Lecture 14 & 15

Modern theory of solids: Band structure

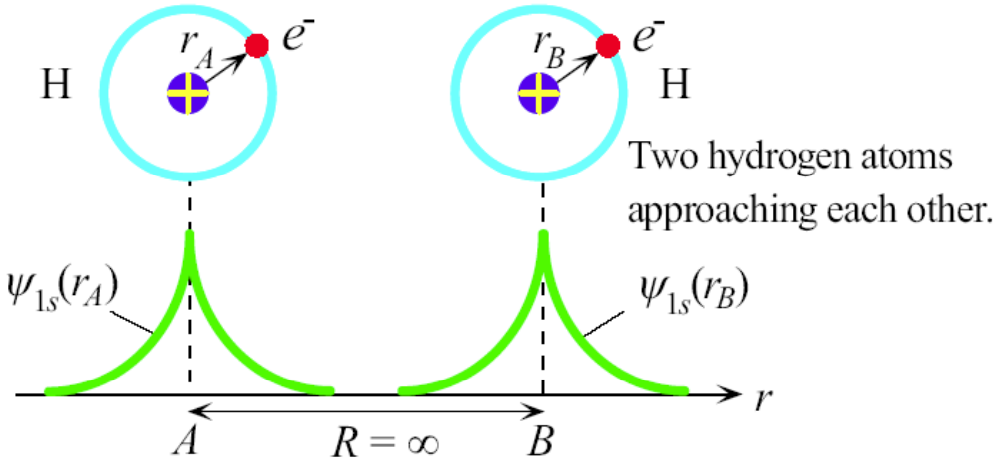
Recap So Far

- Classical electrical & thermal conduction in solids
- Diffusion & doping
- Temperature dependence of resistivity
- Sensors (i.e., Hall sensors)

- Quantum theory of atoms
- Photon and electron diffraction, the photoelectric effect, blackbody radiation
- Lasers

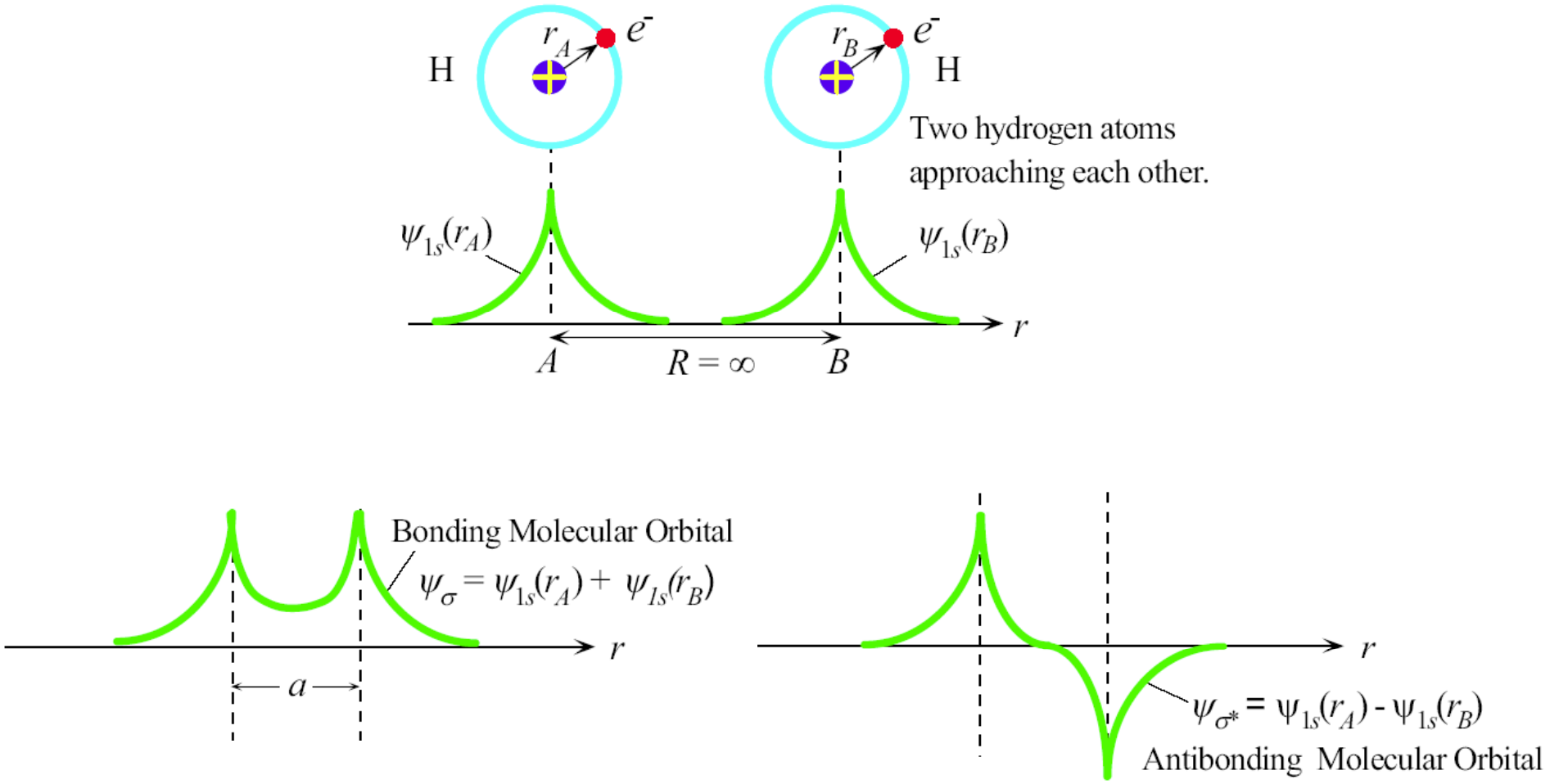
- Interacting electrons and atoms → solids
- Band theory
- Quantum theory of conduction
- Foundation for understanding semiconductors & semiconductor devices

Bonding & Antibonding orbitals



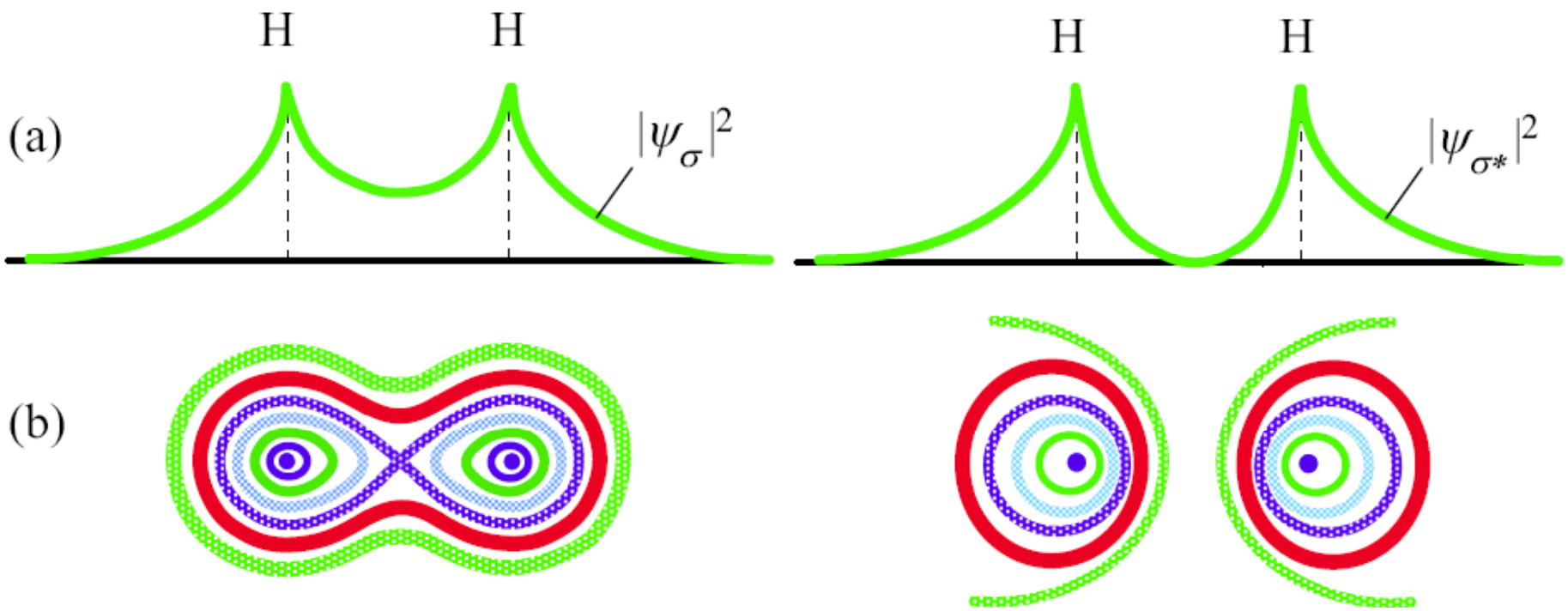
Two H atoms, both in their 1s state.
As they approach, their wavefunctions begin to overlap.

Bonding & Antibonding orbitals



Formation of molecular orbitals - bonding and antibonding (ψ_σ and ψ_{σ^*}) when two H atoms approach each other. The two electrons pair their spins and occupy the bonding orbital ψ_σ

H-H bond: Electron probability distribution



(a) Electron probability distributions for bonding and antibonding orbitals, ψ_σ and ψ_{σ^*}.

(b) Lines representing contours of constant probability (darker lines represent greater relative probability).

Linear combination of atomic orbitals

Two identical atomic orbitals ψ_{1s} on atoms *A* and *B* can be combined linearly in two different ways to generate two separate molecular orbitals ψ_{σ} and ψ_{σ^*}

ψ_{σ} and ψ_{σ^*} generated from a
linear combination of atomic orbitals (LCAO)

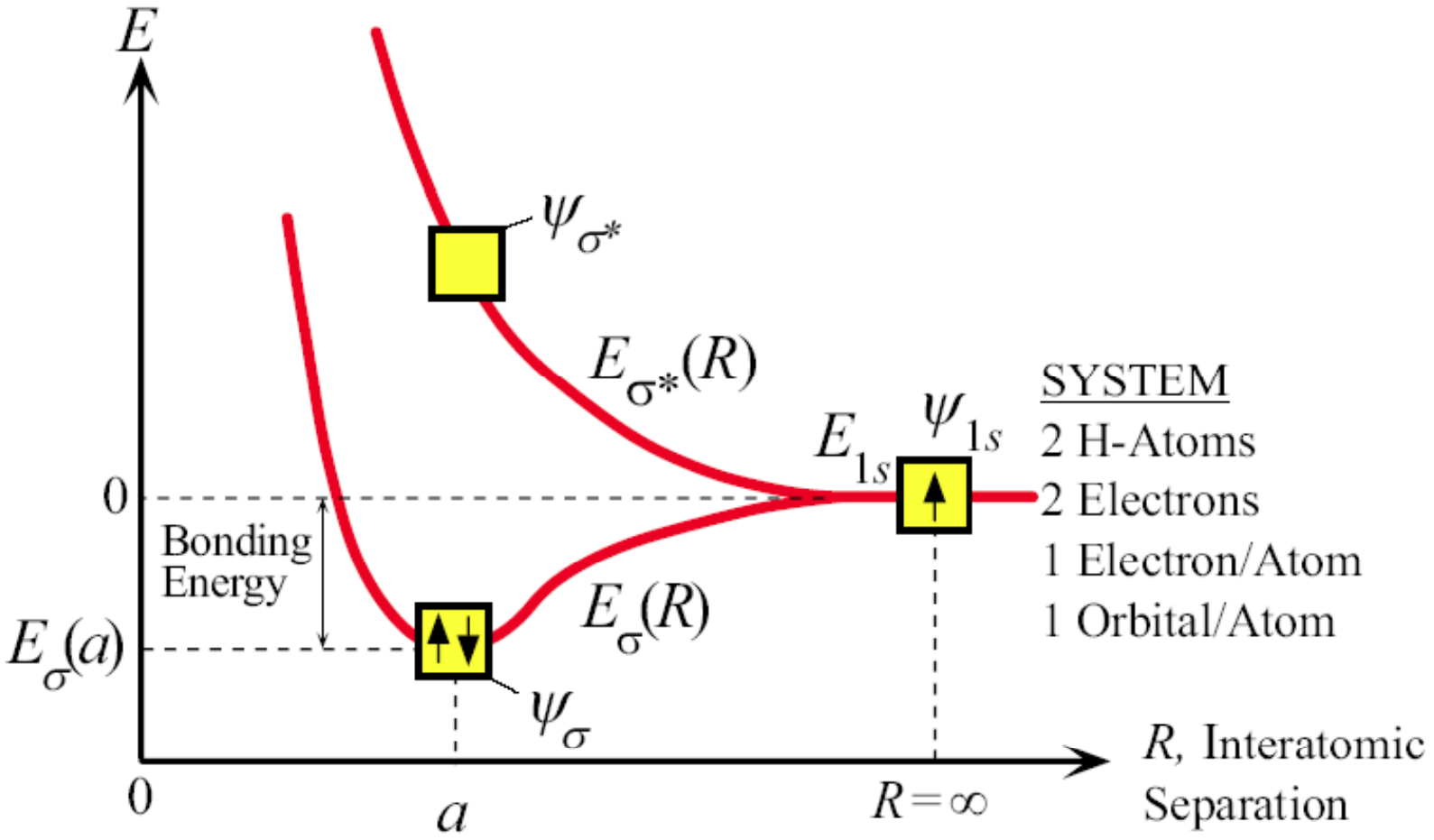
Wavefunction around A

Wavefunction around B

$$\psi_{\sigma} = \psi_{1s}(r_A) + \psi_{1s}(r_B)$$

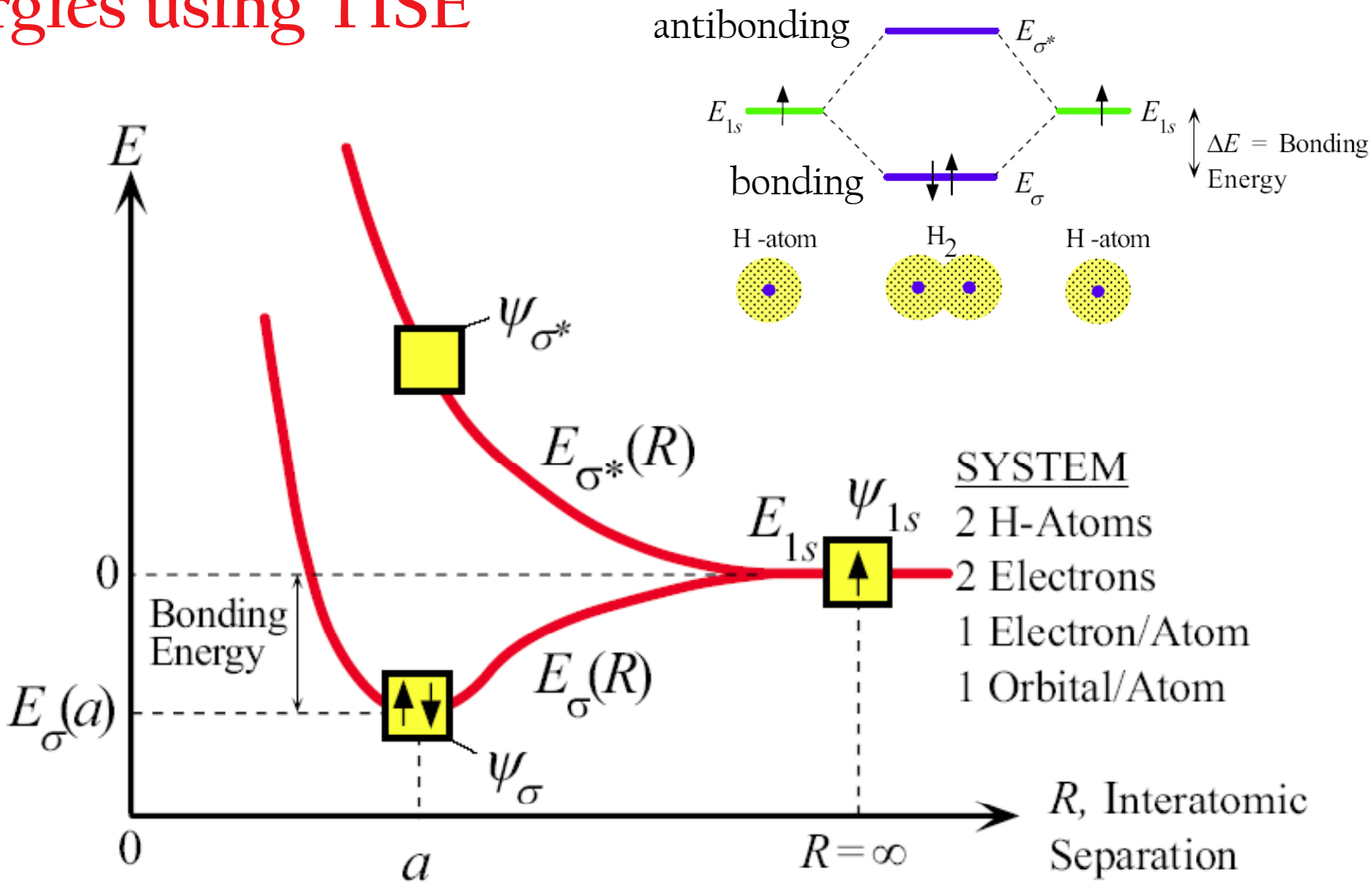
$$\psi_{\sigma^*} = \psi_{1s}(r_A) - \psi_{1s}(r_B)$$

Energies using TISE



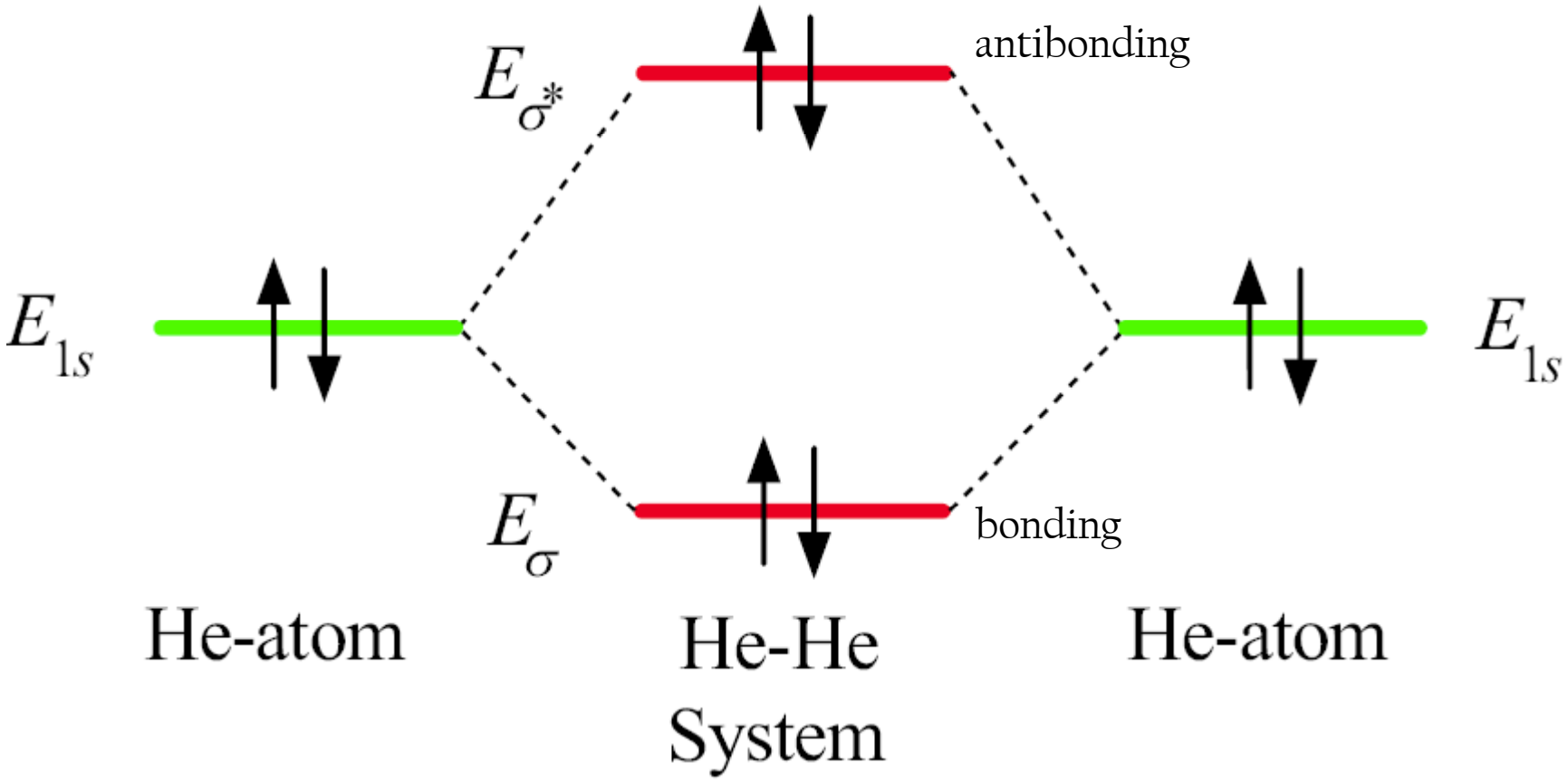
Energy of ψ_σ and ψ_{σ^*} found using the time-independent Schrodinger equation (TISE) vs. the interatomic separation R.

Energies using TISE



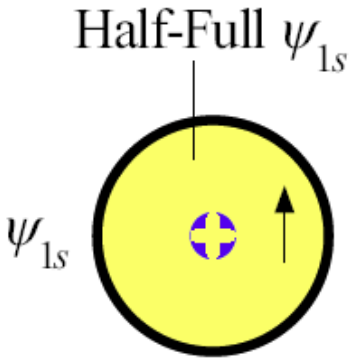
Inset: Pictorial representation of "linear combination of atomic orbitals" (LCAO), showing the changes in the electron energy as two isolated H atoms, far left and far right, come together to form a hydrogen molecule.

He-He bond



Two He atoms have four electrons. When He atoms come together, two of the electrons enter the E_{σ} level and two the E_{σ^*} level, so the overall energy is greater than two isolated He atoms (since $|E_{antibonding}| \gg |E_{bonding}|$).
Therefore, He-He does not exist!

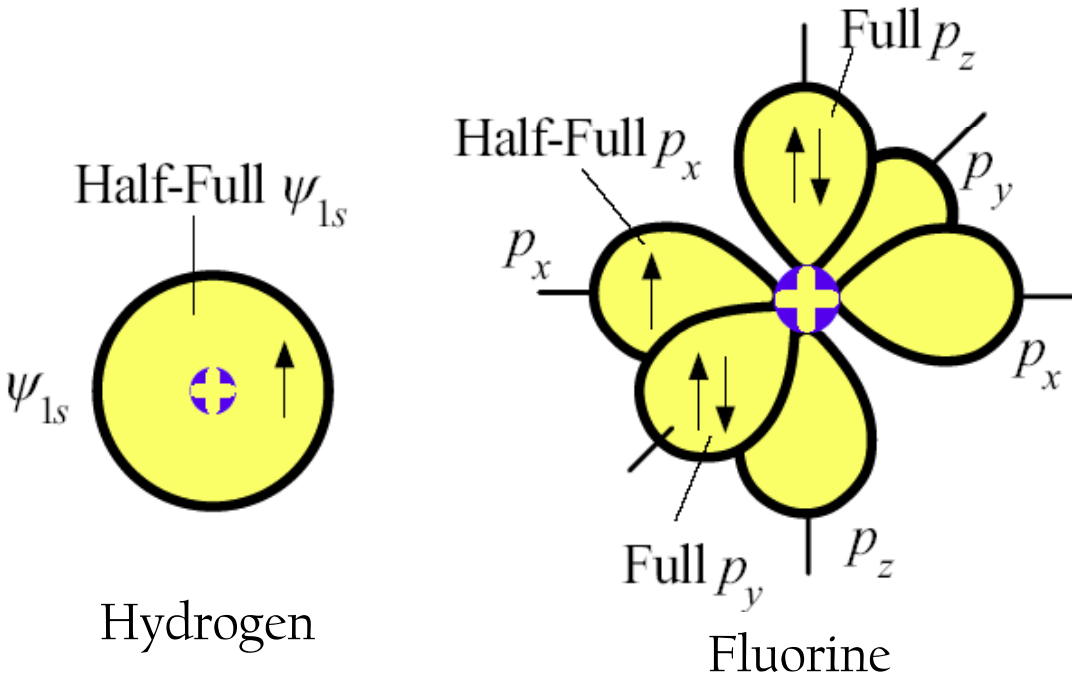
Hydrofluoric Acid



Hydrogen

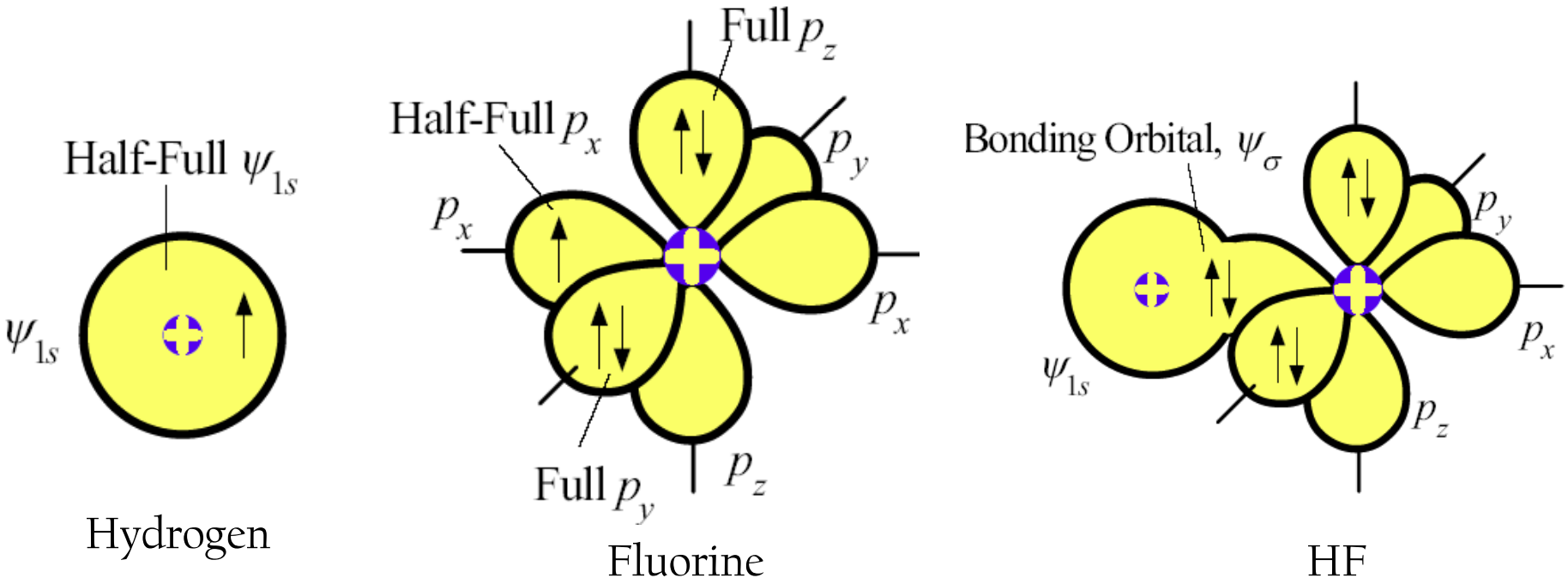
H has one half-empty ψ_{1s} orbital.

Hydrofluoric Acid



H (1s) has one half-empty ψ_{1s} orbital.
F ($1s^2\ 2s^2\ 2p^5$) has one half-empty p_x orbital but full p_y and p_z orbitals.

Hydrofluoric Acid



The overlap between ψ_{1s} and p_x produces a bonding orbital and an antibonding orbital. The two electrons fill the bonding orbital and thereby form a covalent bond between H and F.

Hydrofluoric Etch of SiO_2

Etching SiO_2 in integrated circuits & MEMS

Hydrofluoric Etch of SiO_2 - forming CaF_2

Etching SiO_2 in integrated circuits & MEMS

Hydrofluoric Etch

Etching SiO_2 in integrated circuits & MEMS

Acid-etched cameo glass

Hydrofluoric Etch

Etching SiO_2 in integrated circuits & MEMS

Acid-etched cameo glass

FIGURE 3- Ceramic etching with 10% hydrofluoric acid

FIGURE 4- Application of the silane coupling agent

FIGURE 7- Finishing of the restoration

Dentistry

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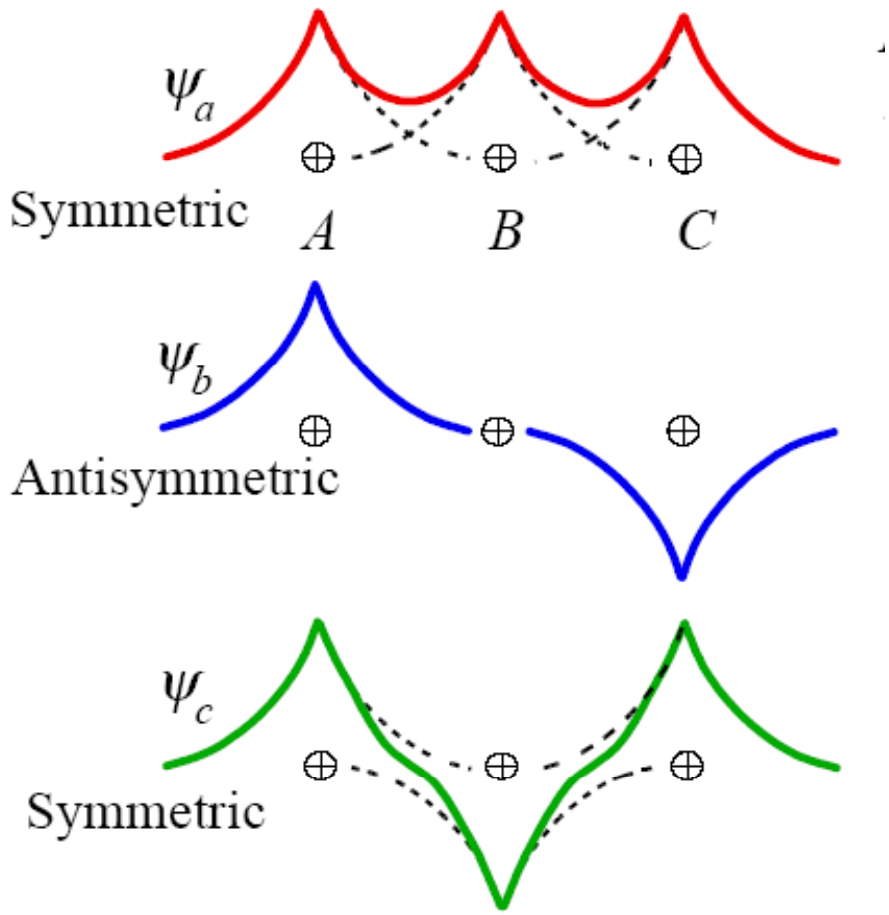
Three-atom system – Band theory of solids



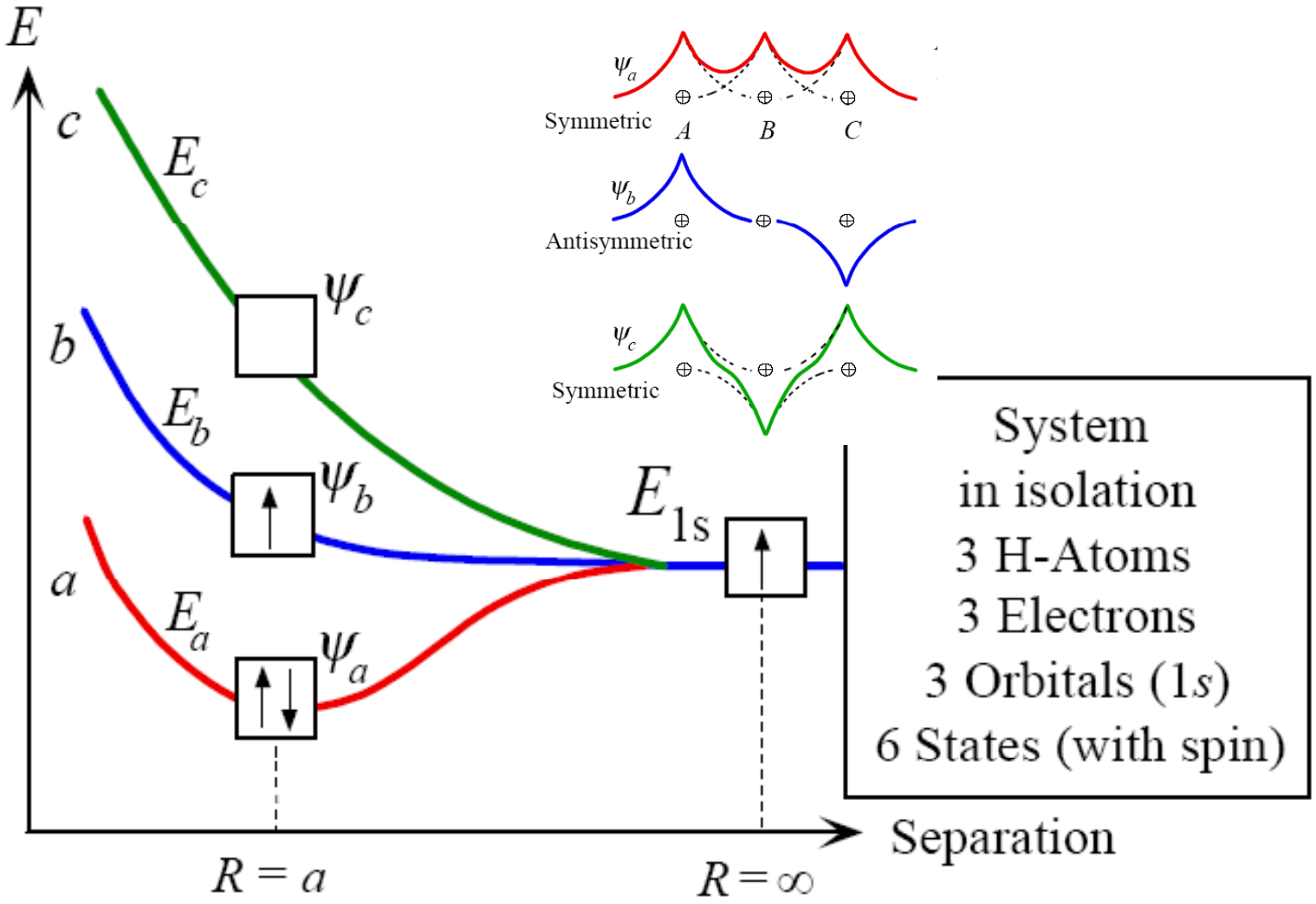
$$\psi_a = \psi_{1s}(r_A) + \psi_{1s}(r_B) + \psi_{1s}(r_C)$$

$$\psi_b = \psi_{1s}(r_A) - \psi_{1s}(r_C)$$

$$\psi_c = \psi_{1s}(r_A) - \psi_{1s}(r_B) + \psi_{1s}(r_C)$$

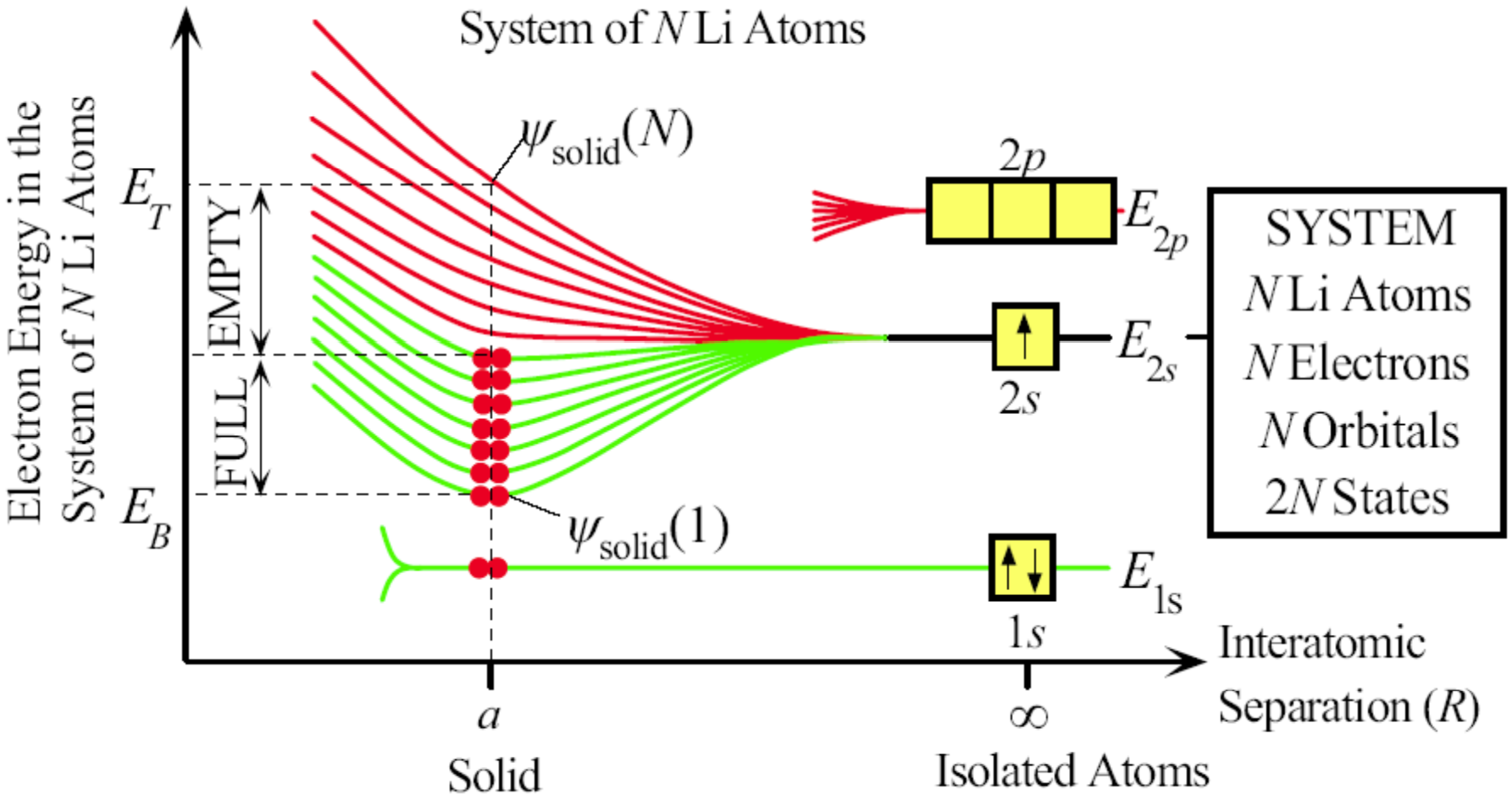
Three molecular orbitals from three ψ_{1s} atomic orbitals overlapping in three different ways.

Three-atom system: three energy levels



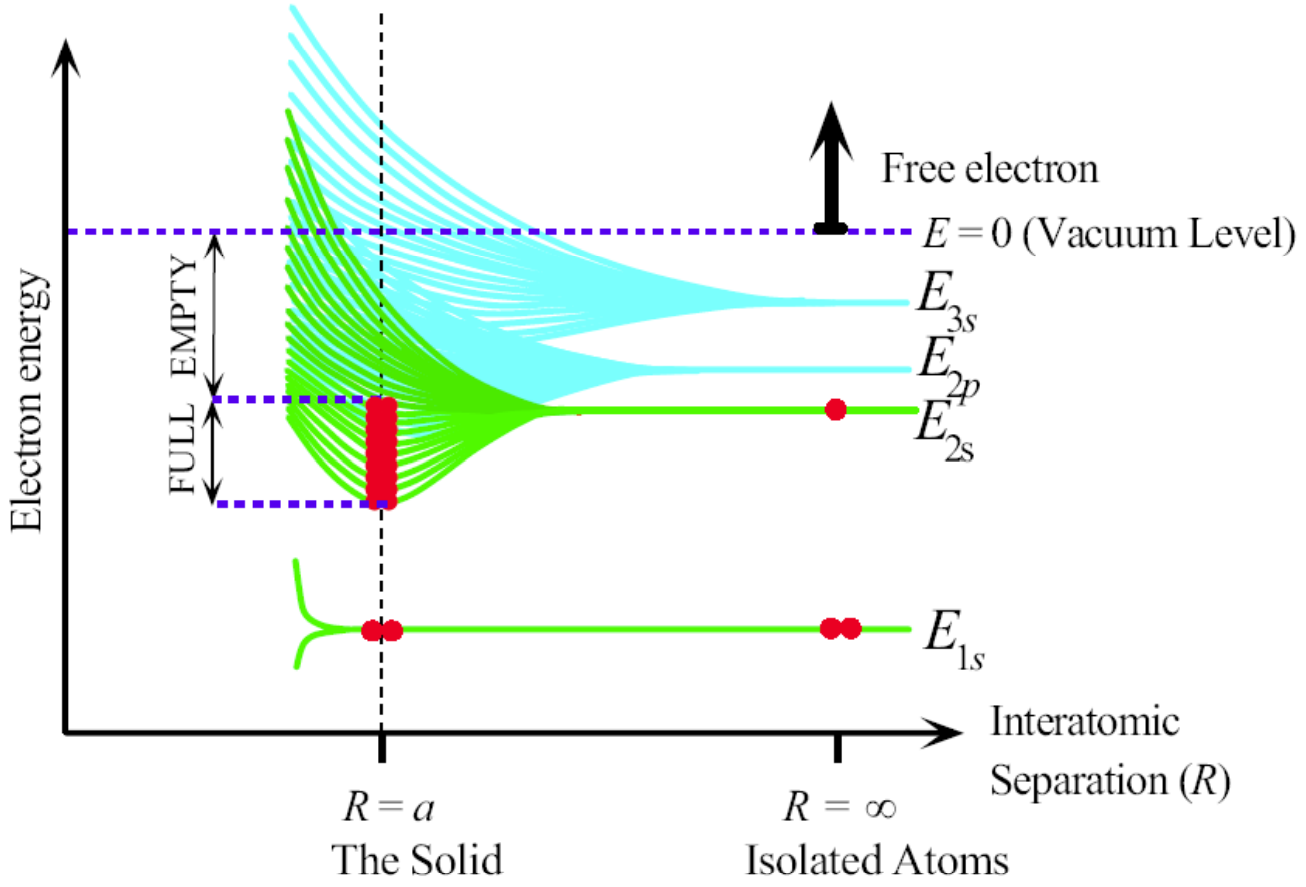
The energies of the three molecular orbitals, labeled a, b, and c, in a system with three H atoms.

N-atom system: N energy levels



The formation of 2*s* energy band from the 2*s* orbitals when *N* Li atoms ($1s^2\ 2s^1$) come together to form the Li solid. There are *N* 2*s* electrons, but 2*N* states in the band. The 2*s* band is therefore only half full. The atomic 1*s* orbital is close to the Li nucleus and remains undisturbed in the solid.

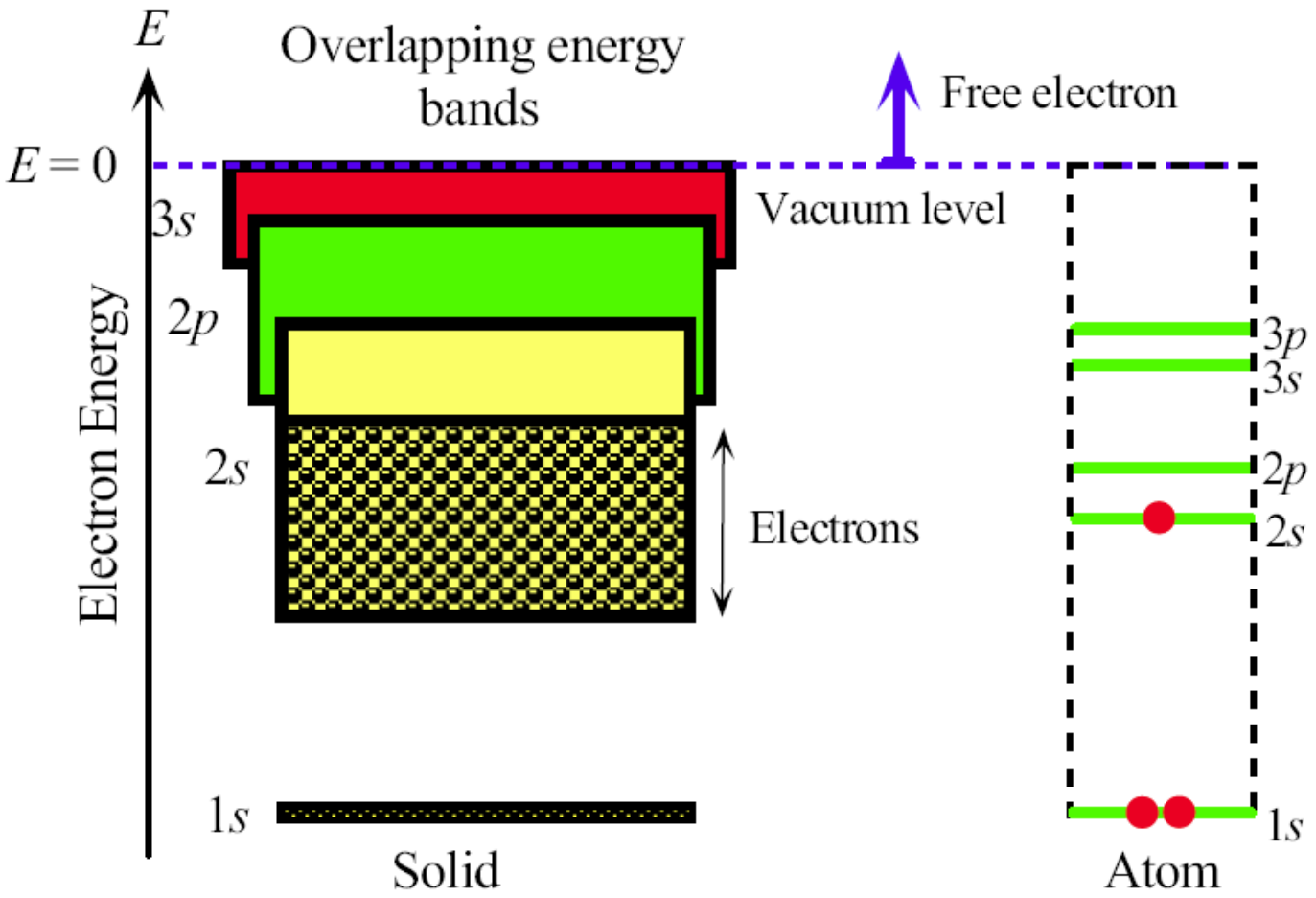
Band theory of solids



As Li atoms are brought together from infinity, the atomic orbitals overlap and give rise to bands. Outer orbitals overlap first. The 3*s* orbitals give rise to the 3*s* band, 2*p* orbitals to the 2*p* band, etc. The various bands overlap to produce a single band in which the energy is nearly continuous.

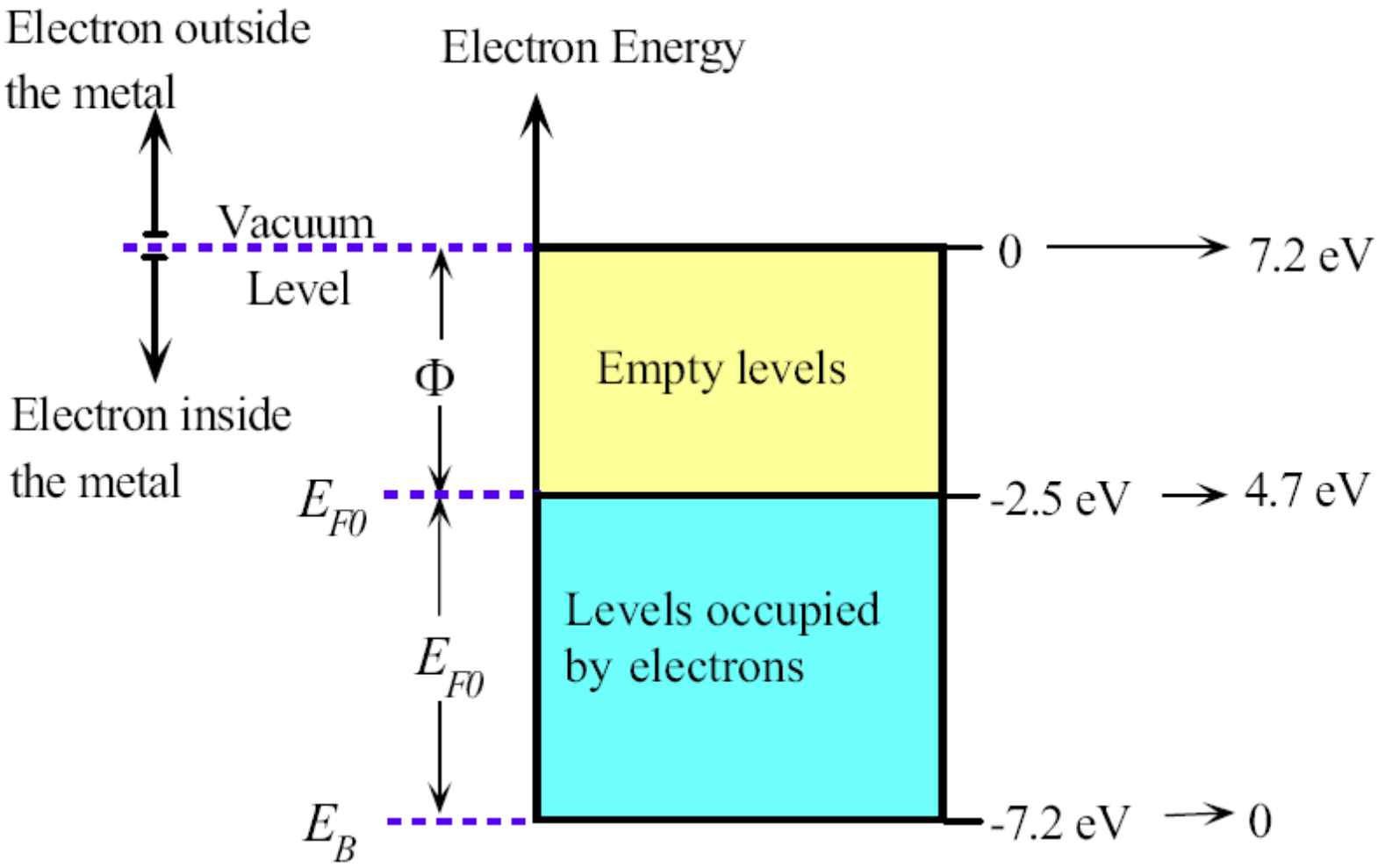
Note: We can no longer consider the electrons as belonging to specific atoms – they are shared among the entire solid.

Band theory of solids



In a metal, the various energy bands overlap to give a single energy band that is only partially full of electrons. There are states with energies up to the vacuum level, where the electron is free.

Band theory of solids: The Fermi Level



Typical electron energy band diagram for a metal. All the valence electrons are in an energy band, which they only partially fill. The top of the band is the vacuum level, where the electron is free from the solid ($PE = 0$).

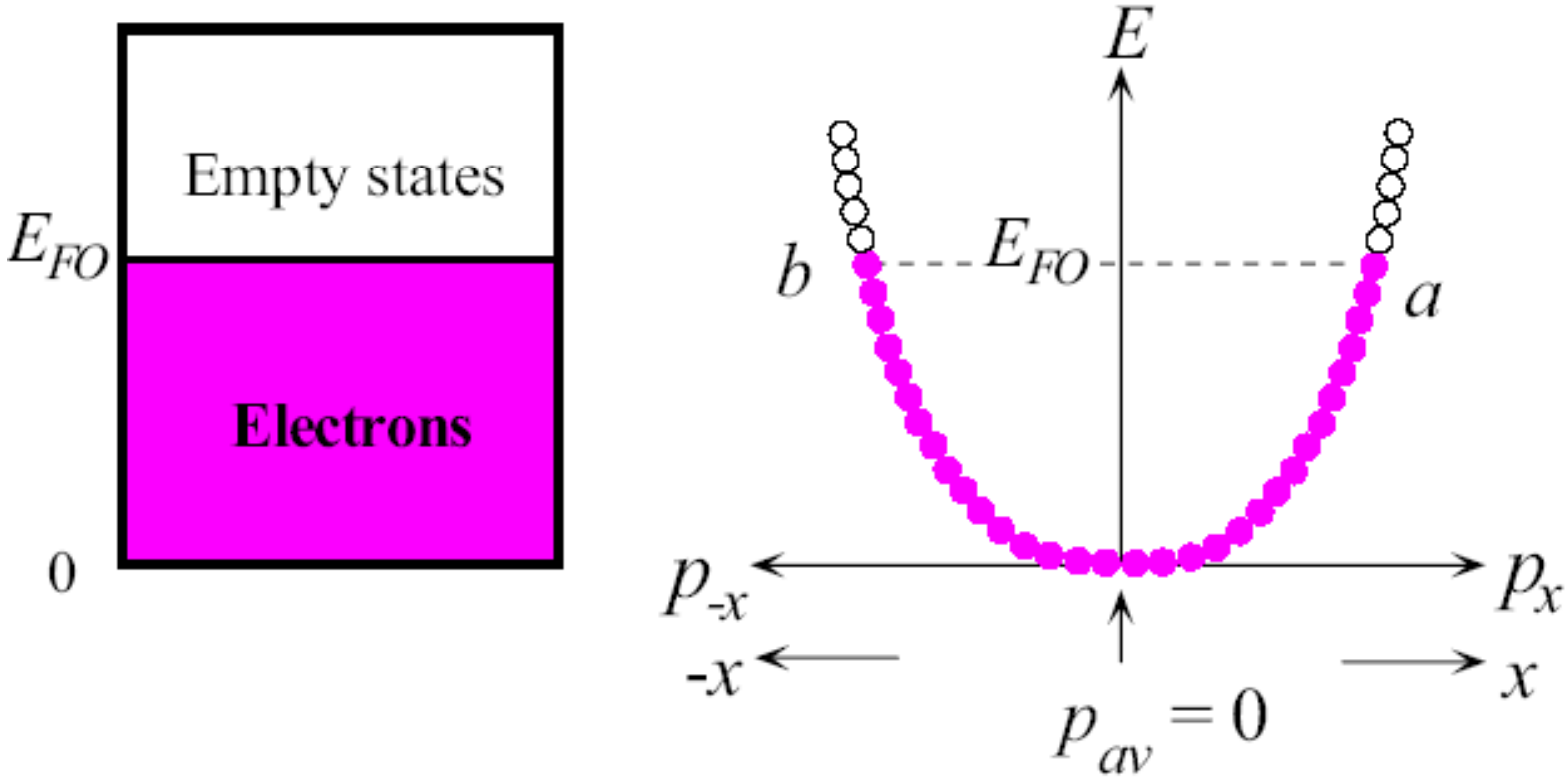
Band theory of solids: Work-function redefined

The energy required to excite an electron from the Fermi level to the vacuum level, that is, to liberate the electron from the metal, is called the **work function** Φ of the metal.

Table 4.1 Fermi energy and work function of selected metals

	Metal							
	Ag	**Al**	**Au**	**Cs**	**Cu**	**Li**	**Mg**	**Na**
Φ (eV)	4.5	4.28	5.0	2.14	4.65	2.3	3.7	2.75
E_{FO} (eV)	5.5	11.7	5.5	1.58	7.0	4.7	7.1	3.2

Band diagram of a metal: 'free' electrons

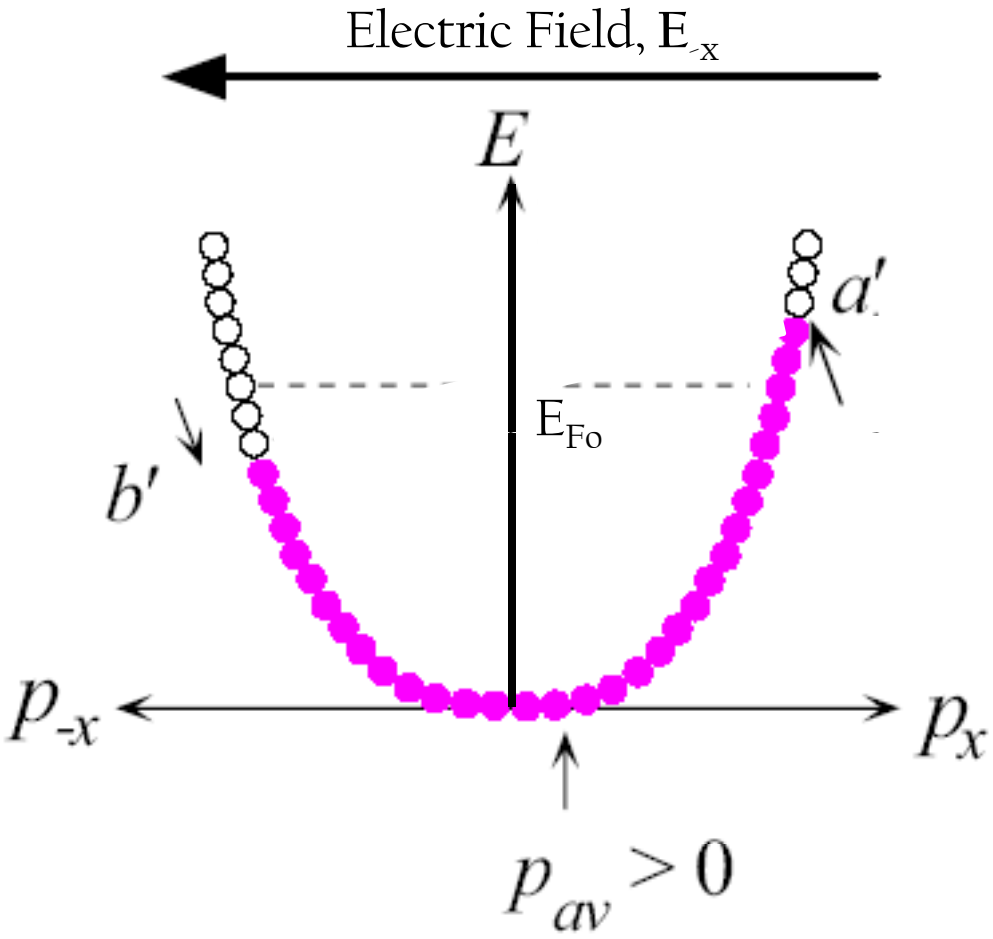


Energy band diagram of a metal.

Energy $E=KE=p^2/2m$

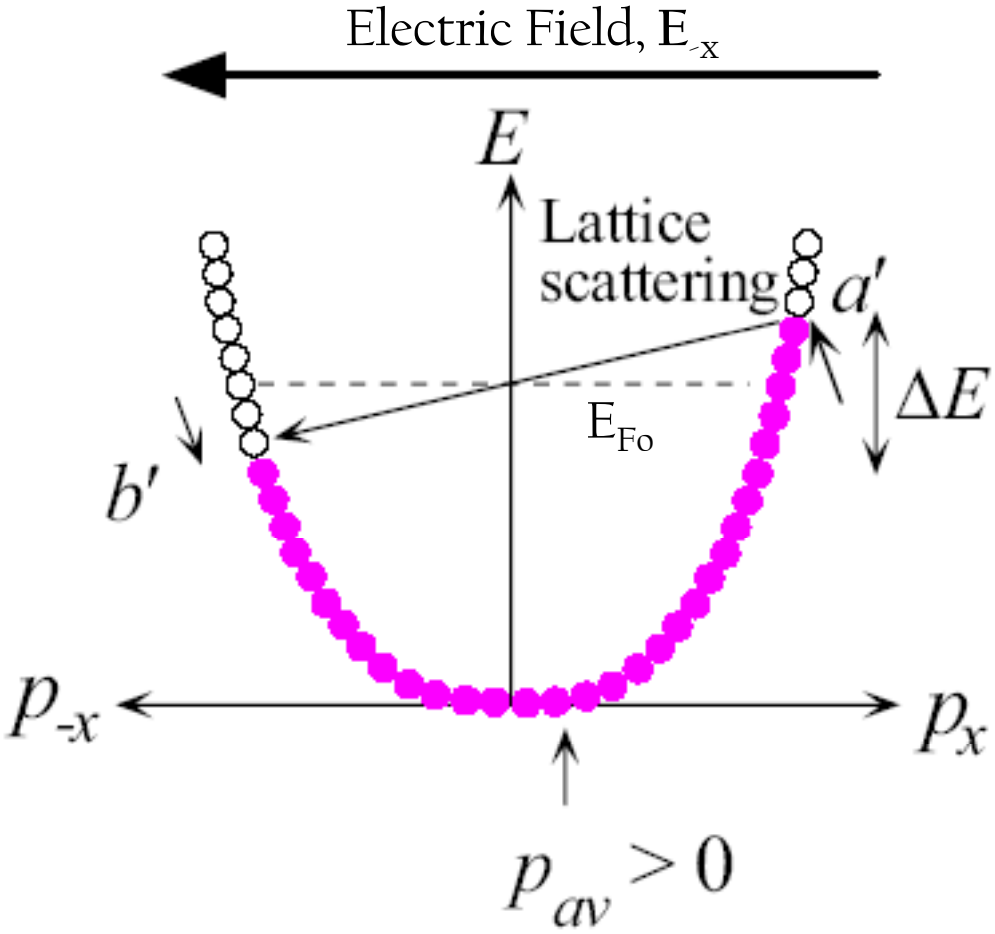
In the absence of a field, there are as many electrons moving right as there are moving left. The motions of two electrons at each energy cancel each other (as for a and b).

Band diagram of a metal: applying an E-field



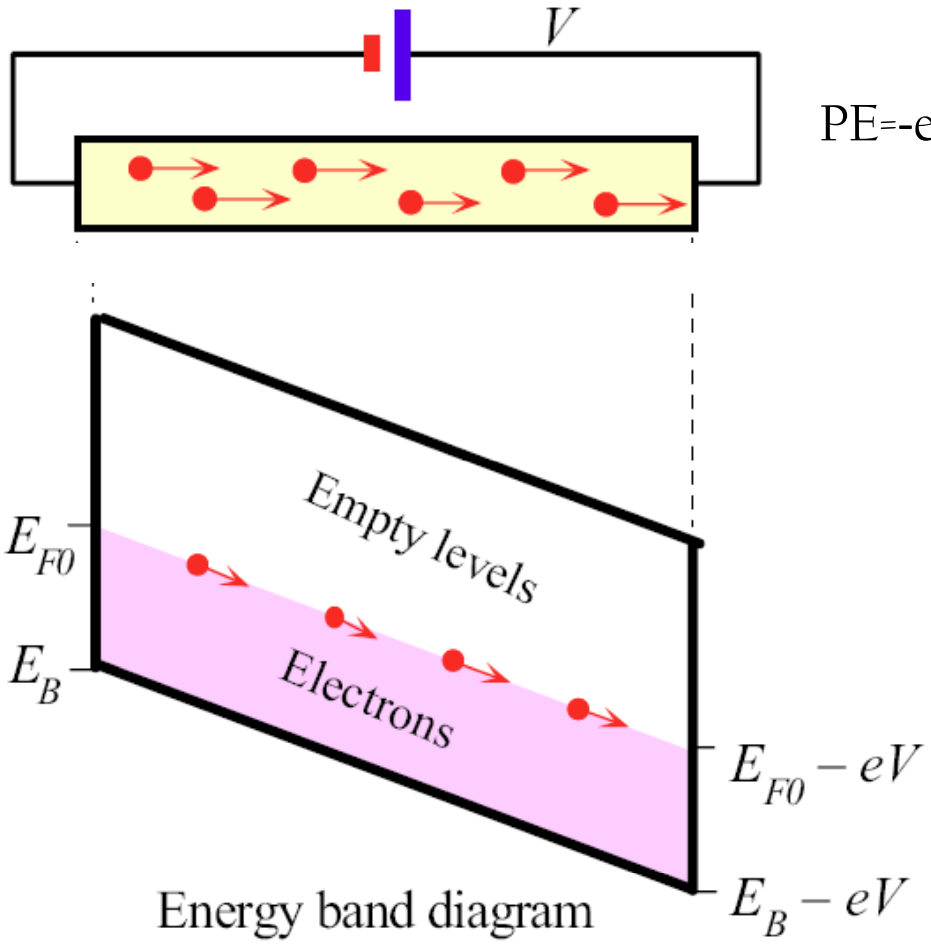
In the presence of an electric field in the $-x$ direction, the electron accelerates and gains energy to a'. The average of all momenta values is along the $+x$ direction and results in a net electrical current.

Band diagram of a metal: only electrons near E_F contribute to conduction!!



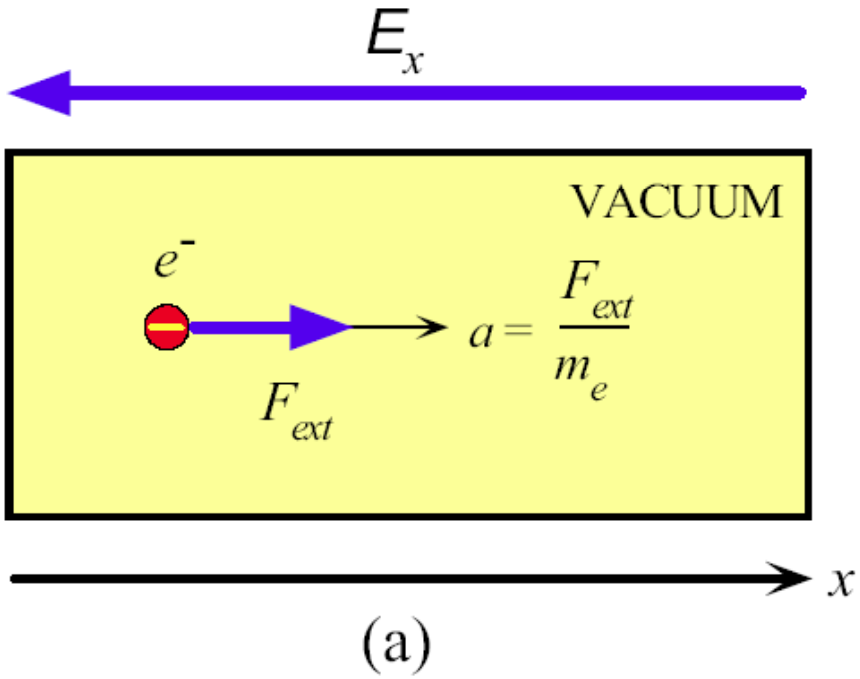
Lattice scattering abruptly changes the momentum of an electron, but conserves energy. Therefore, an electron is scattered to an empty state near E_{FO} but moving in the -x direction.

Band diagram of a metal: applying an E-field



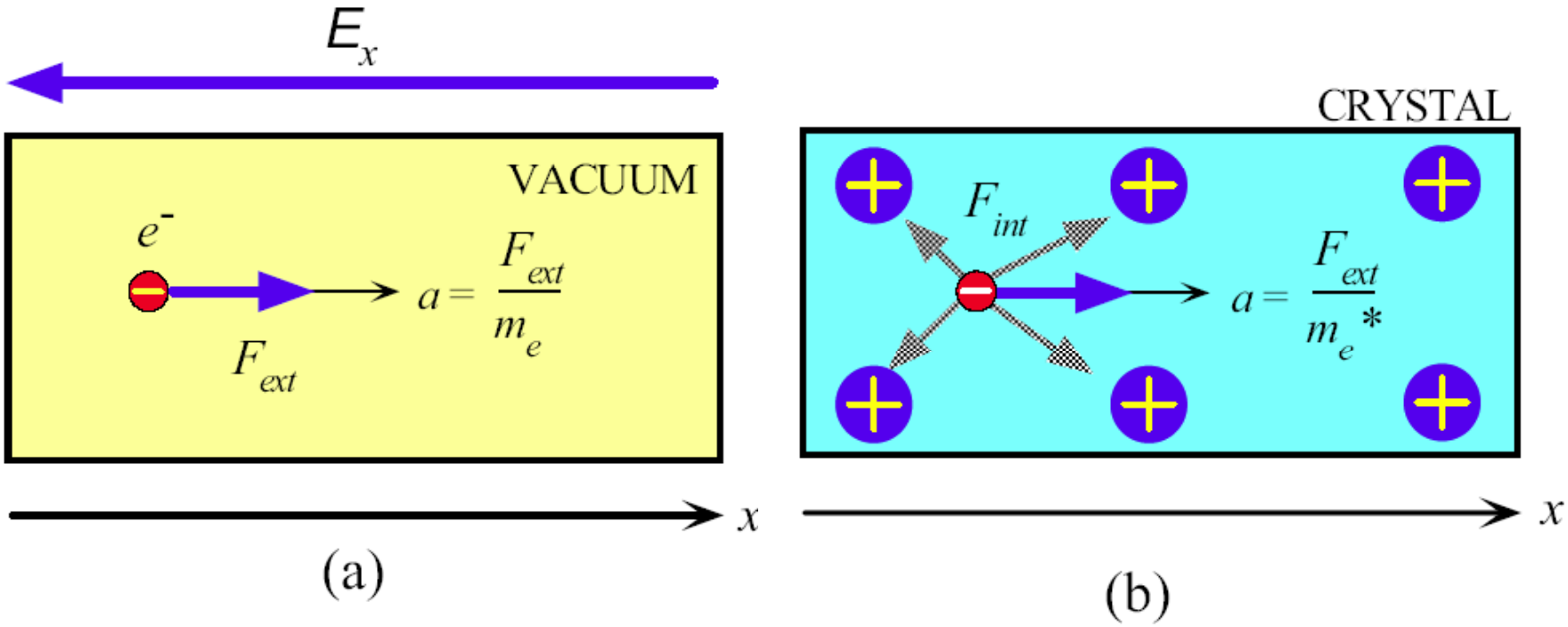
When a voltage is applied to a metal, the energy band is bent to be lower at the positive terminal....i.e., the electron's potential energy decreases as it moves toward the positive terminal.

In vacuum, the electron has mass, m



(a) An external force F_{ext} applied to an electron in a vacuum results in an acceleration $a_{vac} = F_{ext} / m_e$.

In a band, the electron has an effective mass, m*



(a) An external force F_{ext} applied to an electron in a vacuum results in an acceleration $a_{vac} = F_{ext} / m_e$.

(b) An external force Fext applied to an electron in a crystal results in an acceleration $a_{cryst} = F_{cryst} / m_{e*}$

In a band, the electron had an effective mass, m*

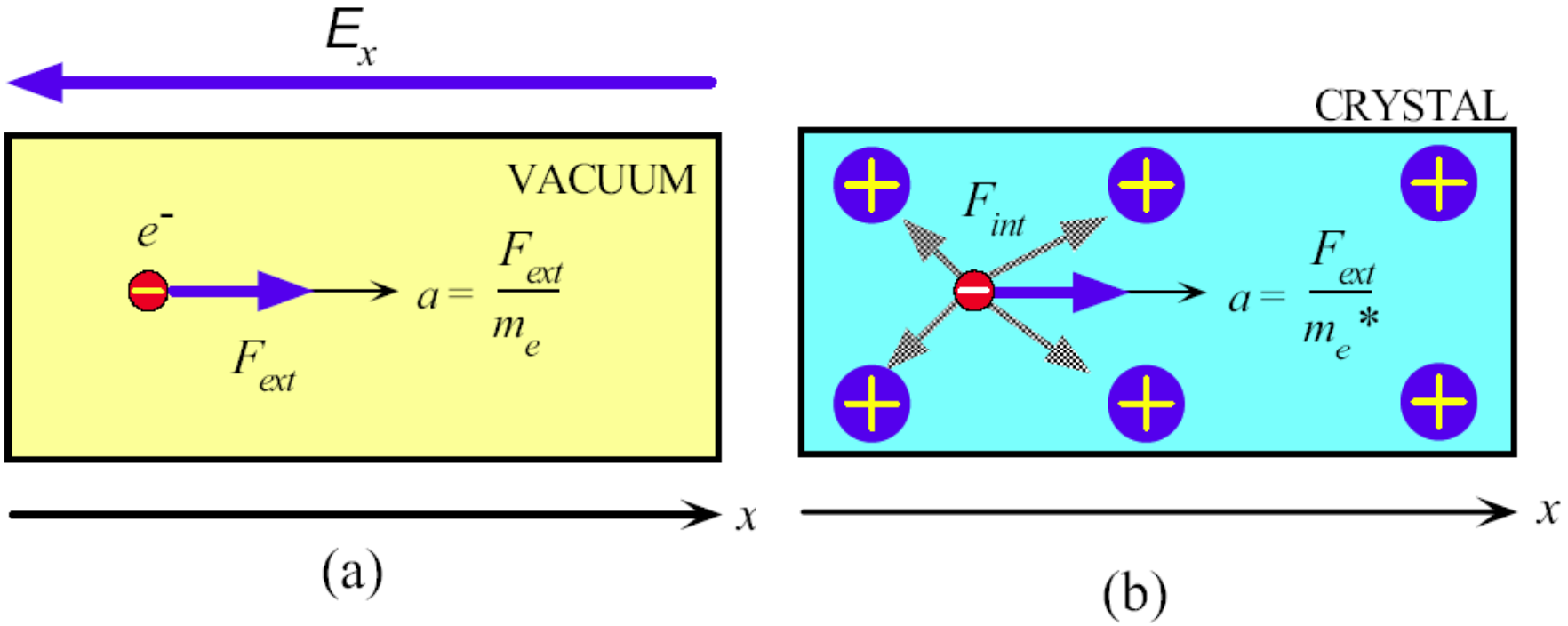
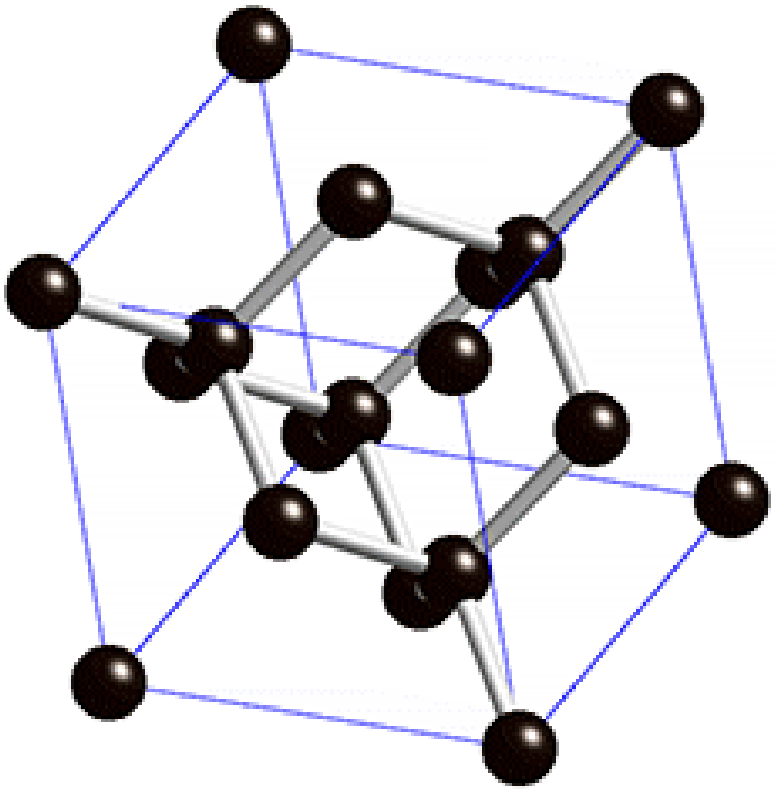


Table 4.2 Effective mass m_e^* of electrons in some metals

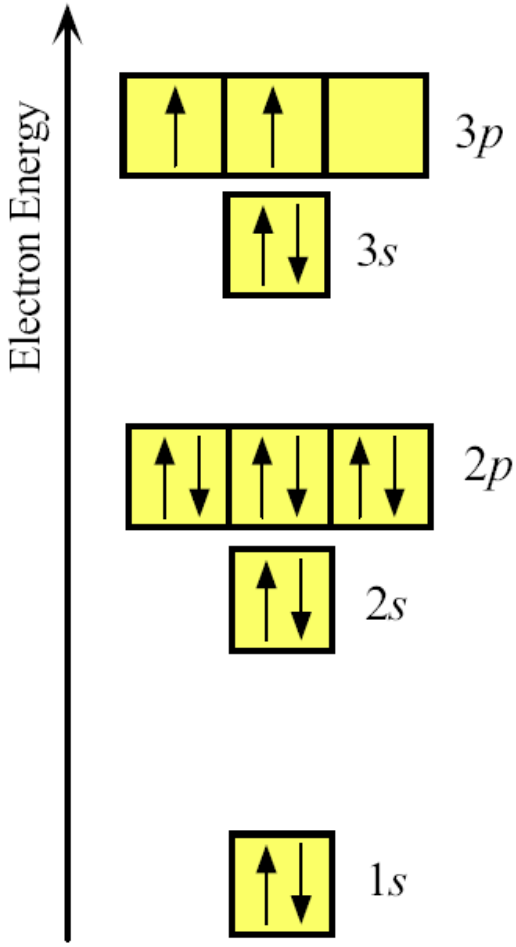
Metal	Ag	Au	Bi	Cu	K	Li	Na	Ni	Pt	Zn
$\frac{m_e^*}{m_e}$	0.99	1.10	0.047	1.01	1.12	1.28	1.2	28	13	0.85

Semiconductors: Silicon

The crystal structure of Si: diamond cubic

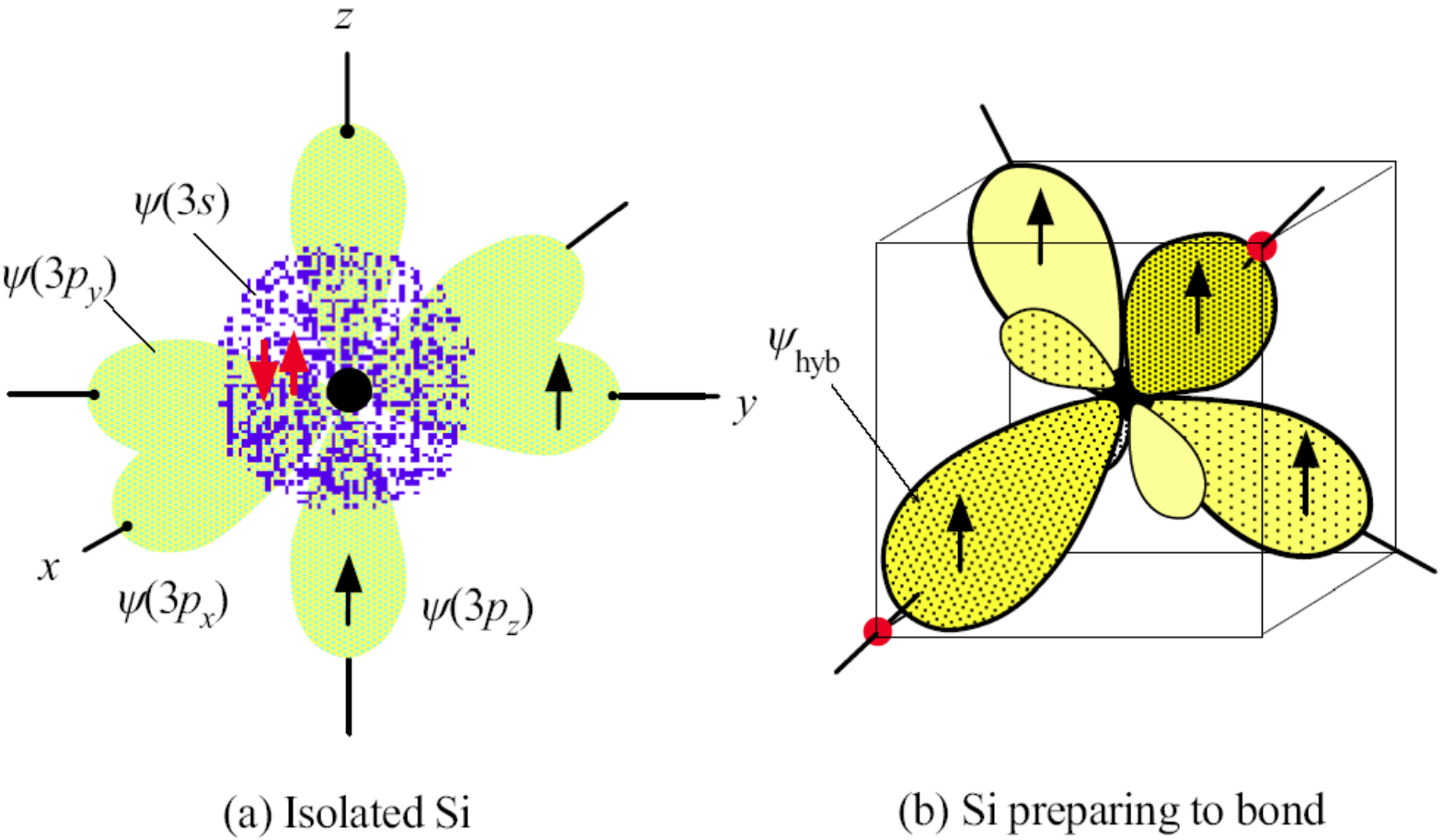


The electronic structure of Si:
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$



Why does Si bond with 4 neighbors, since there are only 2 unpaired electrons?

Hybridization of Si orbitals



(a) Isolated Si

(b) Si preparing to bond

When Si is about to bond, the one 3*s* orbital and the three 3*p* orbitals become perturbed and mixed to form four hybridized orbitals, ψ_{hyb}, called sp^3 orbitals, which are directed toward the corners of a tetrahedron. The ψ_{hyb} orbital has a large major lobe and a small back lobe. Each ψ_{hyb} orbital takes one of the four valence electrons.