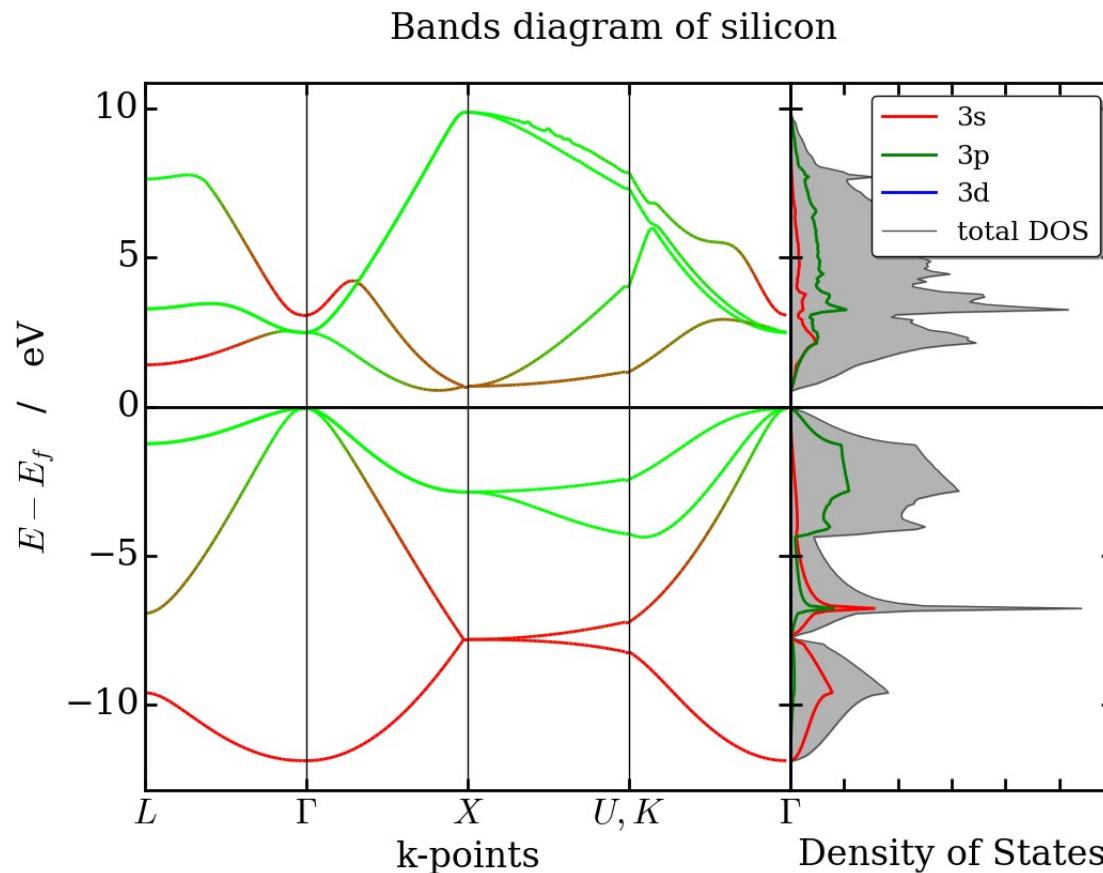
$$E = \hbar\omega = \frac{hc}{\lambda}$$

What is electronic structure?

Part 2: Introduction to electronic band structure (of solids)

 "spaghetti diagrams"

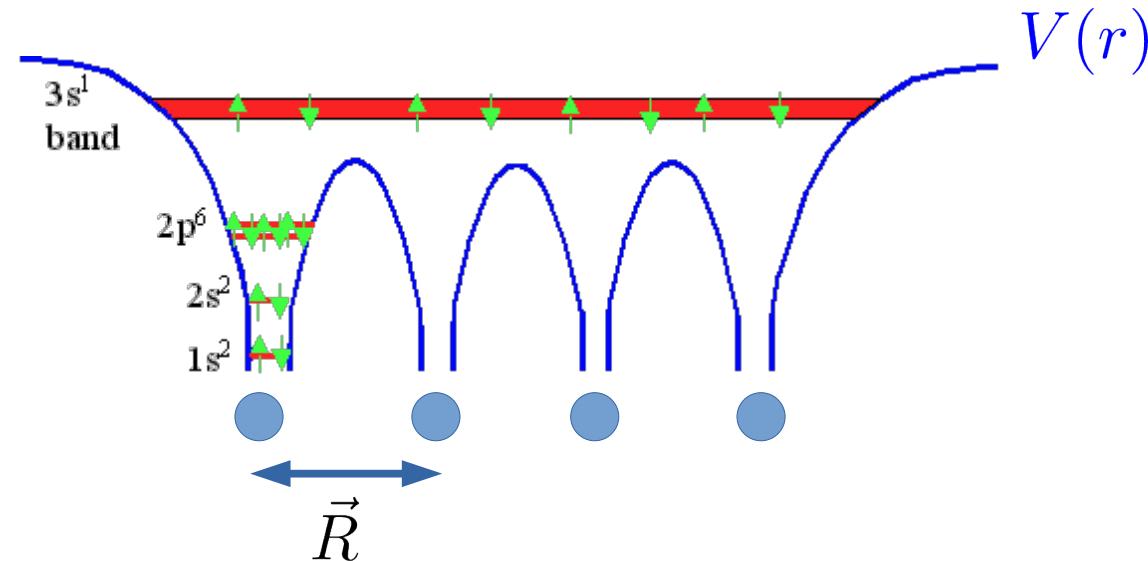
Example Electronic Band Structures



Crystallography: Bloch's Theorem

Electrons in crystalline solids exist in a **periodic potential**

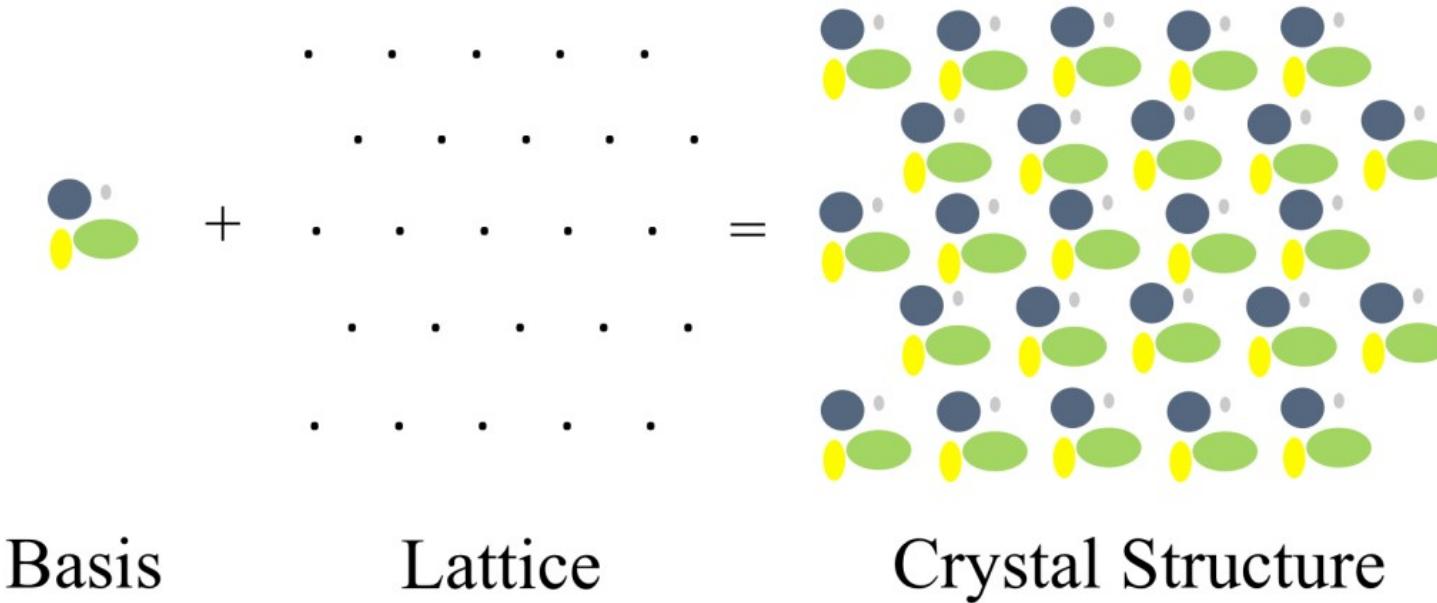
e.g., metallic Na



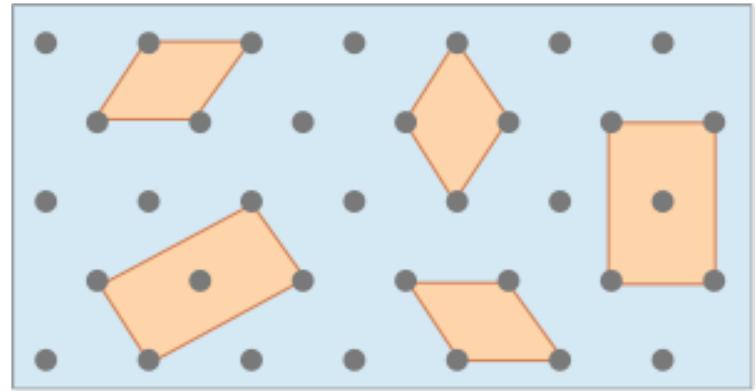
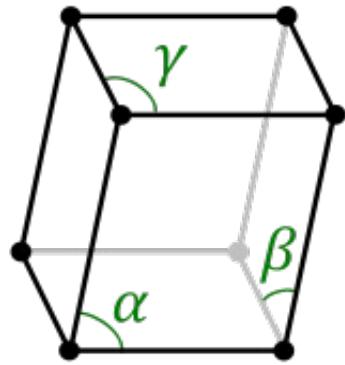
$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi = E \psi$$

$$V(\vec{r} + \vec{R}) = V(\vec{r})$$

Crystal Structure = Basis + Lattice



The Unit Cell



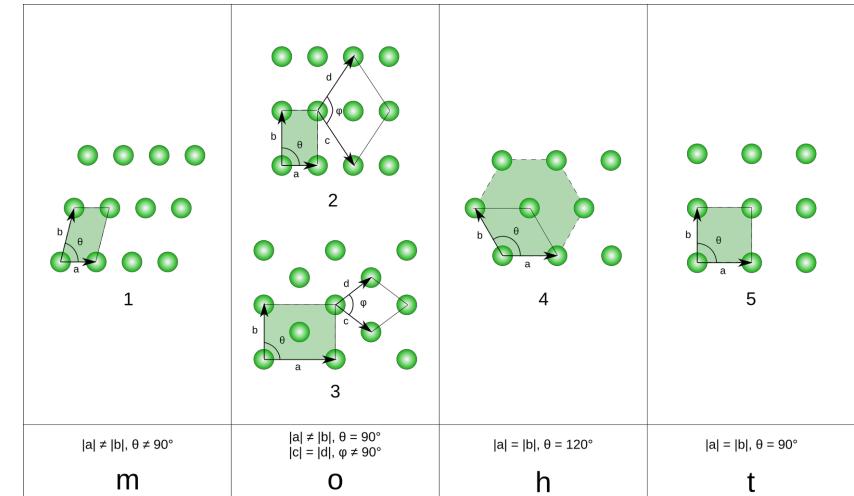
Primitive Unit Cell

Conventional Unit Cell

Bravais Lattice (in 3D)

Bravais lattice cells	Axes and interaxial angles	Examples
Cubic P Cubic I Cubic F	Three axes at right angles; all equal: $a = b = c; \alpha = \beta = \gamma = 90^\circ$	Copper (Cu), silver (Ag), sodium chloride (NaCl)
Tetragonal P Tetragonal I	Three axes at right angles; two equal: $a = b \neq c; \alpha = \beta = \gamma = 90^\circ$	White tin (Sn), rutile (TiO_2), β -spodumene ($\text{LiAlSi}_2\text{O}_6$)
P C I F Orthorhombic	Three axes at right angles; all unequal: $a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$	Gallium (Ga), perovskite (CaTiO_3)
Monoclinic P Monoclinic C	Three axes, one pair not at right angles, of any lengths: $a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
Triclinic P	Three axes not at right angles, of any lengths: $a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ$	Potassium chromate (K_2CrO_7)
Trigonal R (rhombohedral)	Rhombohedral: three axes equally inclined, not at right angles; all equal: $a = b = c; \alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO_3), arsenic (As), bismuth (Bi)
Trigonal and hexagonal C (or P)	Hexagonal: three equal axes coplanar at 120° , fourth axis at right angles to these: $a_1 = a_2 = a_3 \neq c; \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Zinc (Zn), cadmium (Cd), quartz (SiO_2) [P]

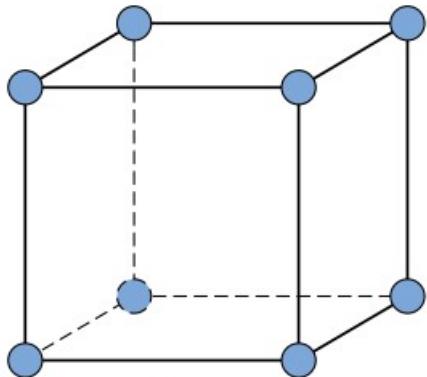
Bravais Lattice (in 2D)



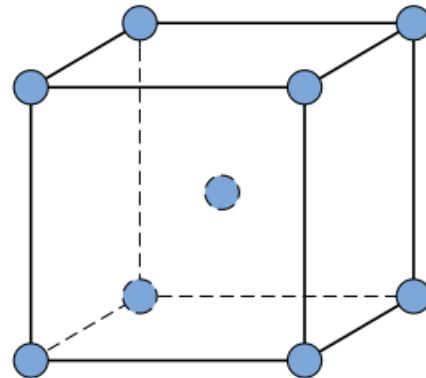
These assume single-atom basis

Cubic crystal structures (monoatomic)

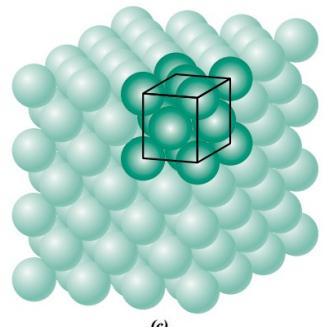
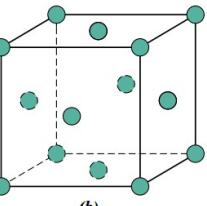
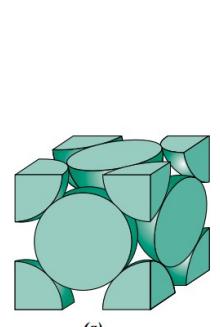
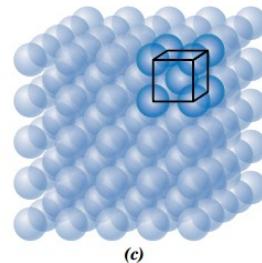
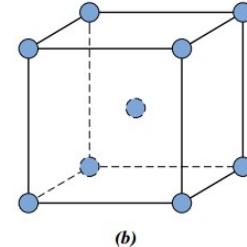
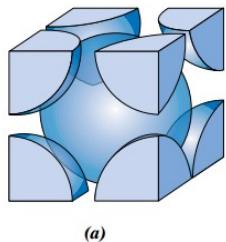
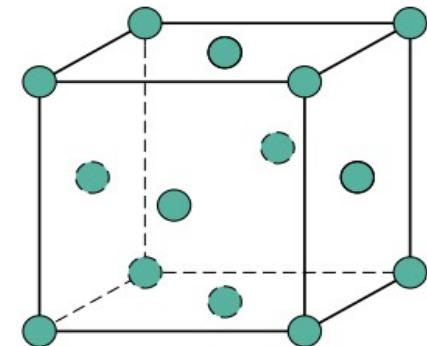
Simple Cubic



Body-Centered Cubic

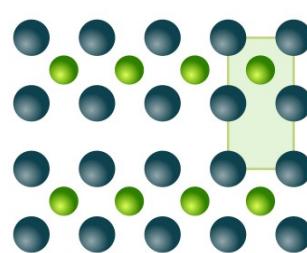
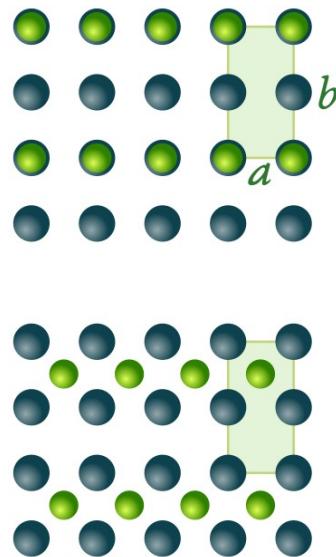
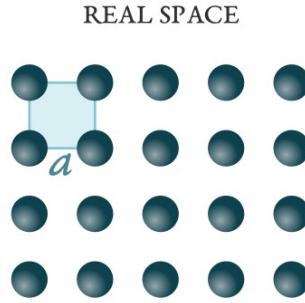


Face-Centered Cubic

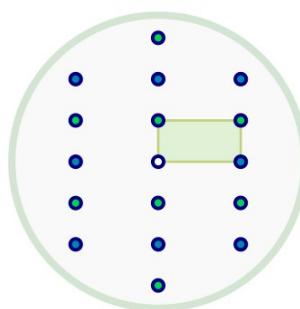
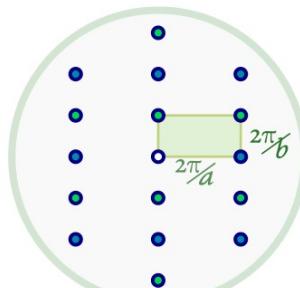
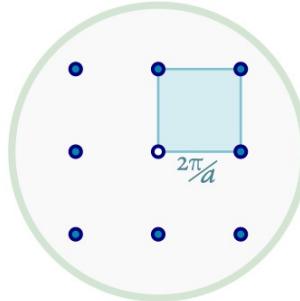


Crystallography: Reciprocal Space

XRD



RECIPROCAL SPACE - LEED



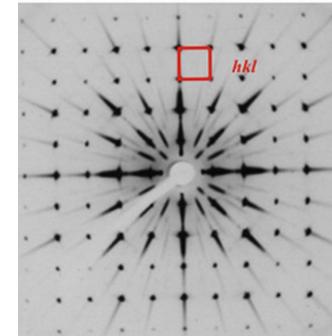
$$\mathbf{b}_1 = \frac{2\pi}{V} \mathbf{a}_2 \times \mathbf{a}_3$$

$$\mathbf{b}_2 = \frac{2\pi}{V} \mathbf{a}_3 \times \mathbf{a}_1$$

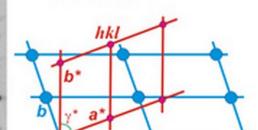
$$\mathbf{b}_3 = \frac{2\pi}{V} \mathbf{a}_1 \times \mathbf{a}_2$$

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$

Reciprocal space

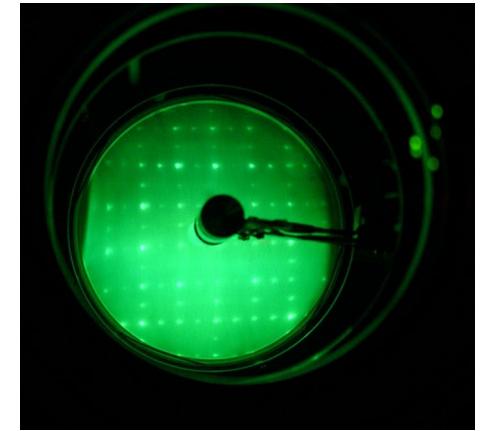


reciprocal cell
vs.
direct cell



direct cell
space group

LEED



A side note on space groups

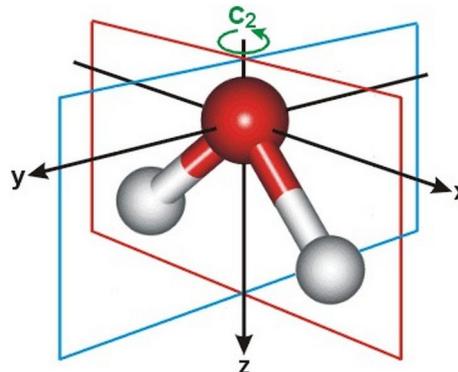
Neumann's principle:

'the symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal'.

Space group:

combination of crystallographic point groups + Bravais lattice
(230 combinations in 3D, if count chiral structures distinct)

Example: crystallographic point group of water molecule Common notation: Hermann-Mauguin or Schoeflies used



Looking up info on space space groups
e.g.,
<http://img.chem.ucl.ac.uk/sgp/medium/sgp.htm>

Crystallography: Bloch's Theorem

Electrons in crystalline solids exist in a **periodic potential**

Bloch's theorem gives a general form of the wavefunction in a periodic potential

Eigenfunctions/wavefunctions can have any periodicity but should adhere to the translational symmetry of the underlying crystal potential

Crystallography: Bloch's Theorem

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Bloch's theorem

Solutions to the Schrodinger equation in a periodic potential
can be expressed as a Bloch function

$$\psi(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \underline{u(\vec{r})} \quad \xrightarrow{\hspace{1cm}} \quad u(\vec{r} + \vec{R}) = u(\vec{r})$$

$$\psi(\vec{r} + \vec{R}) = e^{i\vec{k}(\vec{r} + \vec{R})} u(\vec{r} + \vec{R}) = u(\vec{r}) e^{i\vec{k}\vec{r}} e^{i\vec{k}\vec{R}} = \psi(\vec{r}) e^{i\vec{k}\vec{R}}$$

Periodic function
having same periodicity of the crystal

$$|\psi(\vec{r} + \vec{R})|^2 = \psi^*(\vec{r}) e^{-i\vec{k}\cdot\vec{R}} \psi(\vec{r}) e^{+i\vec{k}\cdot\vec{R}} = |\psi(\vec{r})|^2$$

phase factor

Crystallography: Bloch's Theorem

Electrons in crystalline solids exist in a **periodic potential**

Eigenfunctions/wavefunctions can have any periodicity but should adhere to the translational symmetry of the underlying crystal potential

We define a translation operator $\hat{T}_{\vec{R}} f(\vec{r}) = f(\vec{r} - \vec{R})$

If the potential V is periodic, then the Hamiltonian is periodic as well

$$\hat{H}\psi = E\psi$$

$$\hat{T}\hat{H}\psi = E\psi^{(0)}$$

$\hat{T}_{\vec{R}}$ → satisfies

$$\hat{T}_{\vec{R}} \hat{T}_{\vec{R}'} \psi = \hat{T}_{\vec{R}' - \vec{R}} \psi$$

$$\hat{T}_{\vec{R}}^{-1} = \hat{T}_{-\vec{R}}$$

$$\hat{T}_{\vec{R}}^+ = \hat{T}_{\vec{R}}^{-1}$$
 unitary → preserves length, distance

Crystallography: Bloch's Theorem

We define a translation operator $\hat{T}_{\vec{R}} f(\vec{r}) = f(\vec{r} - \vec{R})$

$$\hat{T}_{\vec{R}} \psi(\vec{r}) = \underbrace{c(\vec{R})}_{\text{---}} \psi(\vec{r})$$

↳ successive translations
inverse
unitary


$$c(\vec{R}) = e^{\frac{i\pi}{2} \vec{R} \cdot \vec{R}} = e^{i\vec{k} \cdot \vec{R}}$$
$$\vec{R} = n_1 \bar{a}_1 + n_2 \bar{a}_2 + n_3 \bar{a}_3$$
$$n_1, n_2, n_3 \in \mathbb{Z}$$

$$c(\vec{R}) = c(\bar{a}_1)^{n_1} c(\bar{a}_2)^{n_2} c(\bar{a}_3)^{n_3}$$

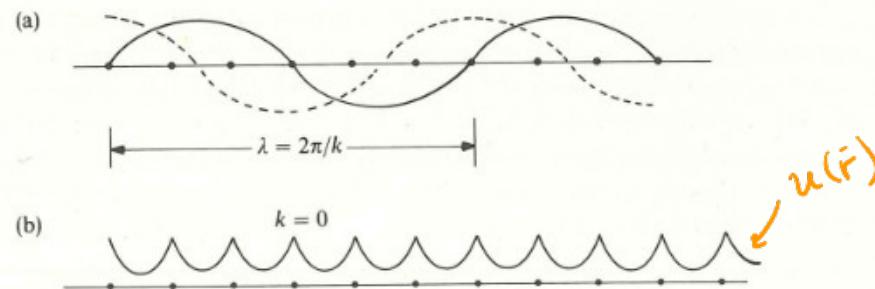
define $\bar{k} = x_1 \bar{b}_1 + x_2 \bar{b}_2 + x_3 \bar{b}_3$

reciprocal lattice vectors

$$\bar{b}_i \cdot \bar{a}_j = \delta_{ij} \cdot 2\pi \rightarrow \text{orthonormal up to a constant}$$

$$c(\vec{R}) = e^{i2\pi x_1 n_1} e^{i2\pi x_2 n_2} e^{i2\pi x_3 n_3} \Rightarrow \boxed{e^{i\vec{k} \cdot \vec{R}}}$$

Crystallography: Bloch's Theorem-Interpretation



$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \underbrace{u(\vec{r})}_{}$$

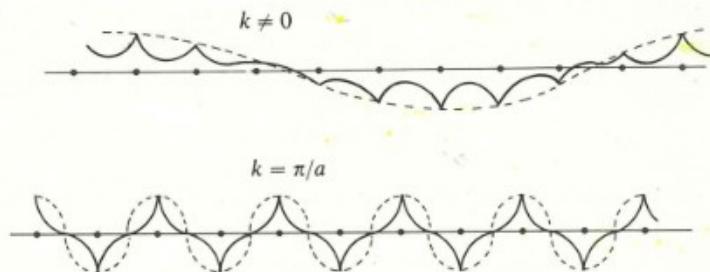
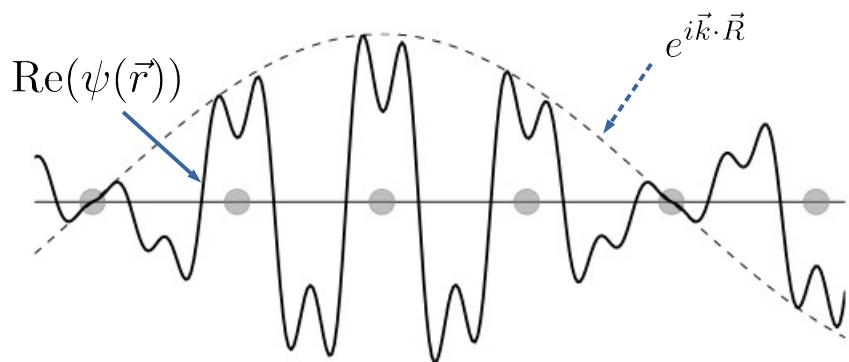


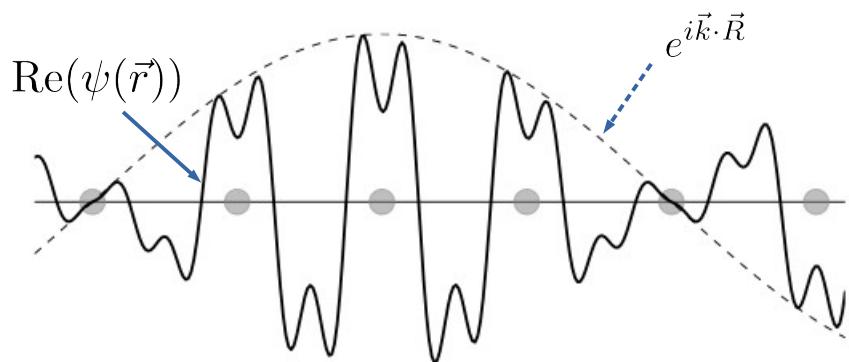
Fig. 4.2 Wave functions for electrons along a chain. (a) Real (—) and imaginary (---) parts of a free-electron wave function. (b) Bloch functions with different k values, formed from overlapping atomic orbitals. Only the real part of the wave function is shown.

Crystallography: Bloch's Theorem-Interpretation



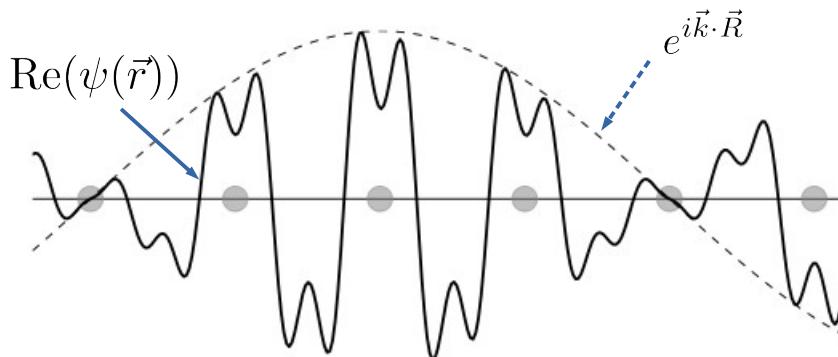
Every solution to the Schrodinger equation in a periodic potential is a plane wave times some function with the periodicity of the lattice

Crystallography: Bloch's Theorem-Interpretation



Every solution to the Schrodinger equation in a periodic potential is a plane wave times some function with the periodicity of the lattice

Crystallography: Bloch's Theorem-Interpretation



Every solution to the Schrodinger equation in a periodic potential is a plane wave times some function with the periodicity of the lattice

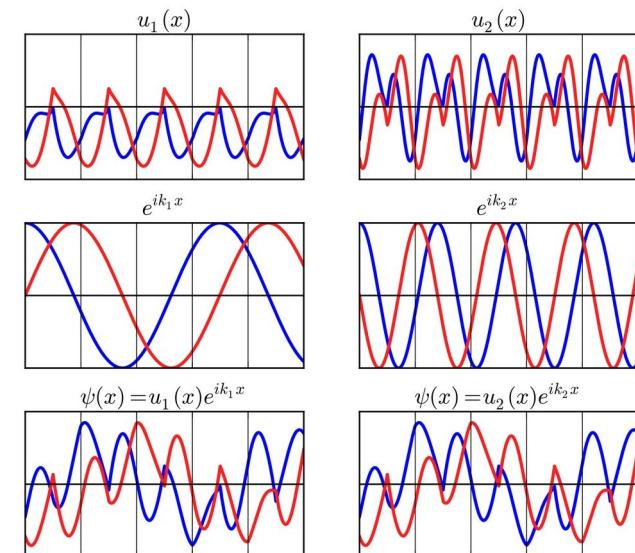
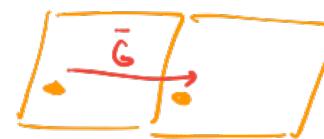
The k vectors are not unique

k_1 and k_2 can differ by a reciprocal wave vector G

$$\vec{k}_1 = \vec{k}_2 + \vec{G}$$

$$\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}+\vec{G}}(\vec{r})$$

$$\varepsilon_{\vec{k}} = \varepsilon_{\vec{k}+\vec{G}}$$

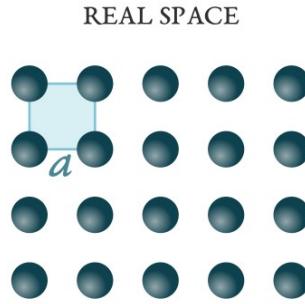


Because the k vectors differ by a vector G , then we can find the set of all non-equivalent k vectors
We also use each non-equivalent k vector to index each non-equivalent ψ

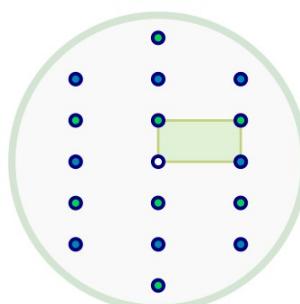
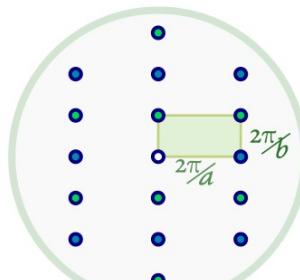
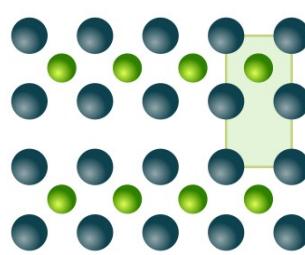
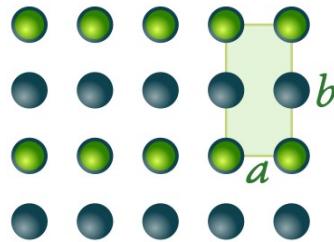
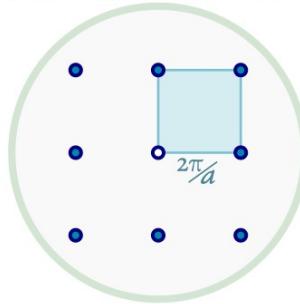
Re(ψ)
Im(ψ)

Crystallography: Reciprocal Space

XRD



RECIPROCAL SPACE - LEED

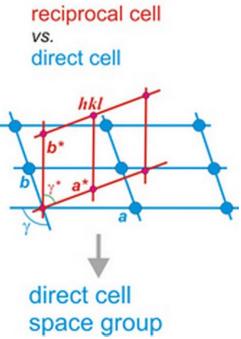
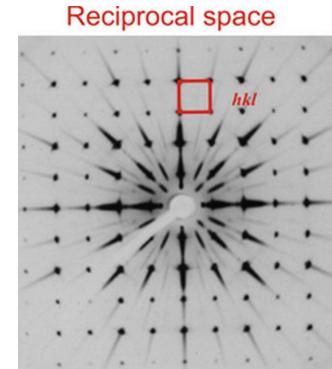


$$\mathbf{b}_1 = \frac{2\pi}{V} \mathbf{a}_2 \times \mathbf{a}_3$$

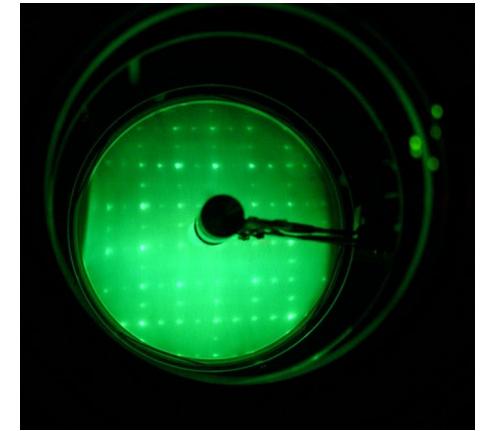
$$\mathbf{b}_2 = \frac{2\pi}{V} \mathbf{a}_3 \times \mathbf{a}_1$$

$$\mathbf{b}_3 = \frac{2\pi}{V} \mathbf{a}_1 \times \mathbf{a}_2$$

→ $\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$



LEED



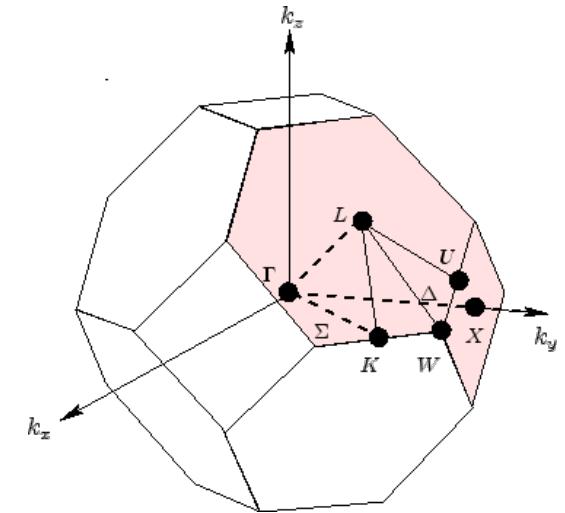
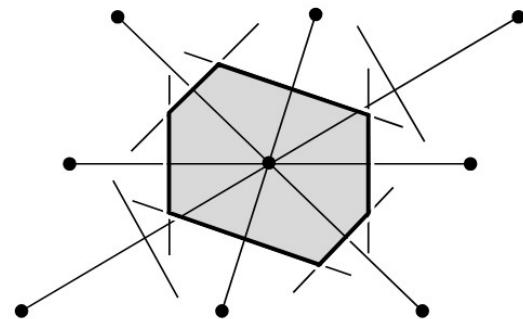
Crystallography: Brillouin Zone

Wigner-Seitz cell of reciprocal lattice = first Brillouin zone

The first Brillouin Zone (BZ) defines the space containing all non-equivalent k vectors

The shape of the BZ depends on the symmetry of the crystal (i.e., space group, Bravais lattice)

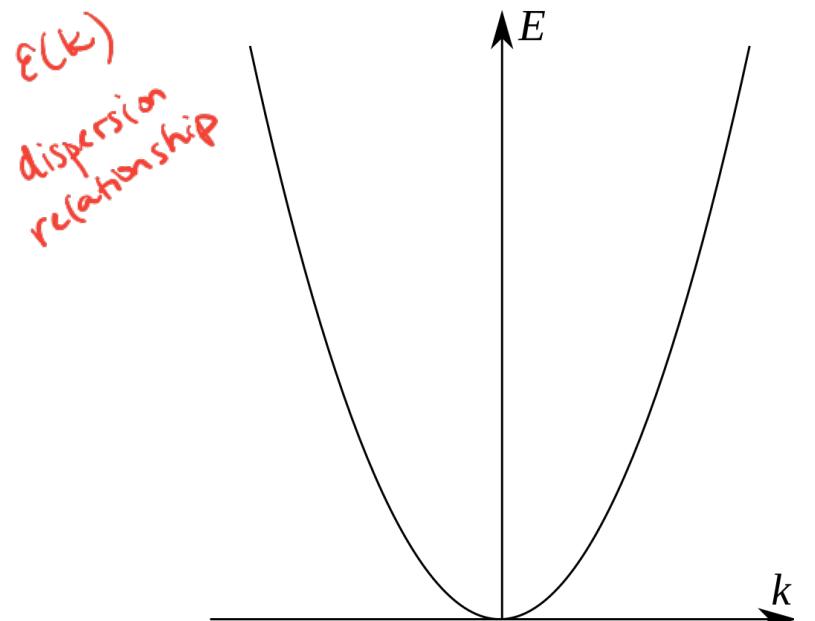
Figure 4 A primitive cell may also be chosen following this procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All space may be filled by these cells, just as by the cells of Fig. 3.



Reciprocal Wigner-Seitz cell of FCC lattice,
aka first Brillouin Zone

Dispersion relation $E(k)$ for Free-electron model (1D)

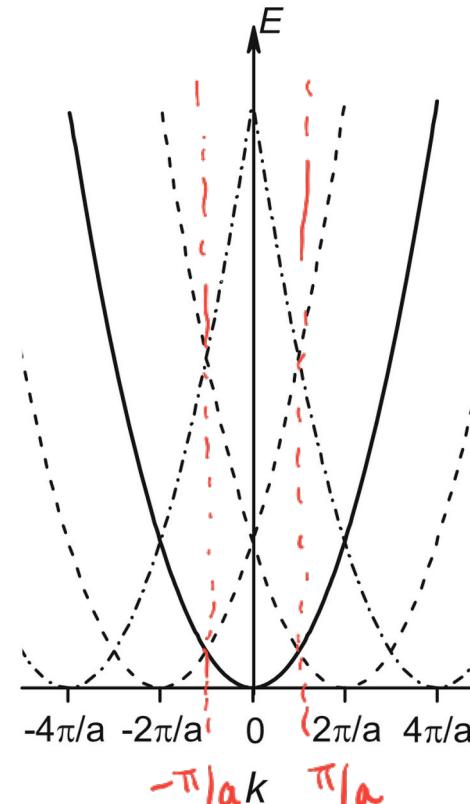
Free electron
(non-periodic potential)



$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x)$$

$$E = \frac{\hbar^2 k^2}{2m}$$

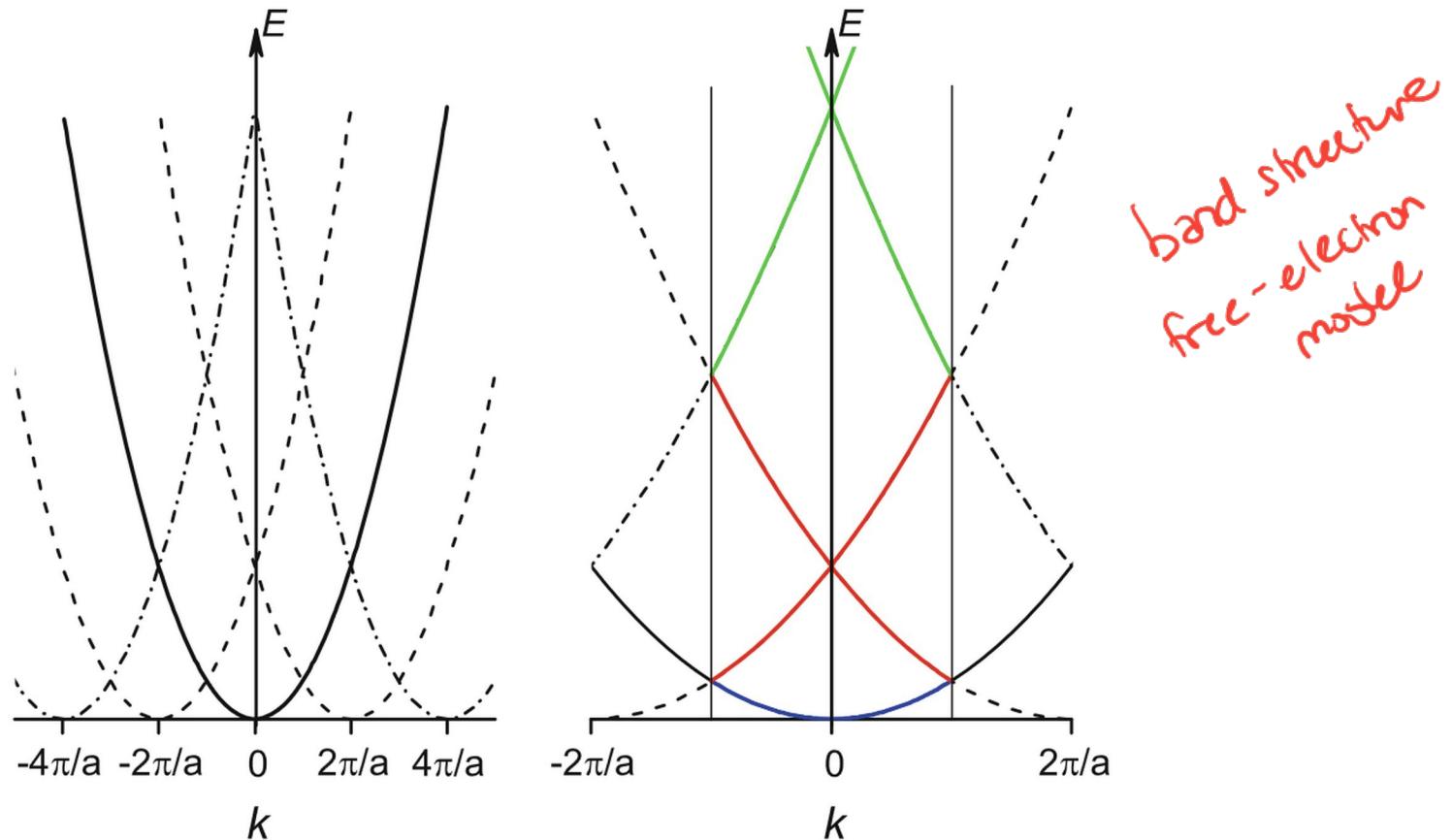
Free electron
(periodic potential)



Dispersion relation $E(k)$ for Free-electron model (1D)

First Brillouin Zone and band folding

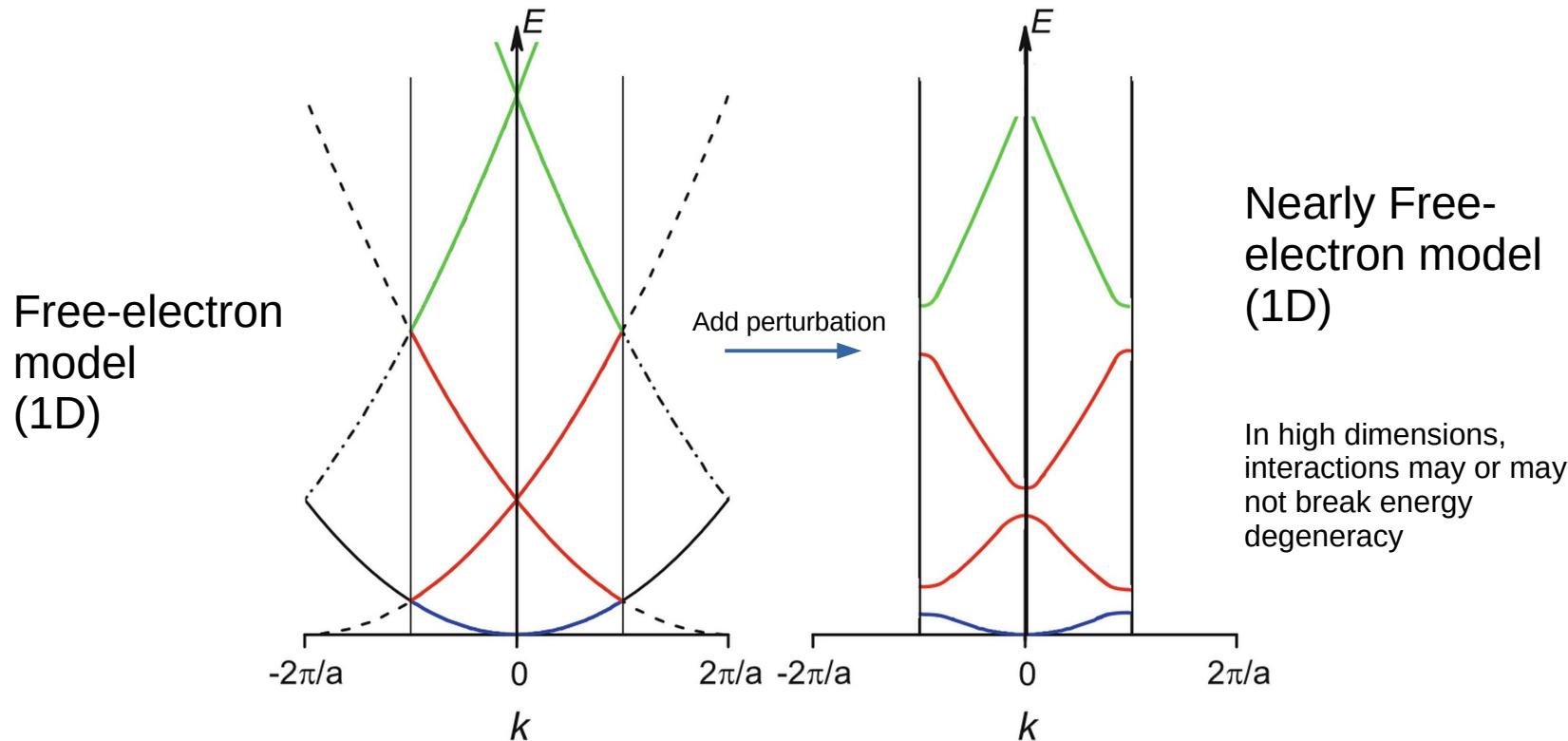
Energetically degenerate states
at BZ edge $(-\pi/a, +\pi/a)$



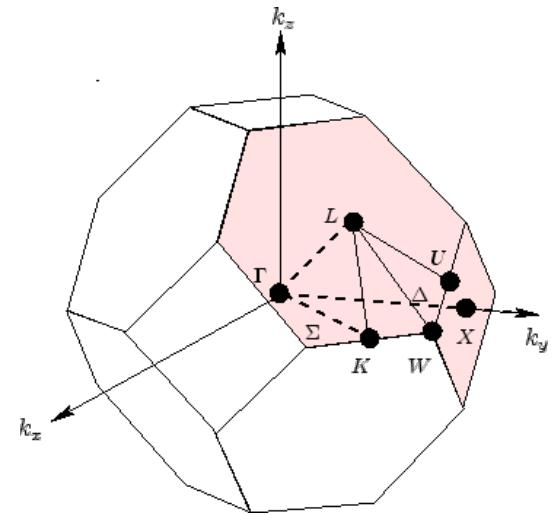
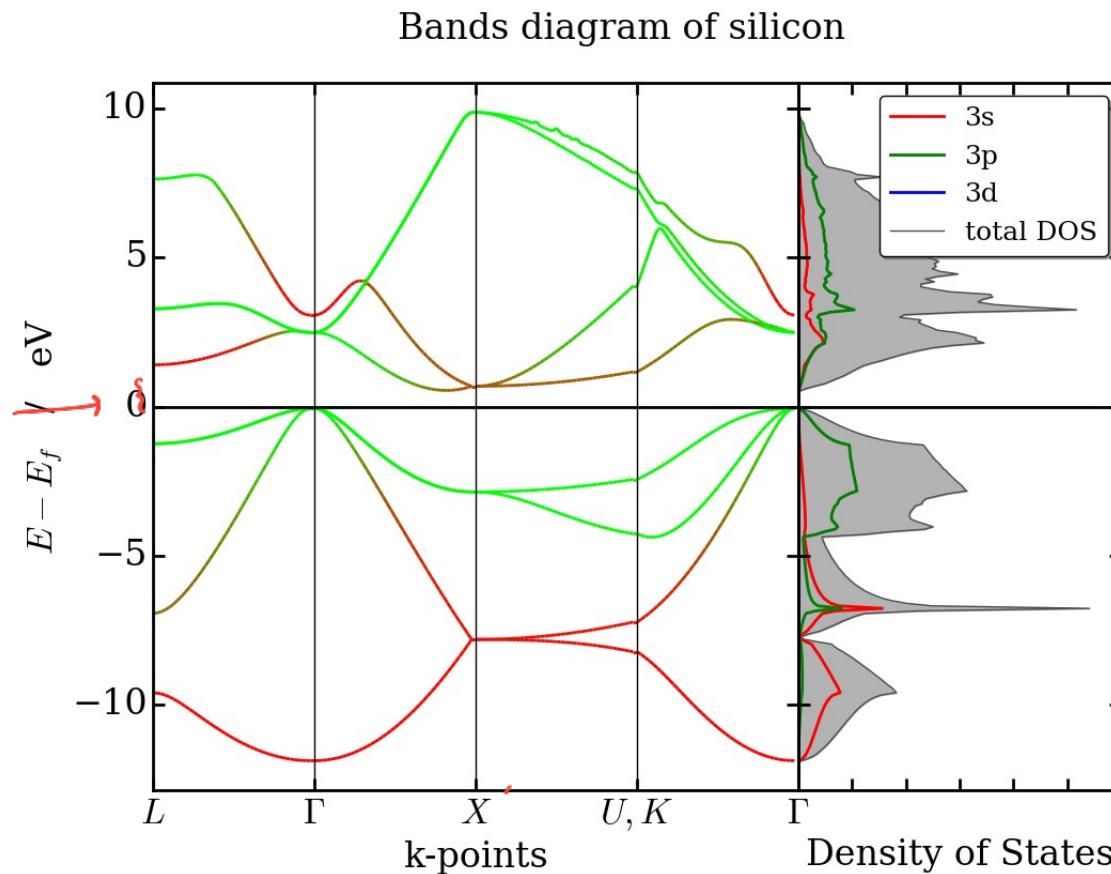
Dispersion relation for *nearly* free-electron model

Add a weak, perturbative potential → break energetic degeneracies at BZ edge
→ energy band gap

A simple model that introduces electron band structure in *solids*



Example Electronic Band Structures



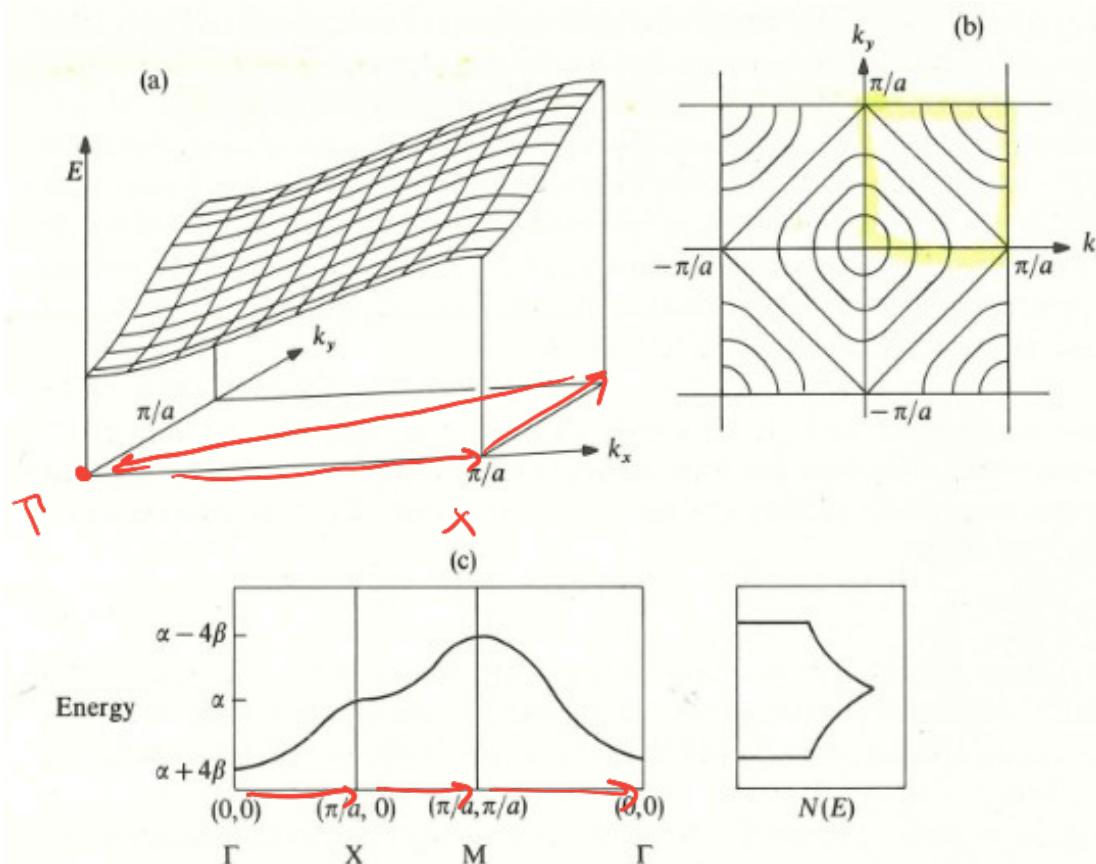
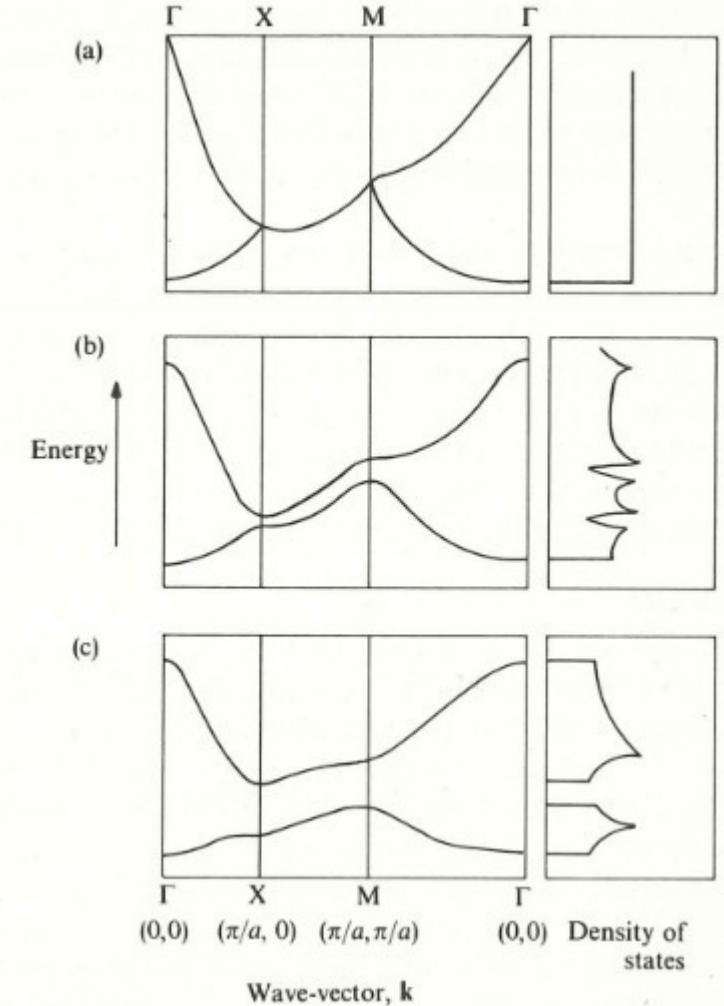
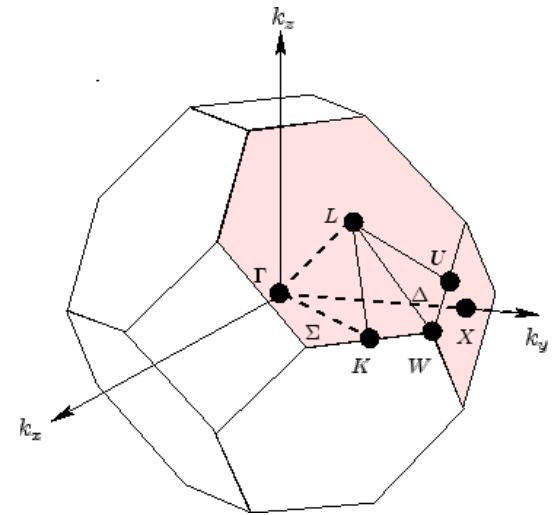
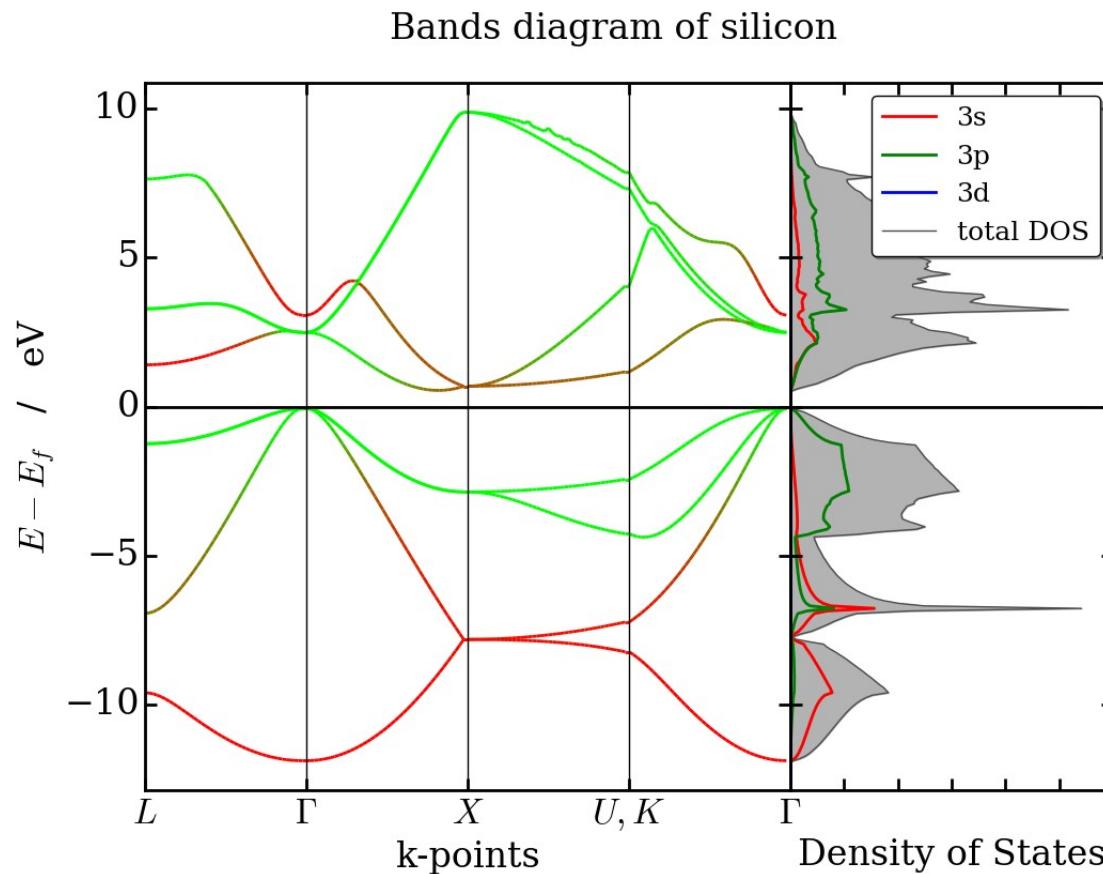


Fig. 4.19 Three representations of $E(\mathbf{k})$ for the s band. (a) Energy surface for one-quarter of the Brillouin zone. (b) Constant-energy contours, illustrating the symmetry of the zone. (c) Energy plotted over a triangular path of \mathbf{k} values, showing minimum and maximum energies, and density of states.



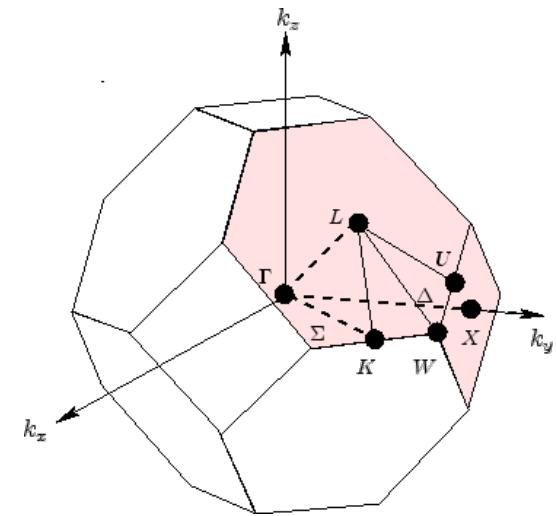
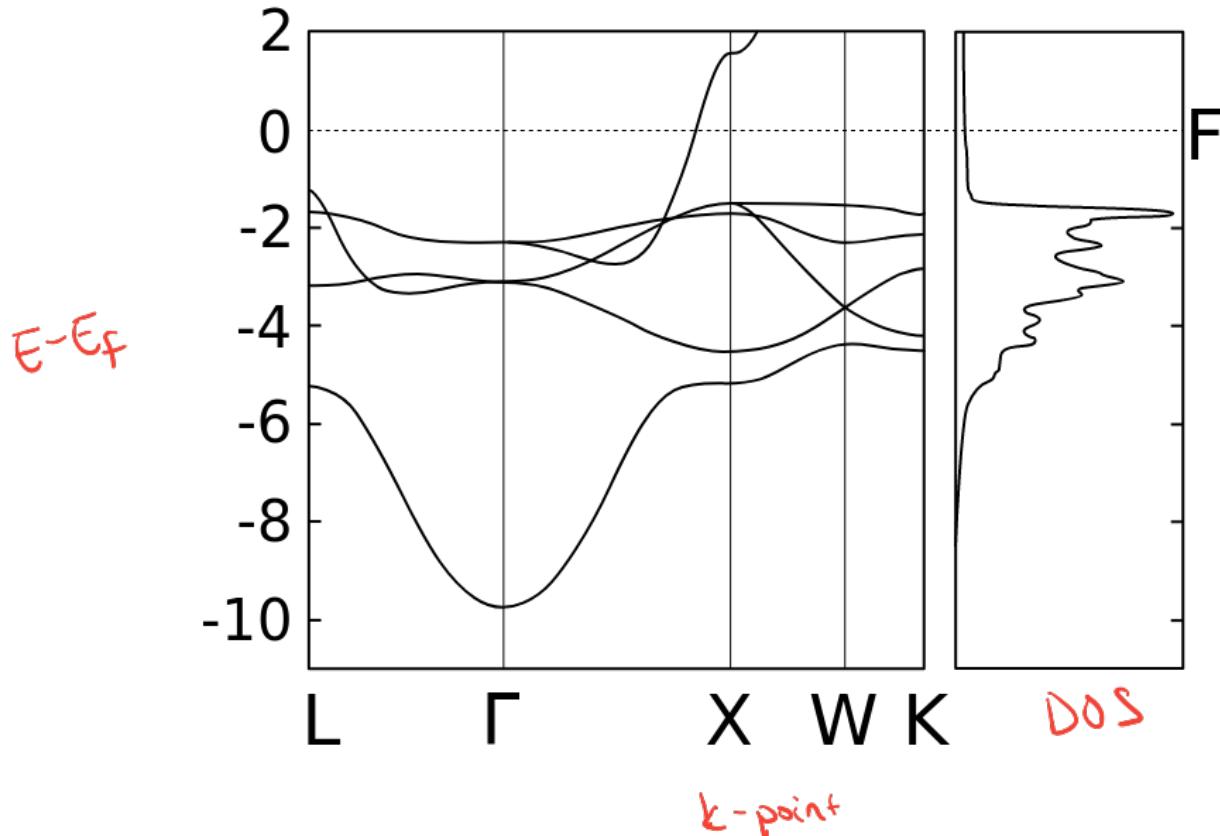
Band structures and density of states of nearly-free electron model, with increasing strengths of a periodic potential;
 (a) zero, (b) weak, (c) strong

Example Electronic Band Structures



Example Electronic Band Structures

FCC Copper



Example Electronic Band Structures

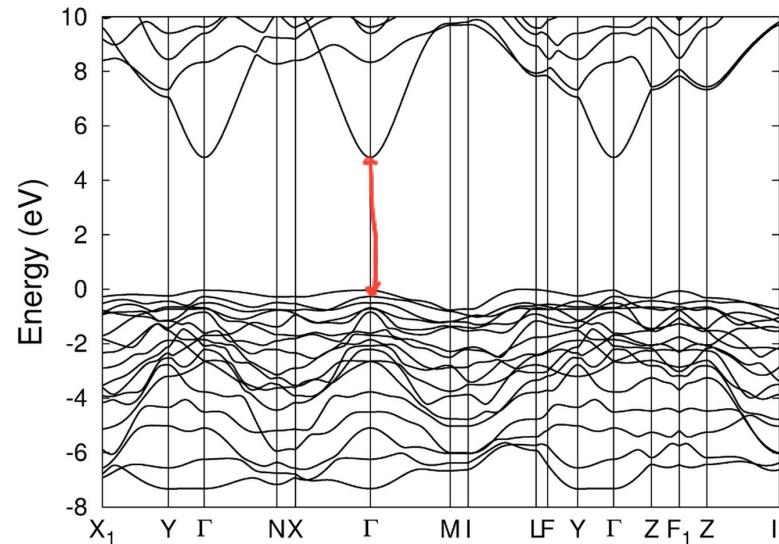
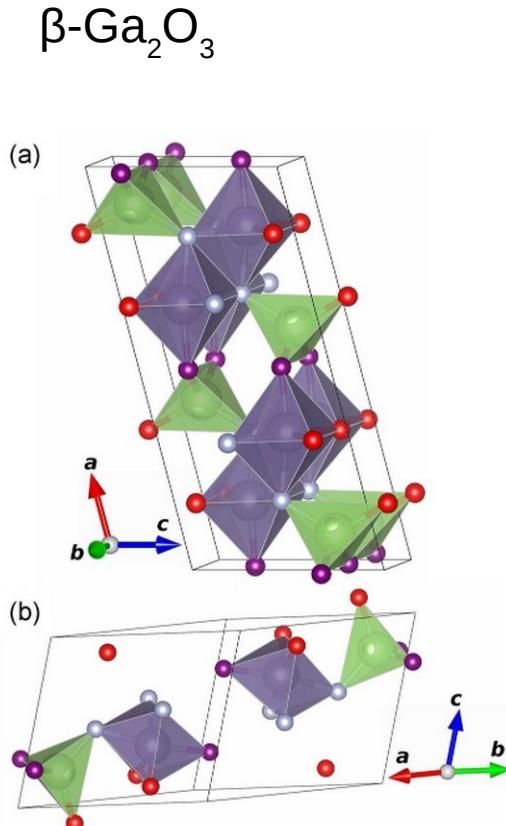


Figure 3 Band structure of $\beta\text{-Ga}_2\text{O}_3$ along a continuous path in the Brillouin zone. High-symmetry points are labeled according to Fig. 2, with coordinates in Table 2. The zero of energy is set at the valence-band maximum, which is on the I - L line.

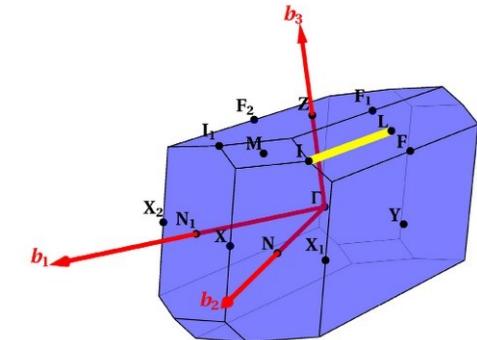


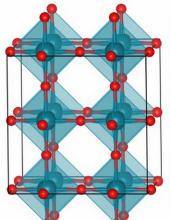
Figure 2 The Brillouin zone corresponding to the relaxed monoclinic $\beta\text{-Ga}_2\text{O}_3$. Labels indicate high-symmetry points. The axes of the reciprocal unit cell are also shown. The I - L line is indicated by a (yellow) line.

Indirect $E_g = 4.84$ eV

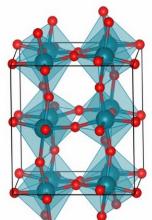
Direct $E_g = 4.88$ eV

Things you can compute using the electronic structure

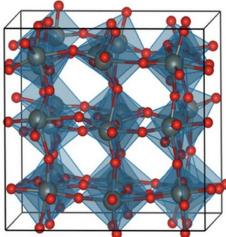
Optical Properties



cubic



monoclinic



amorphous

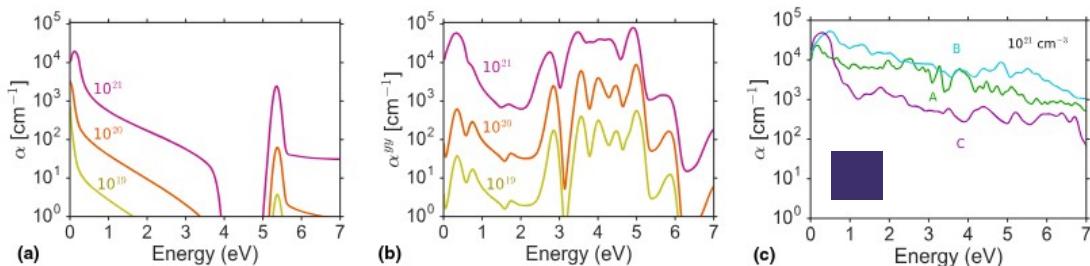
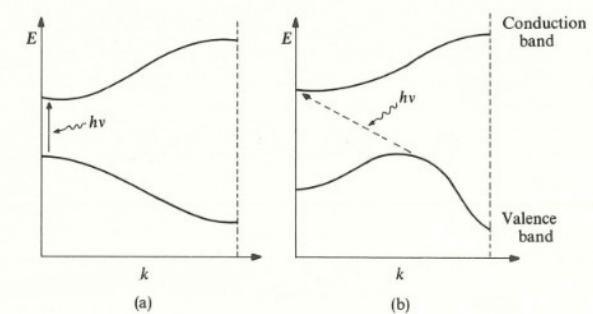


Figure 3. Absorption coefficient (on a logarithmic scale) for CB → CB transitions for (a) the cubic, (b) the monoclinic phase, and (c) for three disordered structures of WO_3 . For the cubic and monoclinic phases, results are shown for three doping levels (10^{19} , 10^{20} , and 10^{21} cm^{-3}); for the disordered phase, the doping level is 10^{21} cm^{-3} .

Designing solar cells



Direct v Indirect Band gaps

Indirect optical transitions weak compared to direct optical transitions

Silicon has an indirect band gap.
→ thicker active layer needed to absorb enough sunlight

Things you can compute using the electronic structure

Transport Properties

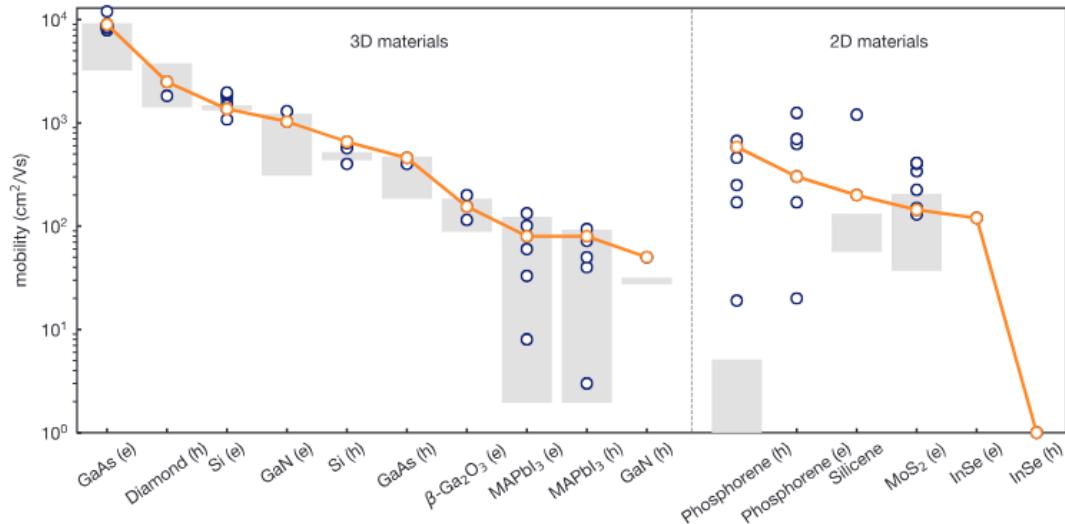


Figure 19. Range of measured electron (e) and hole (h) mobilities at room temperature (shaded region), and calculated values (blue dots). The results highlighted in orange can be considered to be the most accurate calculations reported so far. Materials are sorted with the mobility decreasing towards the right hand side: electron mobility of GaAs, theory [16, 125, 126, 186, 187, 189, 189] and experiments [188, 189, 193]; hole mobility of diamond, theory [69, 169] and experiments [165, 167, 168, 174, 175, 355]; electron mobility of silicon, theory [60, 62, 84, 84, 94, 126, 127] and experiments [32, 152–154]; electron mobility of w-GaN, theory [186, 200] and experiments [201, 210, 356, 357]; hole mobility of silicon, theory [60, 84, 84, 126] and experiments [152–155]; hole mobility of GaAs, theory [126, 185] and experiments [182, 192–194, 196–198]; electron mobility of β -Ga₂O₃, theory [223–225] and experiments [221, 227]; electron mobility of MAPbI₃, theory [234] and experiments [228–233, 358]; hole mobility of MAPbI₃, theory [234] and experiments [228–233, 358]; hole mobility of w-GaN, theory [200] and experiments [211, 359]; hole mobility of phosphorene, theory [89, 303–305, 307, 308] and experiments [299]; electron mobility of phosphorene, theory [89, 303–306, 308]; electron mobility of silicene, theory [105, 291] and experiments [289]; electron mobility of MoS₂, theory [62, 89, 105, 272, 280, 291, 321] and experiments [316–318, 320]; electron mobility of InSe, theory [332] and experiments [332].

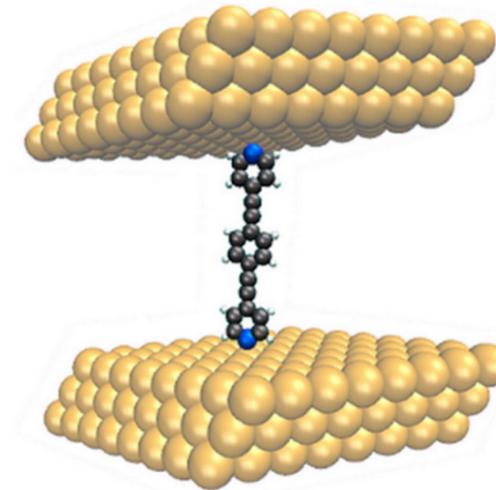


Figure 5. Structural model employed in first-principles calculations of charge transport in 1,2-bis(2-phenylethynyl)benzene bonded to Au electrodes. Different anchoring groups including pyridine, thiolate, and isocyanide have been studied. Reproduced from [107]. CC BY 3.0.

* requires the use of localized basis sets to be computationally feasible

Variational Principle

For an arbitrary (and realistic) potential, how do we solve the Schrodinger equation (i.e., solve for the ground state)?

1) Use WKB theory:

obtain approximate solutions in 1D; particularly useful for computing bound states and tunneling rates through potential barriers- used in semiconductor physics community

2) Use perturbation theory:

use known solutions of simpler Hamiltonians such as hydrogen atom or harmonic oscillator to generate solutions for more complex potentials

3) (After some assumptions and simplifications,) Expand wavefunction onto a ‘reasonable’ basis and solve self-consistently

→ Variational principle

Matrix formalism of QM

To implement QM in a computer, need to discretize the problem into a numerical solution

Functional form $\hat{H}\psi = E\psi$

Vector/matrix form $\hat{H}|\psi\rangle = E|\psi\rangle$

Expand a wavefunction as a linear combination of basis vectors

$$|\psi\rangle = \sum_{n=1,\dots,k} c_n |\phi_n\rangle \quad \{|\phi_n\rangle\} \text{ k orthogonal basis functions}$$

$$= c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + \dots$$

e.g., plane waves, Gaussian functions

$$\langle \phi_m | \hat{H} | \psi \rangle = E \langle \phi_m | \psi \rangle$$

$$= E \sum_{n=1,\dots,k} c_n \langle \phi_m | \phi_n \rangle$$

$$= E c_m$$

Variational Principle

$$\psi = \sum_n c_n \phi_n \quad \langle \phi_n | \phi_m \rangle = \delta_{nm} \quad \xrightarrow{\text{orthonormality}} \sum_n |c_n|^2 = 1$$

$$E[\psi] = \langle \psi | H | \psi \rangle = \left\langle \sum_n c_n \phi_n \middle| H \middle| \sum_m c_m \phi_m \right\rangle \geq E_0$$

$$= \sum_{n,m} \langle c_n \phi_n | H | c_m \phi_m \rangle \quad \begin{matrix} \uparrow \\ \text{iff guessed} \end{matrix}$$

$$= \sum_{n,m} \langle c_n \phi_n | E_m | c_m \phi_m \rangle \quad \begin{matrix} \uparrow \\ \text{exact } \psi_0 \end{matrix}$$

$$= \sum_{n,m} c_n^* c_m E_m \underbrace{\langle \phi_n | \phi_m \rangle}_{\delta_{nm}}$$

$$= \sum_n |c_n|^2 E_n$$

$$= |c_0|^2 E_0 + \underbrace{(E_n - E_0) \sum_{n>0} |c_n|^2}_{> 0 \text{ for } n > 0}$$

Matrix formalism of QM

To implement QM in a computer, need to discretize the problem into a numerical solution

Matrix elements

$$\sum_{n=1,\dots,k} c_n \langle \phi_m | \hat{H} | \phi_n \rangle = E c_m$$

H_{mn}

Recast Hamiltonian operator as a matrix

$$\begin{pmatrix} H_{11} & \dots & H_{1k} \\ \vdots & & \vdots \\ H_{k1} & \dots & H_{kk} \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_k \end{pmatrix} = E \begin{pmatrix} c_1 \\ \vdots \\ c_k \end{pmatrix}$$

Hamiltonian operator
is Hermitian
 $(H^*)^T = H$

Diagonalize to determine the eigenvalue and corresponding eigenvector

Basis sets: in Quantum Chemistry

Quantum Chemistry often uses localized basis sets

e.g., Linear Combination of Atomic Orbitals (LCAO)

$$\psi = \sum_k c_k \chi_k$$

c_k Molecular orbital coefficients

Atom-centered basis functions
that mimic those of H atom

Determine coefficients c_k through a numerical procedure

Solving the Schrodinger equation becomes a linear algebra diagonalization problem

Basis sets: in Quantum Chemistry

Quantum Chemistry often uses localized basis sets

e.g., “Slater type” orbitals (STO): use exact form of radial part for H atom

$$R(r) = \underline{N} r^{n-1} e^{-\zeta r}$$

Normalizing constant Constant, effective charge of nucleus

Natural number
Stand-in for principle quantum number

A common variant is the double-zeta basis set:
use two STO to describe charge that is near and far from nucleus

$$R_{2s}(r) = C_1 r e^{-\zeta_1 r} + C_2 r e^{-\zeta_2 r}$$

Slater type orbitals are accurate but not frequently used
because multi-centered integrals are difficult to compute

Basis sets: in Quantum Chemistry

Gaussian Type Orbitals (GTO)

$$G_{nlm}(r, \theta, \phi) = N_n \underbrace{r^{n-1} e^{-\alpha r^2}}_{\text{radial part}} \overbrace{Y_l^m(\theta, \phi)}^{\text{angular part}}$$

GAUSSIAN

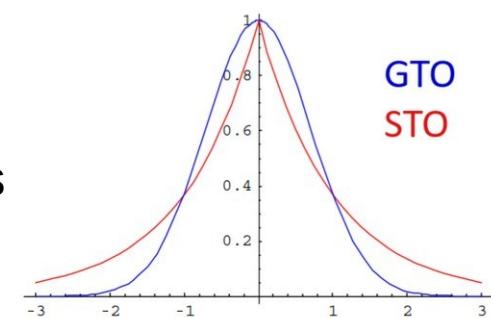
Gaussian functions are used due to the ease of evaluating multi-centered integrals
(product of two Gaussians is a shifted Gaussian)

However, Gaussians approximate atomic orbitals inexactly

To compensate for this, replace each STO with a set of Gaussians

Table 11.2.1: Different Gaussian Basis sets

Basis set	# functions	Basis set	# functions	Basis set	# functions
STO-3G	5	6-31G	9	6-311G	13
3-21G	9	6-31G*	15	6-311G*	18*
4-31G	9	6-31+G*	19	6-311+G*	22*



GTO
STO

N-MPG*

N = # Gaussian primitives (inner shell)
M = # Gaussian primitives (inner valence shell)
P = # Gaussian primitives (outer valence shell)
* = polarization functions included

Basis sets: in Quantum Chemistry

Gaussian Type Orbitals (GTO)

Many basis sets have been made for various elements
An open library of basis sets is available:
<https://www.basissetexchange.org/>

Basis Set Exchange Download GitHub Feedback About Help Request a Basis set

All roles All Total found: 712 basis sets Select All Reset Selection

1 H	2 He																		
3 Li	4 Be																		
5 Na	6 Mg																		
7 K	8 Ca	9 Sc	10 Ti	11 V	12 Cr	13 Mn	14 Fe	15 Co	16 Ni	17 Cu	18 Zn	19 Ga	20 Ge	21 As	22 Sb	23 Te	24 I	25 Br	26 Kr
27 Rb	28 Sr	29 Y	30 Zr	31 Nb	32 Mo	33 Tc	34 Ru	35 Rh	36 Pd	37 Ag	38 Cd	39 In	40 Sn	41 Sb	42 Te	43 I	44 Xe	45 At	46 Ra
47 Cs	48 Ba	49 Hf	50 Ta	51 W	52 Re	53 Os	54 Ir	55 Pt	56 Au	57 Hg	58 Tl	59 Pb	60 Bi	61 Po	62 At	63 Rn	64 Fr	65 Ra	
66 La	67 Ce	68 Pr	69 Nd	70 Pm	71 Eu	72 Gd	73 Tb	74 Dy	75 Ho	76 Er	77 Tm	78 Yb	79 Lu	80	81	82	83	84	
85 Ac	86 Th	87 Pa	88 U	89 Np	90 Pu	91 Am	92 Cm	93 Bk	94 Cf	95 Es	96 Fm	97 Md	98 No	99 Lr	100	101	102	103	

search basis sets...

References for selected basis

Plain Text Get References

Selected Basis Set: (none)

Description: Basis Set Notes Family Notes

Latest Version: Function Types:

Last Update: Basis Set Notes Family Notes

Role: Function Types:

Family: Basis Set Notes Family Notes

Download basis set

Format NWChem Advanced Get Basis Set

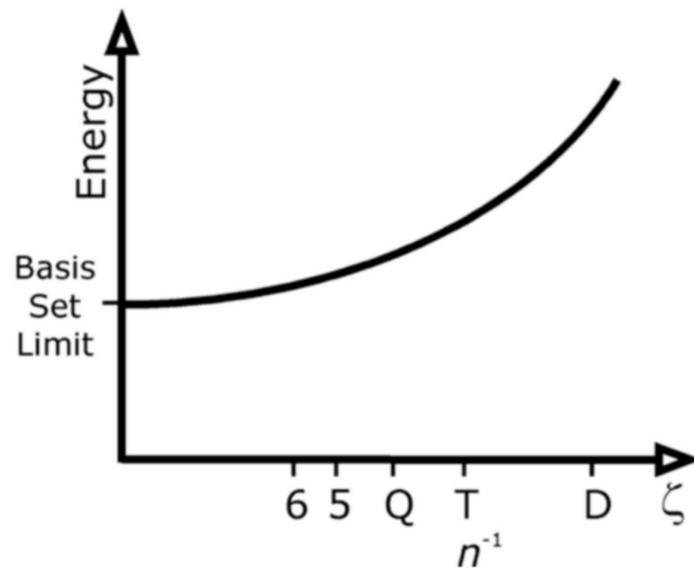
Citation

When publishing results obtained from use of the Basis Set Exchange software, please cite:

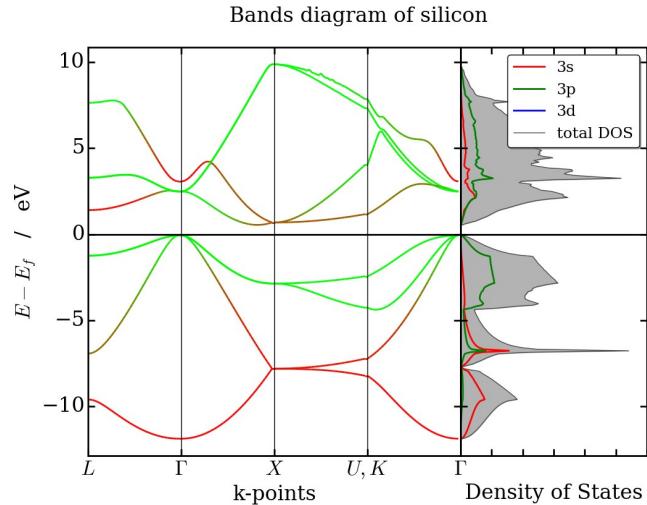
- A New Basis Set Exchange: An Open, Up-to-date Resource for the Molecular Sciences Community. Benjamin Pritchard, Doaa Altarawiy, Brett Didier, Tara D. Gibson, Theresa L. Windus. *J. Chem. Inf. Model.* **2019**, 59(11), 4814-4820, doi:10.1021/acs.jcim.9b00725.
- Basis Set Exchange: A Community Database for Computational Sciences Schuchardt, K.L., Didier, B.T., Elsethagen, T., Sun, L., Gurumoothri, V., Chase, J., Li, J., and Windus, T.L. *J. Chem. Inf. Model.* **2007**, 47(3), 1045-1052, doi:10.1021/ci600510j.

Convergence of basis sets

The limit of the complete basis set can be approximated by plotting a relevant quantity using basis sets of different sizes and extrapolating the fitted trend



Electronic band structure in solids



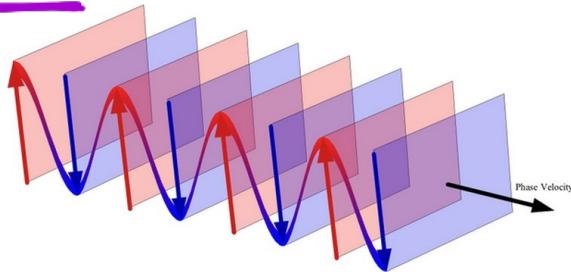
For each k -point, there are n solutions (aka, bands) to the Schrodinger equation.

Each of these quantum states evolves continuously with k

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi_{n,\vec{k}}(\vec{r}) = \varepsilon_{n,\vec{k}} \psi_{n,\vec{k}}$$

Basis sets: in condensed matter systems

Plane waves



$$\text{Bloch's theorem: } \psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n,\vec{k}}(\vec{r})$$

Expand all cell-periodic functions in terms of plane waves (Fourier analysis)

$$\begin{aligned} u_{n,\vec{k}}(\vec{r}) &= \frac{1}{V^{\frac{1}{2}}} \sum_{\vec{G}} c_{\vec{G}n\vec{k}} e^{i\vec{G}\cdot\vec{r}} \\ \{ \Rightarrow \psi_{n,\vec{k}}(\vec{r}) &= \frac{1}{V^{\frac{1}{2}}} \sum_{\vec{G}} c_{\vec{G}n\vec{k}} e^{i(\vec{G}+\vec{k})\cdot\vec{r}} \quad \left. \begin{array}{c} \bar{c}_{\vec{G}_1, n_1, \vec{k}_1} \\ \bar{c}_{\vec{G}_2, n_2, \vec{k}_2} \\ \vdots \end{array} \right\} \\ V(\vec{r}) &= \sum_i v_i e^{i\vec{G}_i \cdot \vec{r}} \quad \rho_{n,\vec{k}}(i) = |\psi_{n,\vec{k}}|^2 = \sum_{\vec{G}} p_{\vec{G}n\vec{k}} e^{i\vec{G}\cdot\vec{r}} \end{aligned}$$

Why use plane waves (for solids)?

- Historical reasons:
 - Study of materials began with metallic s and p elements
 - Many such elements exhibit electronic band structures with features similar to the free or nearly-free electron picture
- Practical reasons:
 - Extended solids lend themselves easily to plane waves (Bloch's theorem)
 - Total energy and Hamiltonian expressions are straightforward to implementation
- Computational reasons:
 - Many efficient FFT libraries for evaluating Hamiltonian
 - Monotonic improvement in numerical accuracy

Plane wave basis sets: energy cutoff

Computationally, need to truncate the expansion into plane wave basis at some k

Determined by the **energy cutoff**

(also can consider as related to the resolution of the Fourier representation)

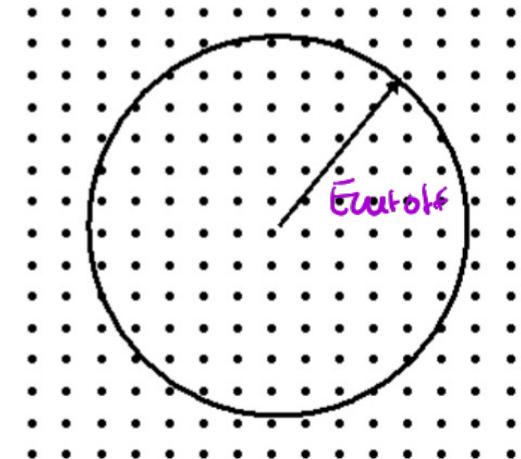
Why is the basis set truncation called the energy cutoff?

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_{n,k}(\vec{r}) \rightarrow -\frac{\hbar^2}{2m} \nabla^2 \left(\frac{1}{V^{1/2}} \sum_{\vec{G}} C_{\vec{G}+\vec{k}} e^{i(\vec{G}+\vec{k})\vec{r}} \right)$$

$$\sim \frac{\hbar^2}{2m} |\vec{G} + \vec{k}|^2 C_{\vec{G}+\vec{k}} e^{i(\vec{G}+\vec{k})\vec{r}}$$

$$E_{\text{cutoff}} > \frac{\hbar^2}{2m} |\vec{E} + \vec{G}|^2$$

→ 50 eV - 100 eV



k -point integration

Many quantities (e.g., total energy, densities, optical absorption, carrier mobilities) all involve integrating over space, i.e., over the Brillouin Zone (BZ)

For a periodic solid, only need to sample within the 1st BZ.

e.g., density

Integral form

$$\rho(r) = \frac{1}{\Omega_{BZ}} \sum_n \int_{BZ} f_{n,\vec{k}} |\psi_{n,\vec{k}}|^2 d\vec{k}$$

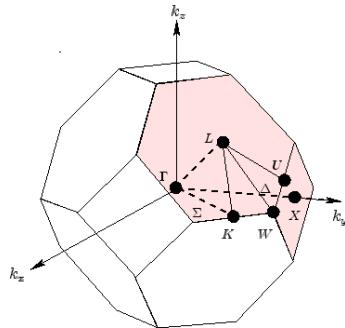
Discrete form

$$\rho(r) = \sum_{n,\vec{k}} w_{\vec{k}} f_{n,\vec{k}} |\psi_{n,\vec{k}}|^2$$

Integral is approximated by weighted sum over discrete k -points

k -point integration

Goal: Sample the 1st BZ using an equally-spaced mesh (aka Monkhorst-Pack mesh)

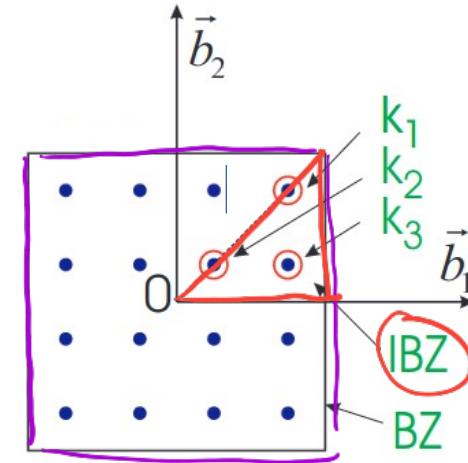


Algorithm:

- 1) Calculate equally spaced mesh
- 2) Shift mesh, if desired
(useful for hexagonal cells or for breaking symmetry)
- 3) Apply symmetry operations of Bravais lattice
- 4) Extract the irreducible k -points (aka, **irreducible Brillouin zone, IBZ**)
- 5) Calculate weights

Example: 4x4 k -point mesh on square 2D lattice

- 16 points total
- Only 3 are symmetry inequivalent points
 - 4 equivalent \mathbf{k}_1 , $w_{k_1} = 1/4$
 - 4 equivalent \mathbf{k}_2 , $w_{k_2} = 1/4$
 - 8 equivalent \mathbf{k}_3 , $w_{k_3} = 1/2$



See also: VASP basics

Summary of convergence parameters (in DFT)

Preparation of your computational samples

Minimum set of convergence parameters:

- Energy cutoff (start from recommended value)
- k-point sampling
- Simulation cell size (finite-size effects)

The choice of your calculation parameters will depend on the material system you are working with and the problem for which you are running calculations.

e.g.,

- Systems containing oxygen tend to need higher energy cutoffs
- Transport properties versus total energies and relaxation
- Defects that exhibit local versus delocalized characteristics
- Excited state properties often involve an separate set of convergence parameters

Convergence tests tell you what parameters to use and also the approximate numerical error to expect from your calculations.