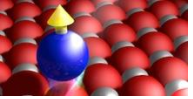
# 1

# Review of electronic properties: from atoms to bulk



# Review of electronic properties: from atoms to bulk

atoms

quantum numbers
electron configuration
orbitals

exchange interaction

molecular orbitals

hybrid orbitals

---

bulk

tight binding model

band structure
density of states

Physical Chemistry
Peter Atkins and Julio de Paula

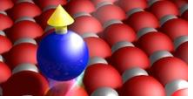
Modern Physics
Paul A. Tipler and Ralph A. Llewellyn

https://chem.libretexts.org/

---

Solid State Physics
Philip Hofmann

EPFL lectures: Physique du Solide (2024-2025)
H. Brune and M. Pivetta



# Analytical solution for hydrogen and hydrogenic atoms (one electron)

EPFL

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \qquad -\frac{\hbar^2}{2m_e}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

Hamiltonian and Schrödinger equation for the motion of one electron relative to the nucleus, approx $m_N \gg m_e$
$Z$: atomic number

→ variable separation, radial and angular parts of wavefunctions $\psi(r,\theta,\phi) = R(r) \times Y(\theta,\phi)$

$n = 1, 2, 3, 4 \ldots$ principal quantum number; average distance of an electron from the nucleus; energy of the electron: $E_n \propto -{}^{Z^2}/_{n^2}$

$l = 0, 1, \ldots n-1$ orbital (angular momentum) quantum number; magnitude of the angular momentum of the electron: $|\boldsymbol{l}| = \sqrt{l(l+1)}\hbar$

$m_l = l, l-1, \ldots, -l$ magnetic quantum number; $(2l+1)$ values; direction of the angular momentum (with respect to an applied magnetic field, usually along $z$): $l_z = m_l\hbar$

electron configurations, identified by the **shell**: $n$ = 1 (K) 2 (L) 3 (M) 4 (N) … and the **subshell**: $l$ = 0 (s) 1 (p) 2 (d) 3 (f) …

Exercise 1.1

| Orbital | $n$ | $l$ | $R_{n,l}$ |
|---|---|---|---|
| 1s | 1 | 0 | $2\left(\frac{Z}{a}\right)^{3/2} e^{-\rho/2}$ |
| 2s | 2 | 0 | $\frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (2-\rho)e^{-\rho/2}$ |
| 2p | 2 | 1 | $\frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho e^{-\rho/2}$ |
| 3s | 3 | 0 | $\frac{1}{243^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (6-6\rho+\rho^2)e^{-\rho/2}$ |
| 3p | 3 | 1 | $\frac{1}{486^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (4-\rho)\rho e^{-\rho/2}$ |
| 3d | 3 | 2 | $\frac{1}{2430^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho^2 e^{-\rho/2}$ |

$m_e \rightarrow a \approx a_0$

$\rightarrow$

$\rho = \frac{2Zr}{na_0}$

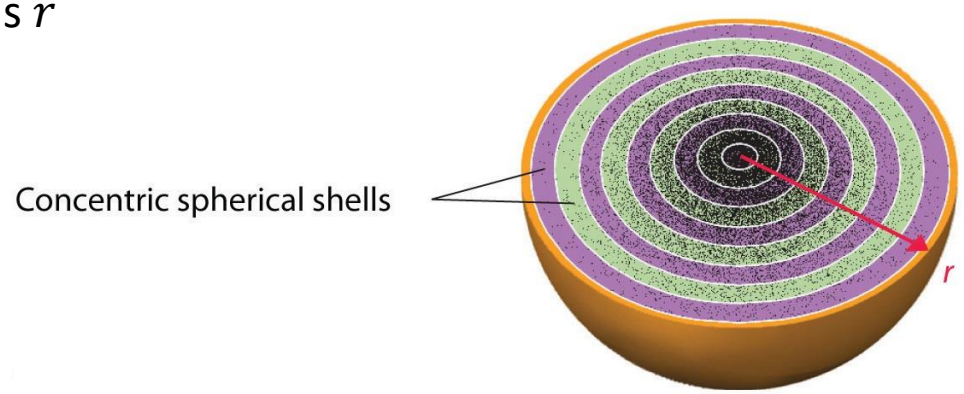
$a_0 =$ 52.9 pm
Bohr radius

# Radial probability function

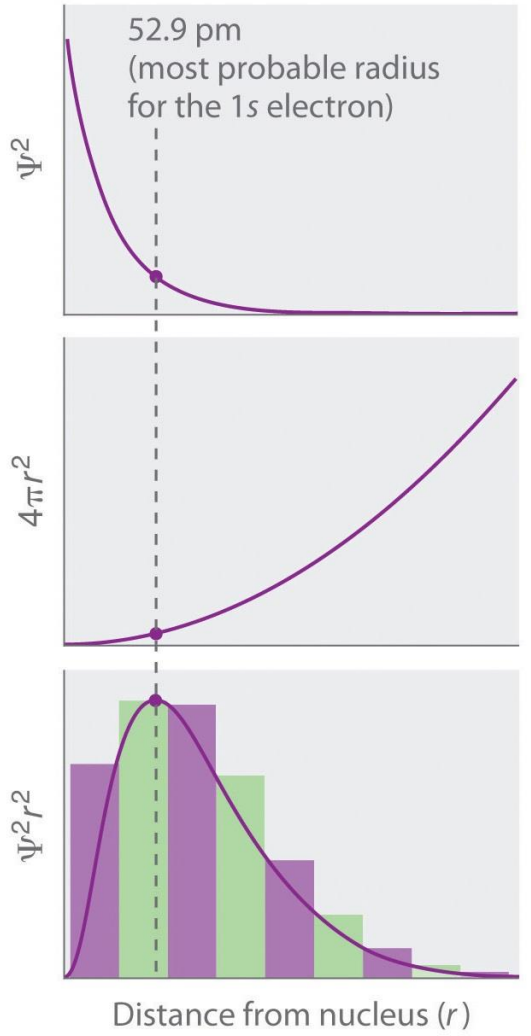
Exercises 1.2 – 1.3

$$P(r) = r^2 R^2\,(r)$$

also $P(r)$ is a probability density:
multiplied by $dr$, it gives the probability of finding the electron anywhere between the two walls of a spherical shell of thickness $dr$ at the radius $r$




(a) 1*s* orbital imagined as an onion




(b) Probability density

(c) Spherical surface area

(d) Radial probability

# Radial wave functions and radial probability density

$e^{-\rho/2}$

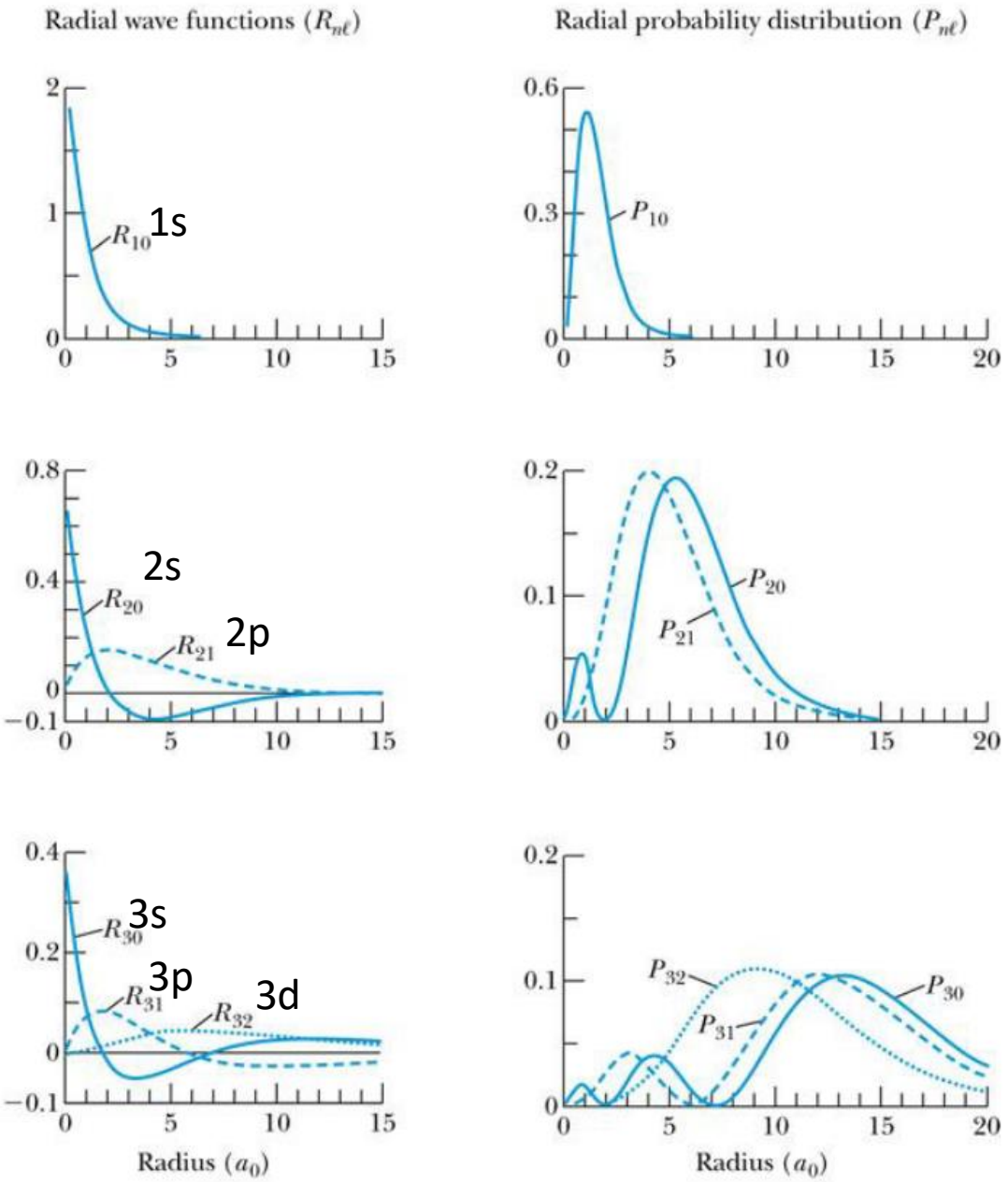
$(2-\rho)e^{-\rho/2}$

$\rho e^{-\rho/2}$

$(6-6\rho+\rho^2)e^{-\rho/2}$

$(4-\rho)\rho e^{-\rho/2}$

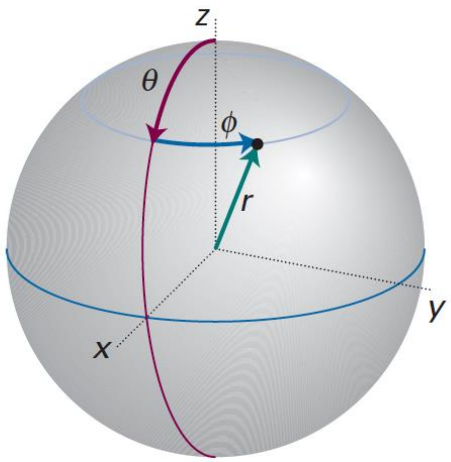
$\rho^2 e^{-\rho/2}$




$$P_{nl}(r) = r^2 R_{nl}^2(r)$$

The zero at $r = 0$ is not a radial node

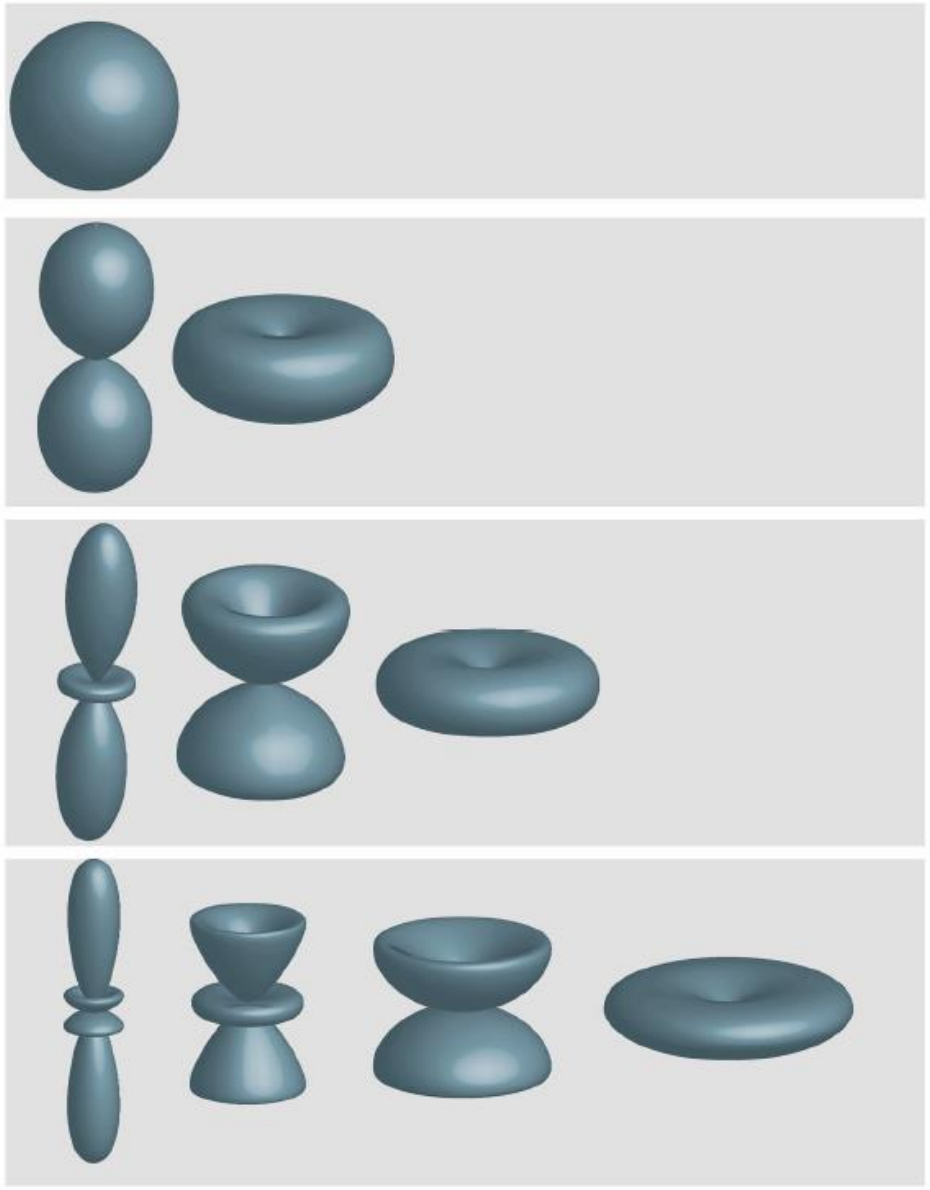
# Hydrogenic angular wavefunctions: Spherical harmonics




| | $l$ | $m_l$ | $Y_{l,m}(\theta,\phi)$ |
|---|---|---|---|
| s | 0 | 0 | $\left(\frac{1}{4\pi}\right)^{1/2}$ |
| p | 1 | 0 | $\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$ |
| | | ±1 | $\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$ |
| d | 2 | 0 | $\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$ |
| | | ±1 | $\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$ |
| | | ±2 | $\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$ |
| f | 3 | 0 | $\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$ |
| | | ±1 | $\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\, e^{\pm i\phi}$ |
| | | ±2 | $\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$ |
| | | ±3 | $\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$ |

# Angular momentum

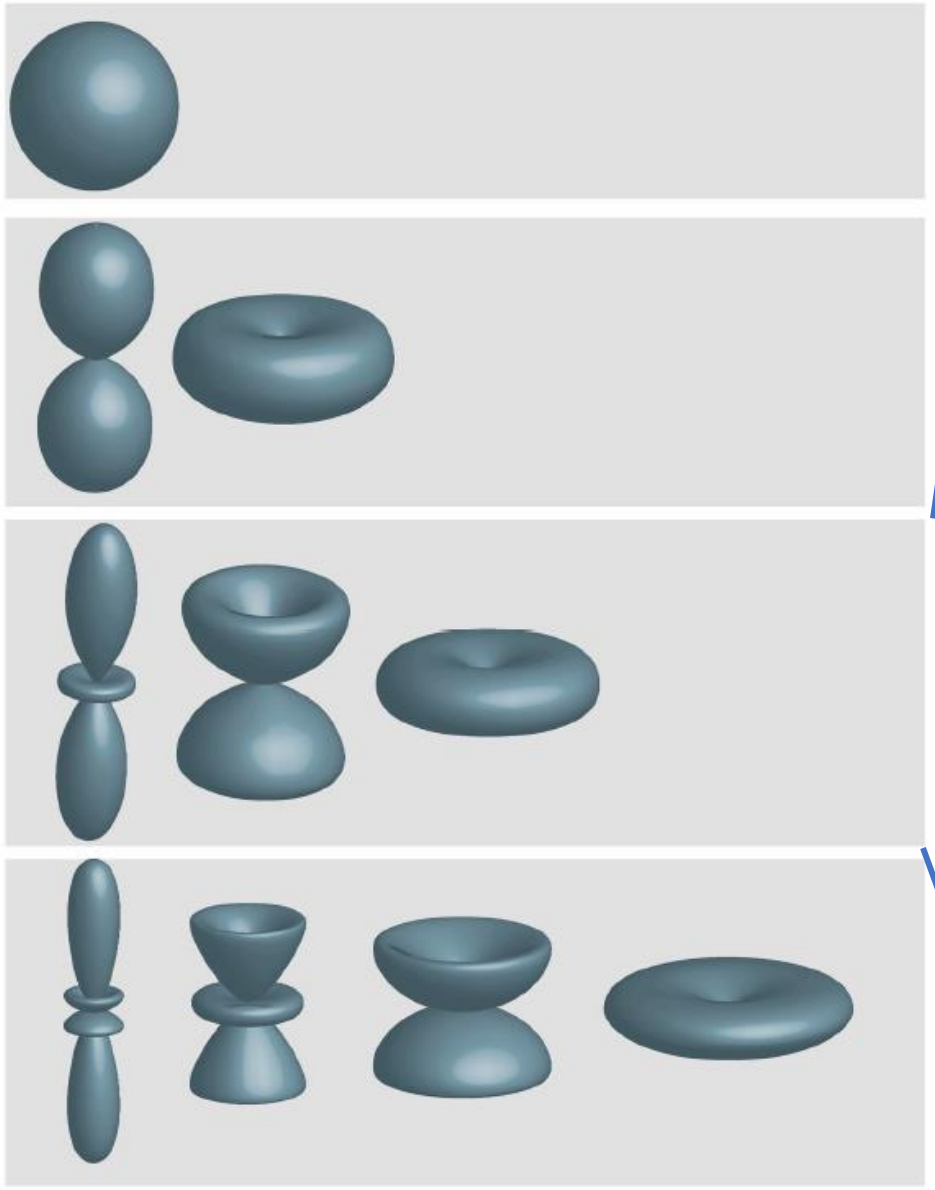
electron density angular distribution

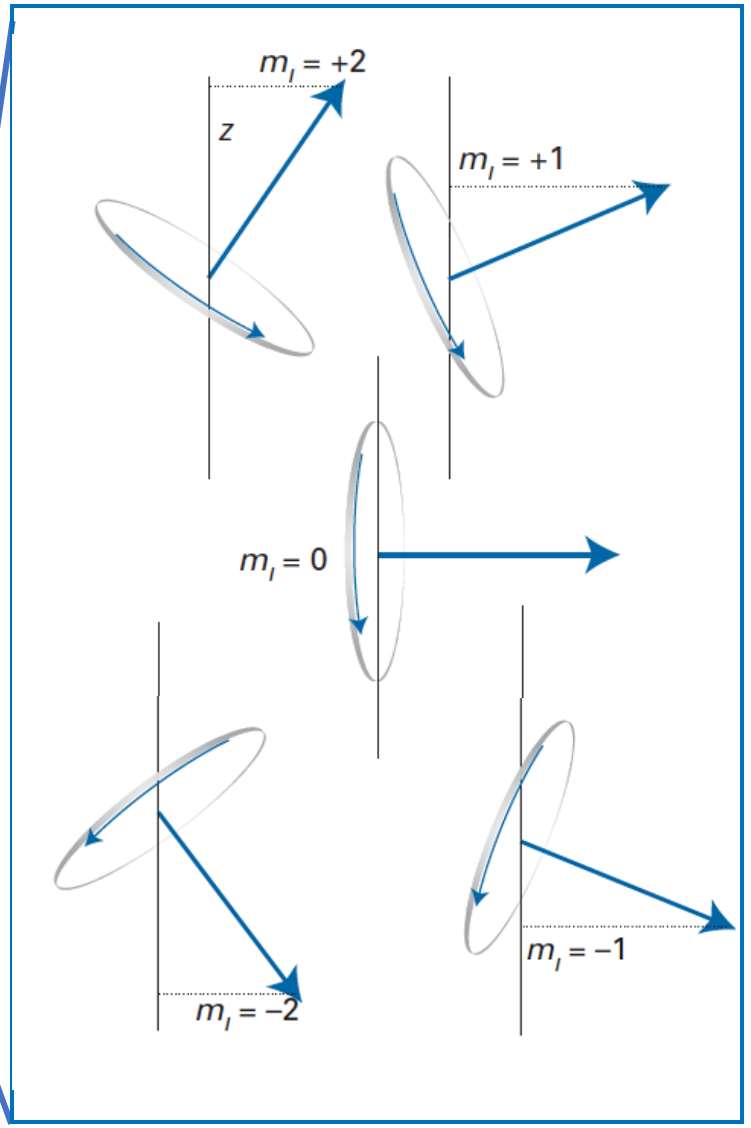


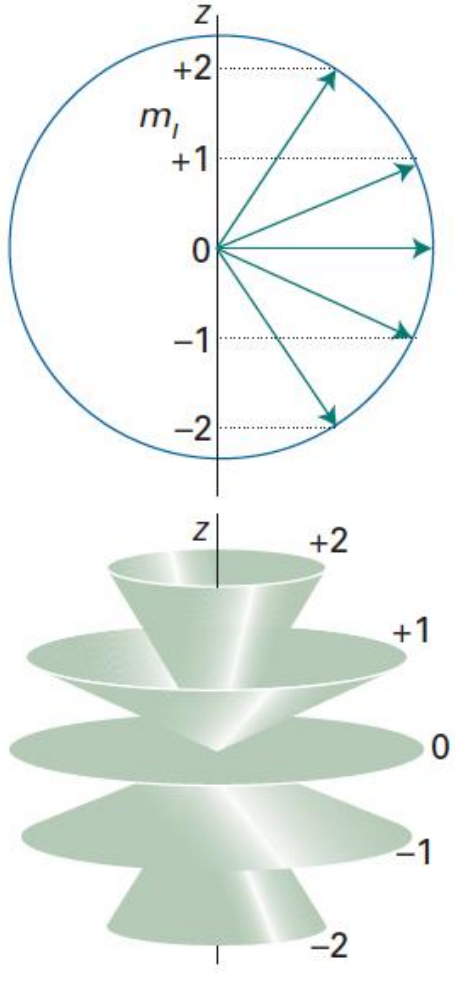

| | $l$ | $m_l$ | $Y_{l,m_l}(\theta,\phi)$ |
|---|---|---|---|
| s | 0 | 0 | $\left(\frac{1}{4\pi}\right)^{1/2}$ |
| p | 1 | 0 | $\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$ |
| | | $\pm 1$ | $\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$ |
| d | 2 | 0 | $\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$ |
| | | $\pm 1$ | $\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$ |
| | | $\pm 2$ | $\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$ |
| f | 3 | 0 | $\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$ |
| | | $\pm 1$ | $\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta - 1)\sin\theta\, e^{\pm i\phi}$ |
| | | $\pm 2$ | $\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$ |
| | | $\pm 3$ | $\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$ |

# Angular momentum

electron density angular distribution



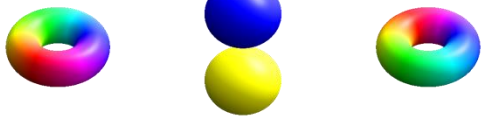

The angular part of the wave function describes the angular distribution of the electron during its precessional motion

# Atomic orbitals

Complex wavefunctions

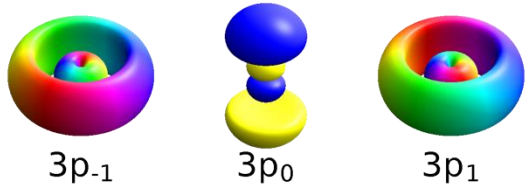
$1s_0$

$2s_0$

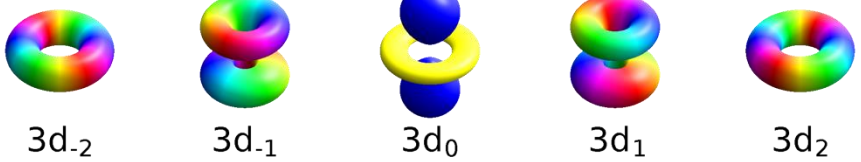


$2p_{-1}$ $2p_0$ $2p_1$

$3s_0$

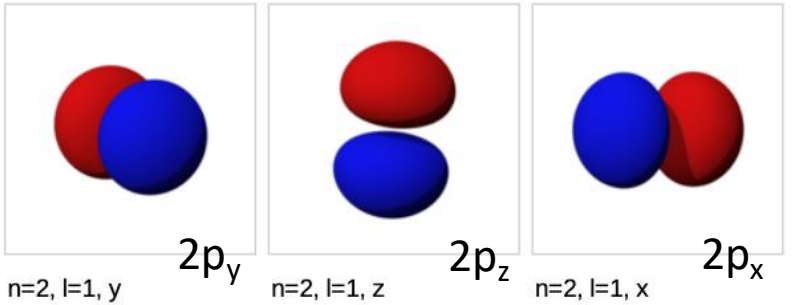


$3p_{-1}$ $3p_0$ $3p_1$



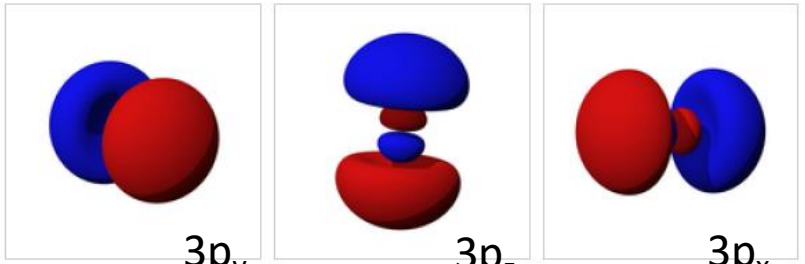
$3d_{-2}$ $3d_{-1}$ $3d_0$ $3d_1$ $3d_2$

Real wavefunctions (linear combinations)



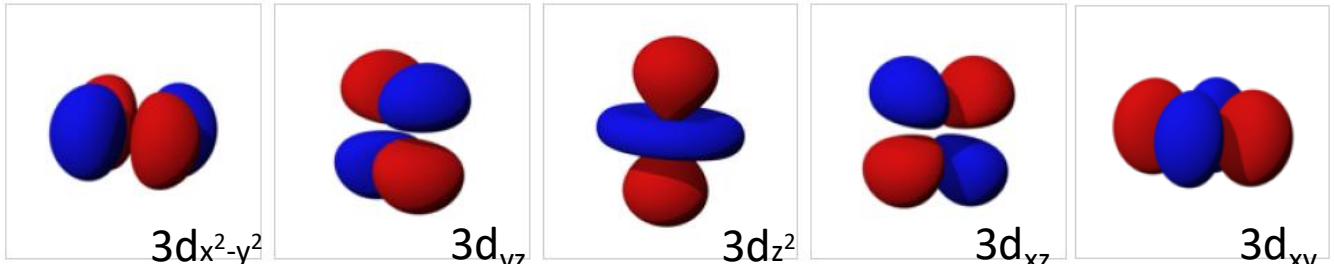
$2p_y$ $2p_z$ $2p_x$

n=2, l=1, y n=2, l=1, z n=2, l=1, x



$3p_y$ $3p_z$ $3p_x$

n=3, l=1, y n=3, l=1, z n=3, l=1, x



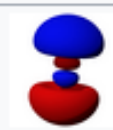
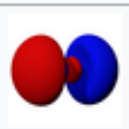
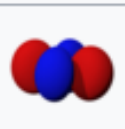
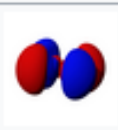
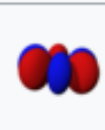
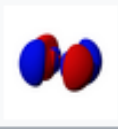
$3d_{x^2-y^2}$ $3d_{yz}$ $3d_{z^2}$ $3d_{xz}$ $3d_{xy}$

n=3, l=2, $x^2-y^2$ n=3, l=2, yz n=3, l=2, $z^2$ n=3, l=2, xz n=3, l=2, xy

https://commons.wikimedia.org/wiki/Hydrogen_orbitals_3D

https://commons.wikimedia.org/wiki/Hydrogen_orbitals_3D_real

# Orbitals (real wave functions): used in crystals and molecules

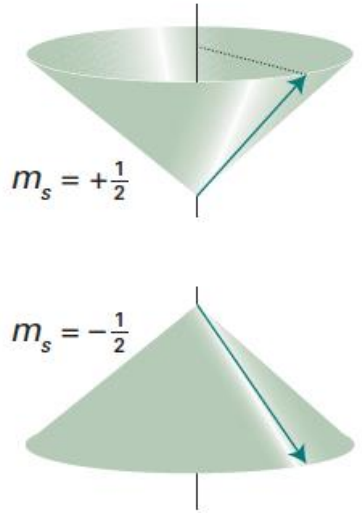
| | s ($\ell = 0$) | p ($\ell = 1$) | | | d ($\ell = 2$) | | | | | f ($\ell = 3$) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $m = 0$ | $m = 0$ | $m = \pm 1$ | | $m = 0$ | $m = \pm 1$ | | $m = \pm 2$ | | $m = 0$ | $m = \pm 1$ | | $m = \pm 2$ | | $m = \pm 3$ | |
| | s | $p_z$ | $p_x$ | $p_y$ | $d_{z^2}$ | $d_{xz}$ | $d_{yz}$ | $d_{xy}$ | $d_{x^2-y^2}$ | $f_{z^3}$ | $f_{xz^2}$ | $f_{yz^2}$ | $f_{xyz}$ | $f_{z(x^2-y^2)}$ | $f_{x(x^2-3y^2)}$ | $f_{y(3x^2-y^2)}$ |
| $n = 1$ |  | | | | | | | | | | | | | | | |
| $n = 2$ |  |  |  |  | | | | | | | | | | | | |
| $n = 3$ |  |  |  |  |  |  |  |  |  | | | | | | | |
| $n = 4$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| $n = 5$ |  |  |  |  |  |  |  |  |  | ... | ... | ... | ... | ... | ... | ... |

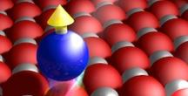
Intrinsic angular momentum of the electron

$s = {}^1/_2$ spin quantum number, magnitude : $|\boldsymbol{s}| = \sqrt{s(s+1)}\hbar = {}^{\sqrt{3}}/_2\,\hbar$

$m_s = \pm {}^1/_2$ spin magnetic quantum number, component along $z$ ,
magnitude: $m_s\hbar = \pm {}^1/_2\,\hbar$

$m_s = +{}^1/_2 = \uparrow, \quad m_s = -{}^1/_2 = \downarrow$





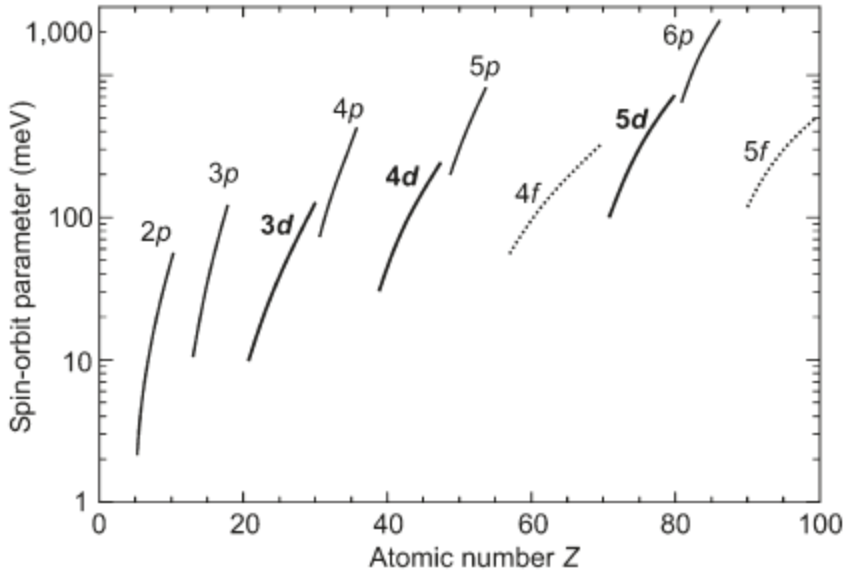
# Spin-orbit coupling

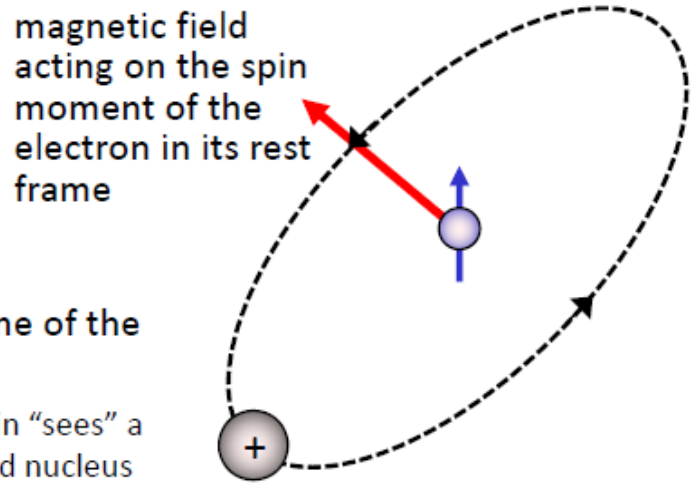
The **spin–orbit interaction** (also called **spin–orbit coupling**) is a relativistic interaction of a particle's spin with the magnetic field generated by its motion inside a potential.

It can be expressed as

$$\mathcal{H}_{SO} \propto \boldsymbol{s} \cdot \boldsymbol{l}$$

The higher the $Z$, the stronger the spin-orbit coupling




**Reference frame of the electron:**

the electron's spin "sees" a positively charged nucleus orbiting around it, giving rise to an electric current and consequently a magnetic field produced by this current

Exercise 1.4

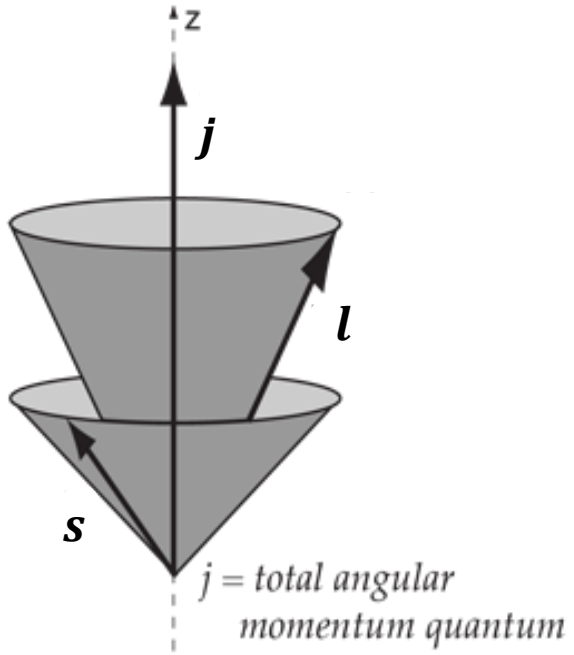
Still only one electron

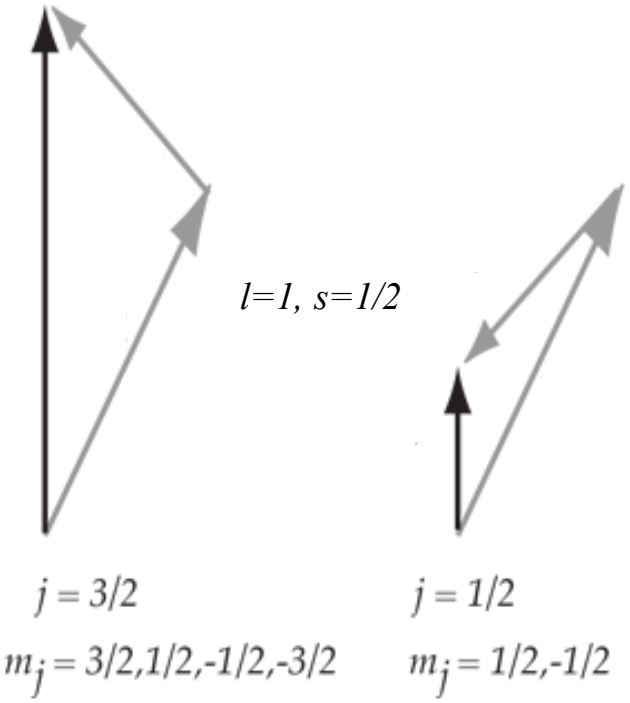
Total angular momentum: $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$

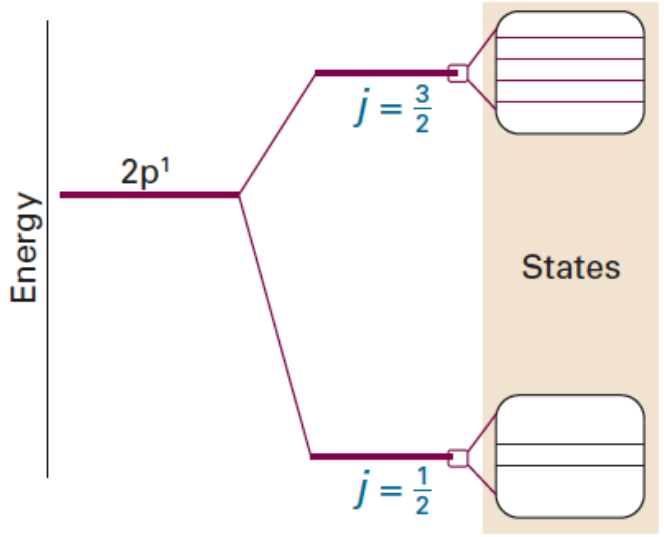
$|\boldsymbol{j}| = \sqrt{j(j+1)}\hbar, \qquad j_z = m_j\hbar$

$j = l + s, \ \ldots, |l - s|$

$m_j = j, \ldots - j$




The electron energy depends on the total angular momentum

The interaction partially lifts the degeneracy of orbitals of a given subshell (same $l$, different $j$ )

Exercise 1.5

all the electrons interact with one another, analytical solution not possible
orbital approximation → electron configuration $(n,\ l)$
Pauli exclusion principle → max two electrons per orbital
Example: Na, 11 electrons: $1s^2\ 2s^2\ 2p^6\ 3s^1$
---

Filling of open subshells? For the ground state it follows the **Hund's rules** (LS-coupling scheme)

1) Total spin $\boldsymbol{S} = \sum_i \boldsymbol{s}_i$ maximized ( $\Rightarrow S = M_S$ max)

2) Total orbital momentum $\boldsymbol{L} = \sum_i \boldsymbol{l}_i$ maximized ( $\Rightarrow L = M_L$ max)

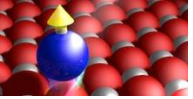
⟺ Coulomb repulsion

3) Total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$
$\boldsymbol{L}$ and $\boldsymbol{S}$ parallel ( $J = L + S$ ) if subshell more than half filled
$\boldsymbol{L}$ and $\boldsymbol{S}$ antiparallel ( $J = |L - S|$ ) if subshell less than half filled

⟺ Spin-orbit interaction

---
Spectroscopic term notation: ${}^{2S+1}L_J$ where

| $L =$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| | S | P | D | F | G | H | I |



# Energy levels in many-electrons atoms

**hydrogenic atom (only one electron):**

$$E_n \propto -\frac{Z^2}{n^2}$$

- orbitals with the same value of $n$ but different values of $l$ are no longer degenerate (consequence of orbital penetration and shielding)
- spin-orbit coupling partially lifts the degeneracy of orbitals of a given subshell (same $l$, different $j$ )

**shell**: $n$ = 1 (K) 2 (L) 3 (M) 4 (N) ...

**subshell**: $l$ = 0 (s) 1 (p) 2 (d) 3 (f) ...

# Core levels energies

***Table 1-1.*** *Electron binding energies, in electron volts, for the elements in their natural forms.*

| Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ | $M_4$ $3d_{3/2}$ | $M_5$ $3d_{5/2}$ | $N_1$ 4s | $N_2$ $4p_{1/2}$ | $N_3$ $4p_{3/2}$ | ... |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H | 13.6 | | | | | | | | | | | | |
| 2 He | 24.6* | | | | | | | | | | | | |
| 3 Li | 54.7* | | | | | | | | | | | | |
| 4 Be | 111.5* | | | | | | | | | | | | |
| 5 B | 188* | | | | | | | | | | | | |
| 6 C | 284.2* | | | | | | | | | | | | |
| 7 N | 409.9* | 37.3* | | | | | | | | | | | |
| 8 O | 543.1* | 41.6* | | | | | | | | | | | |
| 9 F | 696.7* | | | | | | | | | | | | |
| 10 Ne | 870.2* | 48.5* | 21.7* | 21.6* | | | | | | | | | |
| 11 Na | 1070.8† | 63.5† | 30.65 | 30.81 | | | | | | | | | |
| ⋮ | | | | | | | | | | | | | |
| 27 Co | 7709 | 925.1† | 793.2† | 778.1† | 101.0† | 58.9† | 59.9† | | | | | | |
| 28 Ni | 8333 | 1008.6† | 870.0† | 852.7† | 110.8† | 68.0† | 66.2† | | | | | | |
| 29 Cu | 8979 | 1096.7† | 952.3† | 932.7 | 122.5† | 77.3† | 75.1† | | | | | | |
| ⋮ | | | | | | | | | | | | | |
| 79 Au | 80725 | 14353 | 13734 | 11919 | 3425 | 3148 | 2743 | 2291 | 2206 | 762.1† | 642.7† | 546.3† | |
| 80 Hg | 83102 | 14839 | 14209 | 12284 | 3562 | 3279 | 2847 | 2385 | 2295 | 802.2† | 680.2† | 576.6† | ... |
| 81 Tl | 85530 | 15347 | 14698 | 12658 | 3704 | 3416 | 2957 | 2485 | 2389 | 846.2† | 720.5† | 609.5† | |
| 82 Pb | 88005 | 15861 | 15200 | 13035 | 3851 | 3554 | 3066 | 2586 | 2484 | 891.8† | 761.9† | 643.5† | |

K

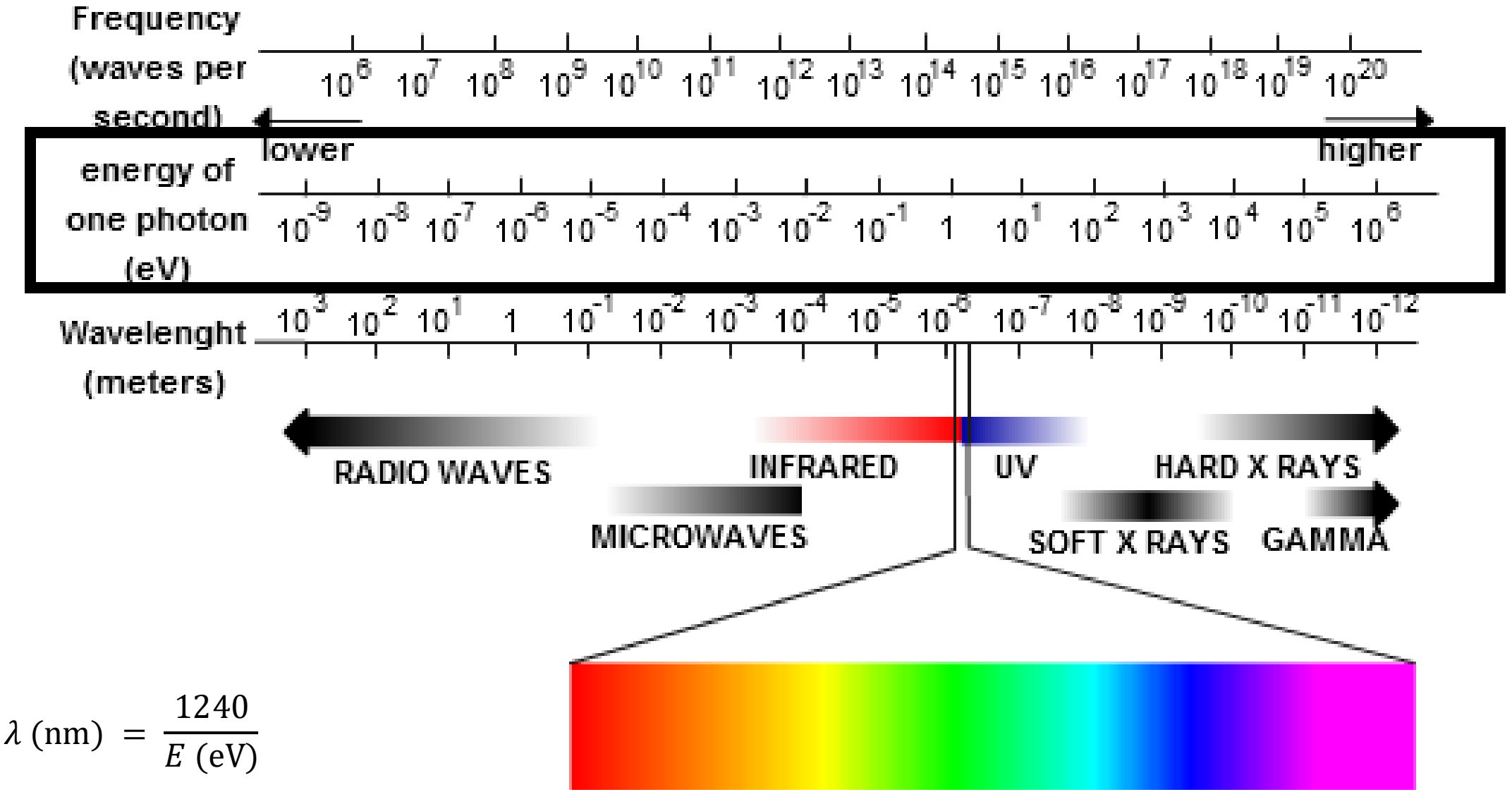
L

M

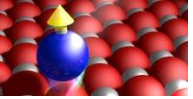
N

X-ray data booklet, *Lawrence Berkeley National Laboratory*
https://xdb.lbl.gov/

# Core levels energies




$$\lambda\,(\mathrm{nm}) = \frac{1240}{E\,(\mathrm{eV})}$$



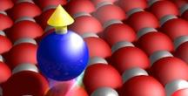
# Molecular orbitals

Approximate solution to the Schrödinger equation for the electrons in the field of the nuclei of the atoms forming the molecule

Usually constructed by combining atomic orbitals or hybrid orbitals from each atom of the molecule

LCAO (Linear Combination of Atomic Orbitals)

Covalent bonds (electron sharing)



# $H_2$ molecule: inter-atomic exchange interaction

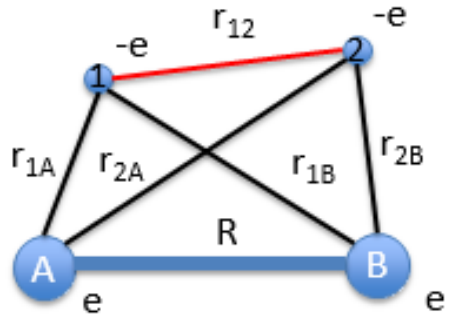
$$\mathcal{H} = \mathcal{H}_{1A} + \mathcal{H}_{2B} \underbrace{- \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1B}} + \frac{1}{r_{2A}} - \frac{1}{r_{12}} - \frac{1}{R}\right)}_{U}$$

$$r_{1A} = |\boldsymbol{R}_A - \boldsymbol{r}_1| \qquad r_{12} = |\boldsymbol{r}_2 - \boldsymbol{r}_1|$$

$$r_{2B} = |\boldsymbol{R}_B - \boldsymbol{r}_2| \qquad R = |\boldsymbol{R}_A - \boldsymbol{R}_B|$$

$$r_{1B} = |\boldsymbol{R}_B - \boldsymbol{r}_1|$$

$$r_{2A} = |\boldsymbol{R}_A - \boldsymbol{r}_2|$$




Atom A with electron 1, atom B with electron 2, $R$ distance between the two nuclei. Additional interactions $U$.

Because electrons are fermions, the total wavefunction (orbital times spin) must be antisymmetric (i.e., it changes sign) upon particle exchange.

Spin wavefunctions are generated by linear combinations of the 4 spin states: $|m_{s1}, m_{s2}\rangle = |\uparrow\uparrow\rangle,\ |\downarrow\downarrow\rangle,\ |\uparrow\downarrow\rangle,\ |\downarrow\uparrow\rangle$

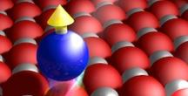
$|S, M_S\rangle$

$|0,0\rangle = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]$ → singlet, antisymmetric upon particle exchange

$|1,+1\rangle = |\uparrow\uparrow\rangle$

$|1,0\rangle = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle]$ → triplet, symmetric upon particle exchange

$|1,+1\rangle = |\downarrow\downarrow\rangle$



# $H_2$ molecule: inter-atomic exchange interaction

the orbital wavefunction associated with the singlet (triplet) must be symmetric (antisymmetric);
such orbital wavefunctions are obtained by different linear combinations of the products of the atomic orbitals $\phi(\boldsymbol{r})$:

$$\psi_{sym}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{\sqrt{2}}[\phi_A(\boldsymbol{r}_1)\phi_B(\boldsymbol{r}_2) + \phi_A(\boldsymbol{r}_2)\phi_B(\boldsymbol{r}_1)]$$

$$\psi_{asym}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{\sqrt{2}}[\phi_A(\boldsymbol{r}_1)\phi_B(\boldsymbol{r}_2) - \phi_A(\boldsymbol{r}_2)\phi_B(\boldsymbol{r}_1)]$$

Combining orbital and spin wavefunctions in the appropriate way, antisymmetric total wavefunctions are obtained:

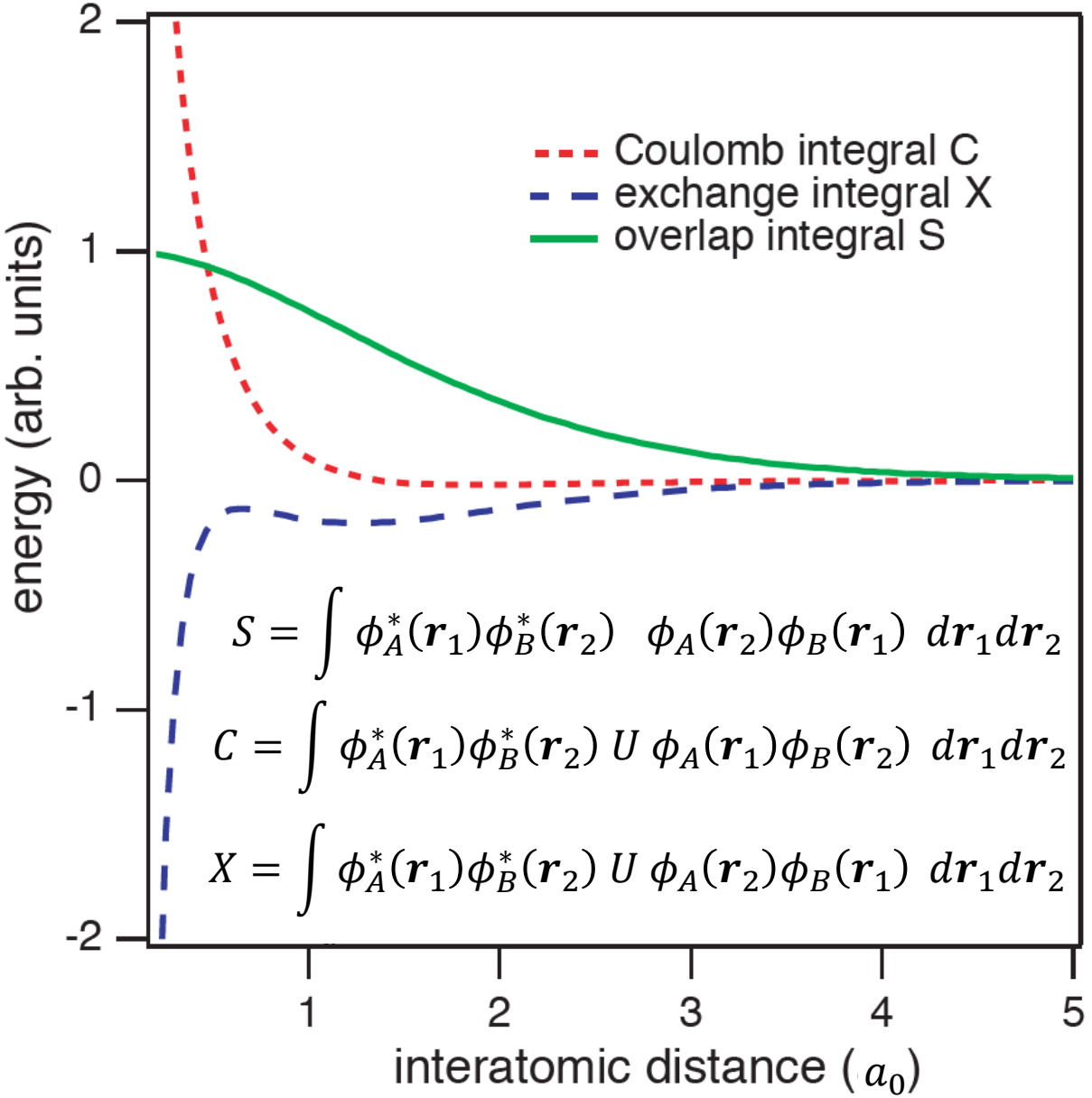
$$\Psi_{singlet} = \psi_{sym}(\boldsymbol{r}_1,\boldsymbol{r}_2)|0,0\rangle$$

$$\Psi_{triplet} = \psi_{asym}(\boldsymbol{r}_1,\boldsymbol{r}_2)|1,M_S\rangle \qquad M_S = -1,0,1$$

Calculate the molecular energy levels for the two orbital wavefunctions:

$$E = \frac{\langle\psi|\mathcal{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

# $H_2$ molecule: inter-atomic exchange interaction




$$E = 2E_{H,1s} + E_{sing/trip}$$

$$E_{trip} = \frac{C(R) - X(R)}{1 - S(R)} \qquad E_{trip} > E_{sing}$$

$$E_{sing} = \frac{C(R) + X(R)}{1 + S(R)}$$

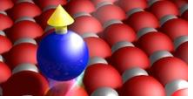
$$E_{H,1s} = \int \phi_A^*(\boldsymbol{r}_1)\mathcal{H}_{1A}\,\phi_A(\boldsymbol{r}_1)\ d\boldsymbol{r}_1 = \int \phi_B^*(\boldsymbol{r}_2)\mathcal{H}_{2B}\,\phi_B(\boldsymbol{r}_2)\ d\boldsymbol{r}_2$$

At large distances $S(R) \approx 0 \Rightarrow E = 2E_{H,1s} + C \pm X$

The energy of the system depends on the spin of the electrons, despite of the fact that the spin does not enter the calculation directly $(E_{sing} - E_{trip} = 2X)$

The $H_2$ molecule can be described by an *effective* Hamiltonian given by:

$$\mathcal{H}_{eff} = 2\mathcal{H}_{H,1s} + \mathcal{H}_{Coul} + \mathcal{H}_{exch}$$



# The Heisenberg Hamiltonian for the $H_2$ molecule

$$\Delta E_{ST} = E_S - E_T = 2X = 2\int \phi_A^*(\boldsymbol{r}_1)\phi_B^*(\boldsymbol{r}_2)\, U\, \phi_A(\boldsymbol{r}_2)\phi_B(\boldsymbol{r}_1)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

Trick: the difference in energy between singlet and triplet states can be parametrized using $\boldsymbol{s}_1 \cdot \boldsymbol{s}_2$

$$\boldsymbol{S}^2 = \boldsymbol{s}_1^2 + \boldsymbol{s}_2^2 + 2\boldsymbol{s}_1 \cdot \boldsymbol{s}_2$$

$$2\boldsymbol{s}_1 \cdot \boldsymbol{s}_2 = \boldsymbol{S}^2 - \boldsymbol{s}_1^2 - \boldsymbol{s}_2^2 = \boldsymbol{S}^2 - \tfrac{3}{4} - \tfrac{3}{4}$$

$S = 1 \rightarrow \boldsymbol{S}^2 = 2 \quad \rightarrow \boldsymbol{s}_1 \cdot \boldsymbol{s}_2 = +1/4$ triplet

$S = 0 \rightarrow \boldsymbol{S}^2 = 0 \quad \rightarrow \boldsymbol{s}_1 \cdot \boldsymbol{s}_2 = -3/4$ singlet

$$\mathcal{H}_{ST} = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T)\, \boldsymbol{s}_1 \cdot \boldsymbol{s}_2 = \underbrace{\frac{1}{4}(E_S + 3E_T)}_{\text{constant } E_0} - 2\, J_{ex}\, \boldsymbol{s}_1 \cdot \boldsymbol{s}_2$$

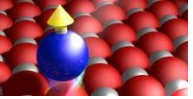
constant $E_0$, absorbed into other constant energy terms

exchange constant
(or exchange integral)
in Heisenberg model
$J_{ex} = X = \Delta E_{ST}/2$

$S = 1 \qquad E_T = E_0 - 1/2\, J_{ex}$

$S = 0 \qquad E_S = E_0 + 3/2\, J_{ex}$

for the $H_2$ molecule, $J_{ex} < 0$
the singlet state is the ground state



# The Heisenberg exchange Hamiltonian

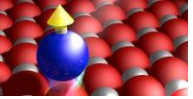
$$\mathcal{H}_{exch} = -2J_{ex}\ \boldsymbol{s}_1 \cdot \boldsymbol{s}_2$$

**Origin of exchange interaction:**

- **Coulomb repulsion** between electrons
- total anti-symmetric wave function (**Pauli exclusion principle**)

- if $J_{ex} > 0$ → ferromagnetic coupling
- if $J_{ex} < 0$ → antiferromagnetic coupling

- Can be extended to higher spins
- Can be extended to more than two spins by summing over pairs



# Simple representation of covalent bonds - Molecular orbitals

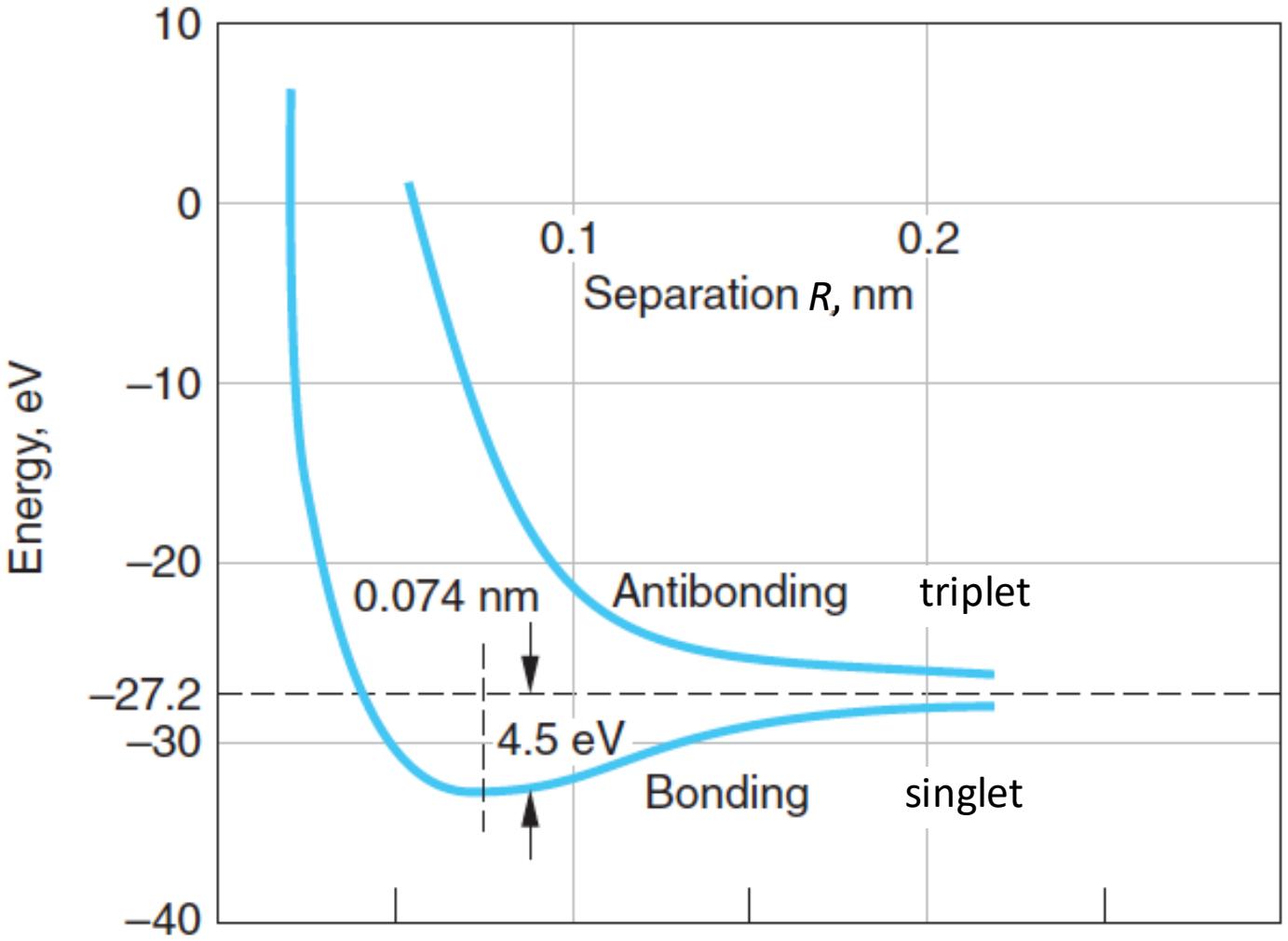
Use the sign (phase) ot the wavefunctions to indicate:

constructive interference → localization of electrons between the atoms, bonding, lower energy

destructive interference → depletion of electrons between the atoms, antibonding, higher energy

The different signs are typically represented by different shades / colors

# $H_2$ molecule: bonding and antibonding orbitals




$$\psi_{sym}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}}[\phi_A(\boldsymbol{r}_1)\phi_B(\boldsymbol{r}_2) + \phi_A(\boldsymbol{r}_2)\phi_B(\boldsymbol{r}_1)]$$

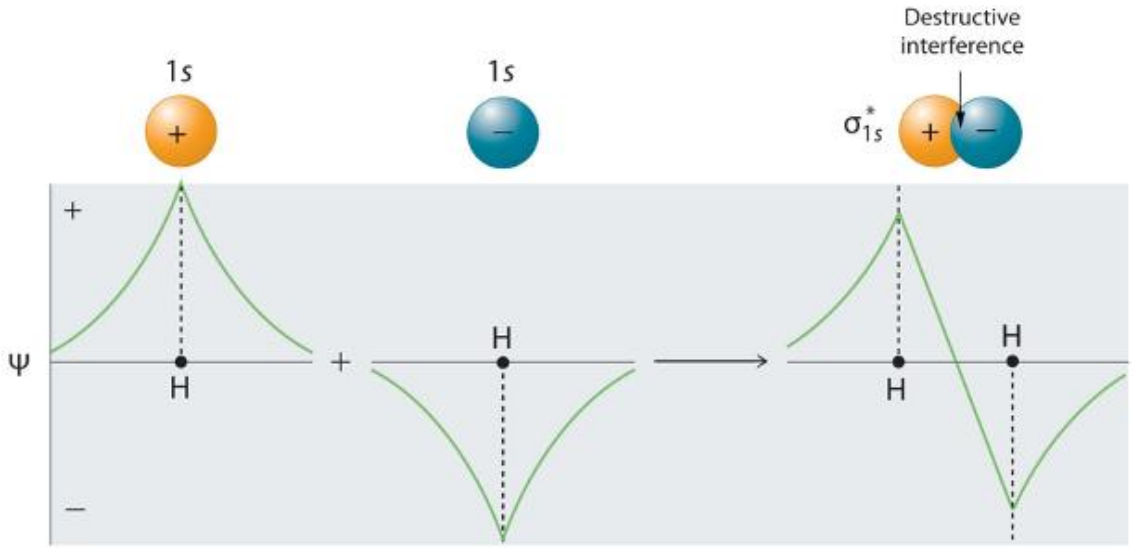
$$\psi_{asym}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}}[\phi_A(\boldsymbol{r}_1)\phi_B(\boldsymbol{r}_2) - \phi_A(\boldsymbol{r}_2)\phi_B(\boldsymbol{r}_1)]$$

$$\Psi_{singlet} = \psi_{sym}(\boldsymbol{r}_1, \boldsymbol{r}_2)\,|\,0,0\rangle$$

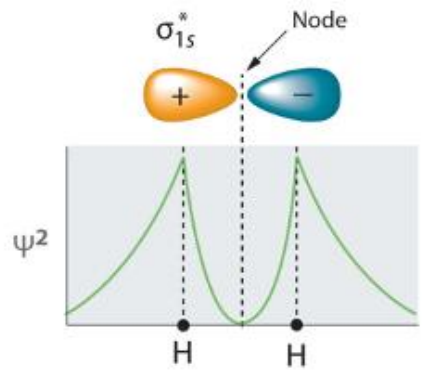
$$\Psi_{triplet} = \psi_{asym}(\boldsymbol{r}_1, \boldsymbol{r}_2)\,|\,1, M_s\rangle$$

# s isotropic orbitals → σ orbitals

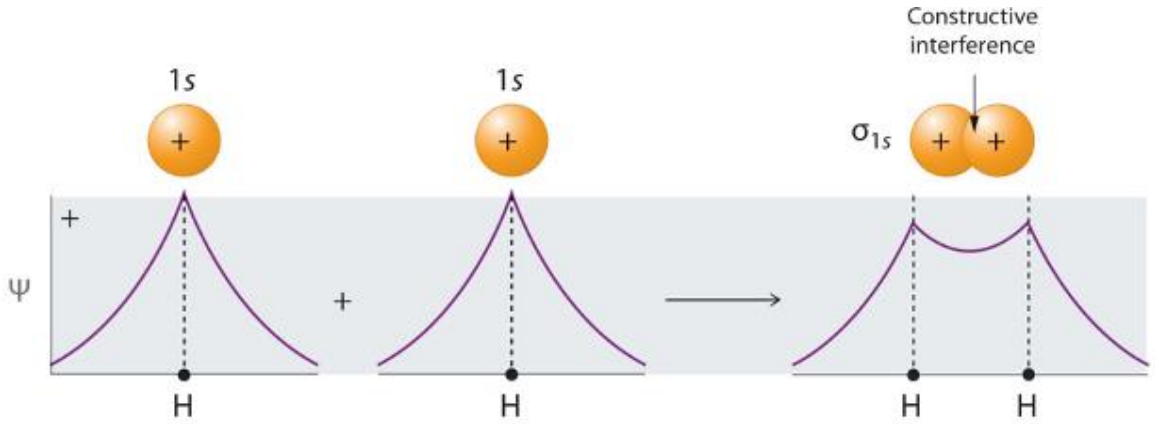
## $H_2$ molecule



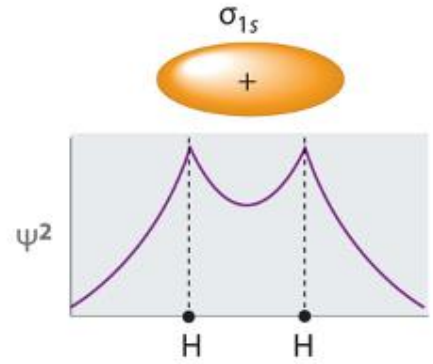

(c) Wave functions combined for $\sigma^*_{1s}$




(d) Antibonding probability density

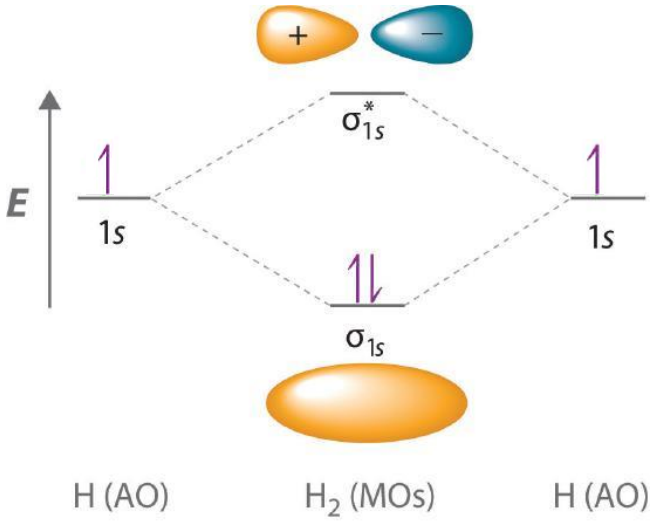



(a) Wave functions combined for $\sigma_{1s}$



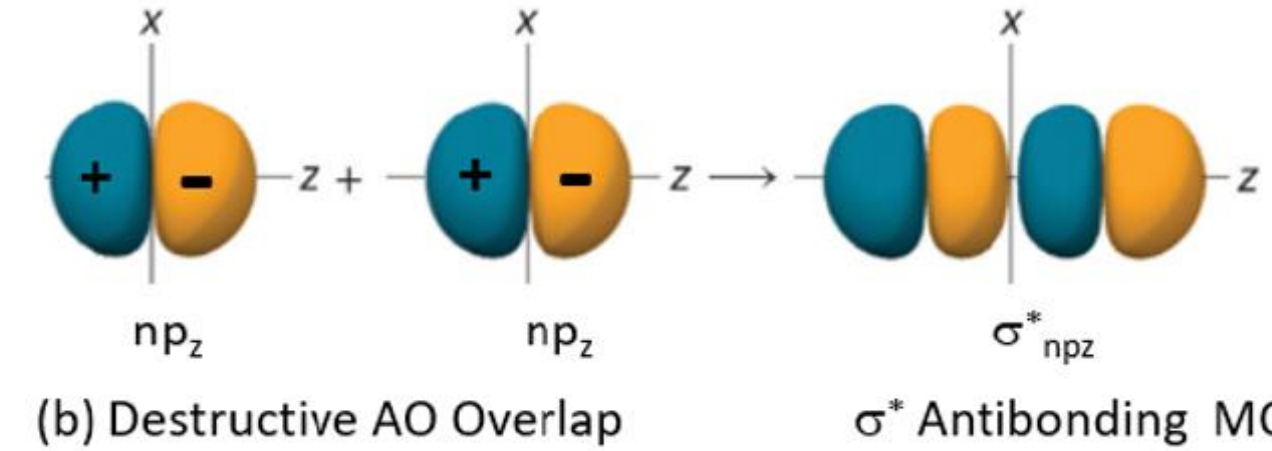

(b) Bonding probability density

## Energy scheme



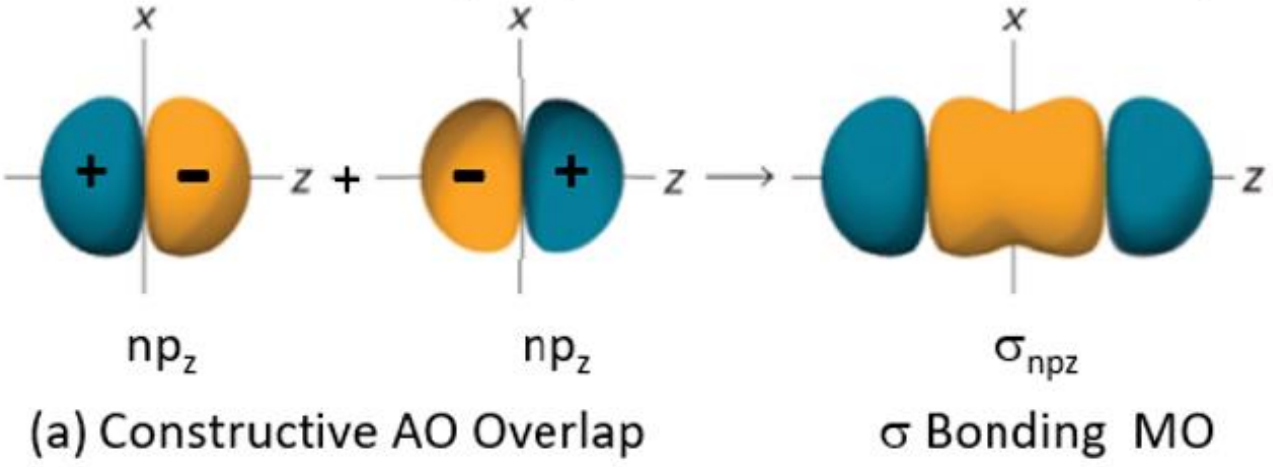
# p orbitals directed along the interatomic axis→ σ orbitals

**example: $p_z$ orbitals, interatomic axis along z**




higher energy

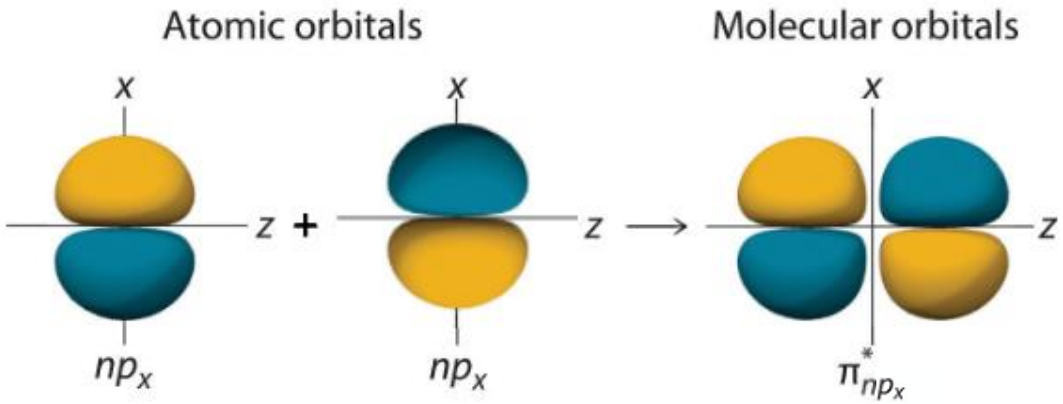
Atomic Orbitals (AOs) Molecular Orbital (MO)



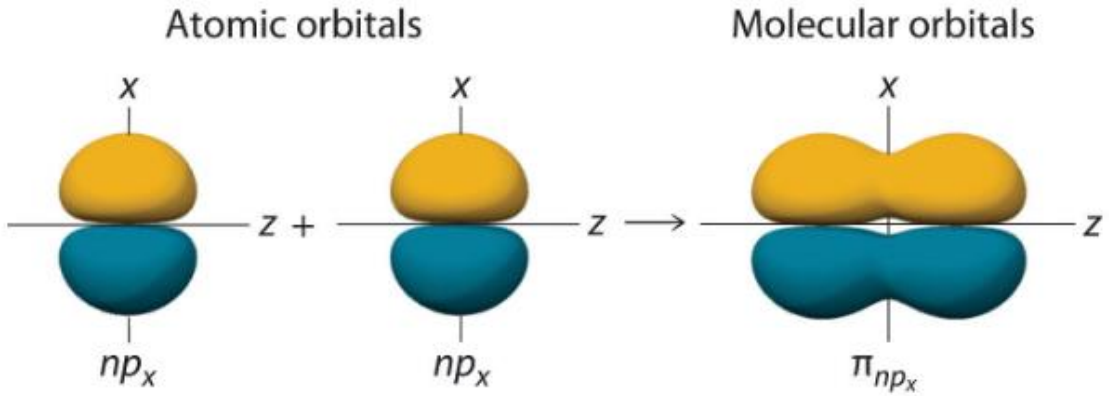

lower energy

# p orbitals perpendicular to the interatomic axis → π orbitals

**example: $p_x$ orbitals, interatomic axis along z**



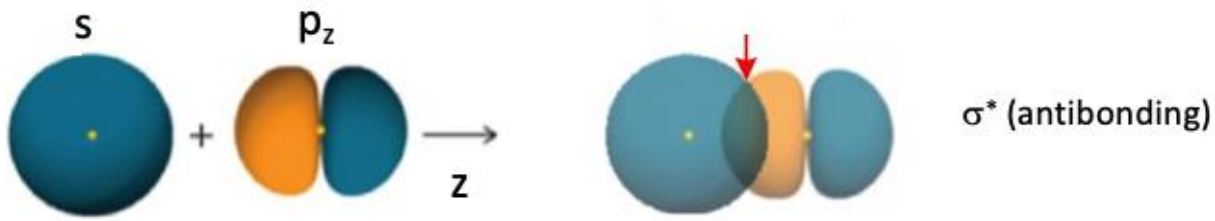

higher energy
anti-bonding, π*

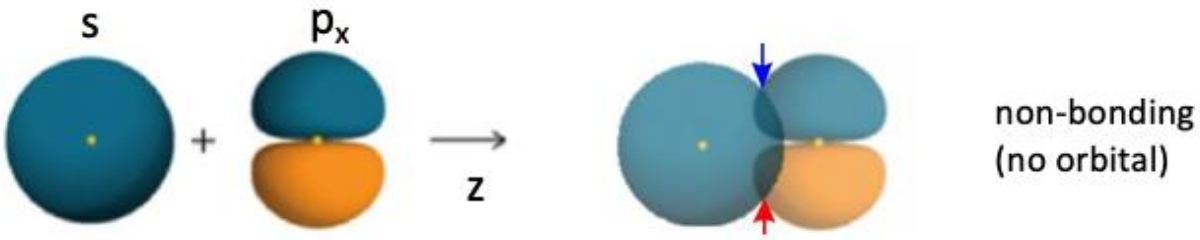


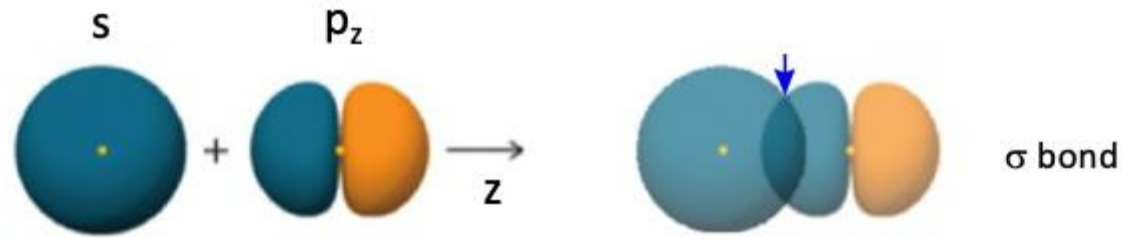

lower energy
bonding, π

# atomic orbitals forming molecular orbitals can have different $l$

**example: s and p orbitals**

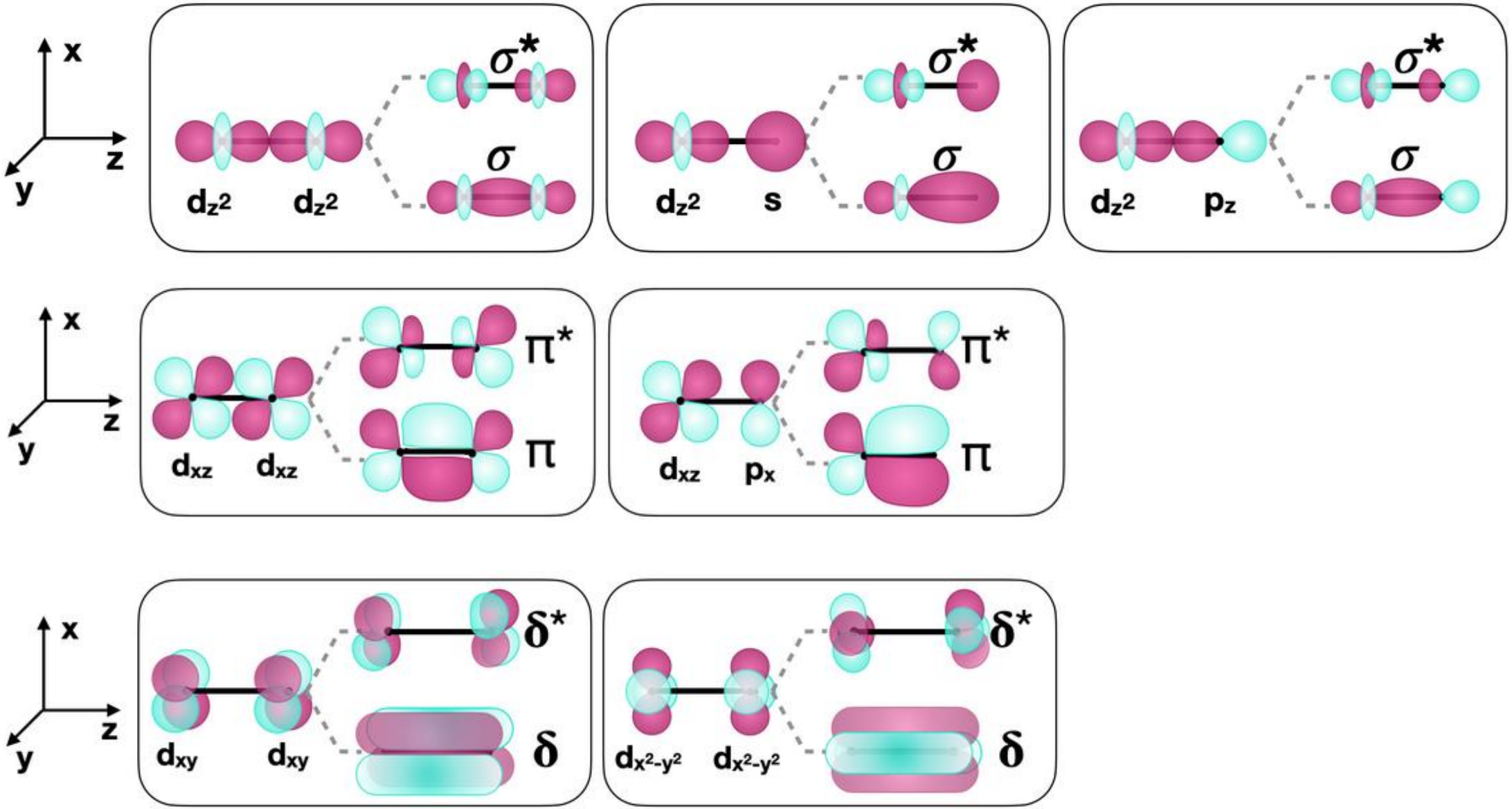



atomic orbitals must have compatible symmetry and orientation to form molecular orbitals

# bonds involving atomic d orbitals



Exercises 1.7 – 1.8

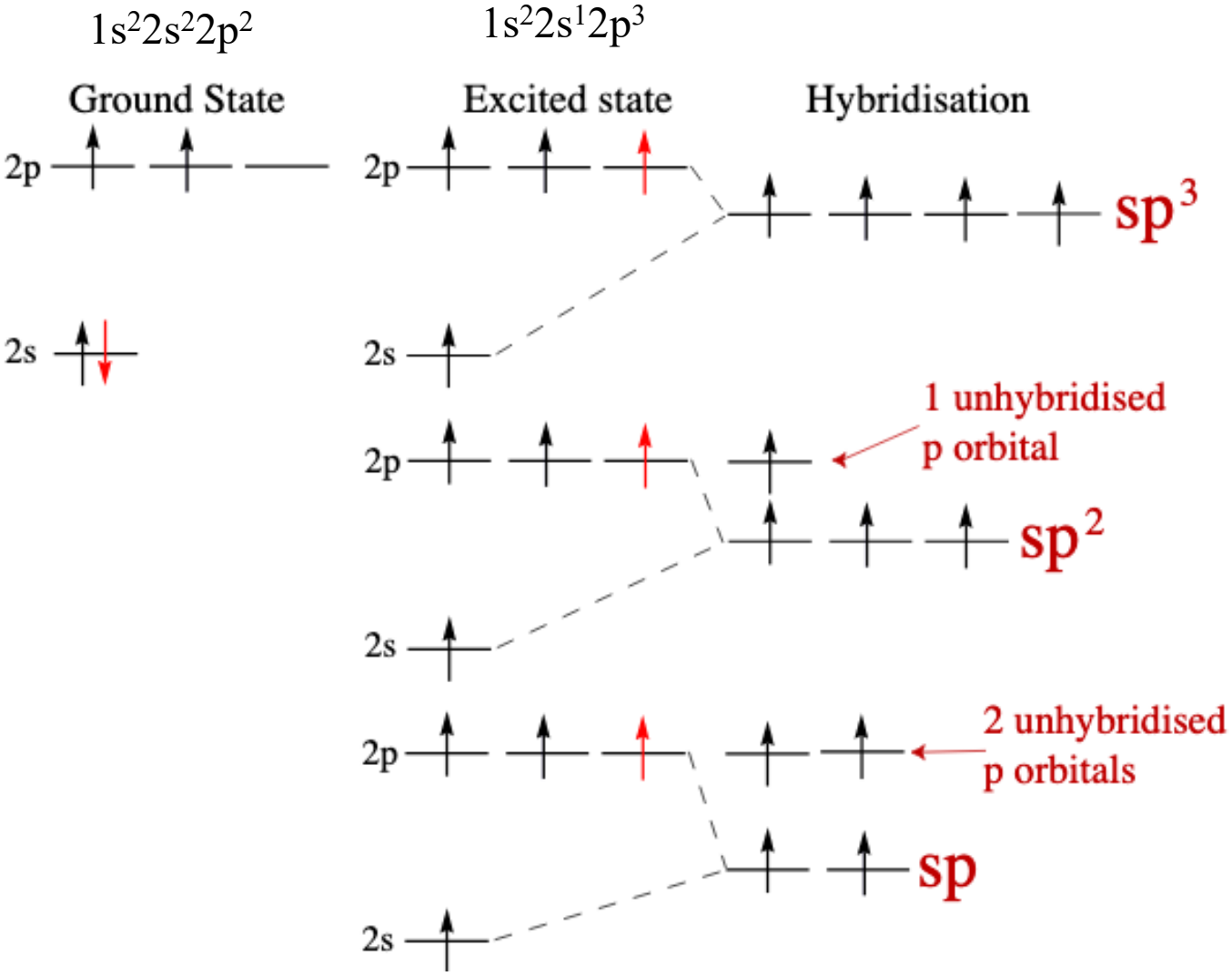
**hybrid orbitals**

perturbation of the description of the atomic orbitals induced by the interaction with the surronding atoms

linear combinations of atomic orbitals that have similar energy to produce sets of equivalent orbitals that are properly oriented to form bonds and favored in energy

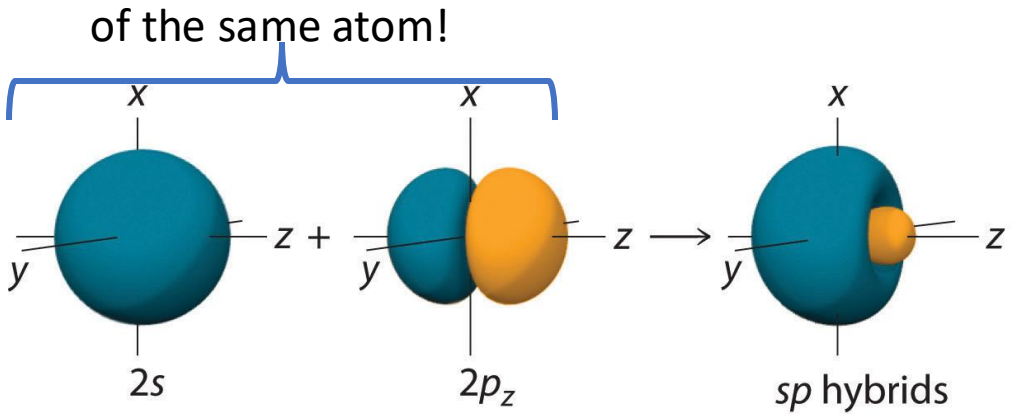
NB: although hybridization makes sense only in the presence of surrounding atoms, it is common to define the hybrid orbitals on single atoms

**example: carbon**

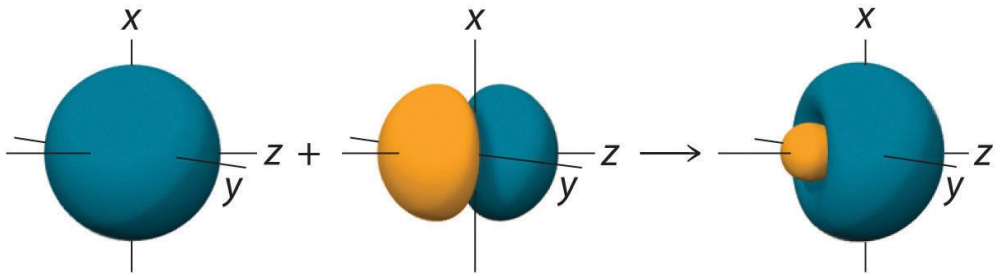


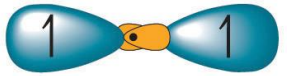
# sp hybridization

the s orbital hybridize with one p orbital, to give **two** sp hybrid orbitals ($sp^1$)




linear bond

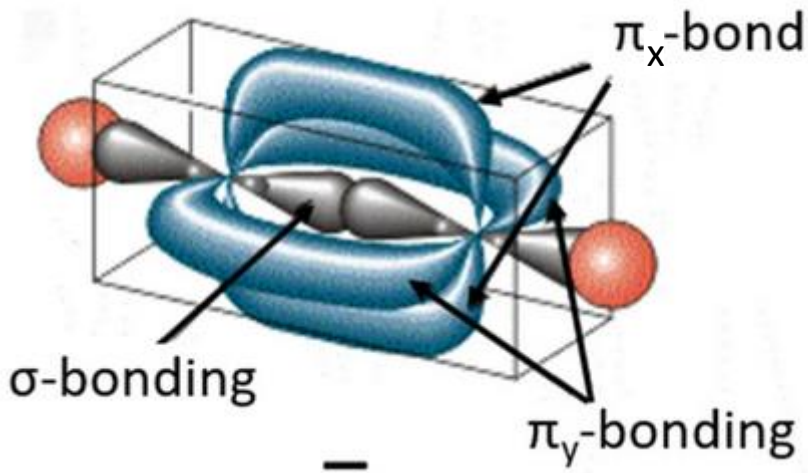


Schematic representation of hybrids shown together

**example: acetylene $C_2H_2$**

H—C≡C—H




σ bond between the sp orbitals (s $p_z$)
σ bonds between sp orbitals and H 1s orbitals
π bonds between the two $p_x$ orbitals and between the two $p_y$ orbitals

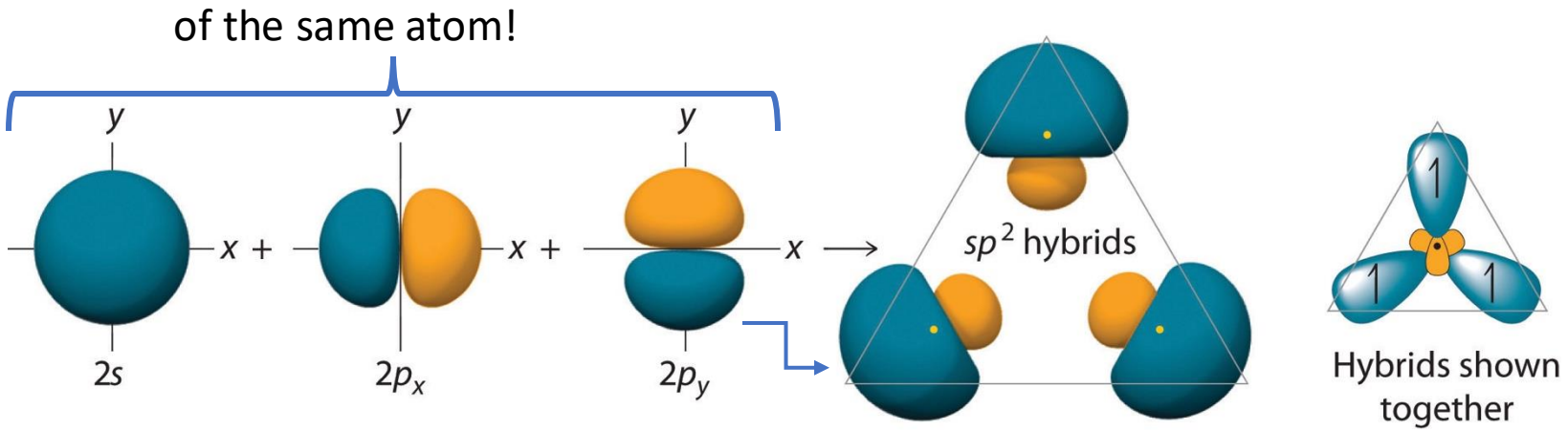


33

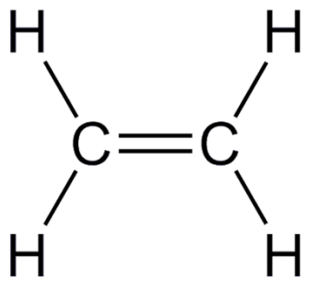
# $sp^2$ hybridization

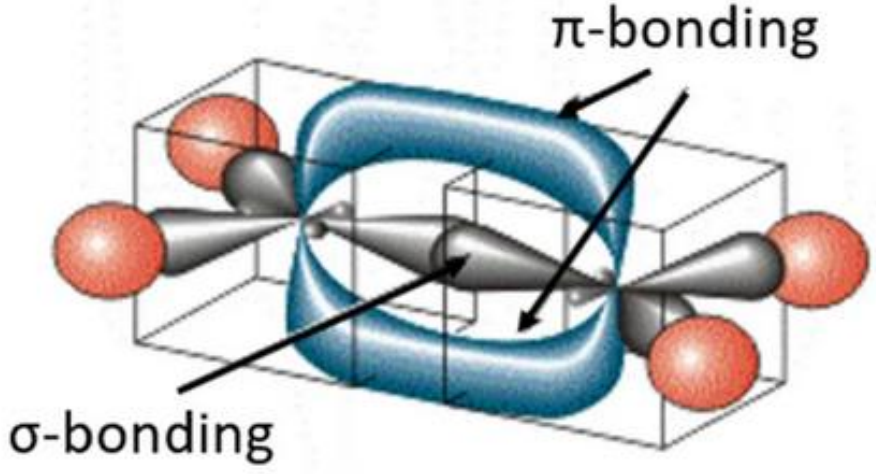
the s orbital hybridize with two p orbitals, to give **three** $sp^2$ hybrid orbitals

trigonal planar bonds




**example: ethylene $C_2H_4$**




σ bond between the $sp^2$ orbitals
σ bonds between $sp^2$ orbitals and H 1s orbitals
π bond between the $p_z$ orbitals

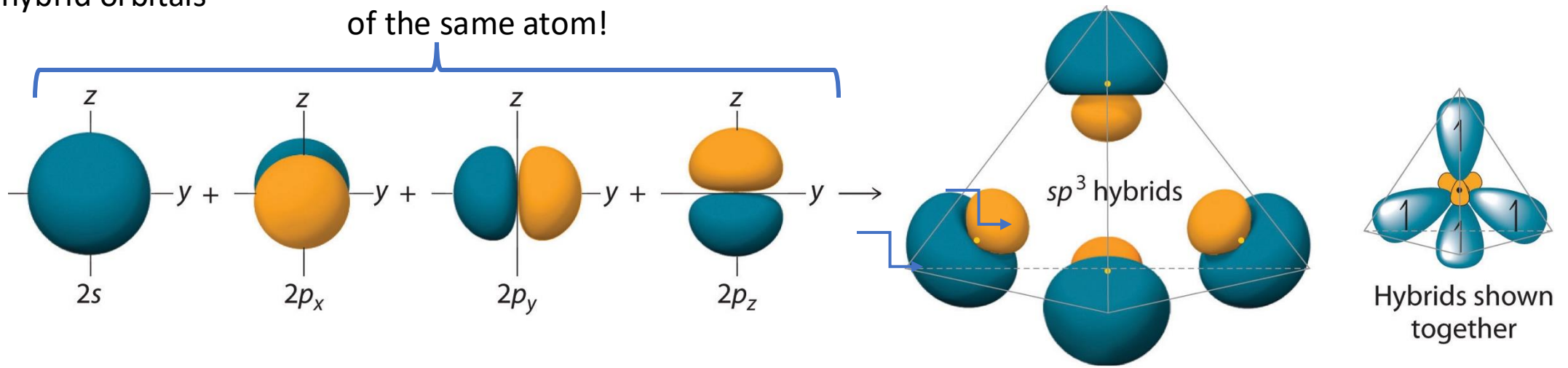

34

# $sp^3$ hybridization

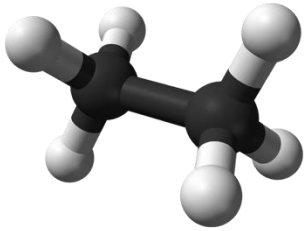
the s orbital hybridize with the three p orbitals,
to give **four** $sp^3$ hybrid orbitals

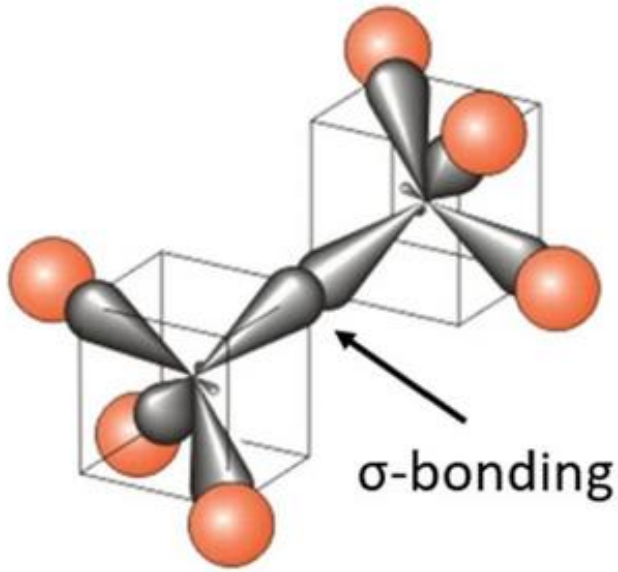
of the same atom!

tetrahedral geometry



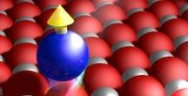

**example: ethane $C_2H_6$**

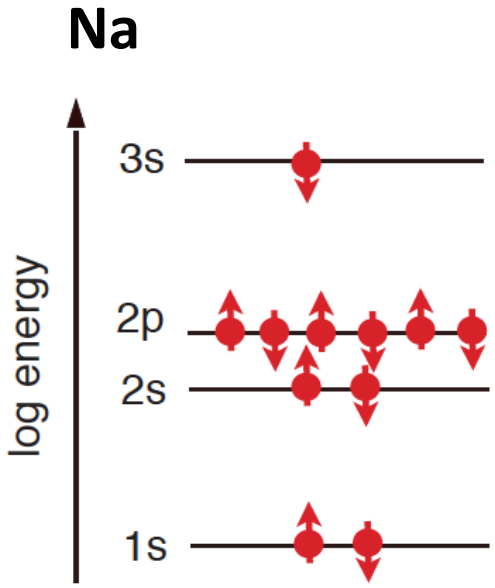


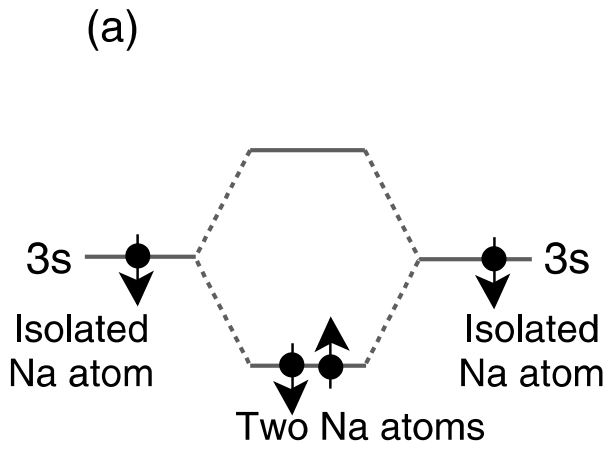


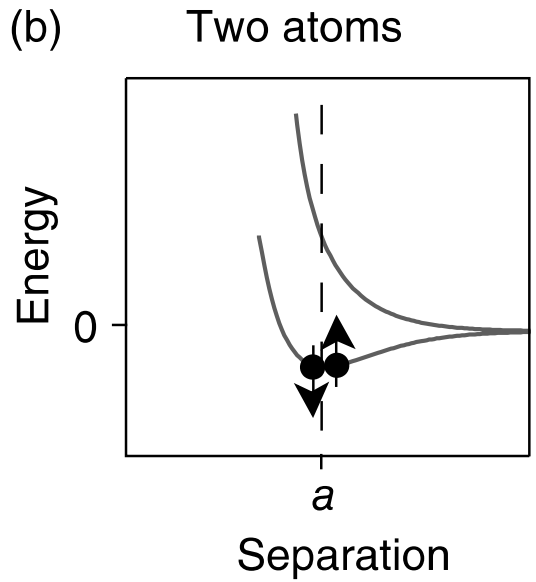

σ bond between the $sp^3$ orbitals
σ bonds between $sp^3$ orbitals and H 1s orbitals

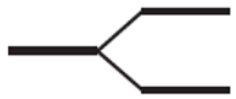

35

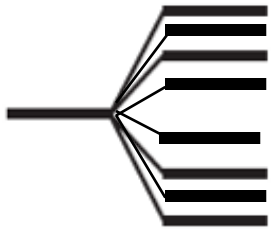


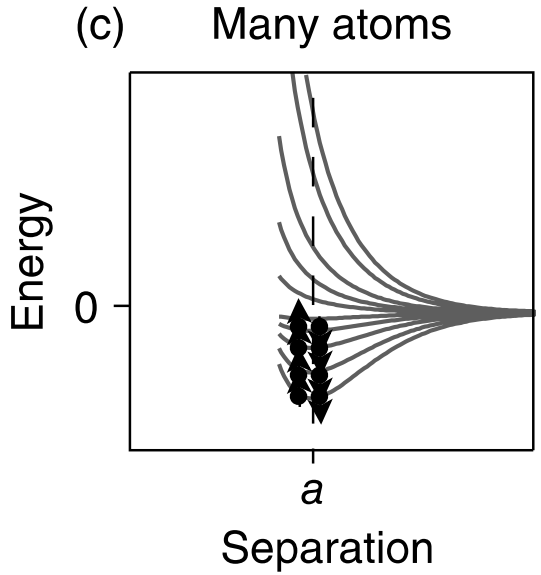

Na
log energy
3s
2p
2s
1s

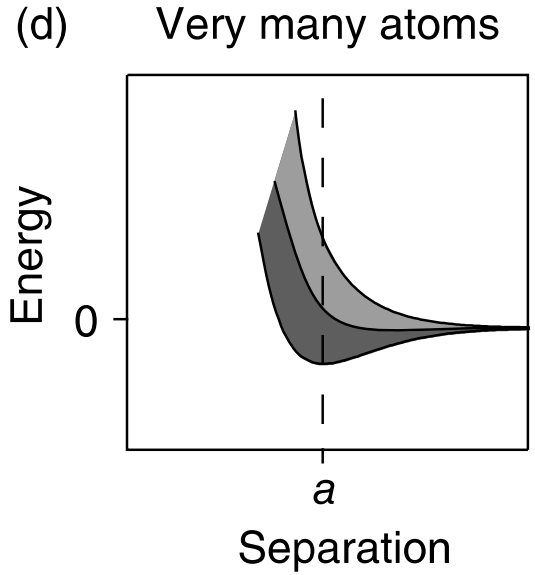

(a)
3s
3s
Isolated
Na atom
Isolated
Na atom
Two Na atoms

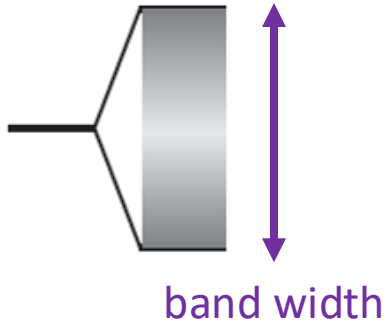

(b)
Two atoms
Energy
0
a
Separation






(c)
Many atoms
Energy
0
a
Separation

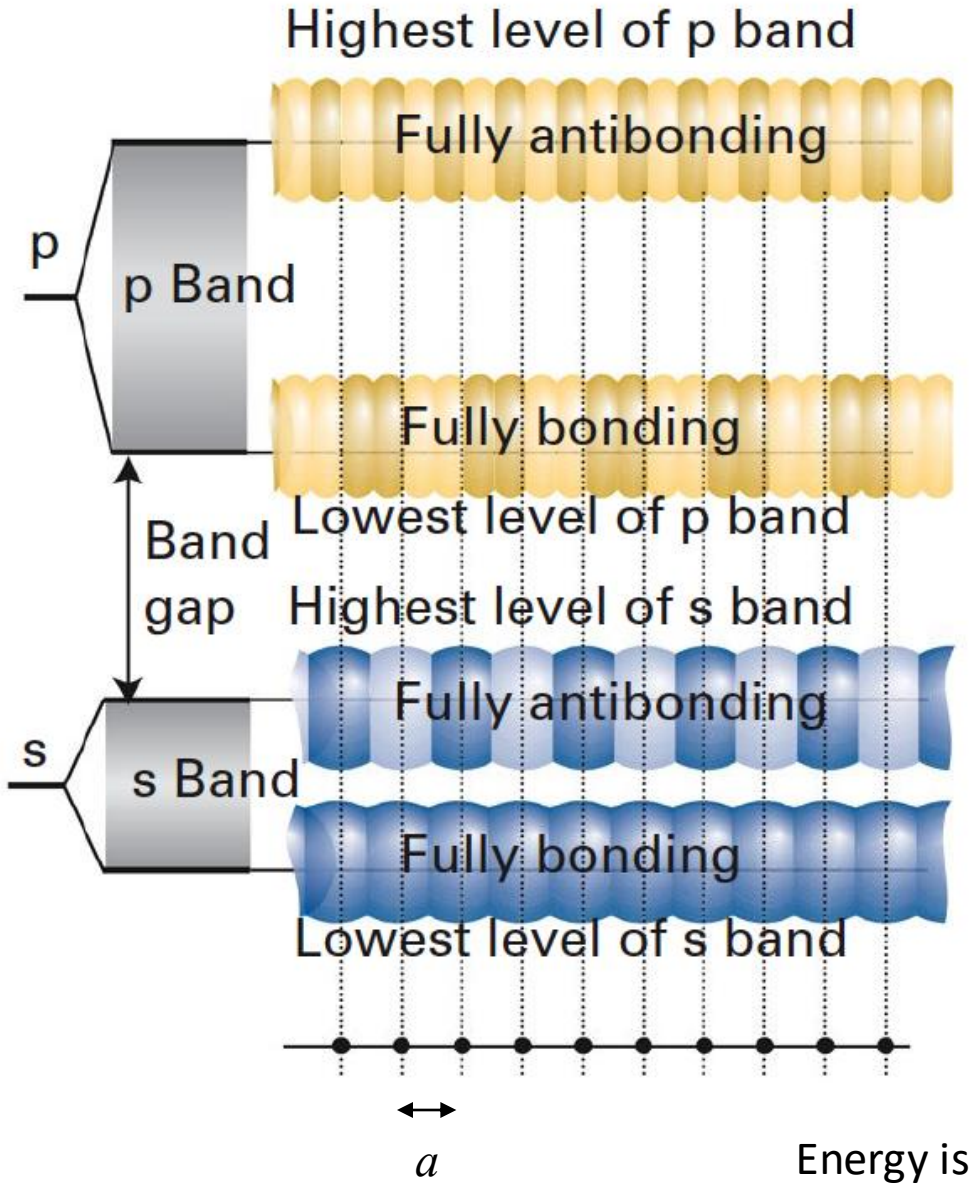

(d)
Very many atoms
Energy
0
a
Separation


band width

## 1D chain

one s orbital

one p orbital
aligned along the chain




wavelenght wavevector $k = 2\pi/\lambda$

$\lambda = \infty \rightarrow \quad k = 0$

$\lambda = 2a \rightarrow \quad k = \pi/a$

$\lambda = 2a \rightarrow \quad k = \pi/a$

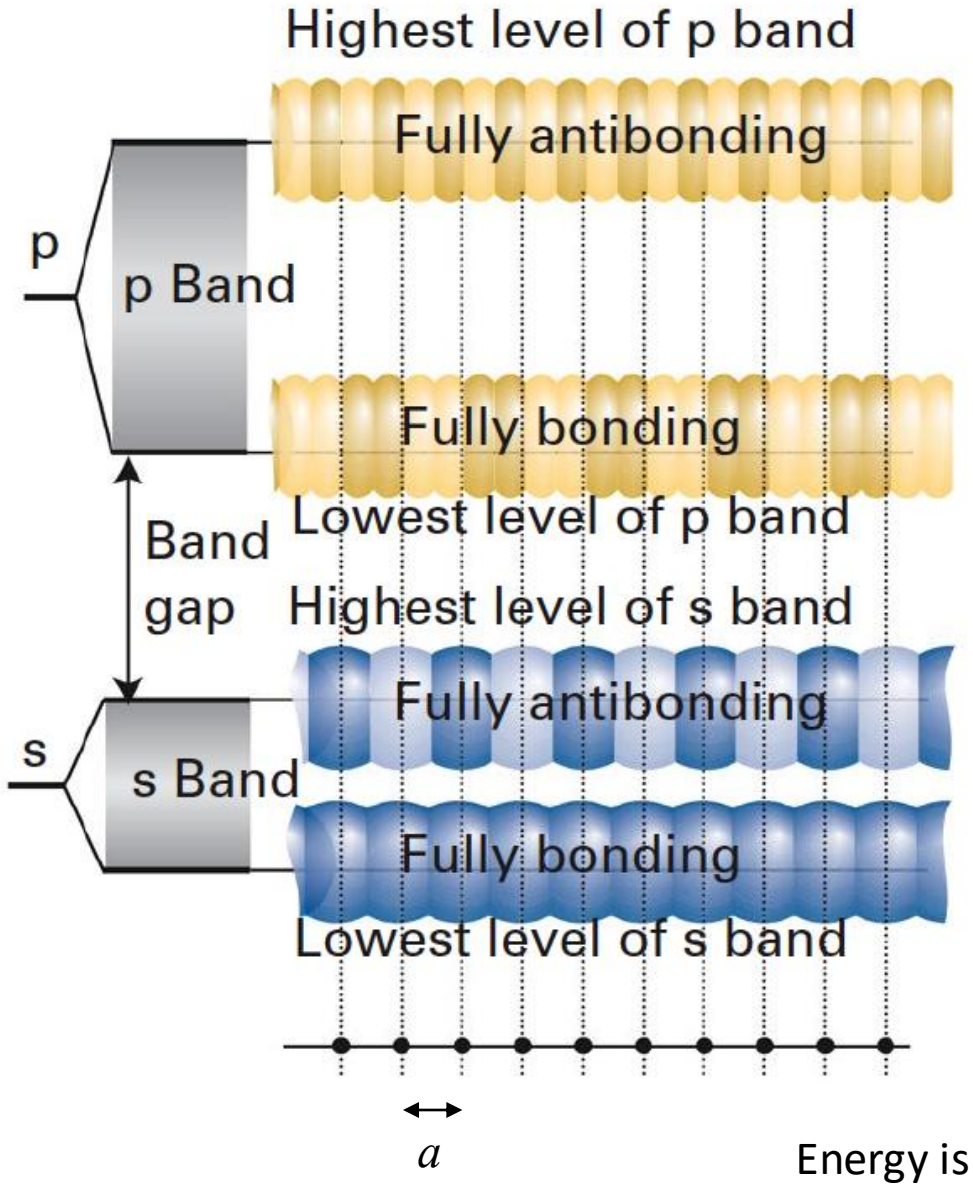
$\lambda = \infty \rightarrow \quad k = 0$

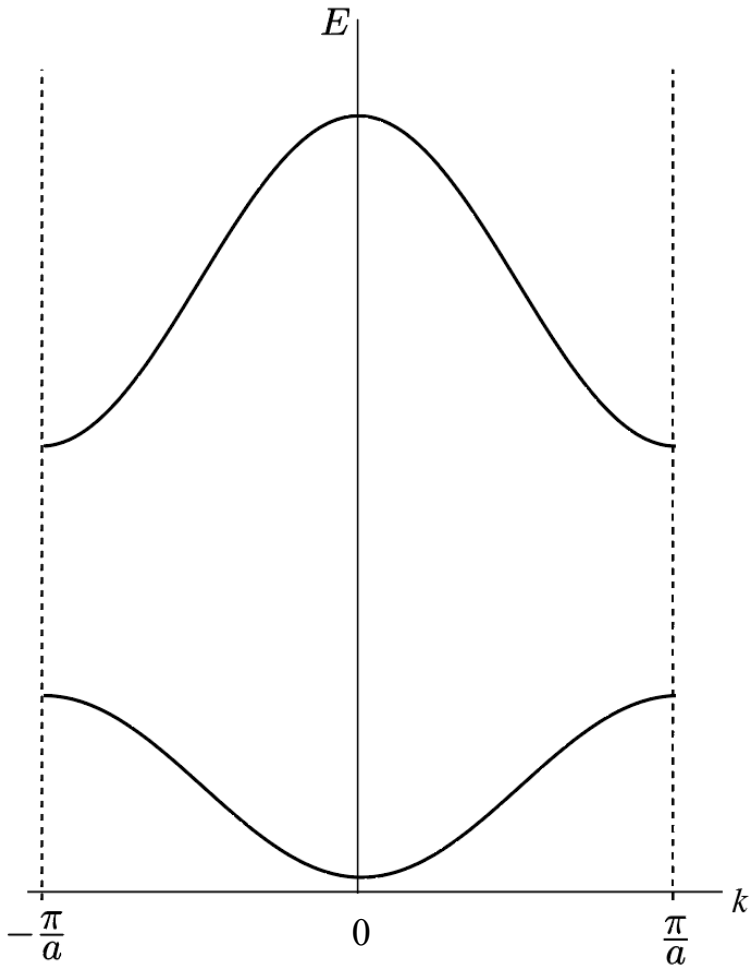
Energy is a function of wavevector: $E(k)$

## 1D chain

one s orbital

one p orbital
aligned along the chain




Energy is a function of wavevector: $E(k)$

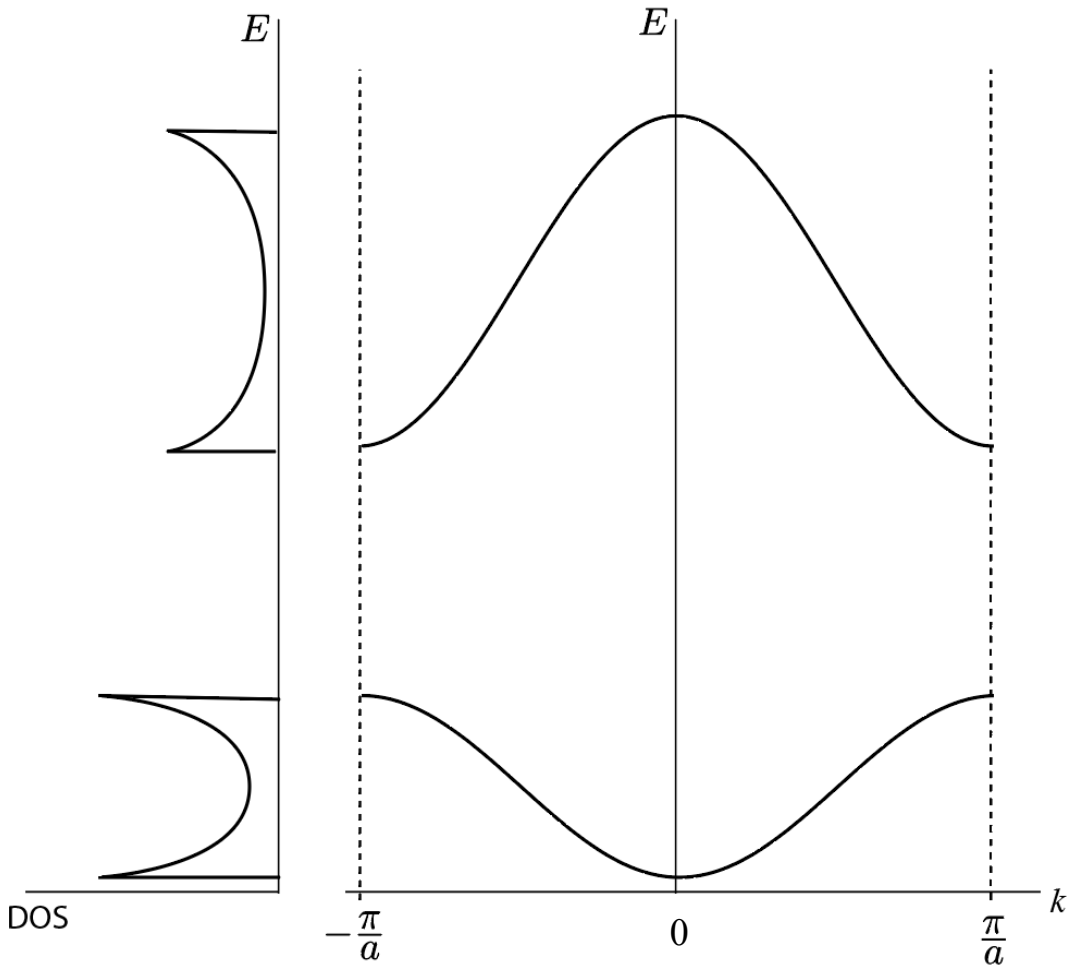
## 1D chain

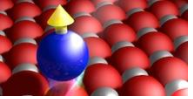
one s orbital

one p orbital
aligned along the chain

Band structure: $E(k)$

$k$-integrated → density of states (DOS) $g(E)$





# Solids: Tight-binding model

To describe the energy of electrons in solid cristals:

Wavefunctions constructed starting from atomic orbitals $\phi(\boldsymbol{r})$
+
Bloch theorem: $\psi_{n,k}(\boldsymbol{r}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r})u_{n,\boldsymbol{k}}(\boldsymbol{r})$ with $u_{n,\boldsymbol{k}}(\boldsymbol{r})$ possessing the lattice periodicity

→ Schrödinger equation can be solved even if the system is composed of a huge number of atoms (~$10^{23}$ / $cm^3$)

→ energy bands: $E(\boldsymbol{k})$

Localized orbitals will not overlap at interatomic distances → atomic-like states
Only orbitals that have sufficient overlap between nearest neighbors will give rise to bands

The bandwidth is proportional to the transfer integral (or hopping matrix element), that reflects the ease with which an electron can transfer from atom to atom.
This integral is related to the overlap between wavefunctions and to the strength of the potential $\Delta U$ originating from the atoms in the cristal at positions $\boldsymbol{R}$.

Transfer integral: $\gamma(\boldsymbol{R}) = \int \phi^*(\boldsymbol{r})\, \Delta U\, \phi(\boldsymbol{r}-\boldsymbol{R})d\boldsymbol{r}$

Other relevant integrals:

Overlap integral: $\alpha(\boldsymbol{R}) = \int \phi^*(\boldsymbol{r})\phi(\boldsymbol{r}-\boldsymbol{R})d\boldsymbol{r}$

Cristal field integral: $\beta = \int \phi^*(\boldsymbol{r})\, \Delta U\, \phi(\boldsymbol{r})d\boldsymbol{r}$

$$E(\boldsymbol{k}) = E_{at} + \frac{\beta + \sum_{\boldsymbol{R}\neq 0} \exp(i\boldsymbol{k}\cdot\boldsymbol{R})\,\gamma(\boldsymbol{R})}{1 + \sum_{\boldsymbol{R}\neq 0} \exp(i\boldsymbol{k}\cdot\boldsymbol{R})\,\alpha(\boldsymbol{R})}$$

simplifications / approximations:

- only nearest neighbors (nn) in the sums
- $\beta$ small offset, can be neglected
- $\alpha$ small and/or does not change strongly the band

→

$$E(\boldsymbol{k}) = E_{at} + \sum_{R_{nn}} \exp(i\boldsymbol{k}\cdot\boldsymbol{R_{nn}})\,\gamma(\boldsymbol{R_{nn}})$$

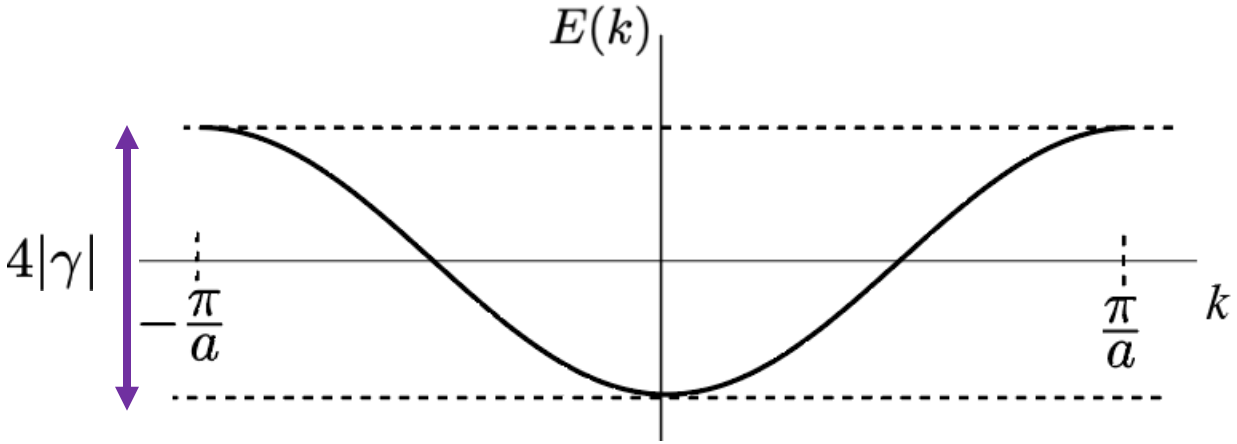
## 1D chain

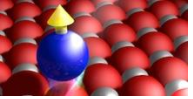
distance $a$
one s orbital

$$E(k) = E_{at} + [\exp(ika) + \exp(-ika)]\gamma(a)$$

$$= E_{at} + 2\,\gamma\cos(ka)$$

$$\gamma < 0$$





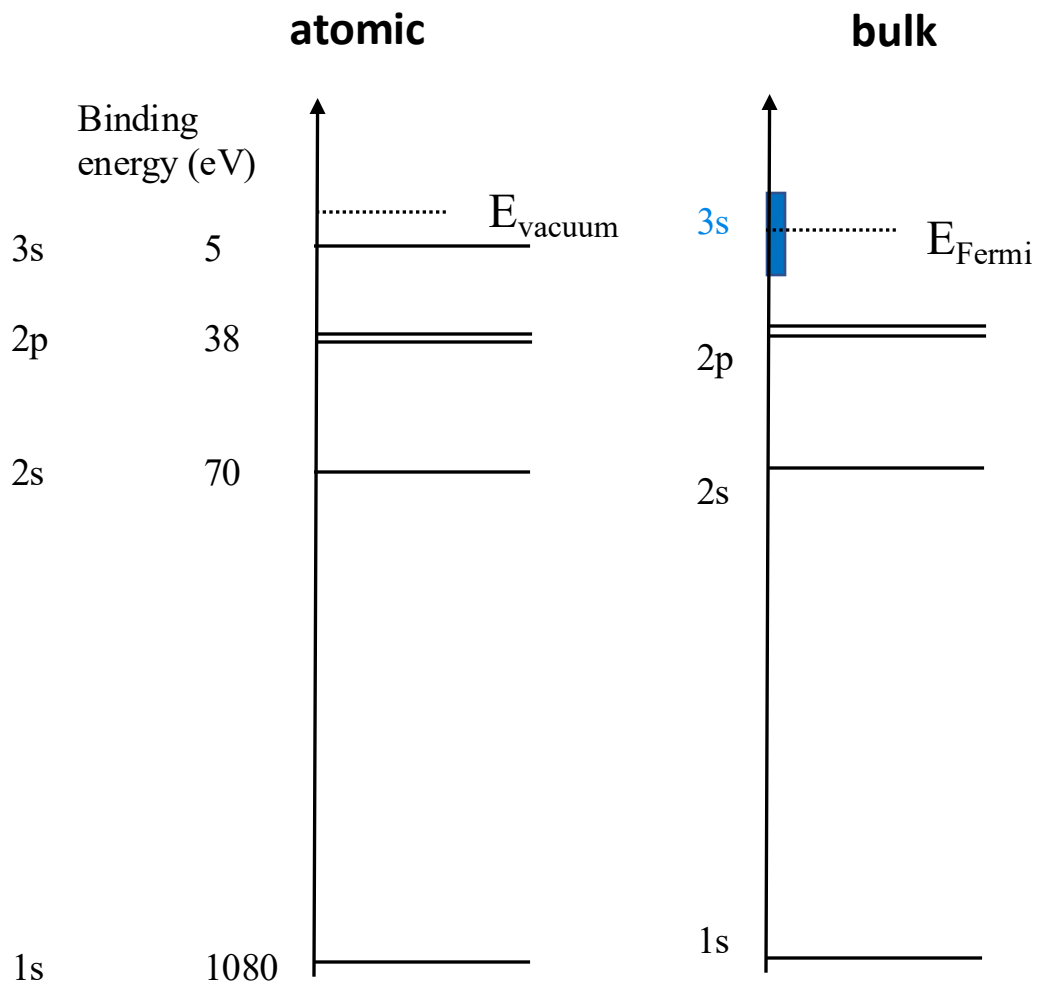
# Na electronic structure

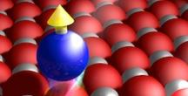
atomic Na:

$1s^2\ 2s^2\ 2p^6\ 3s^1$

[Ne] $3s^1$

energy not to scale

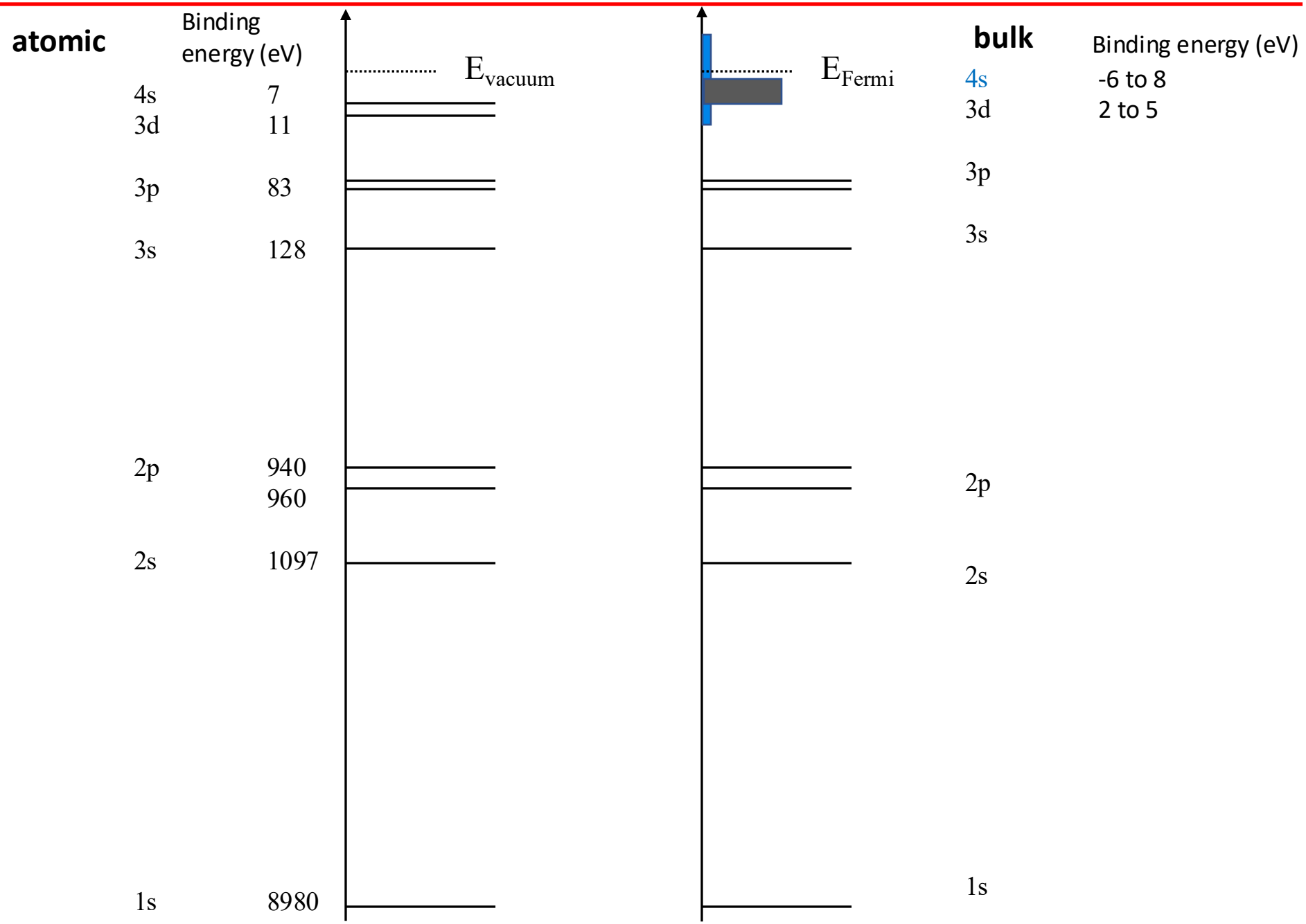




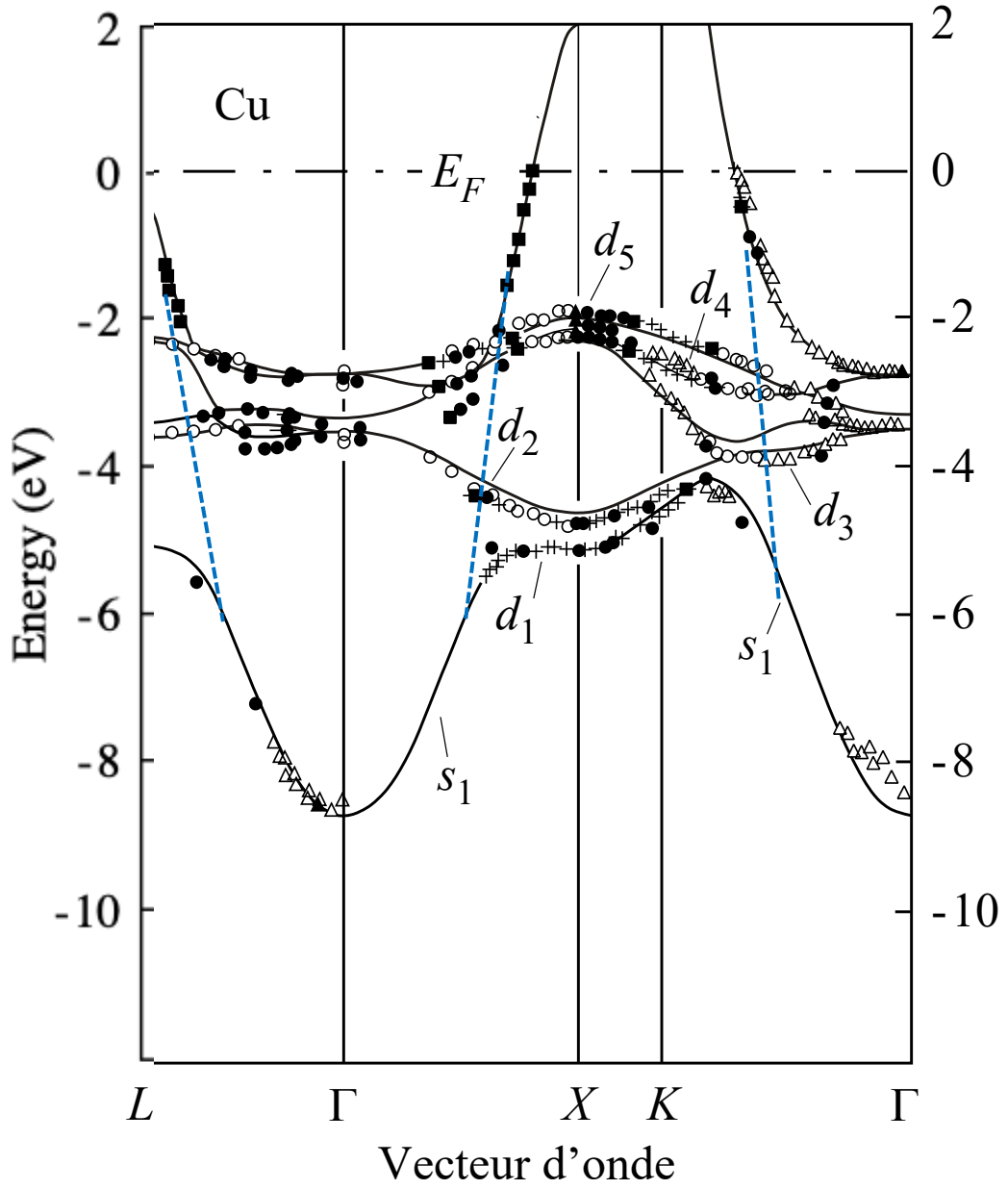
# Cu electronic structure

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

energy not to scale

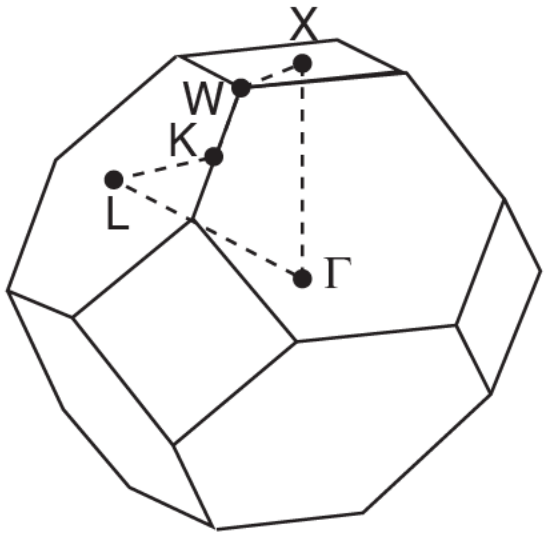


# Cu band structure

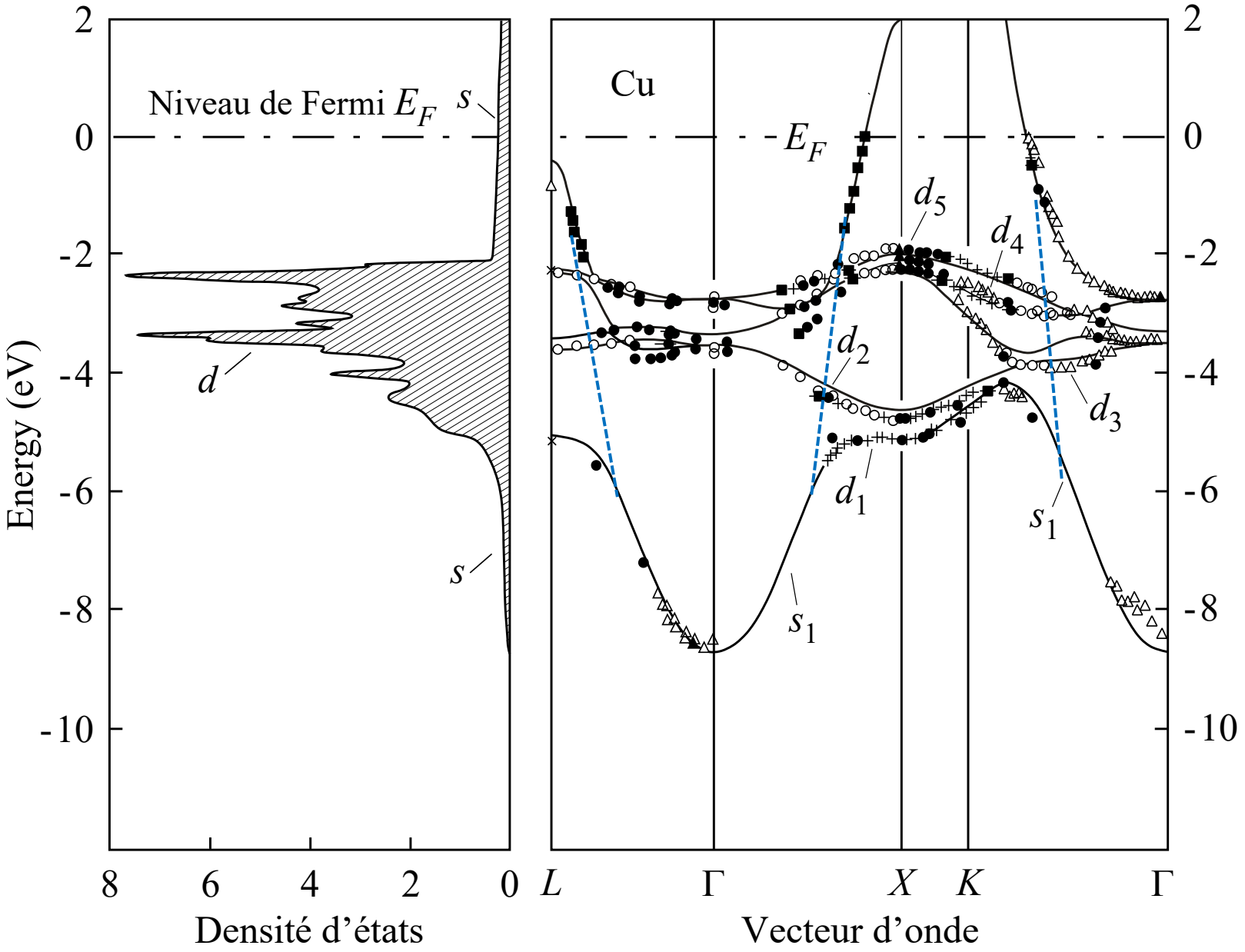



Cu: fcc crystal

first Brillouin zone:

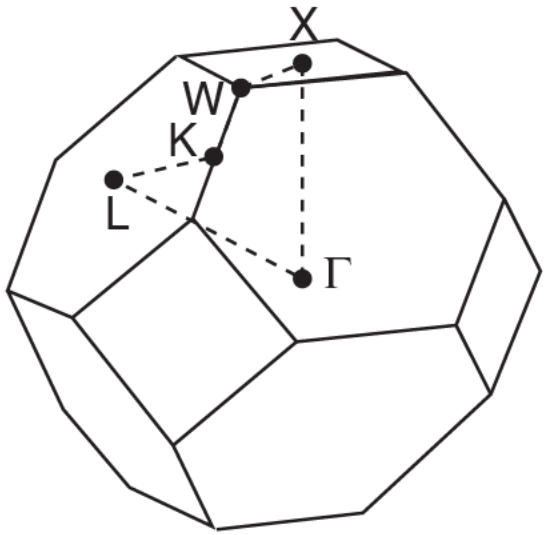


# Cu band structure and density of states (DOS)




Cu: fcc crystal

first Brillouin zone:

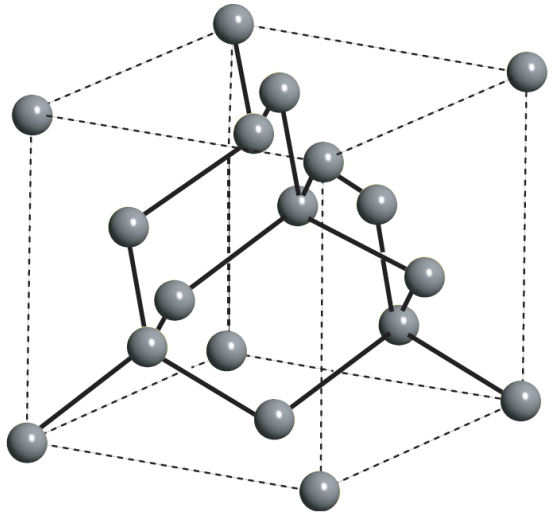


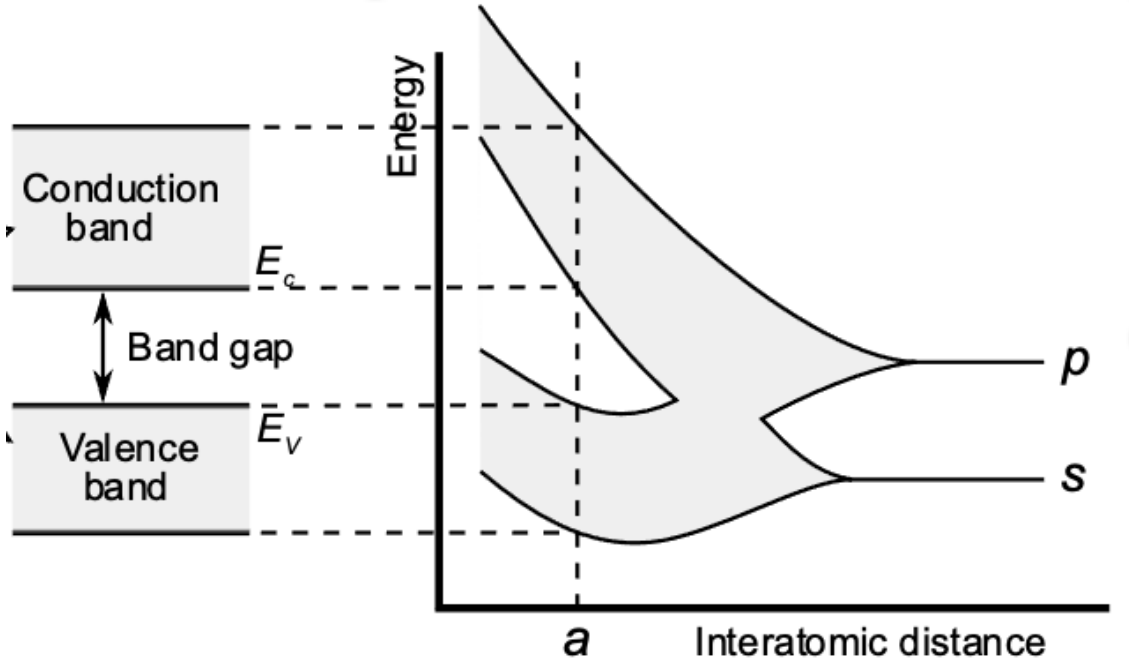
Exercises 1.9 – 1.10

atomic C: $1s^2\ 2s^2\ 2p^2$

formation of **four** $sp^3$ hybrid orbitals

the directional character of the p orbitals is found in the $sp^3$ orbitals → solid with covalent bonds






insulator

$E_{gap}$ = 5.5 eV