From atoms to bulk: Electronic properties

atoms

orbitals
electron configuration

molecular orbitals

hybrid orbitals

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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/

Wikipedia

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Solid State Physics
Philip Hofmann

EPFL lectures: Physique du Solide I et II (2023-2024)
H. Brune and M. Pivetta

Analytical solution for hydrogen and hydrogenic atoms (one electron)

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi \qquad \frac{1}{\mu} = \frac{1}{m_\mathrm{e}} + \frac{1}{m_\mathrm{N}}$$

Schrödinger equation for the motion of one electron relative to the nucleus

Z: atomic number

→ variable separation, radial and angular parts of wavefunctions

$n = 1, 2, 3, 4 \ldots$	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: $\lvert\mathbf{l}\rvert = \sqrt{l(l+1)}\hbar$
$m_l = l, l-1, \ldots, -l$	magnetic quantum number; $(2l+1)$ values; direction of the angular momentum (with respect to an applied magnetic field, usually along z): $\mathrm{l_z} = m_l\hbar$

electron configurations, identified by the **shell**: $\begin{array}{ccccc} n = 1 & 2 & 3 & 4 & \ldots \\ \mathrm{K} & \mathrm{L} & \mathrm{M} & \mathrm{N} & \ldots \end{array}$ and the **subshell**: $\begin{array}{cccccc} l = & 0 & 1 & 2 & 3 & \ldots \\ & \mathrm{s} & \mathrm{p} & \mathrm{d} & \mathrm{f} & \ldots \end{array}$

Hydrogenic wavefunctions

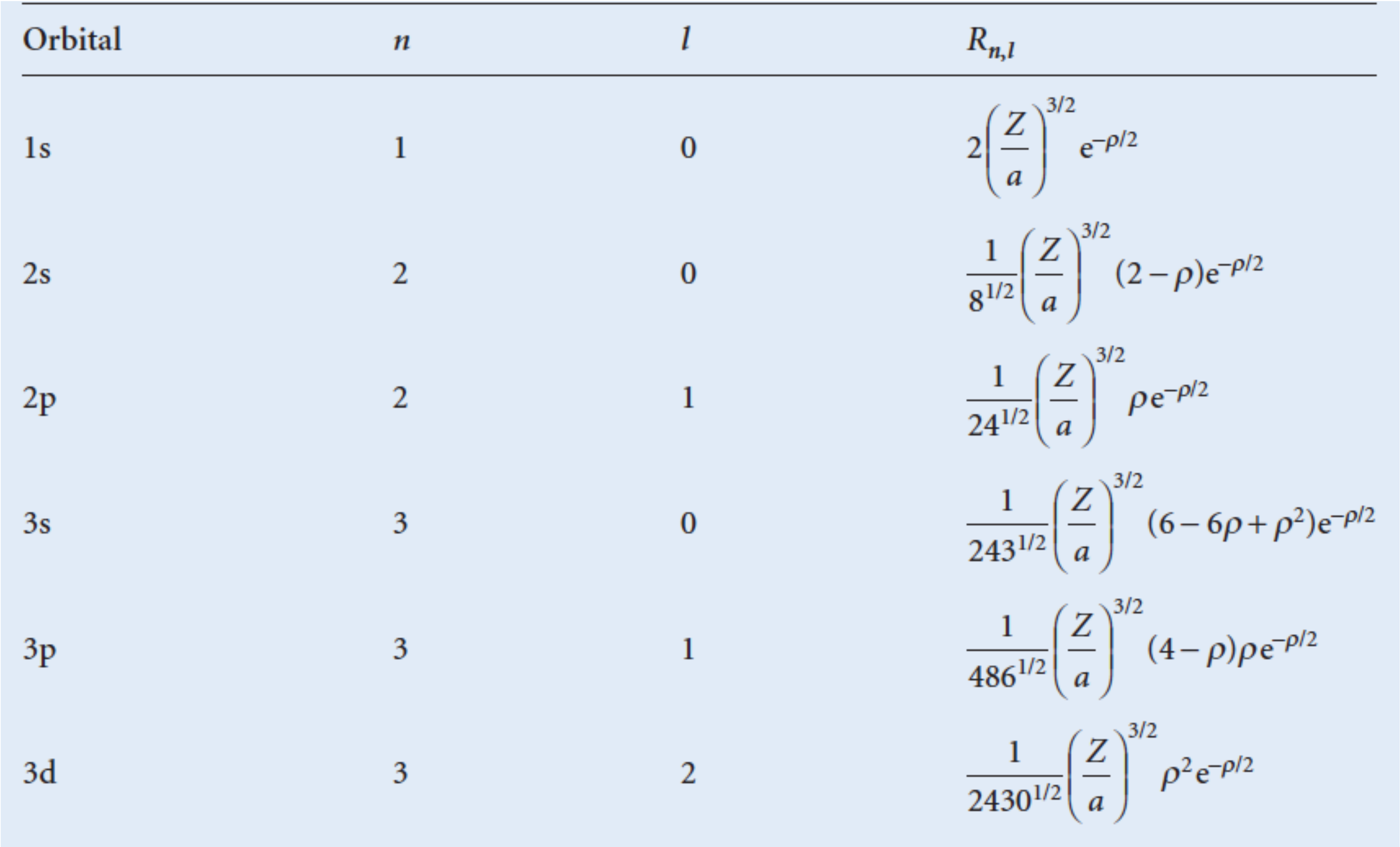
→ variable separation, radial and angular parts of wavefunctions

$$\overbrace{\psi(r,\theta,\phi)}^{\text{Total wavefunction}} = \overbrace{R(r)}^{\text{Radial part}} \times \overbrace{Y(\theta,\phi)}^{\text{Angular part}}$$

$$R(r) = \overbrace{r^l}^{\substack{\text{Dominant close}\\ \text{to the nucleus}}} \times \overbrace{(\text{polynomial in } r)}^{\substack{\text{Bridges the two}\\ \text{ends of the function}}} \times \overbrace{(\text{decaying exponential in } r)}^{\substack{\text{Dominant far from}\\ \text{the nucleus}}}$$

Hydrogenic radial wavefunctions

$$R_{n,l}(r) = N_{n,l}\rho^l L_{n+1}^{2l+1}(\rho)\mathrm{e}^{-\rho/2}$$



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

$$\mu \approx m_\mathrm{e} \rightarrow a \approx a_0$$

$$\rightarrow$$

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

Radial probability distribution

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

$e^{-\rho/2}$

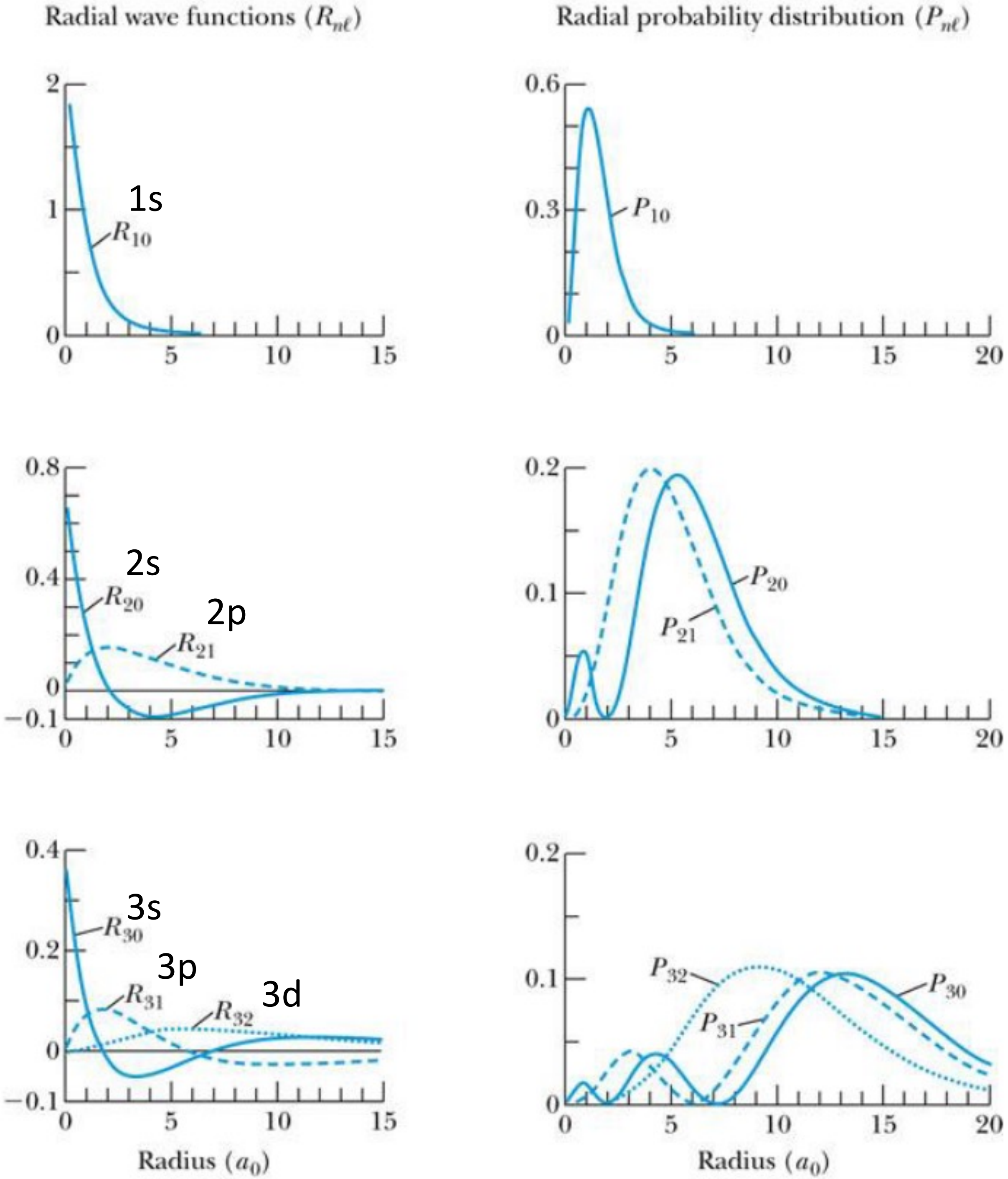
$(2-\rho)e^{-\rho/2}$

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

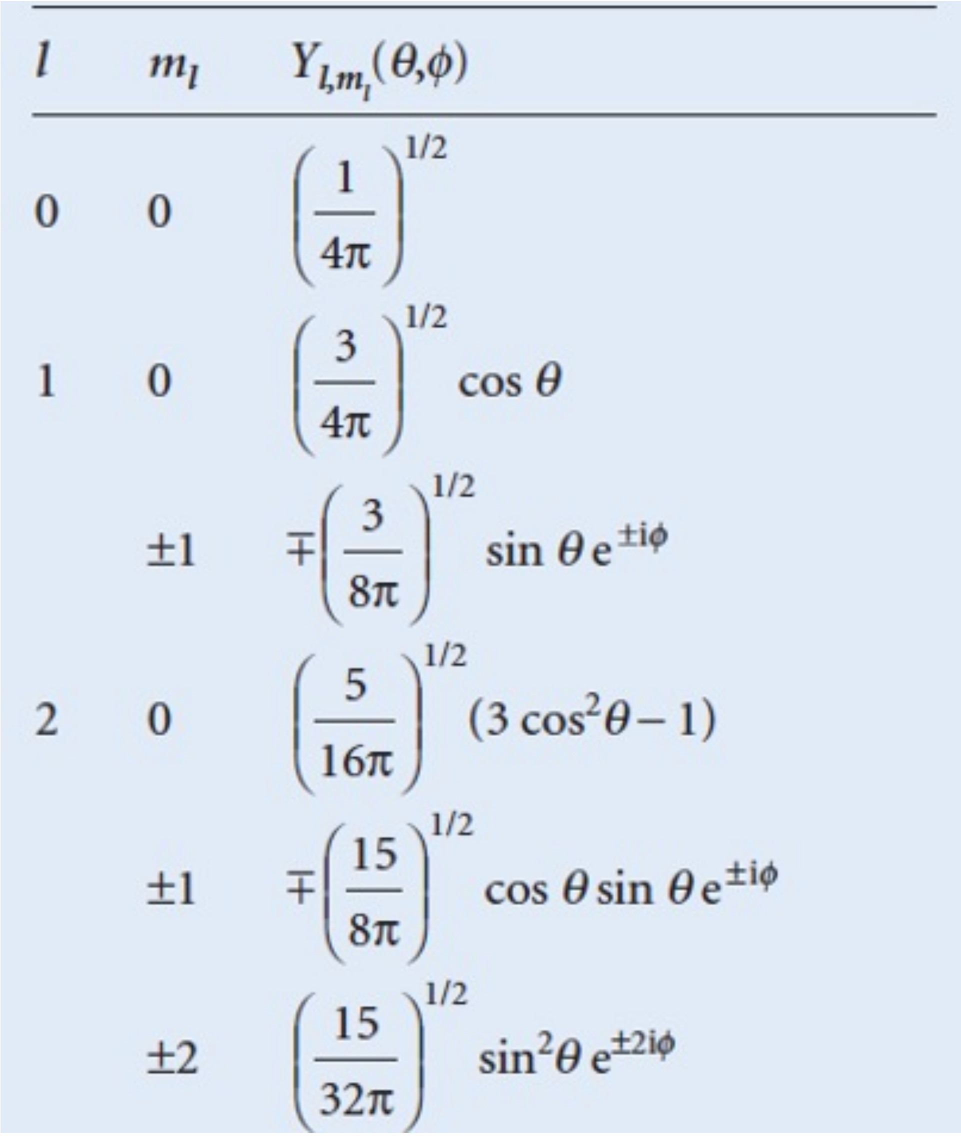
$(6-6\rho+\rho^2)e^{-\rho/2}$

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

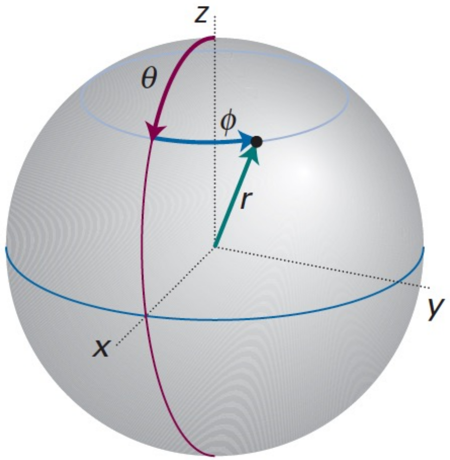
$\rho^2 e^{-\rho/2}$

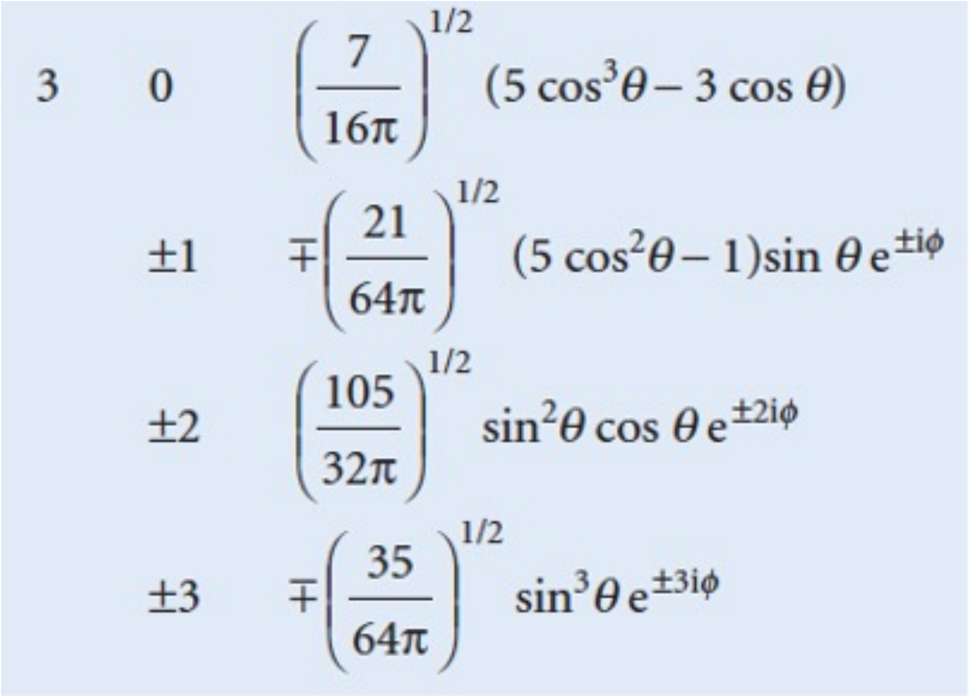


Hydrogenic angular wavefunctions: Spherical harmonics



	l	m_l	$Y_{l,m_l}(\theta,\phi)$
s	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
p	1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
		±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	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$

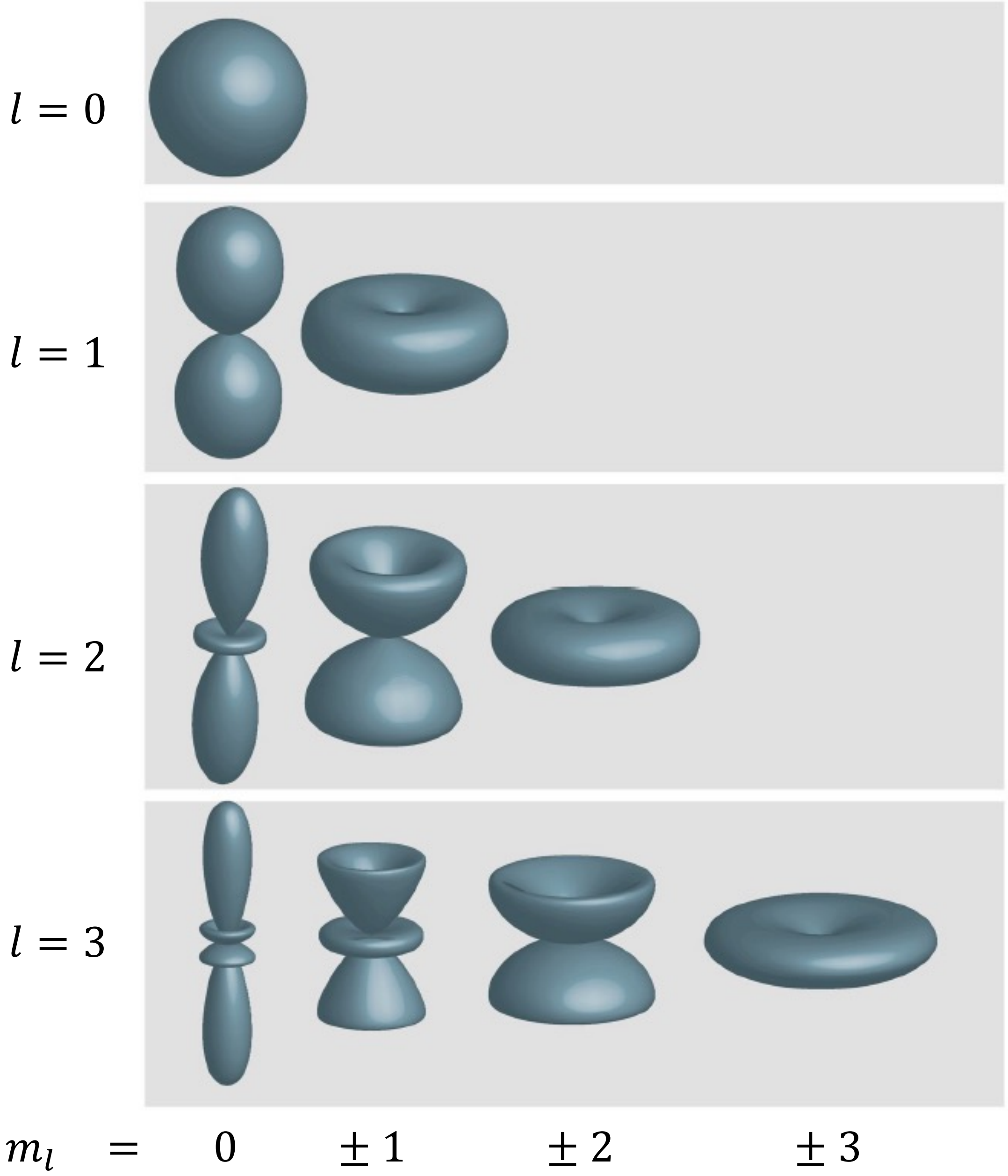


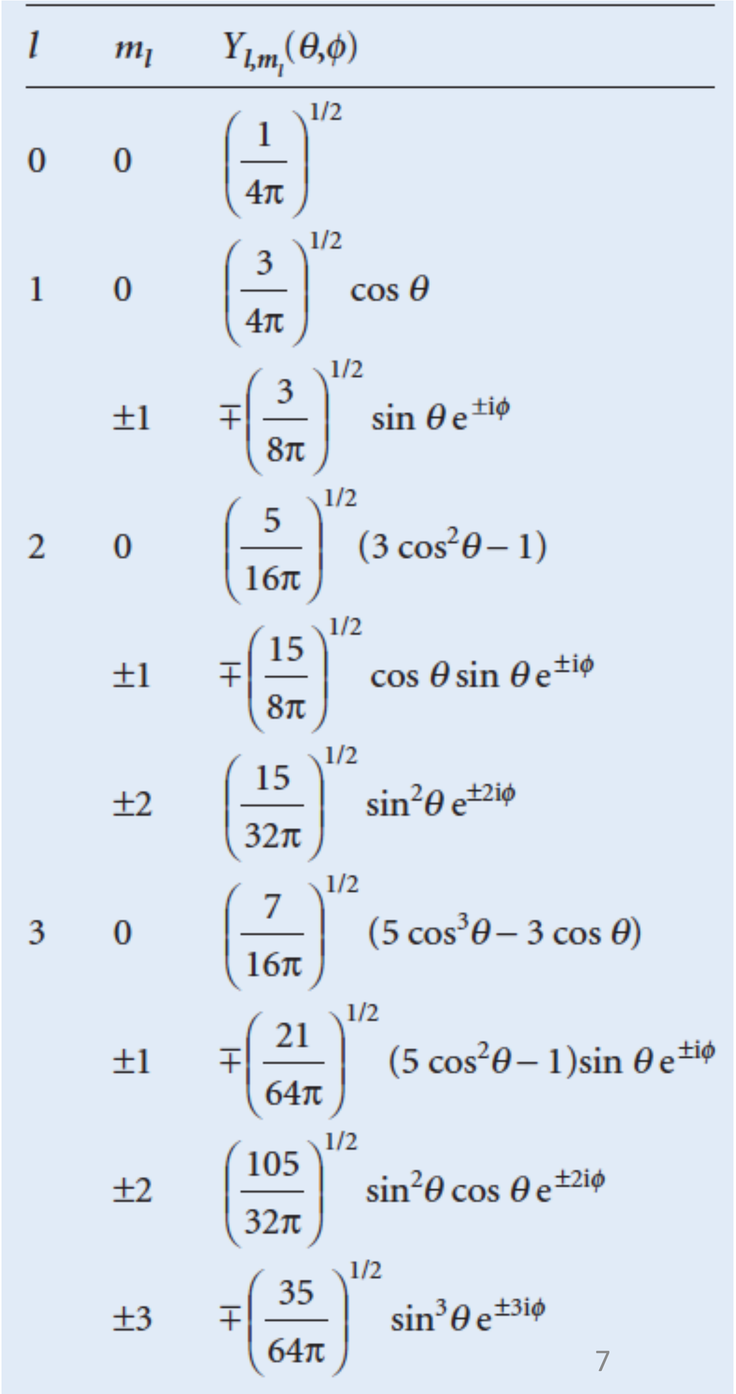


f	3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
		±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\, e^{\pm i\phi}$
		±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
		±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

Angular momentum

electron density angular distribution

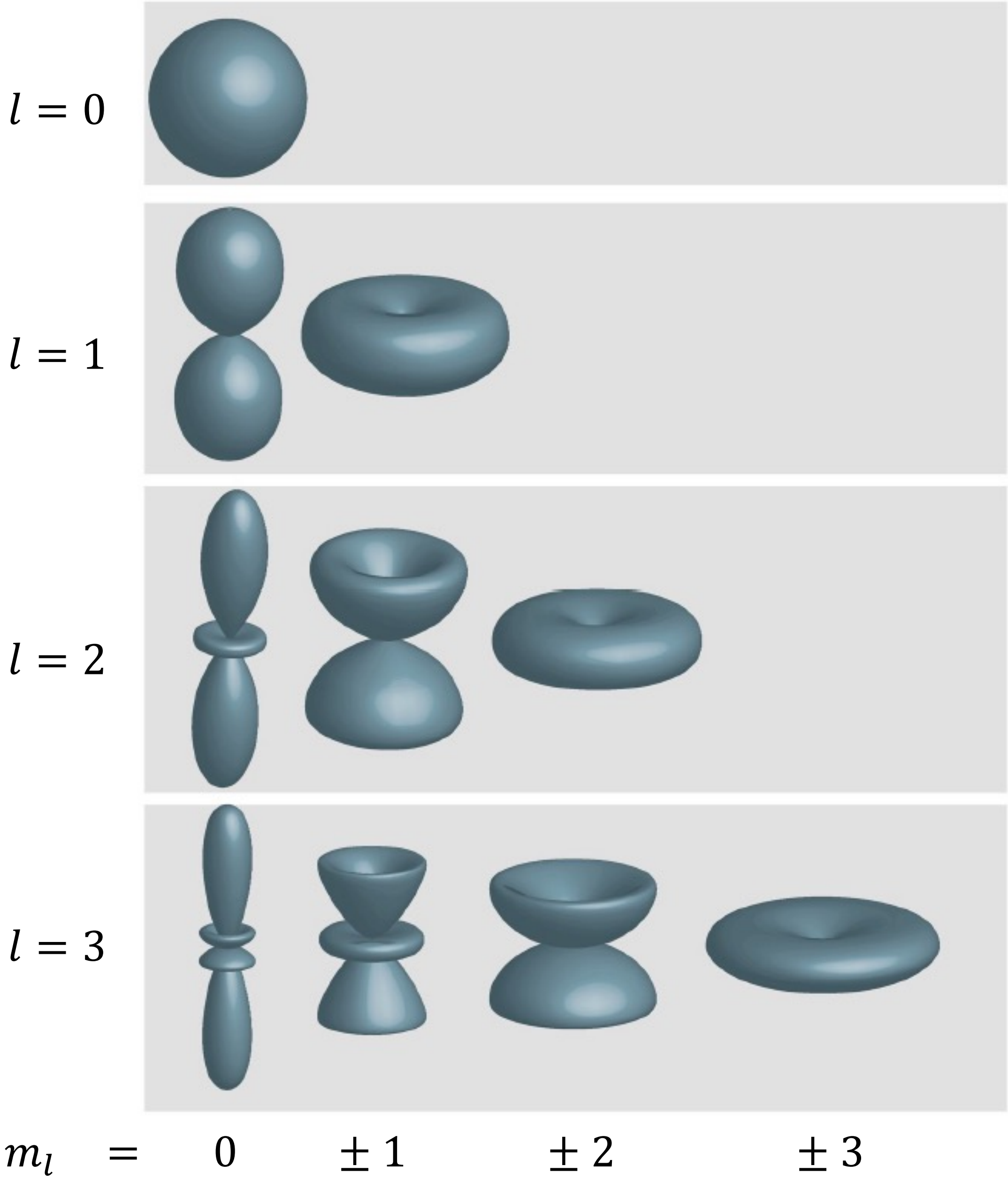


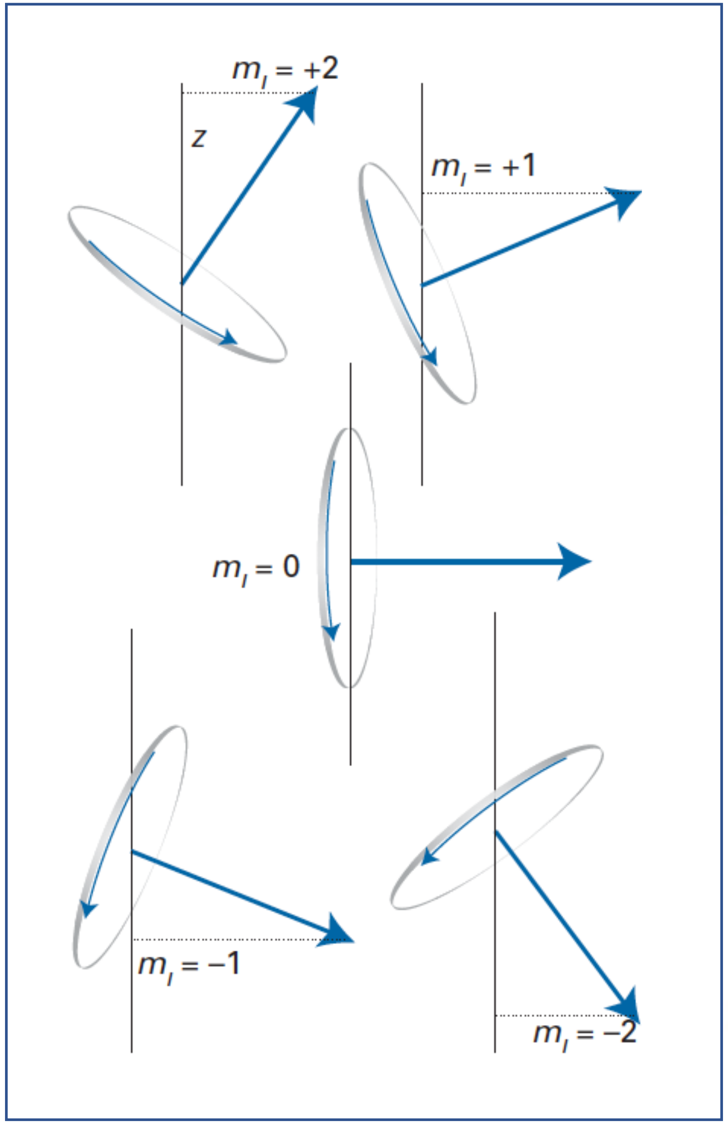


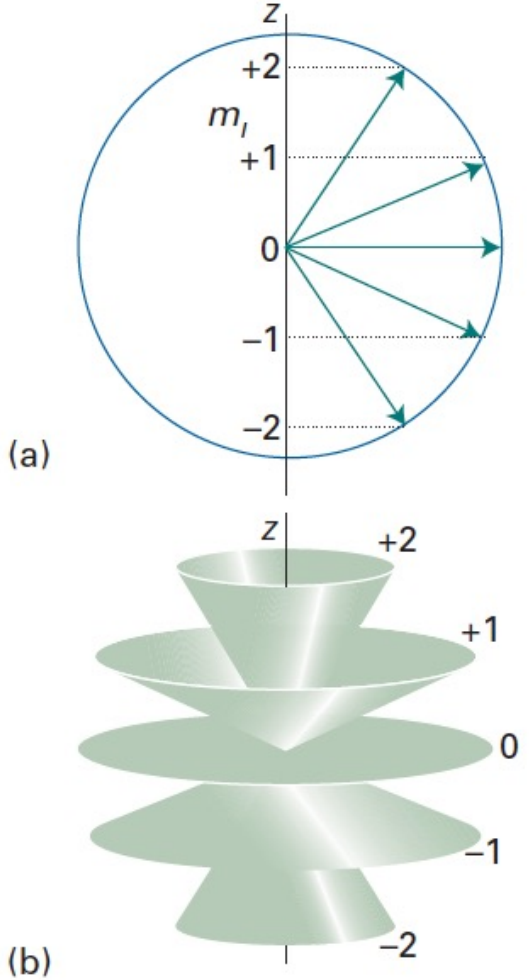
	l	m_l	$Y_{l,m_l}(\theta,\phi)$
s	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
p	1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
		±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$
d	2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
		±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\,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

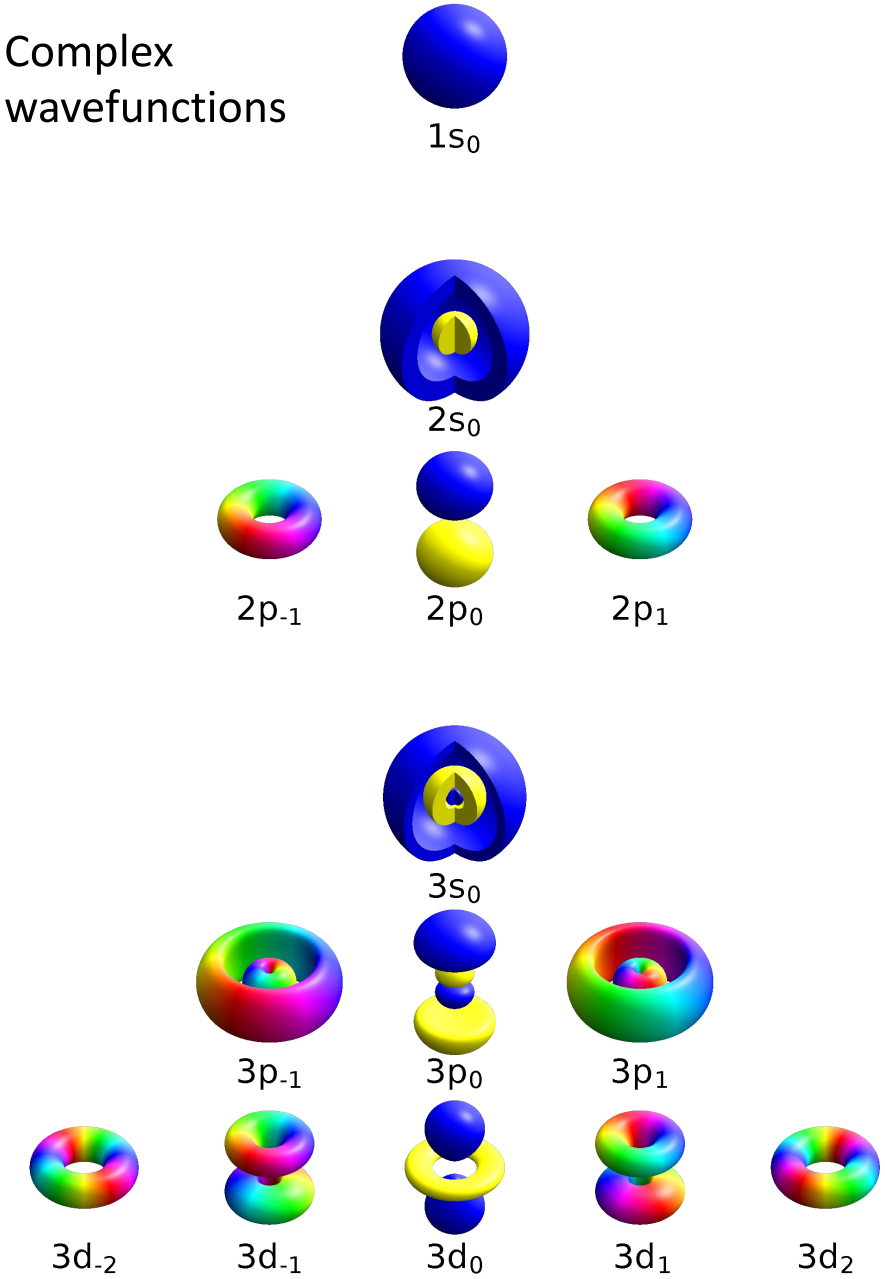






Atomic orbitals

Complex
wavefunctions

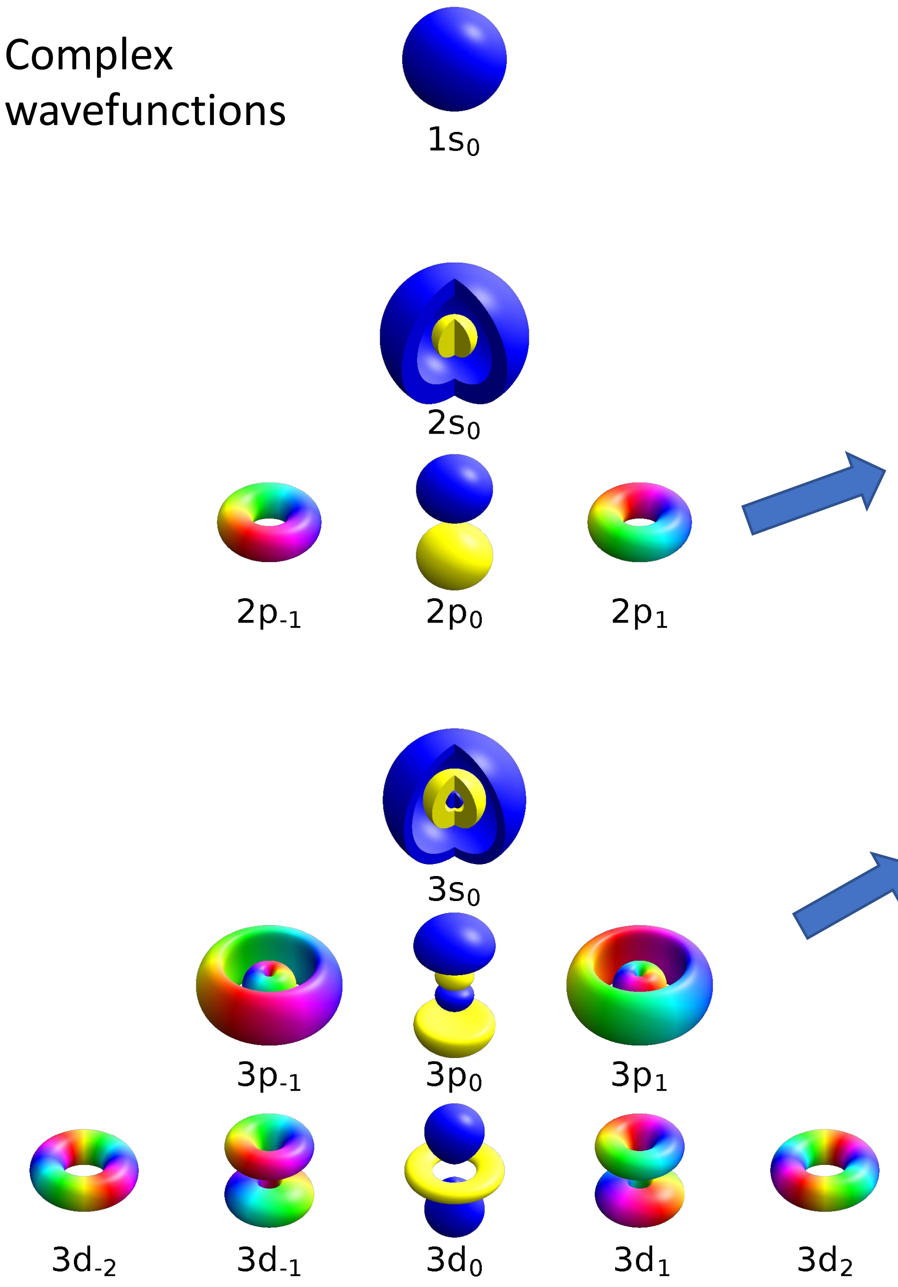


Atomic orbitals

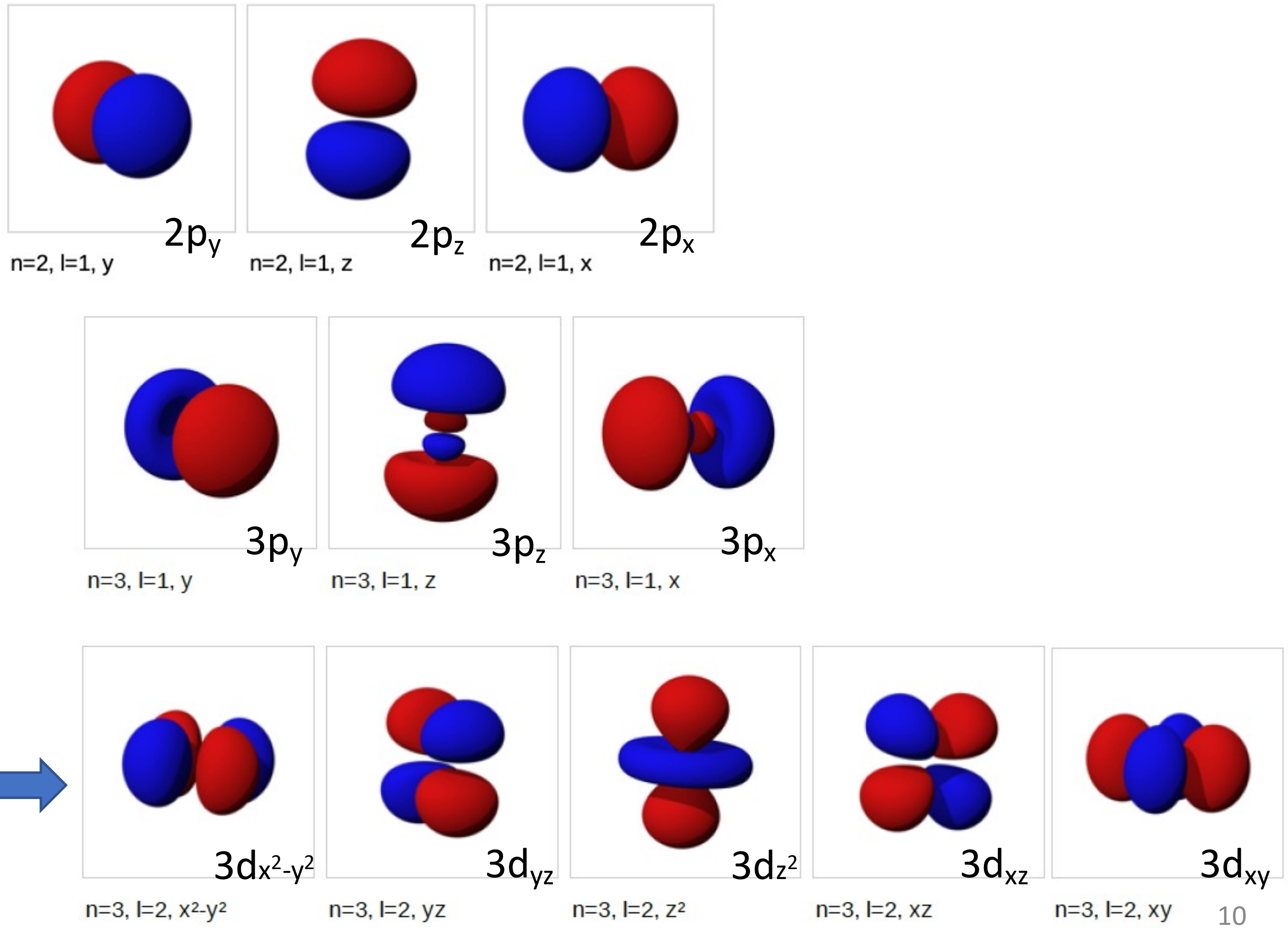
Complex wavefunctions

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

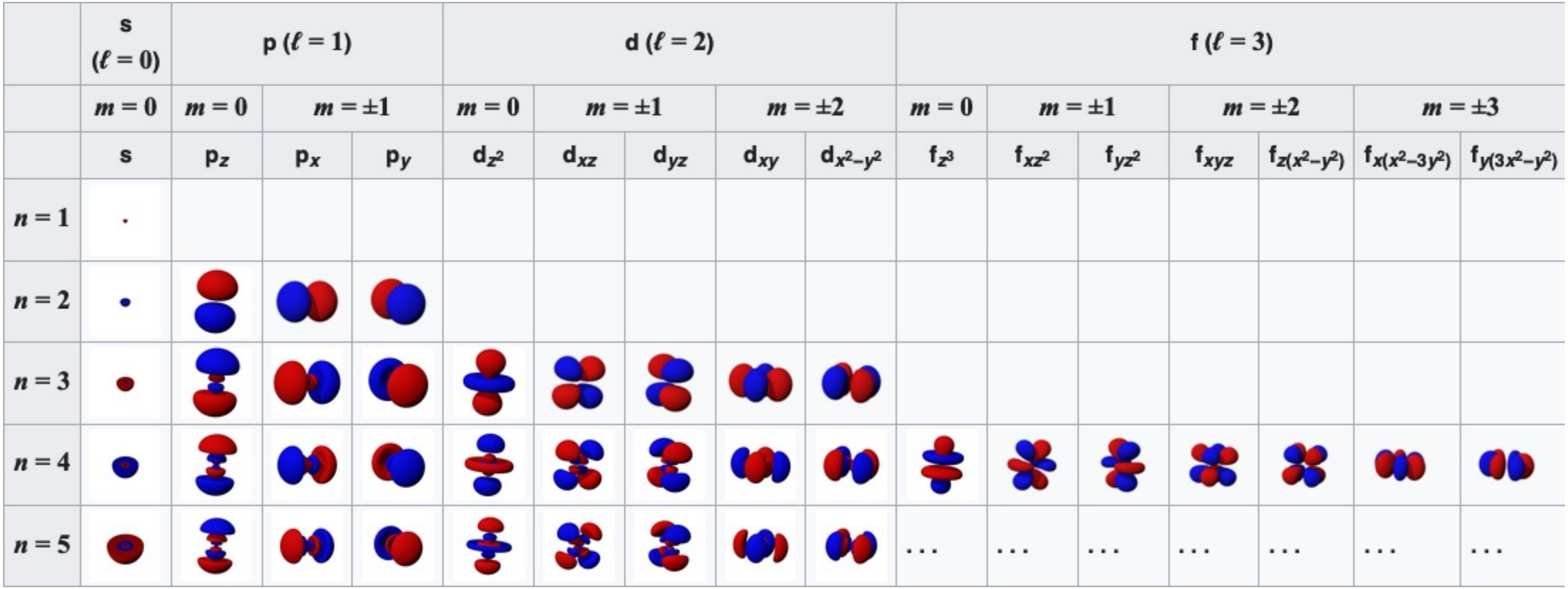
https://commons.wikimedia.org/wiki/Hydrogen_orbitals_3D_real



Real wavefunctions (linear combinations)



Orbitals



	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}	$f_{z(x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{y(3x^2-y^2)}$
$n = 1$																
$n = 2$																
$n = 3$																
$n = 4$																
$n = 5$										…	…	…	…	…	…	…

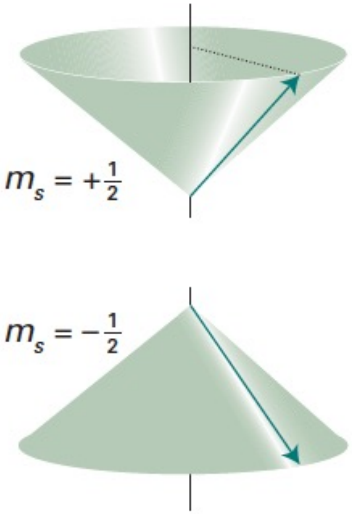
Electron spin

Intrinsic angular momentum of the electron

$s = {}^{1}/_{2}$ spin quantum number, magnitude : $|\mathbf{s}| = \sqrt{s(s+1)}\hbar = {}^{\sqrt{3}}/_{2}\,\hbar$

$m_s = \pm\,{}^{1}/_{2}$ spin magnetic quantum number, component along z ,
magnitude: $m_s\hbar = \pm\,{}^{1}/_{2}\,\hbar$

$m_s = +\,{}^{1}/_{2} = \uparrow, \quad m_s = -\,{}^{1}/_{2} = \downarrow$



Total angular momentum and spin-orbit coupling

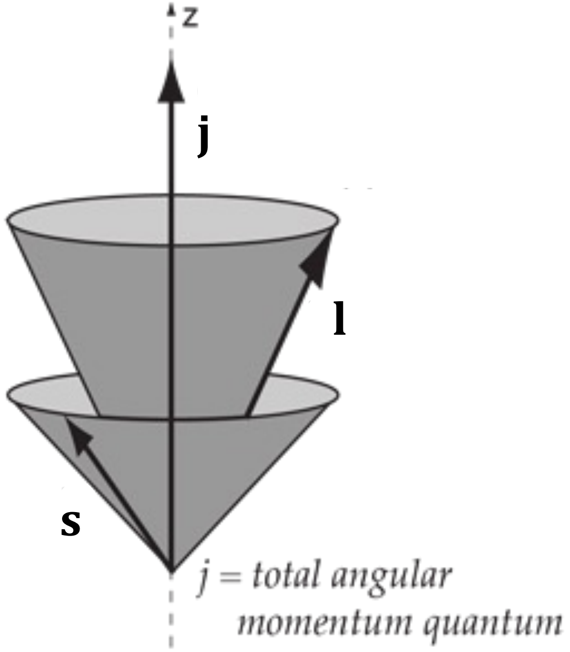
Still only one electron

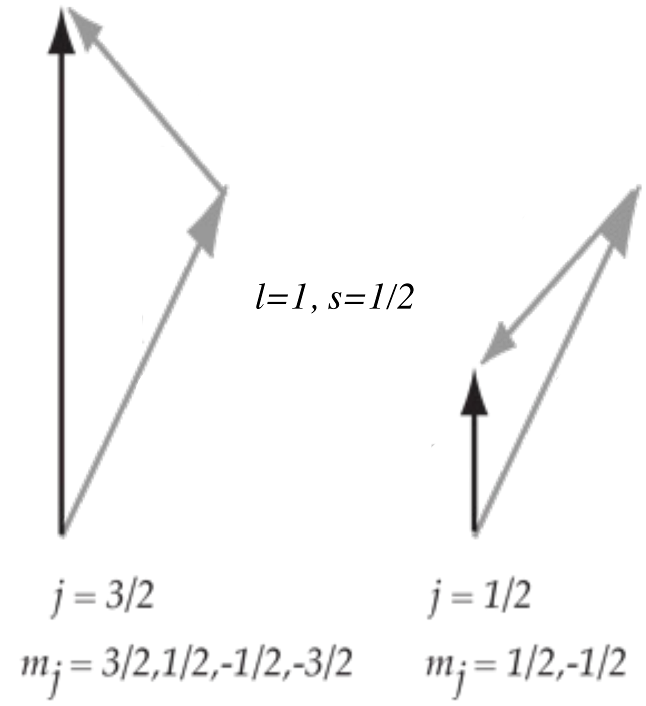
Total angular momentum: $\mathbf{j} = \mathbf{l} + \mathbf{s}$

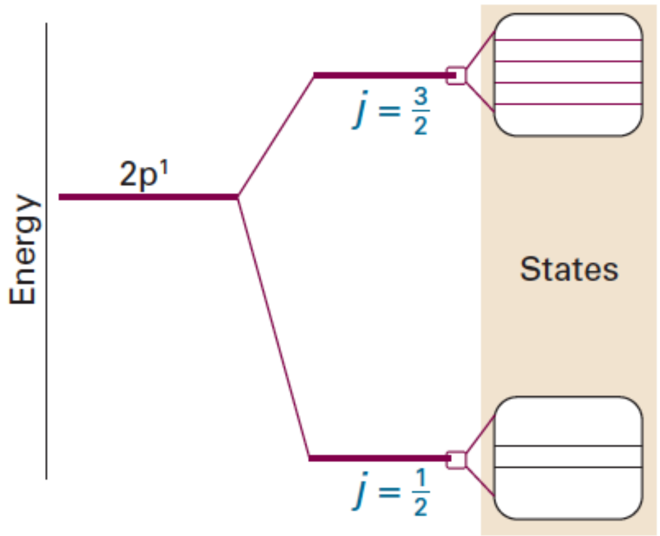
$|\mathbf{j}| = \sqrt{j(j+1)}\hbar,$ $\quad$ $j_z = m_j\hbar$

$$j = l + s, \; \dots, |l - s|$$

$$m_j = j, \dots - j$$







spin-orbit coupling: additional term in the hamiltonian: $V_{SO} \propto (\mathbf{l} \cdot \mathbf{s})\xi_{SO}$

electron energy depends on the total angular momentum

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

Many-electron atoms

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**

Open subshells: how are combined the orbital, spin, and total angular momenta of the electrons?
Two coupling schemes are possible:

- LS-coupling: first find $\mathbf{L}$ and $\mathbf{S}$, then couple them to obtain $\mathbf{J}$ (light elements with small spin-orbit coupling)

Total orbital angular momentum	$\mathbf{L} = \sum \mathbf{l}_i$	quantum number L, and M_L
Total spin momentum	$\mathbf{S} = \sum \mathbf{s}_i$	quantum number S, and M_S
Total angular momentum	$\mathbf{J} = \mathbf{L} + \mathbf{S}$	quantum number J, and M_J

- jj-coupling: couple $\mathbf{l}$ and $\mathbf{s}$ of individual electrons, and then couple the **j**'s (heavy elements, large spin-orbit coupling)

Individual total angular momentum	$\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i$	quantum number j, and m_j
Total angular momentum	$\mathbf{J} = \sum \mathbf{j}_i$	quantum number J, and M_J

Energy levels in many-electron atoms

- orbitals with the same value of n but different values of l are no longer degenerate (consequence of penetration and shielding)

- spin-orbit coupling partially lifts the degeneracy of orbitals of a given subshell (same l, different j)

hydrogenic atom:

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

shell: $n = 1 \quad 2 \quad 3 \quad 4 \quad \ldots$

K L M N …

subshell: $l = 0 \quad 1 \quad 2 \quad 3 \quad \ldots$

s p d f …

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

Core levels energies

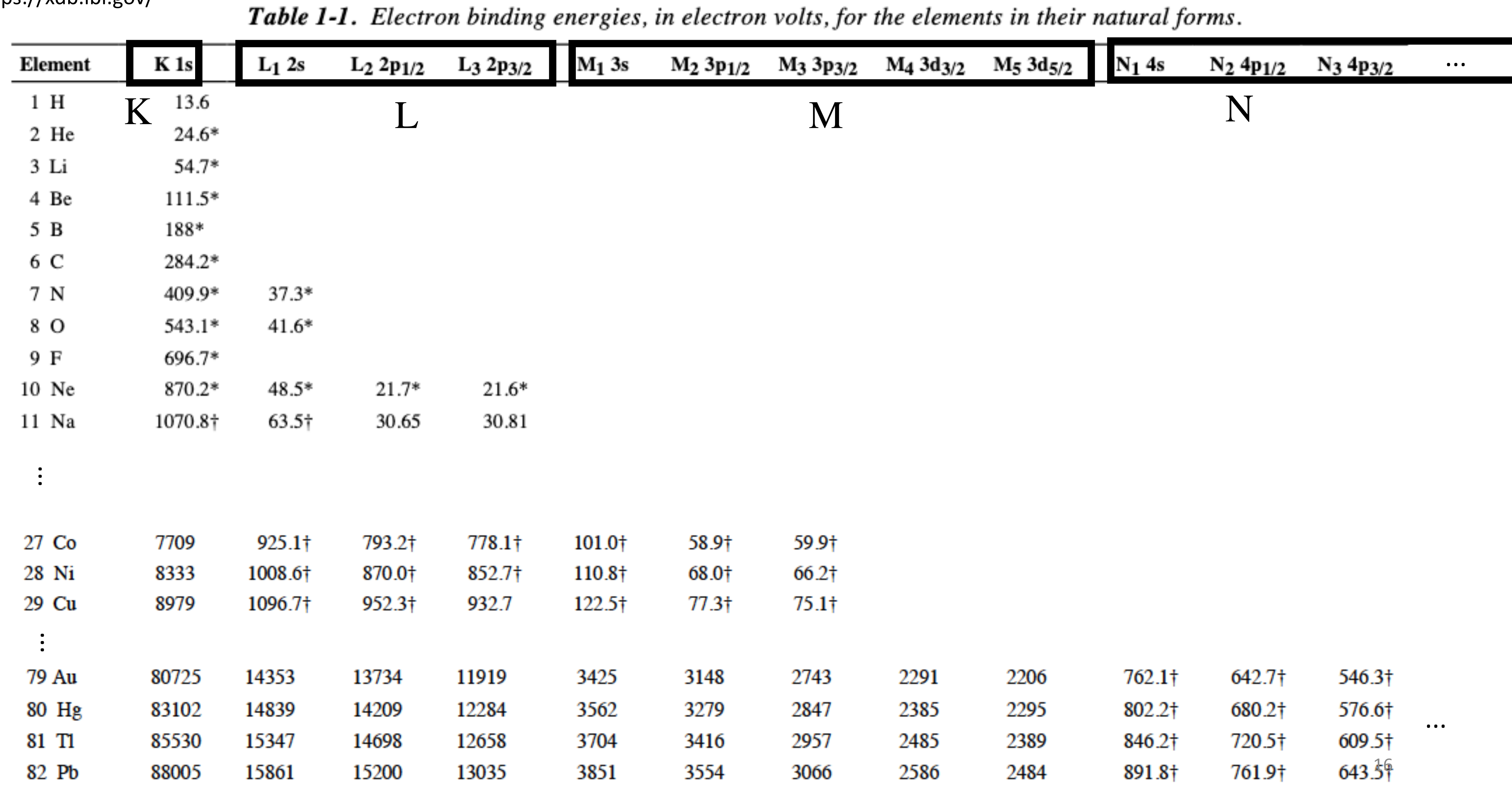
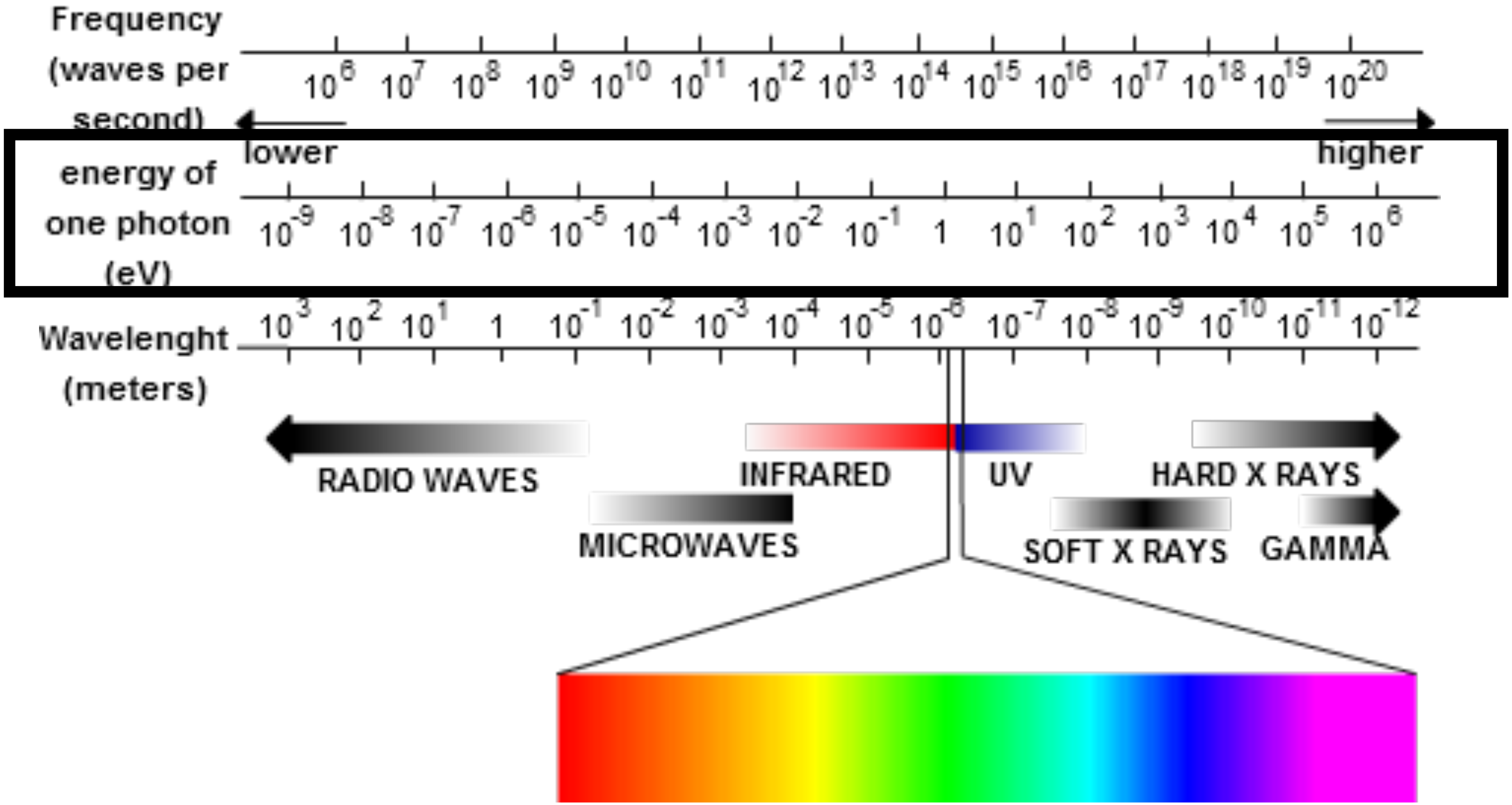


Table 1-1. Electron binding energies, in electron volts, for the elements in their natural forms.

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†	

Core levels energies



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 atomic orbitals or hybrid orbitals from each atom of the molecule

LCAO (Linear Combination of Atomic Orbitals)

Covalent bonds (electron sharing)

H_2 molecule

$$H = -\frac{\hbar^2\nabla_1^2}{2m} - \frac{\hbar^2\nabla_2^2}{2m} + \frac{e^2}{4\pi\epsilon_0}\left\{-\frac{1}{|\mathbf{R}_A - \mathbf{r}_1|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_2|} + \overbrace{\frac{1}{d} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_1|}}^{\text{interaction terms } U}\right\}$$

Atom A with electron 1, atom B with electron 2, at distance d

Because electrons are fermions, the total wavefunction (orbital x spin) must be antisymmetric (change sign) upon particle exchange

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

$$|S, M_S\rangle$$

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

$$\left.\begin{aligned} |1,+1\rangle &= |\uparrow\uparrow\rangle \\ |1,0\rangle &= \frac{1}{\sqrt{2}}\left[\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right] \\ |1,-1\rangle &= |\downarrow\downarrow\rangle \end{aligned}\right\} \rightarrow \text{triplet, symmetric upon particle exchange}$$

H_2 molecule

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:

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

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

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

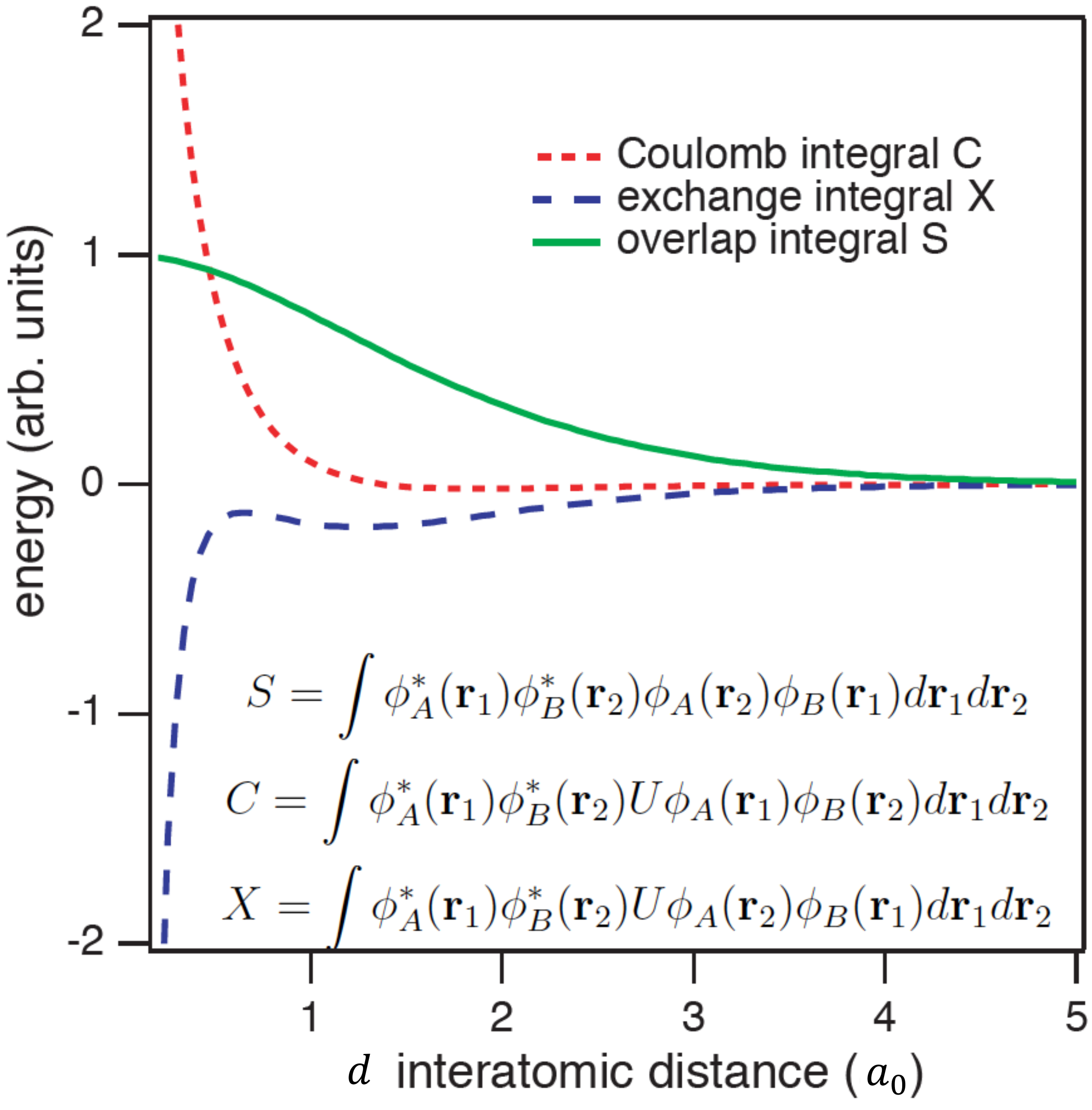
$$\Psi_{\mathrm{singlet}} = \psi_{\mathrm{sym}}(\mathbf{r}_1,\mathbf{r}_2)\,|0,0\rangle$$

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

Heitler - London
Calculate the molecular energy levels
for the two orbital wavefunctions:

$$E = \frac{\int \psi^*\left(\mathbf{r}_1,\mathbf{r}_2\right) H\,\psi\left(\mathbf{r}_1,\mathbf{r}_2\right) d\mathbf{r}_1 d\mathbf{r}_2}{\int \psi^*\left(\mathbf{r}_1,\mathbf{r}_2\right)\psi\left(\mathbf{r}_1,\mathbf{r}_2\right) d\mathbf{r}_1 d\mathbf{r}_2}$$

H_2 molecule



$$S = \int \phi_A^*(\mathbf{r}_1)\phi_B^*(\mathbf{r}_2)\phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2$$

$$C = \int \phi_A^*(\mathbf{r}_1)\phi_B^*(\mathbf{r}_2)U\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

$$X = \int \phi_A^*(\mathbf{r}_1)\phi_B^*(\mathbf{r}_2)U\phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2$$

$$E = 2E_{\mathrm{H,1s}} + \Delta E_{\mathrm{singlet/triplet}}$$

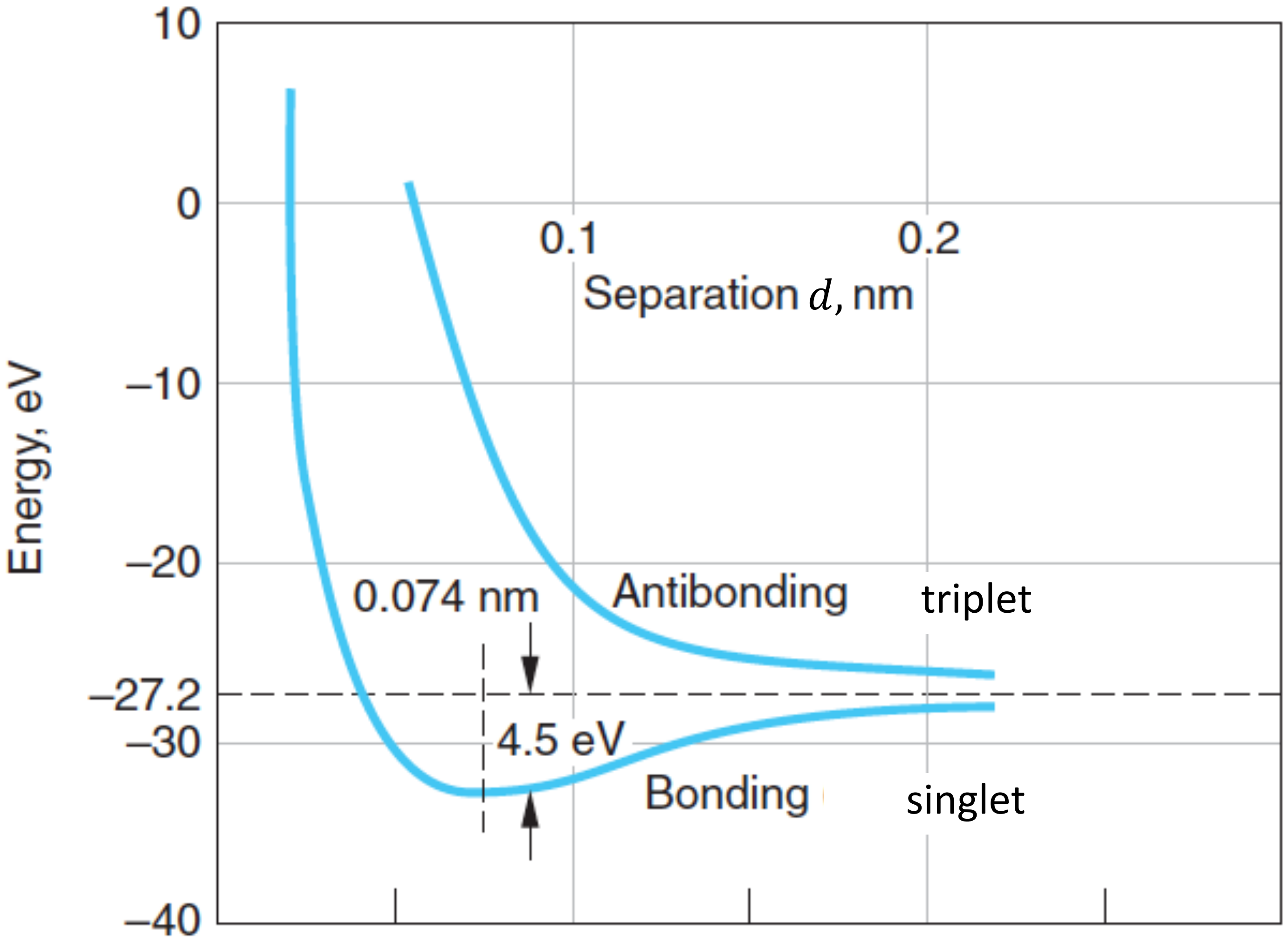
$$\Delta E_{\mathrm{triplet}} = \frac{C(d) - X(d)}{1 - S(d)}$$

$$\Delta E_{\mathrm{singlet}} = \frac{C(d) + X(d)}{1 + S(d)}$$

$$E_{\mathrm{triplet}} > E_{\mathrm{singlet}}$$

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.

H_2 molecule



$$E = 2E_{\mathrm{H,1s}} + \Delta E_{\mathrm{singlet/triplet}}$$

$$\Delta E_{\mathrm{triplet}} = \frac{C(d) - X(d)}{1 - S(d)}$$

$$\Delta E_{\mathrm{singlet}} = \frac{C(d) + X(d)}{1 + S(d)}$$

$$E_{\mathrm{H,1s}} = -13.6\,\mathrm{eV}$$

Simple representation of covalent bonds

Molecular orbitals

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

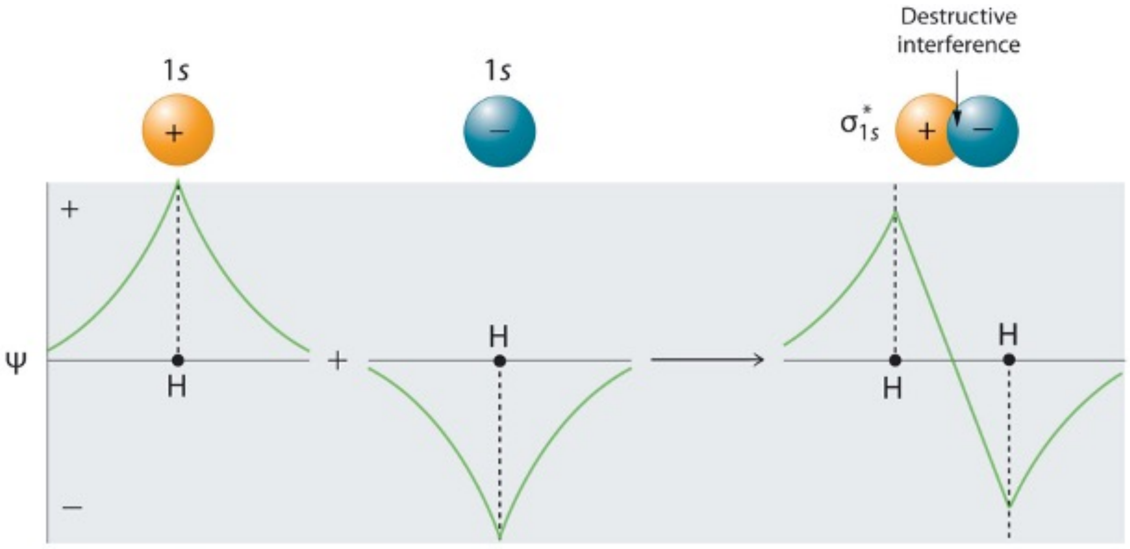
constructive interference -> localization of electrons between the atoms, bonding, lower energy

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

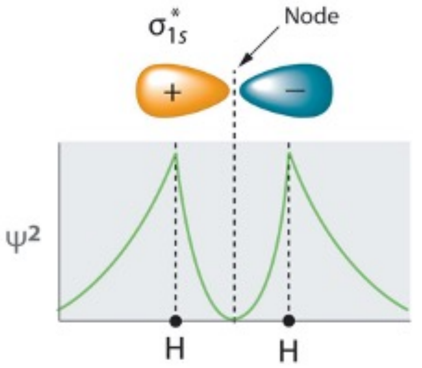
The different signs are typically represented by different shades / colors

s isotropic orbitals → σ orbitals

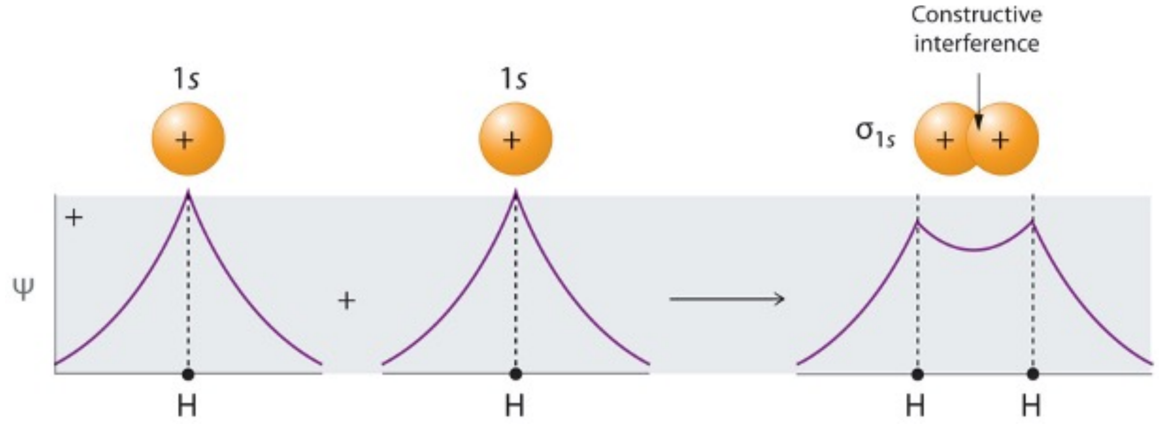
H_2 molecule



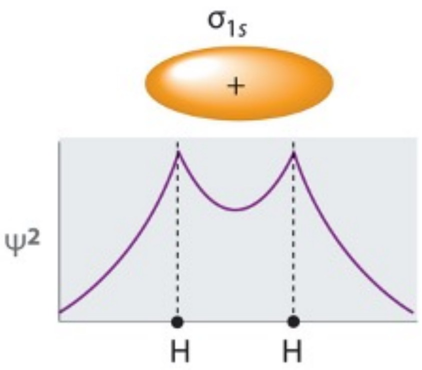
(c) Wave functions combined for σ^*_{1s}



(d) Antibonding probability density

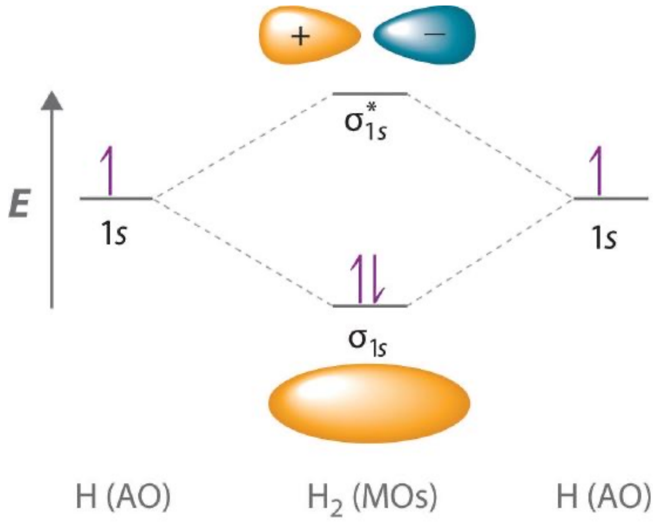


(a) Wave functions combined for σ_{1s}



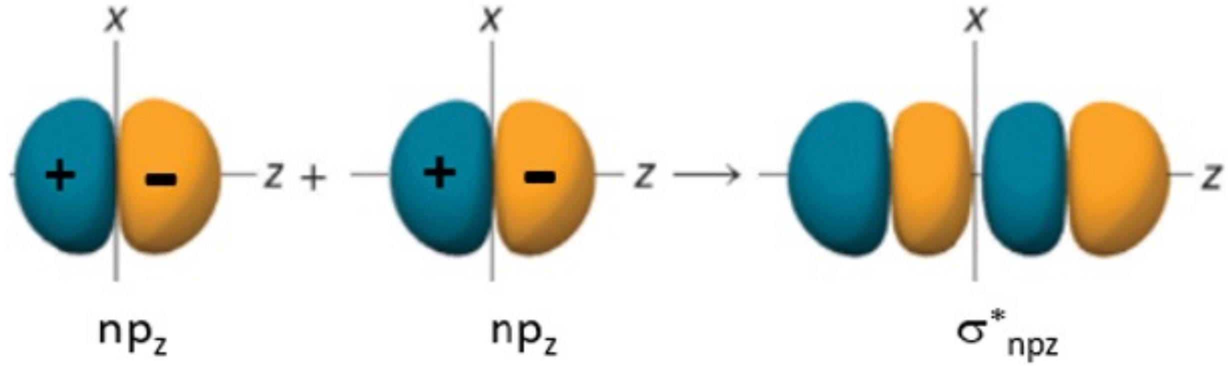
(b) Bonding probability density

Energy scheme



p orbitals directed along the interatomic axis→ σ orbitals

example: p_z orbitals, interatomic axis along z



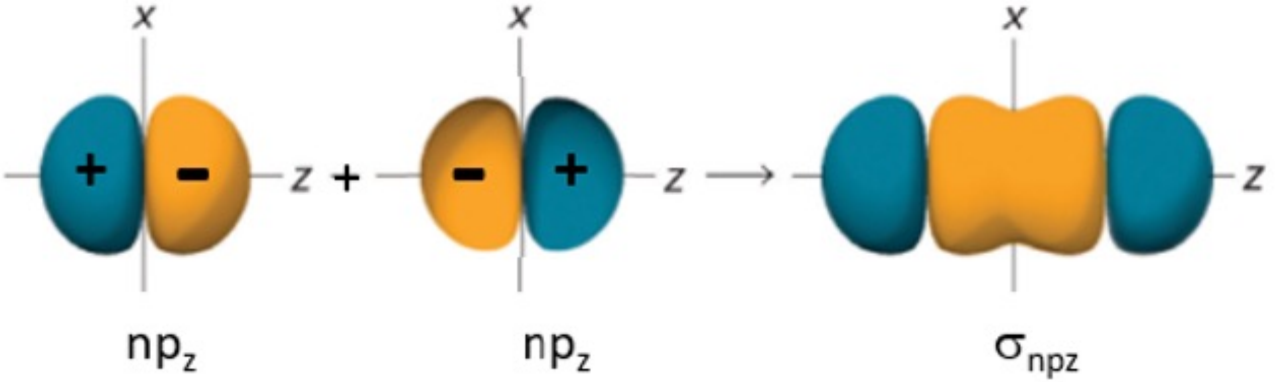
(b) Destructive AO Overlap

σ^* Antibonding MO

higher energy

Atomic Orbitals (AOs)

Molecular Orbital (MO)



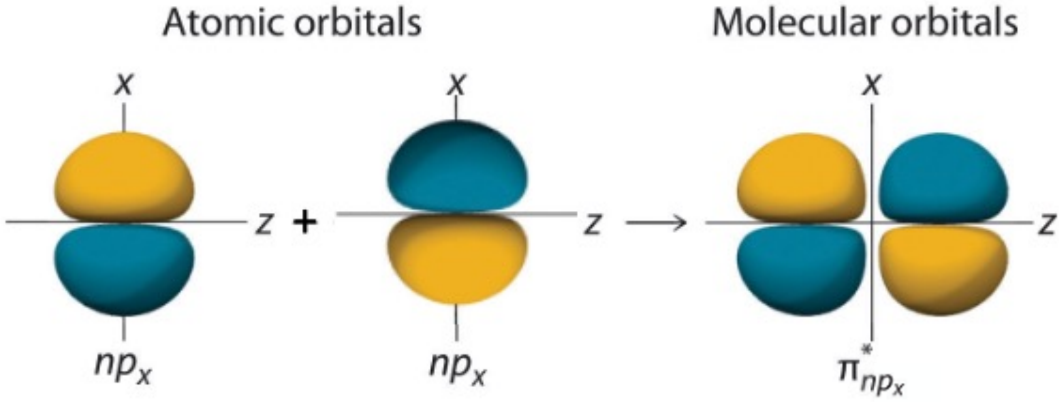
(a) Constructive AO Overlap

σ Bonding MO

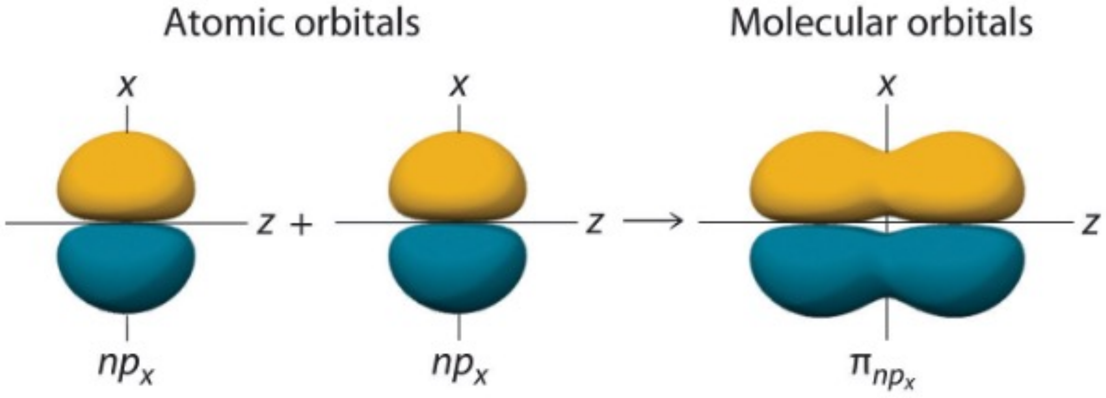
lower energy

p orbitals perpendicular to the internuclear axis → π orbitals

example: p_x orbitals, interatomic axis along z



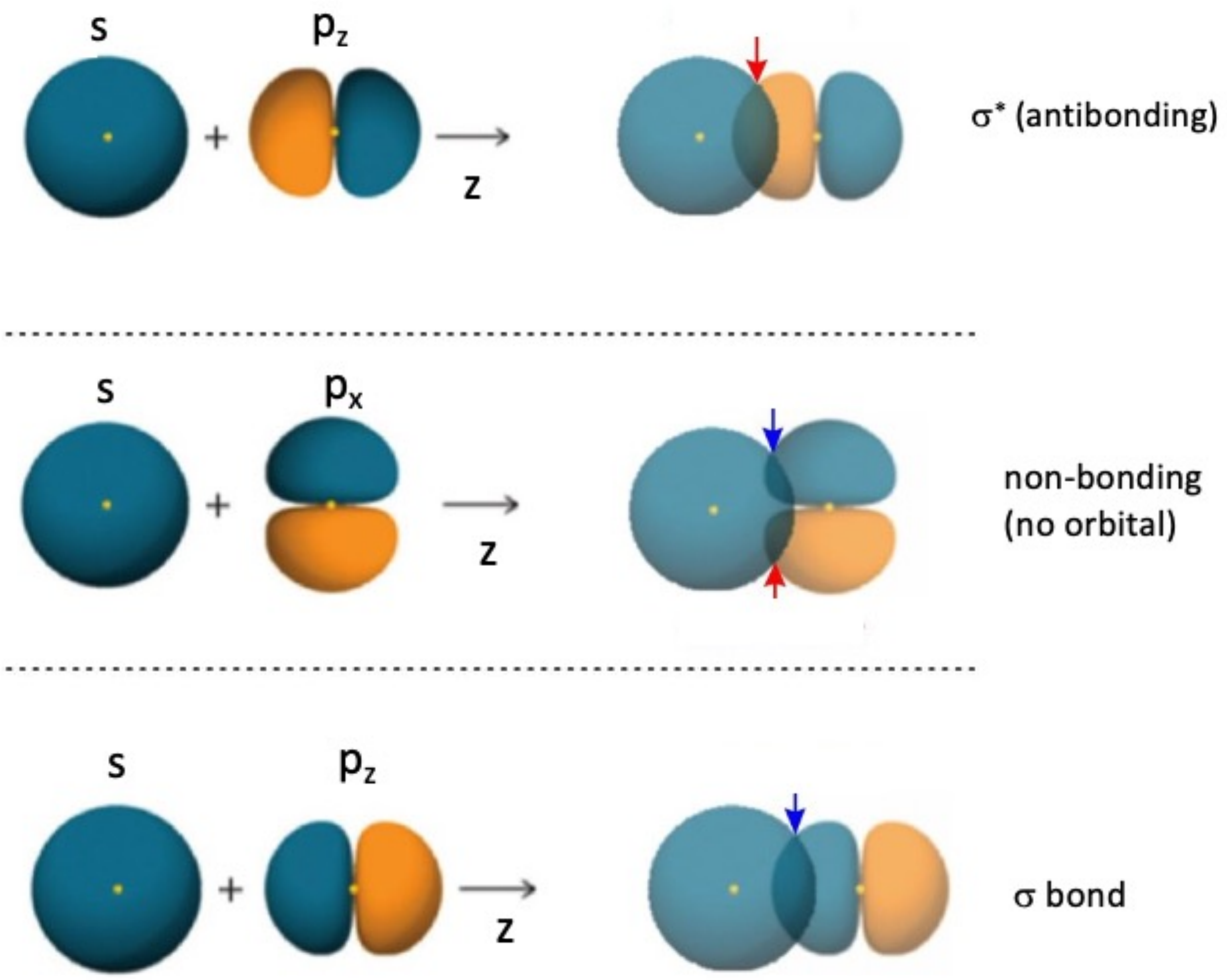
higher energy
anti-bonding, π*



lower energy
bonding, π

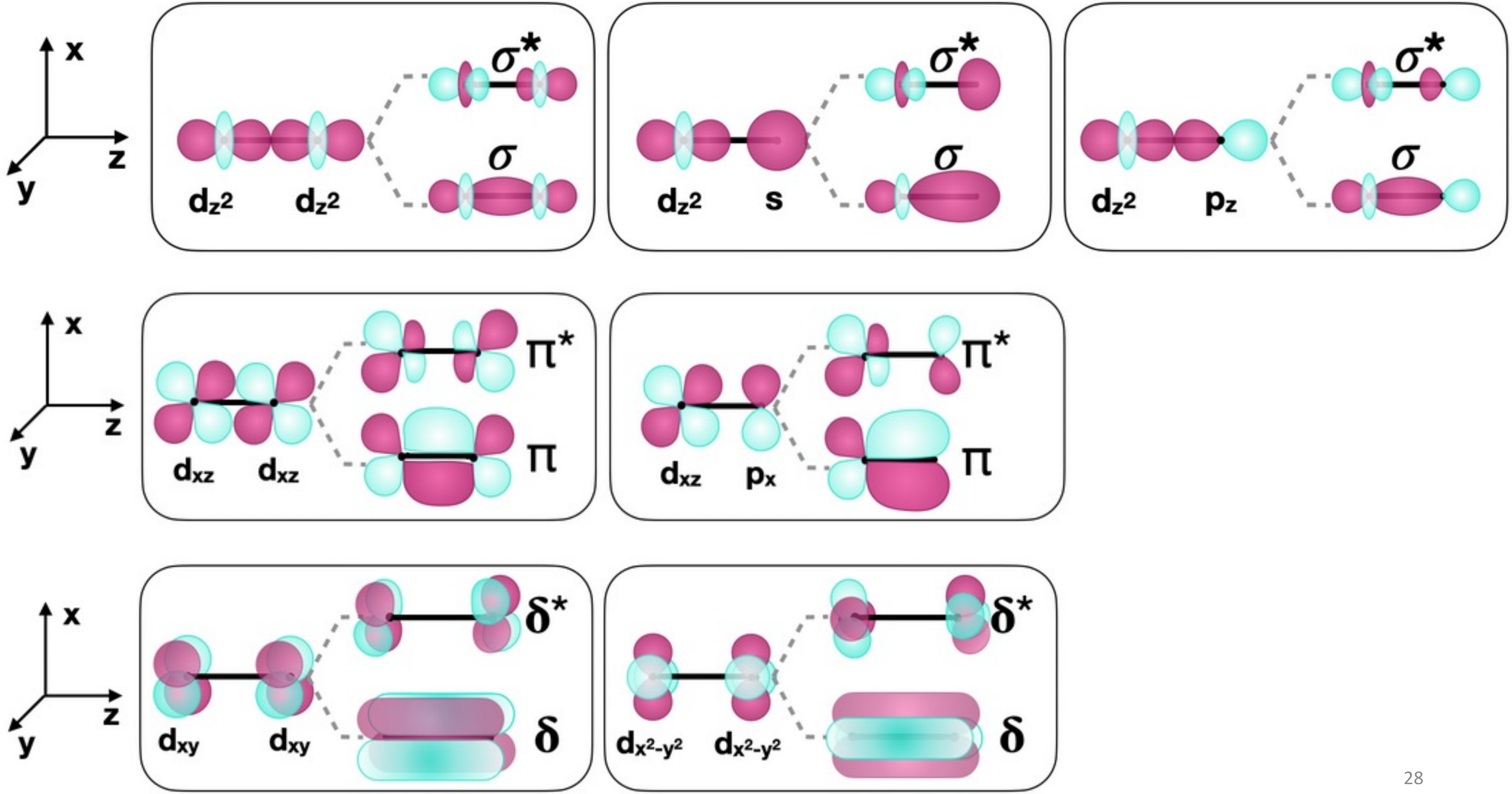
atomic orbitals forming molecular orbitals can have different l

example: s and p orbitals



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

bonds involving atomic d orbitals



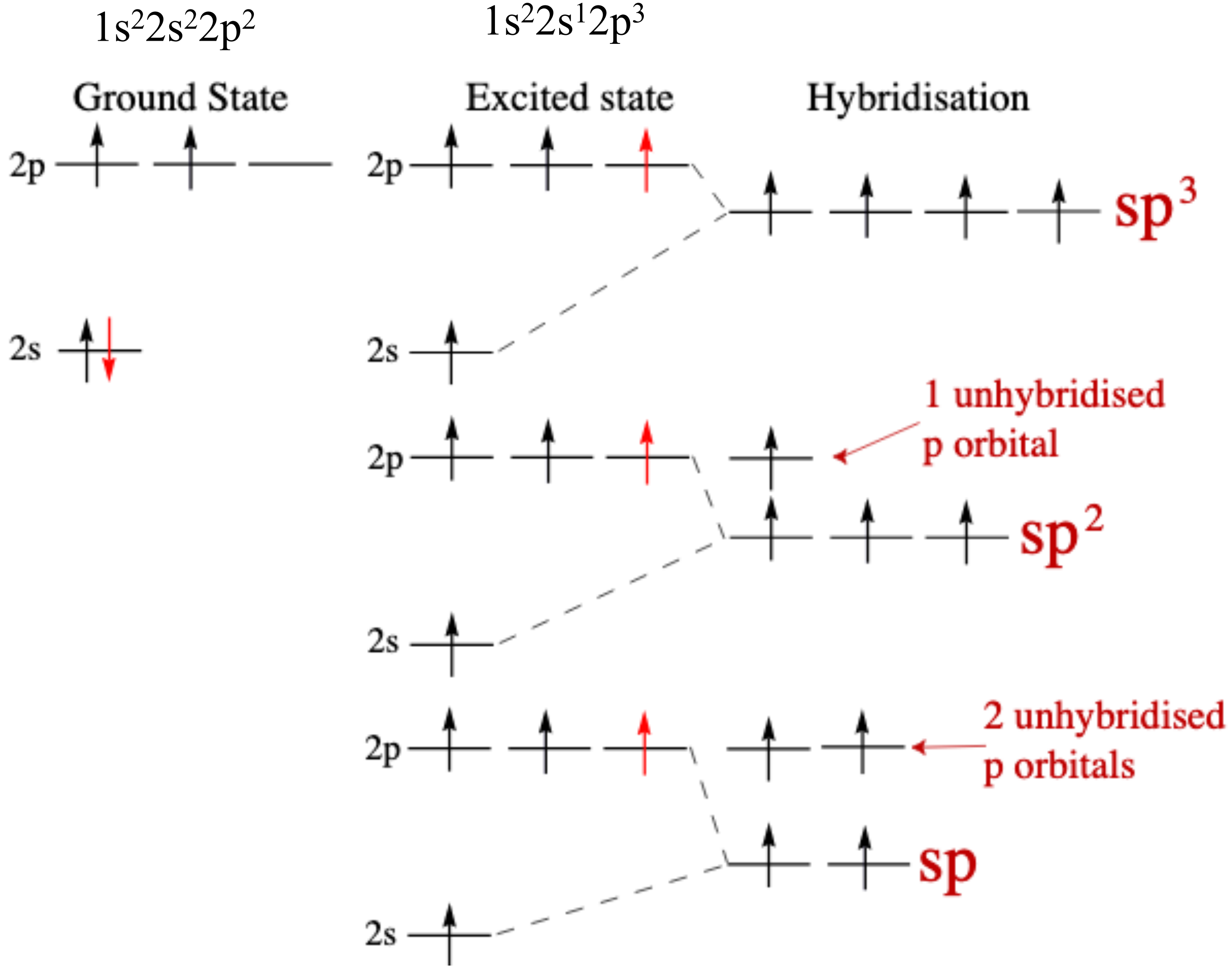
Hybridization

hybrid orbitals

perturbation of the description of the atomic orbitals induced by the interaction with the sourronding 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

example: carbon

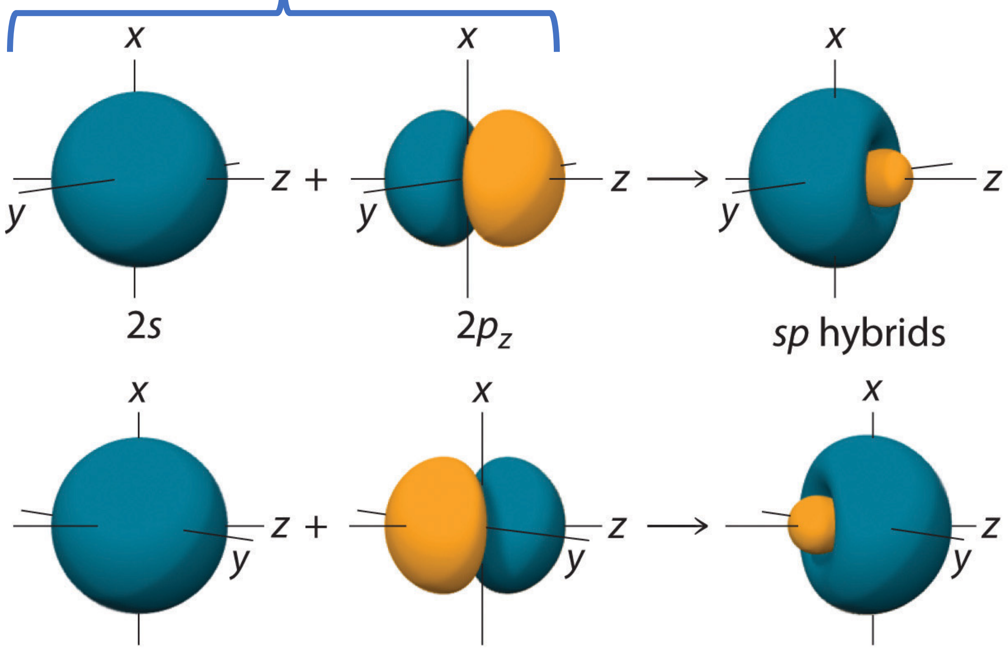


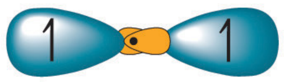
sp hybridization

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

linear bond

of the same atom!

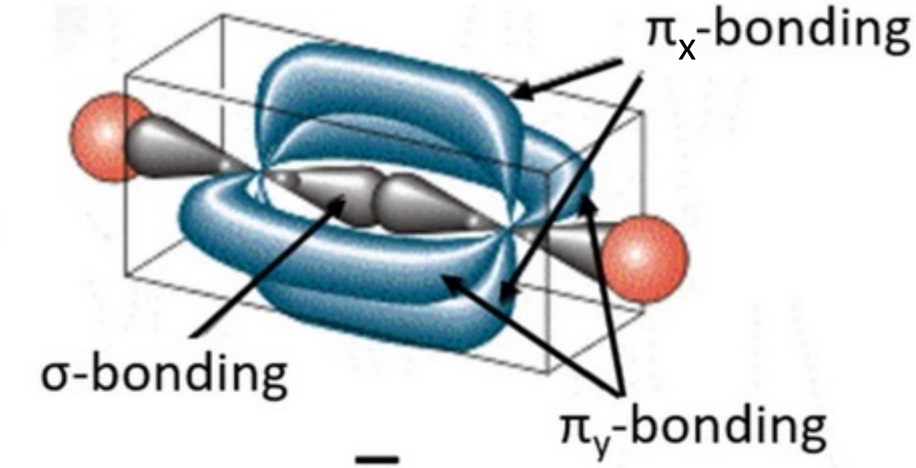




Schematic representation
of hybrids shown together

example: acetylene C_2H_2

H—C≡C—H



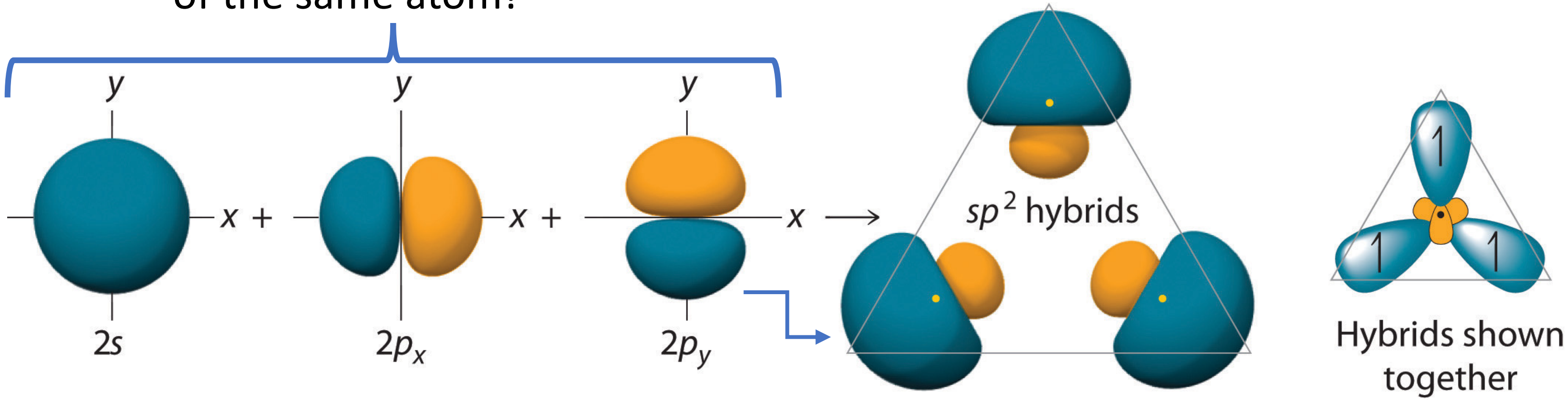
σ bond between the sp orbitals (s p_z)
σ bonds between sp orbitals and H 1s orbitals
π bonds between the two p_x orbitals and
between the two p_y orbitals

sp^2 hybridization

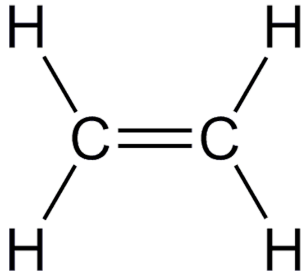
the s orbital hybridize
with two p orbitals,
to give **three** sp^2 hybrid
orbitals

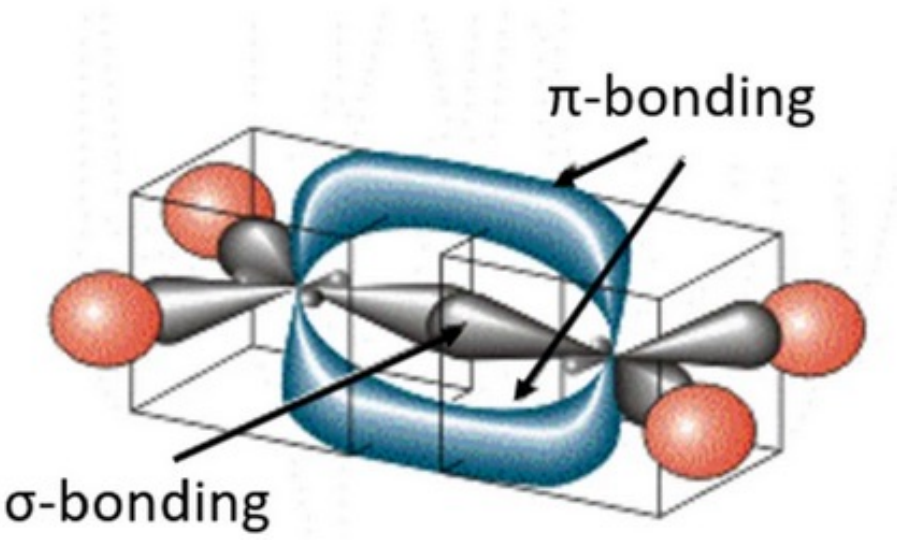
trigonal planar bonds

of the same atom!



example: ethylene C_2H_4





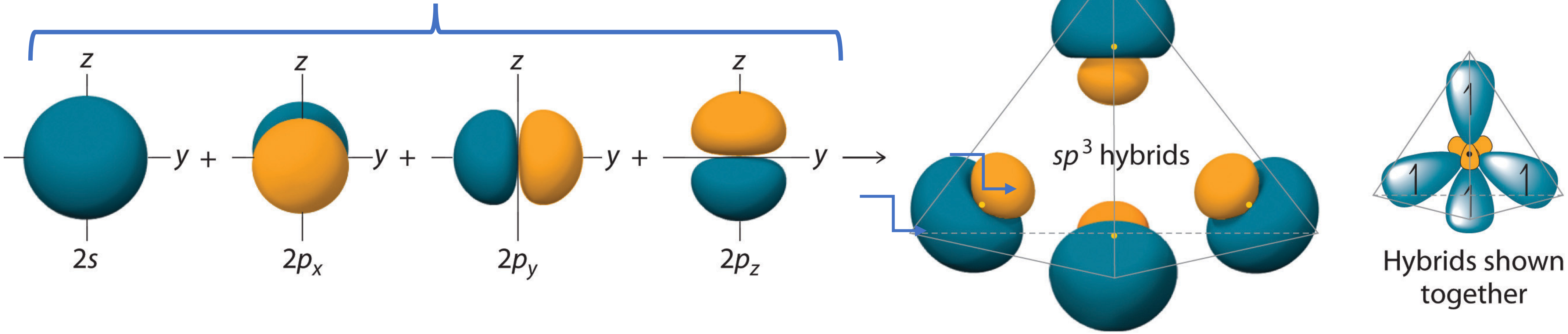
σ bond between the sp^2 orbitals
σ bonds between sp^2 orbitals and H 1s orbitals
π bond between the p_z orbitals

sp^3 hybridization

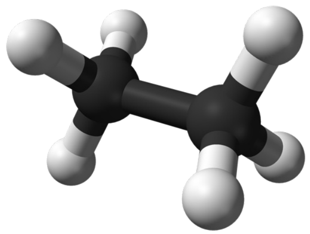
the s orbital hybridize with the three p orbitals,
to give **four** sp^3 hybrid orbitals

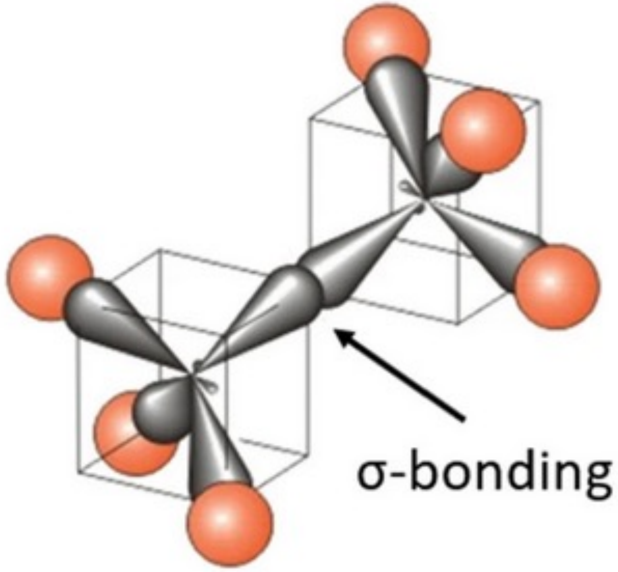
of the same atom!

tetrahedral geometry



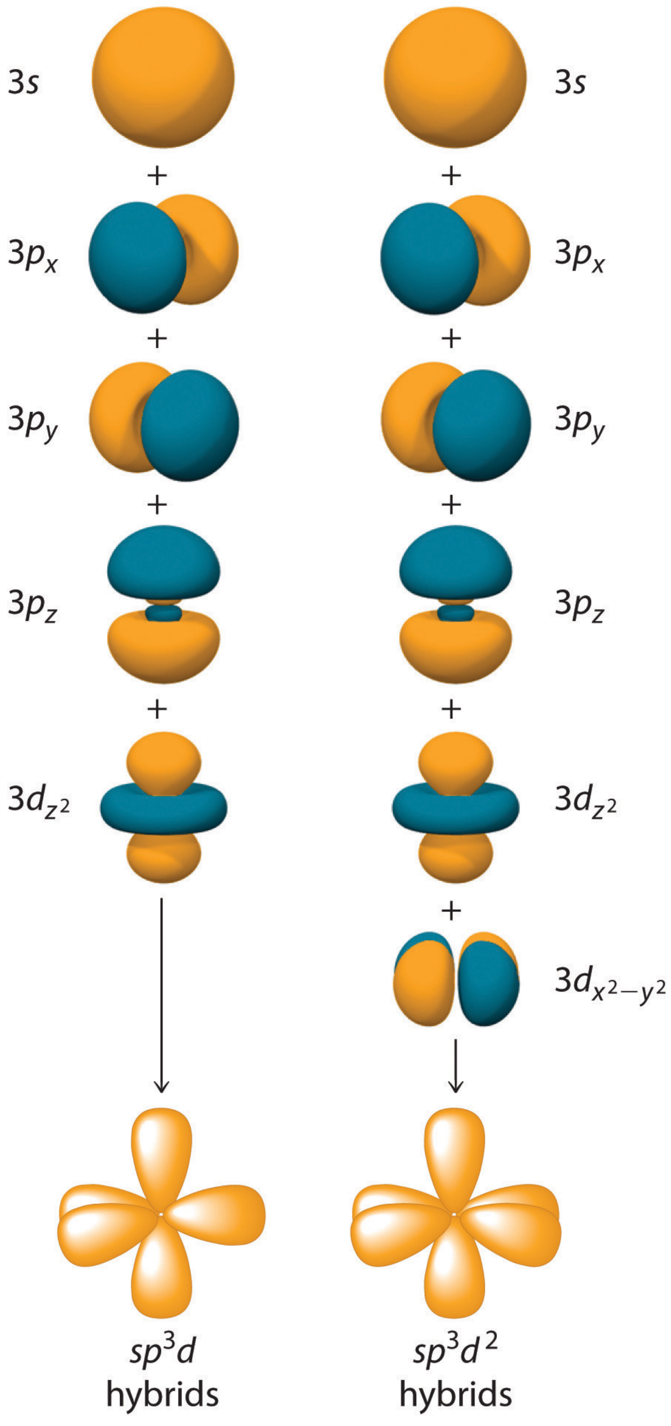
example: ethane C_2H_6





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

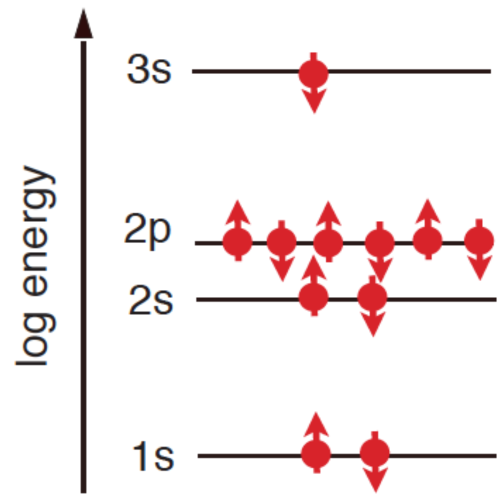
spd hybridization

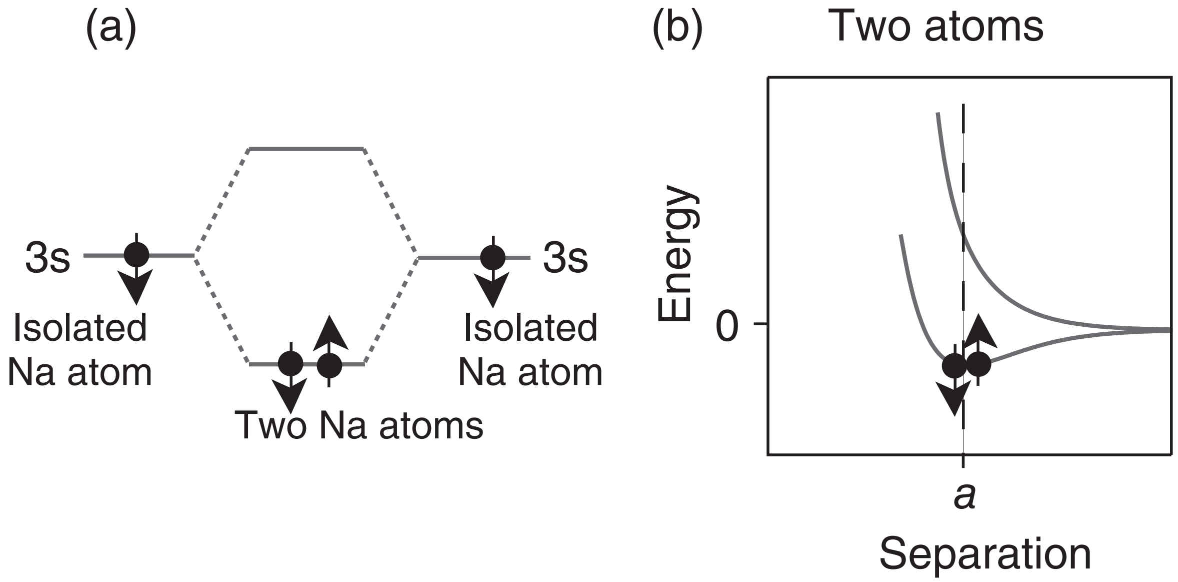


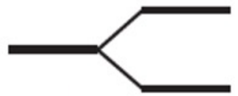
these hybrid orbitals
exist as well

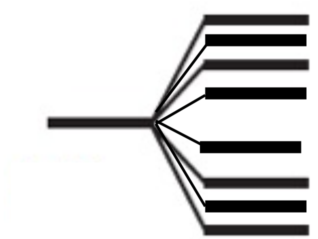
Toward solids: energy bands

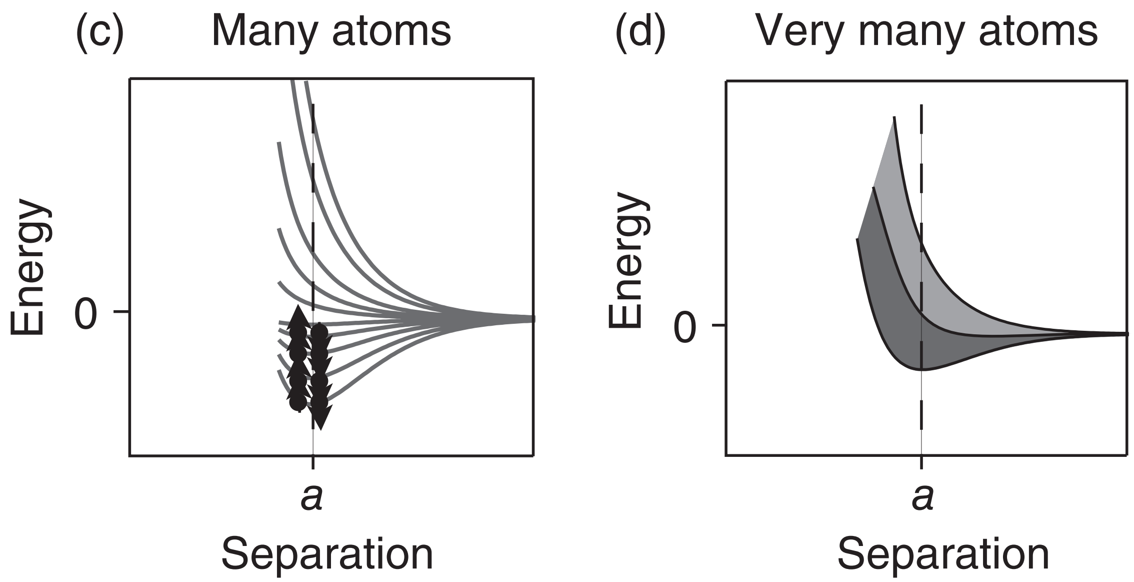
Na

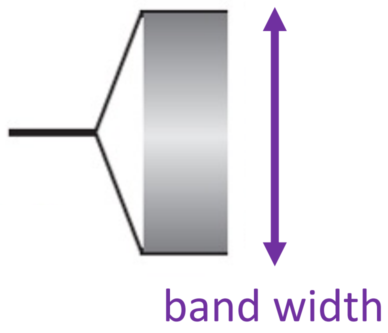










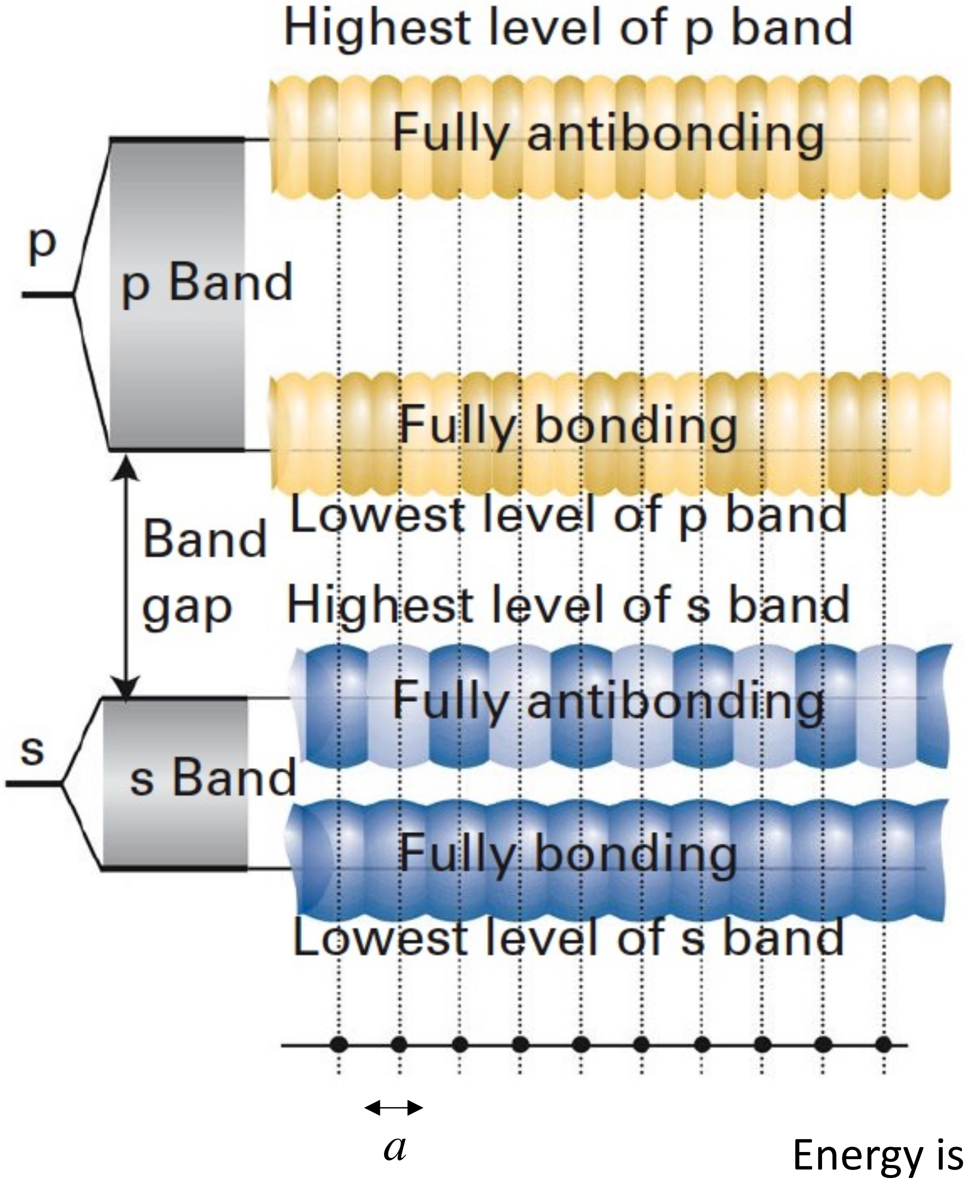


Toward solids: energy bands

1D chain

one s orbital

one p orbital
aligned along the chain



wavelenght	wavevector
$\lambda = \infty \rightarrow$	$k = 0$
$\lambda = 2a \rightarrow$	$k = \pi/a$
$\lambda = 2a \rightarrow$	$k = \pi/a$
$\lambda = \infty \rightarrow$	$k = 0$

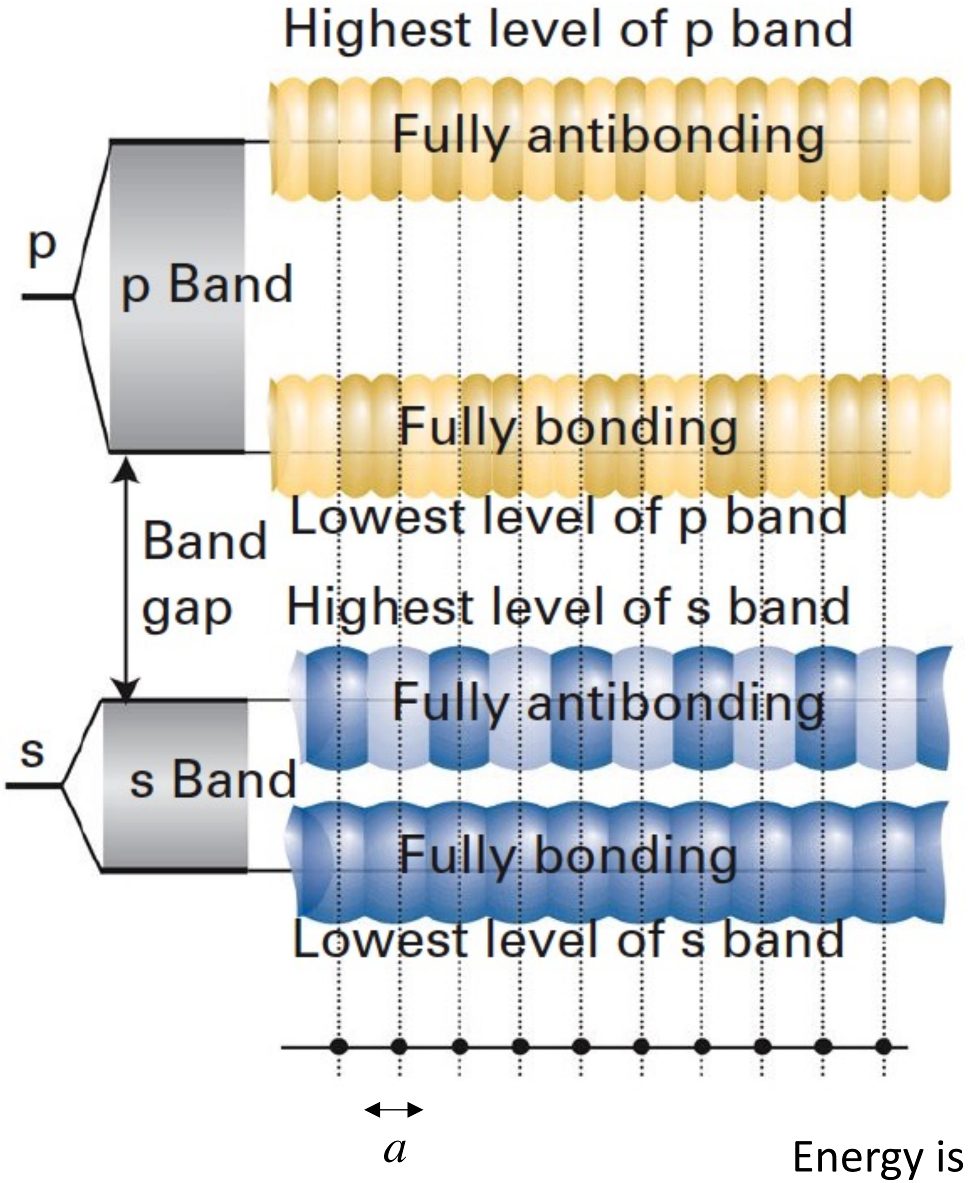
Energy is a function of wavevector: $E(k)$

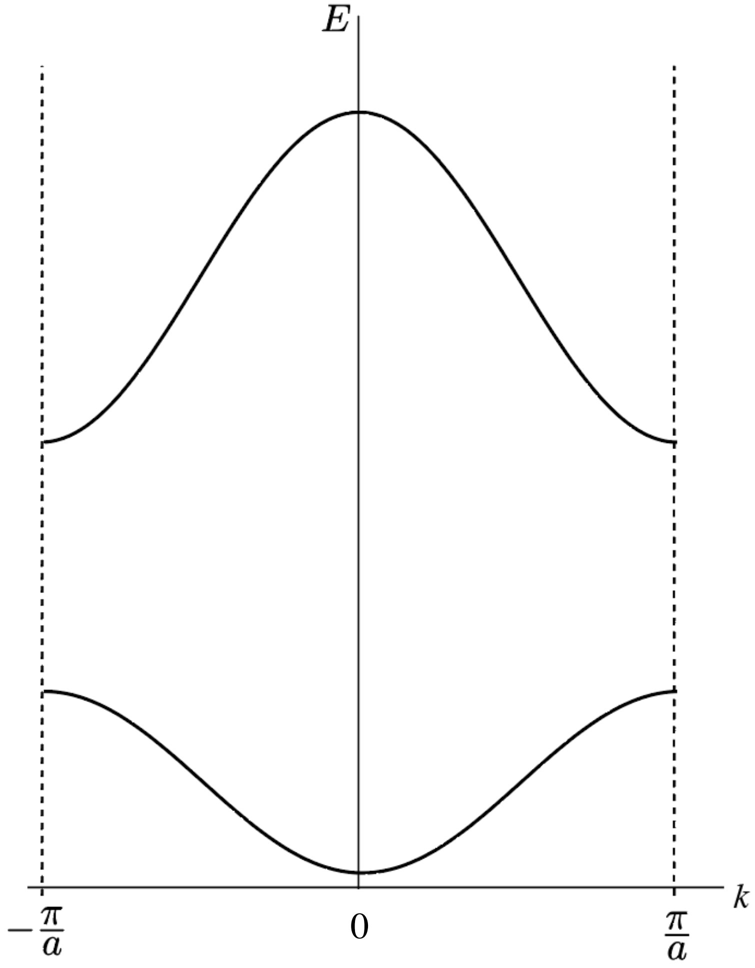
Toward solids: energy bands

1D chain

one s orbital

one p orbital
aligned along the chain





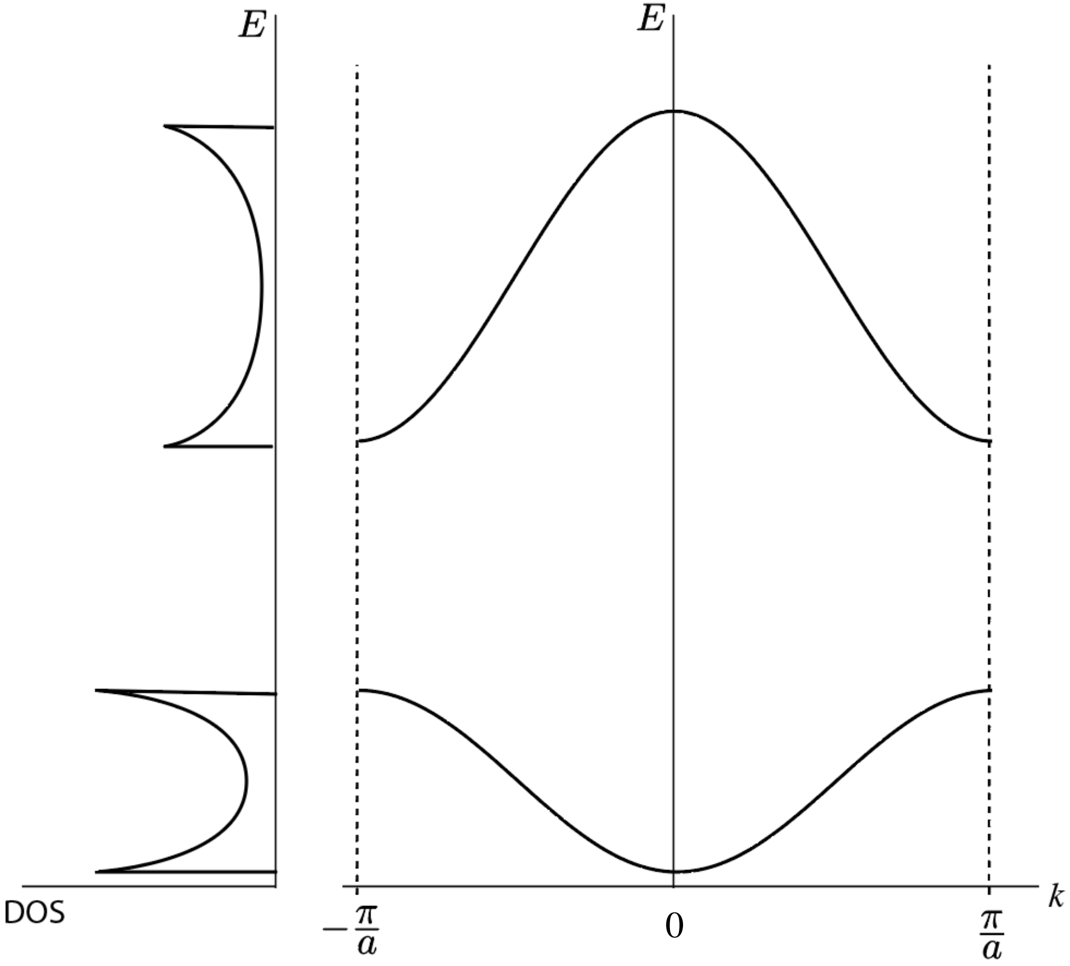
Energy is a function of wavevector: $E(k)$

Toward solids: energy bands and density of states

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 ovelap between wavefunctions and to the strength of the potential ΔU originating from the atoms in the cristal in 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: $\beta = \int \phi^*(\boldsymbol{r})\,\Delta U\,\phi(\boldsymbol{r})d\boldsymbol{r}$

Solids: Tight-binding model

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

simplifications / approximations:

- only nearest neighbors (NN) in the sums
- β small offset, can be neglected
- α small and/or does not change strongly the band

→

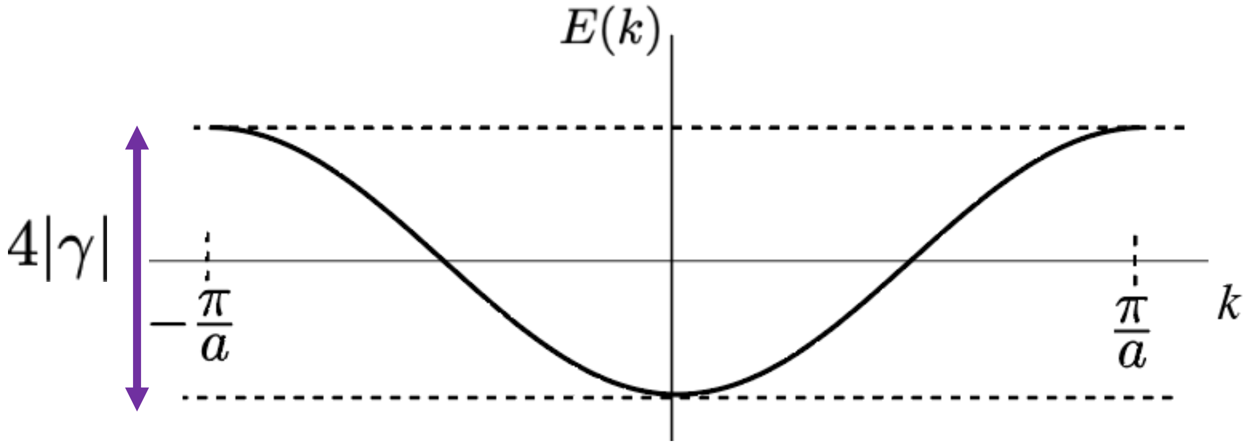
$$E(\mathbf{k}) = E_{at} + \sum_{\mathbf{R}_{NN}} \exp(i\mathbf{k}\cdot\mathbf{R}_{NN})\gamma(\mathbf{R}_{NN})$$

1D chain

distance a
one s orbital

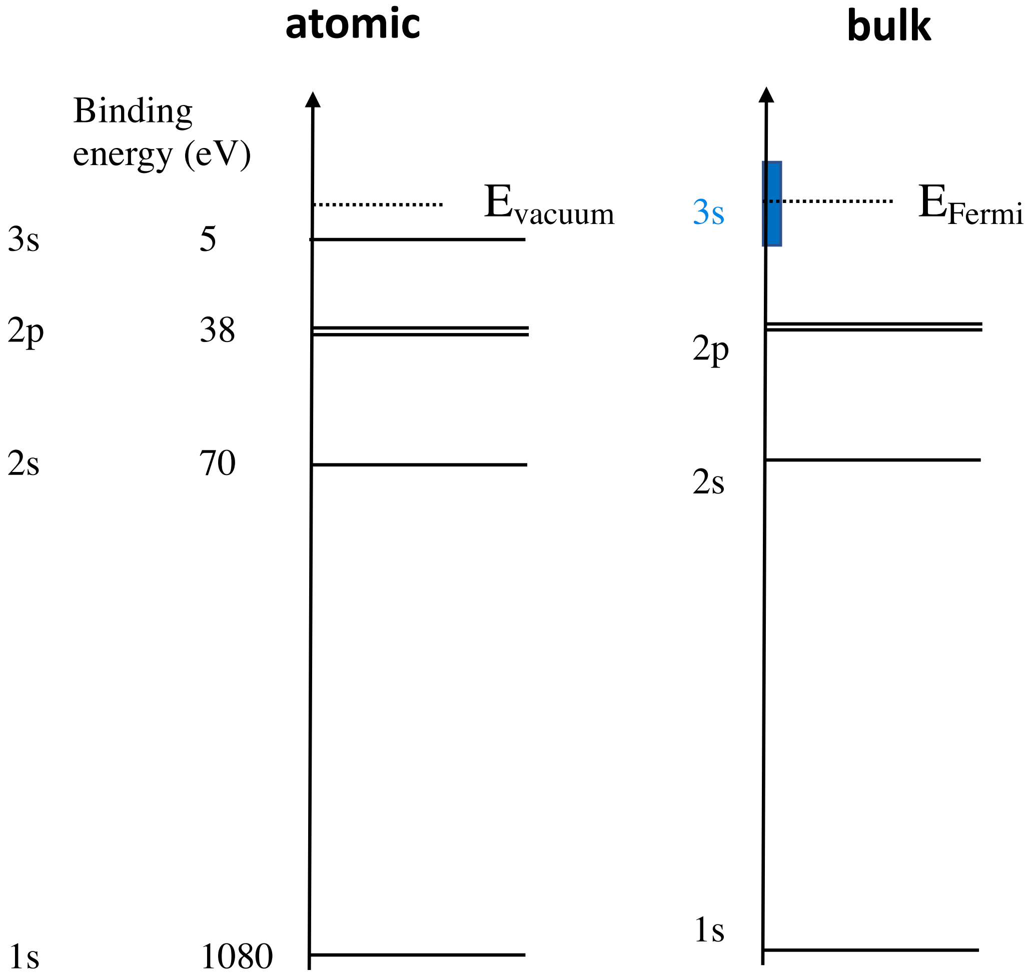
$$\begin{aligned} E(k) &= E_{at,s} + [\exp(ika) + \exp(-ika)]\gamma(a) \\ &= E_{at,s} + 2\gamma\ \cos(ka) \end{aligned}$$

$\gamma < 0$



Na electronic structure

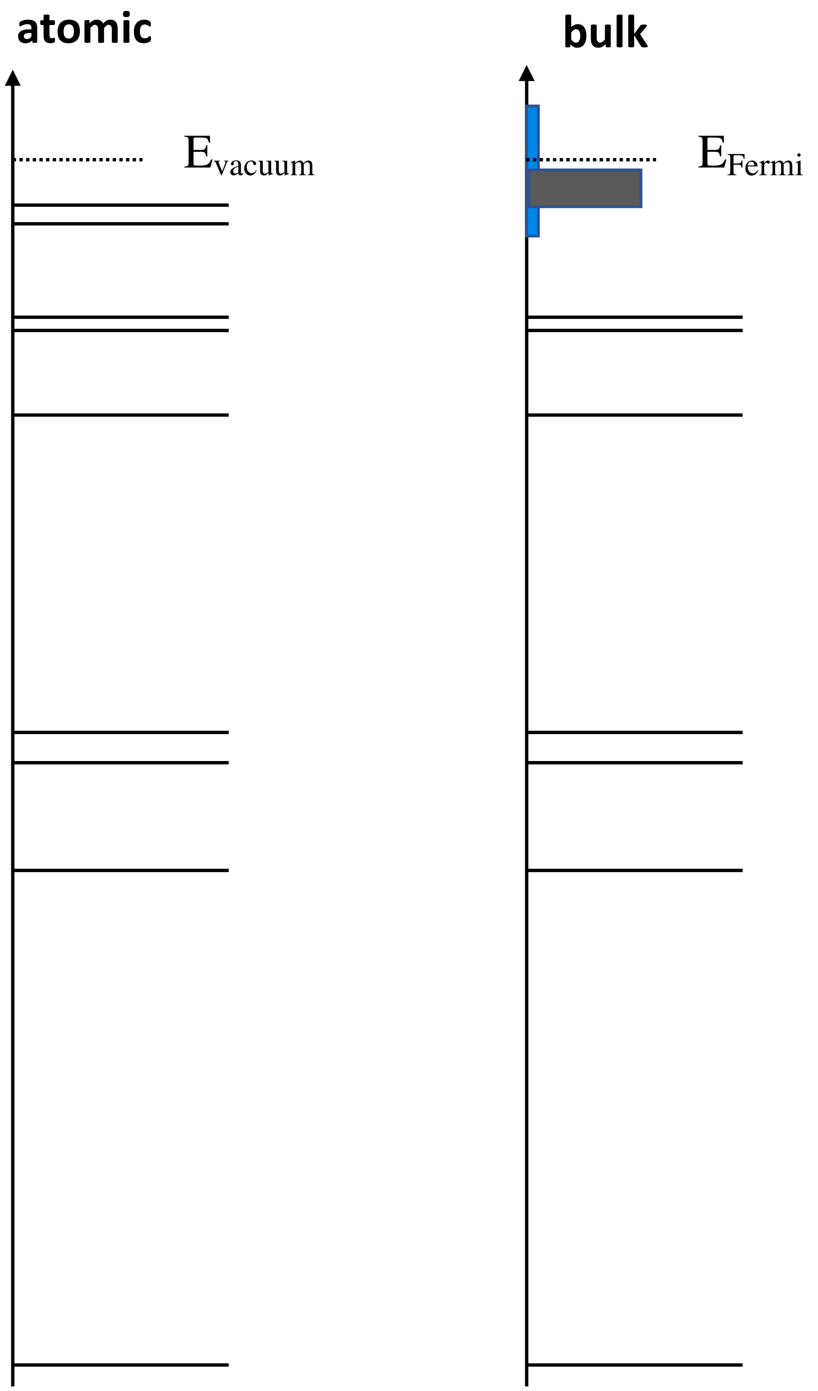
atomic Na:
$1s^2\ 2s^2\ 2p^6\ 3s^1$
[Ne] $3s^1$



energy not to scale

Cu electronic structure

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

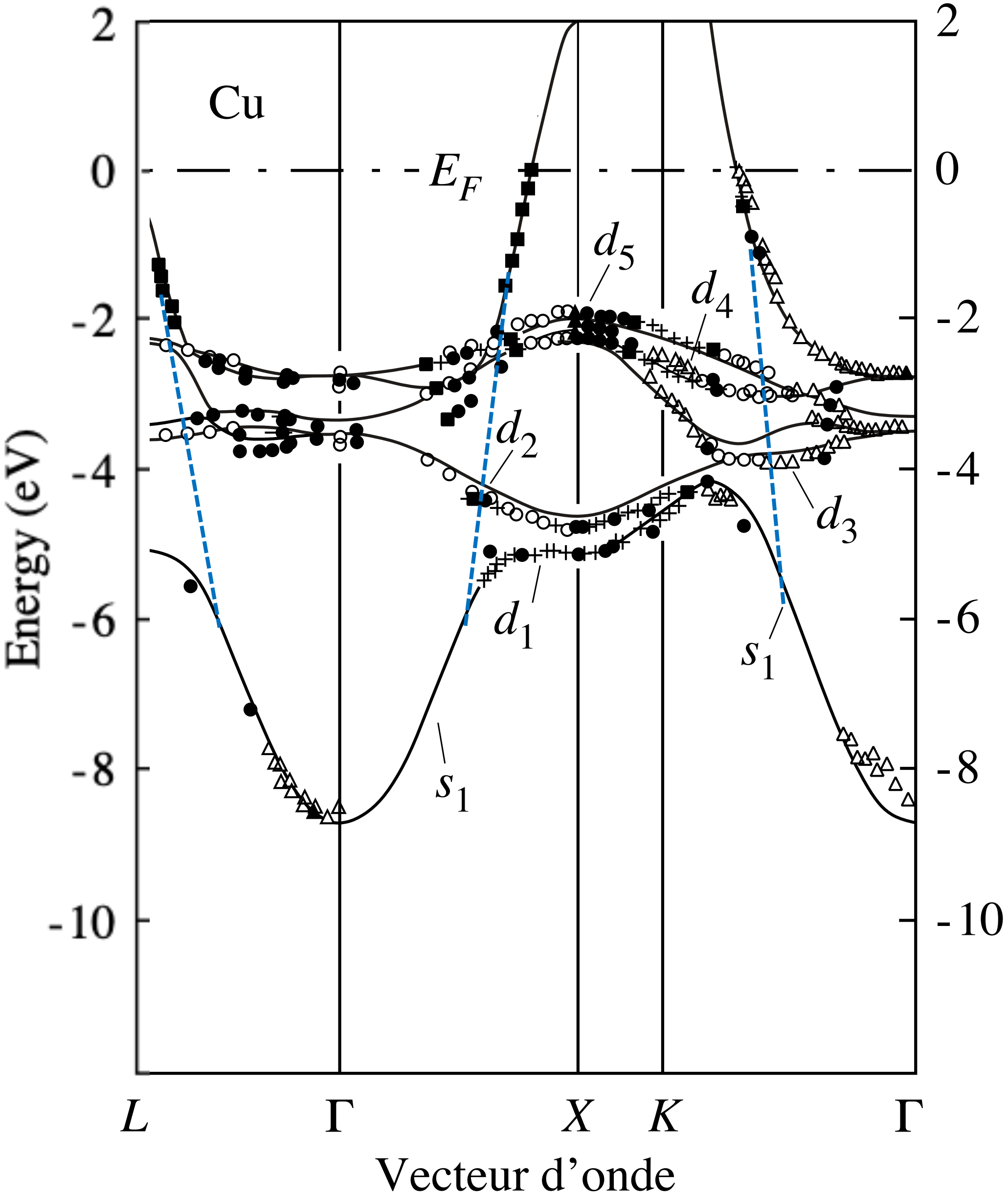


	Binding energy (eV)
4s	7
3d	11
3p	83
3s	128
2p	940 960
2s	1097
1s	8980

	Binding energy (eV)
4s	-6 to 8
3d	2 to 5
3p	
3s	
2p	
2s	
1s	

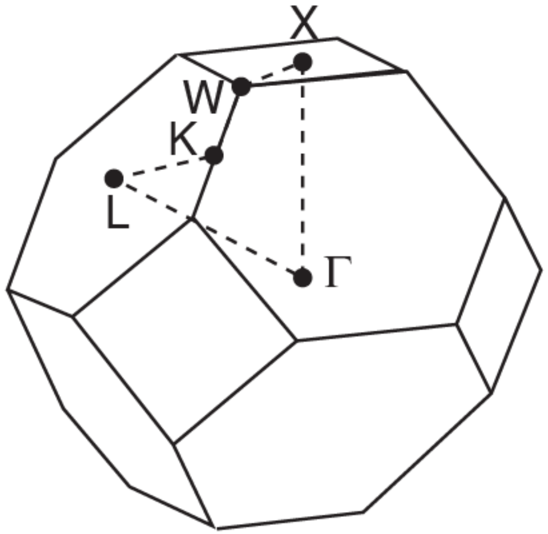
energy not to scale

Cu band structure

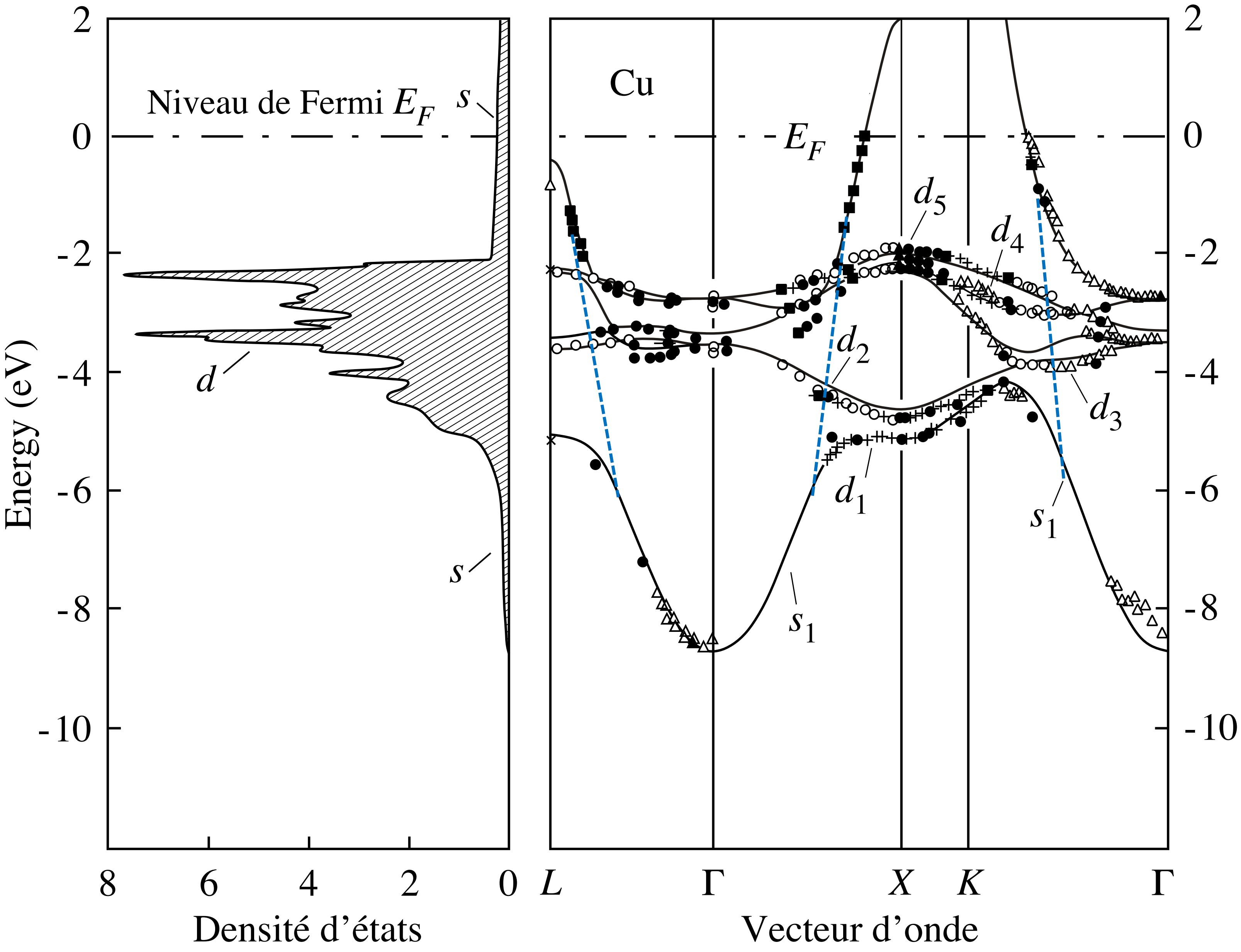


Cu: fcc crystal

first Brillouin zone:

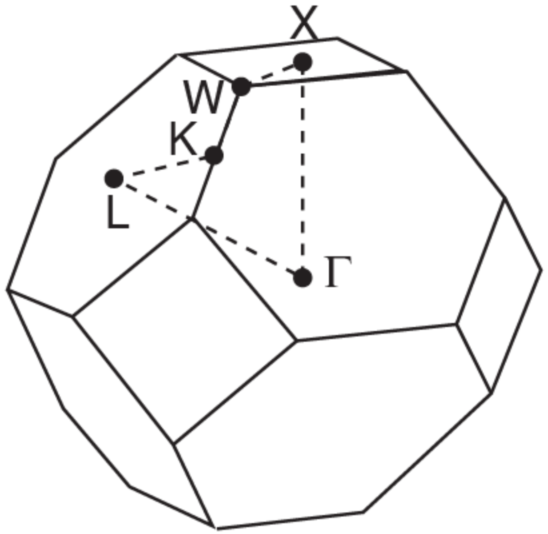


Cu band structure and density of states (DOS)



Cu: fcc crystal

first Brillouin zone:

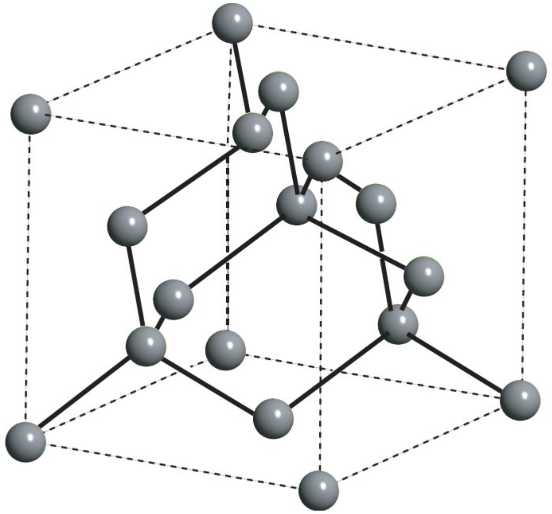


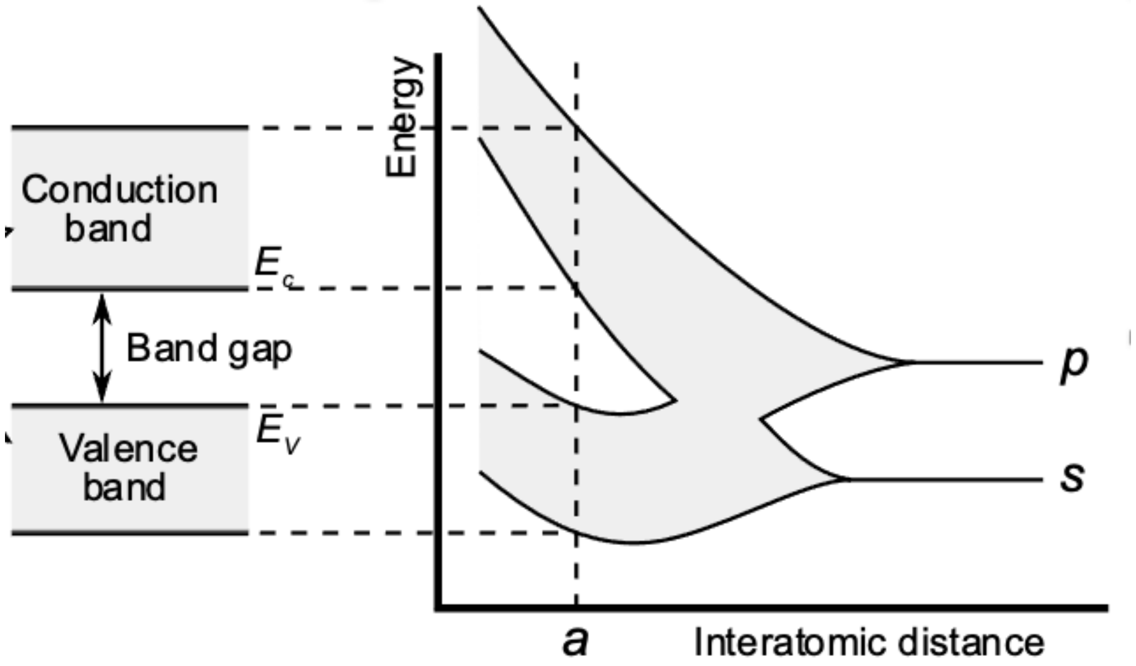
Diamond

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