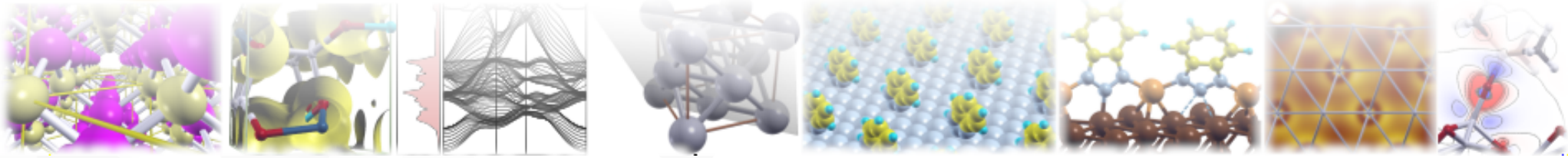
QUANTUMESPRESSO

September 15—20, 2019
Ljubljana, Slovenia

Summer School on Advanced Materials and Molecular Modelling

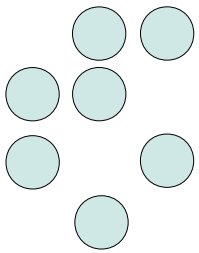


A chemist's view of bonding

&

a very informal intro to Bloch theorem

(*from molecules to solids and back*)



Anton Kokalj
Department of Physical and Organic Chemistry
Jožef Stefan Institute

Basics ...

time-independent Schrödinger equation

Born-Oppenheimer approximation

one-electron approximation

formally exact, but in practice approximative

Hartee-Fock

$$\left[-\frac{1}{2}\nabla^2 + \widehat{V}_{\text{eff}}^{\text{HF}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$

DFT (Kohn-Sham)

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}^{\text{KS}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$

molecular orbitals

Molecular orbitals

- molecular orbital (MO) = linear combination of atomic orbitals (LCAO)

$$\psi_i(\boldsymbol{r}) = \sum_{\mu} c_{\mu,i}\phi_{\mu}(\boldsymbol{r})$$

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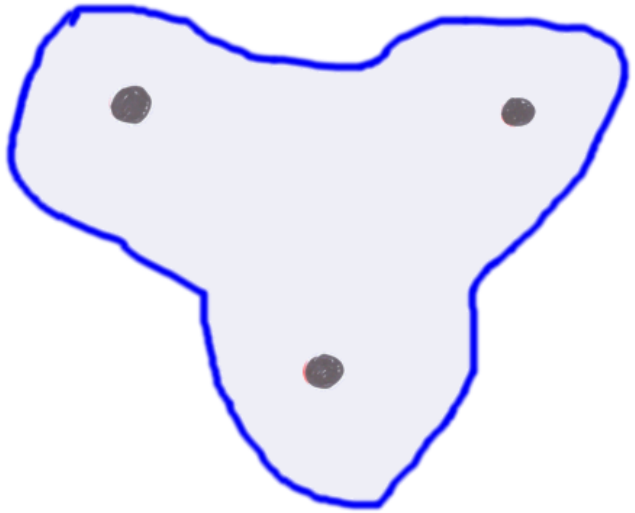
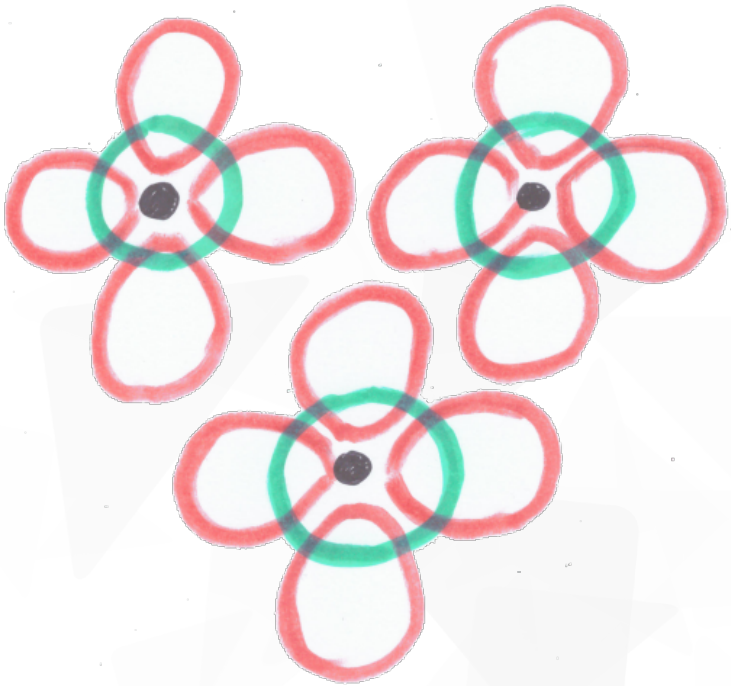


Molecular orbitals

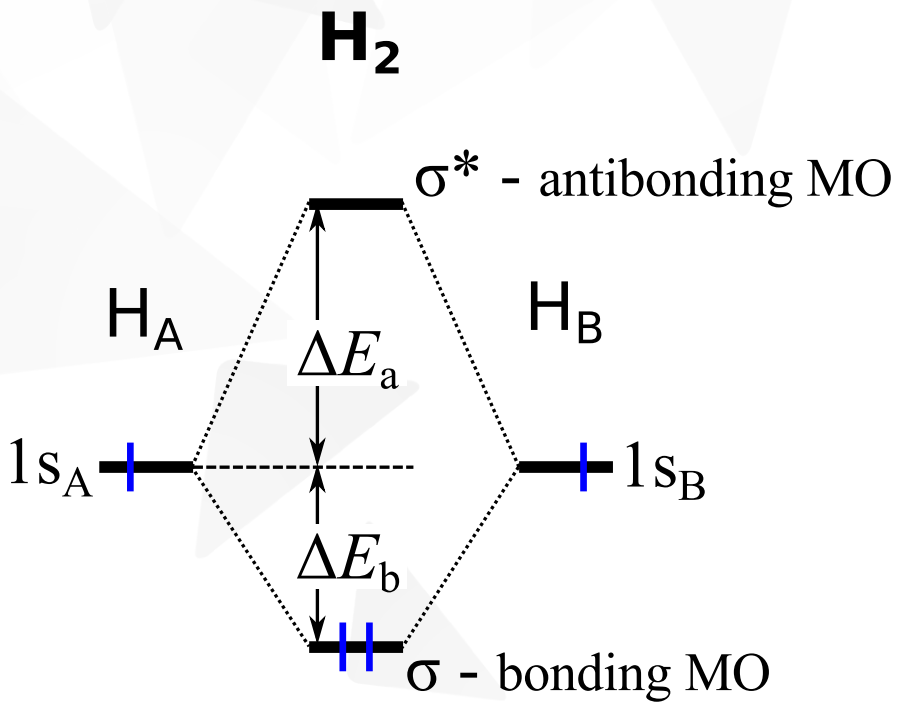
- molecular orbital (MO) = linear combination of atomic orbitals (LCAO)

$$\psi_i(\boldsymbol{r}) = \sum_{\mu} c_{\mu,i}\phi_{\mu}(\boldsymbol{r})$$



A chemist's view of bonding

- molecular orbital (MO) diagram



net attraction

(two-orbital two-electron interaction)

$$\Delta E_a = +\frac{H_{\mathrm{AB}}}{1 - S_{\mathrm{AB}}}$$

$$\Delta E_b = -\frac{H_{\mathrm{AB}}}{1 + S_{\mathrm{AB}}}$$

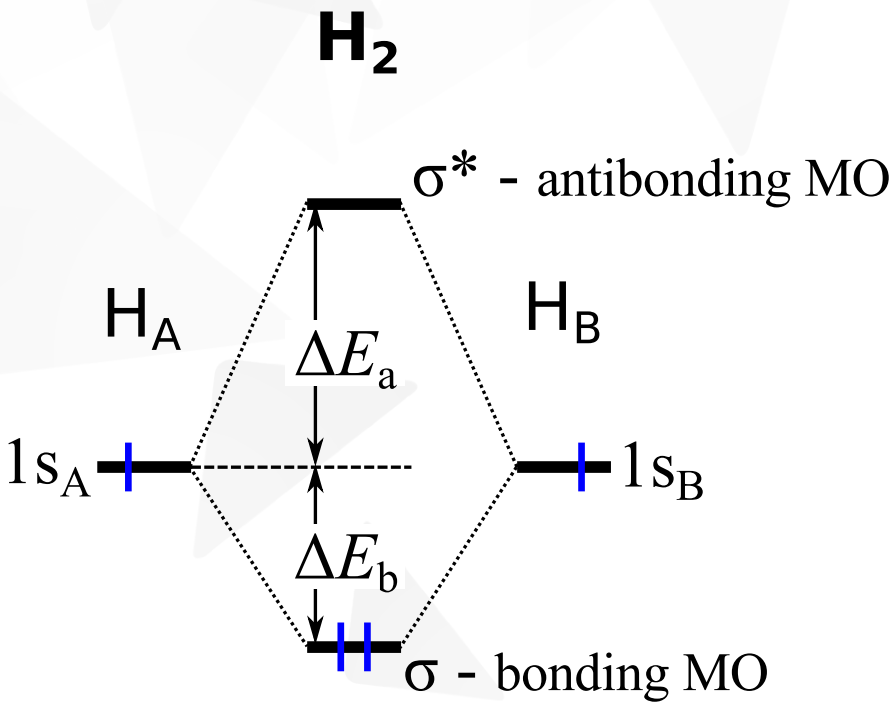
H_{AB} = *interaction between* s_A & s_B

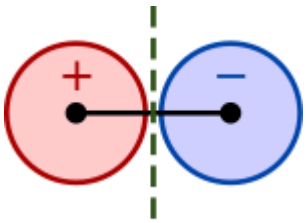
S_{AB} = *overlap between* s_A & s_B

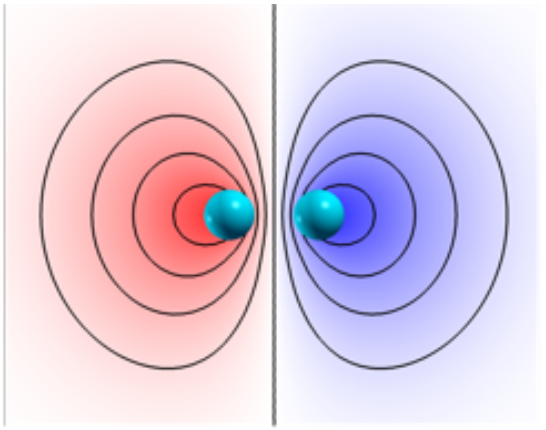
$$H_{\mathrm{AB}} \propto S_{\mathrm{AB}}$$

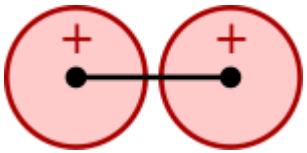
A chemist's view of bonding

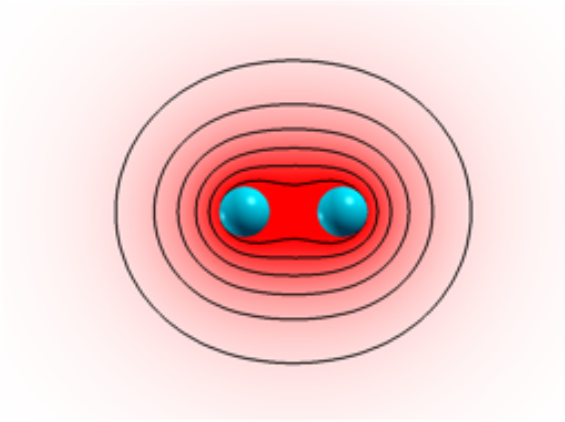
- molecular orbital (MO) diagram











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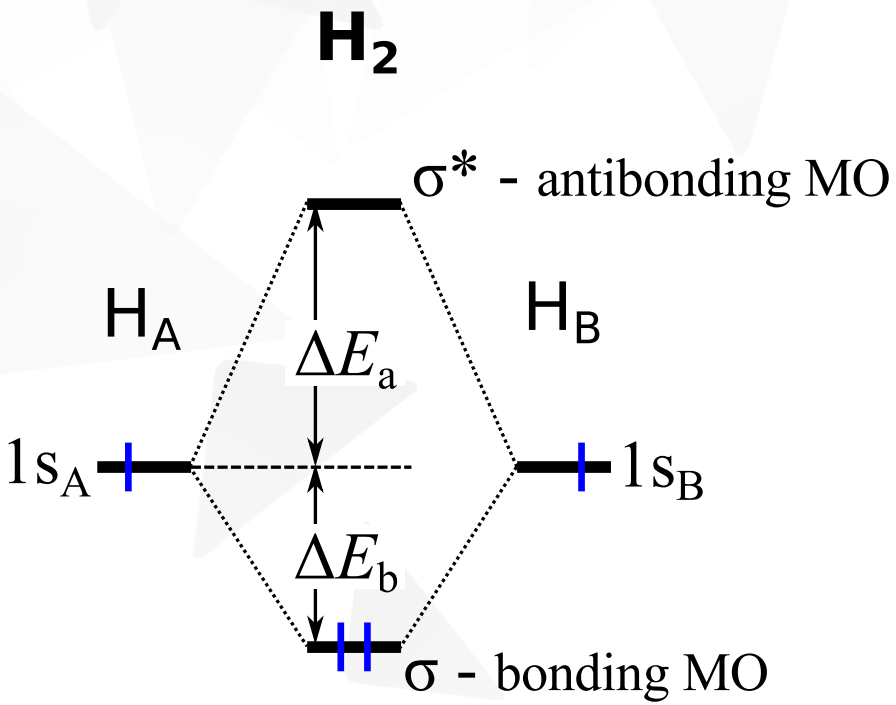
A chemist's view of bonding

- molecular orbital (MO) diagram



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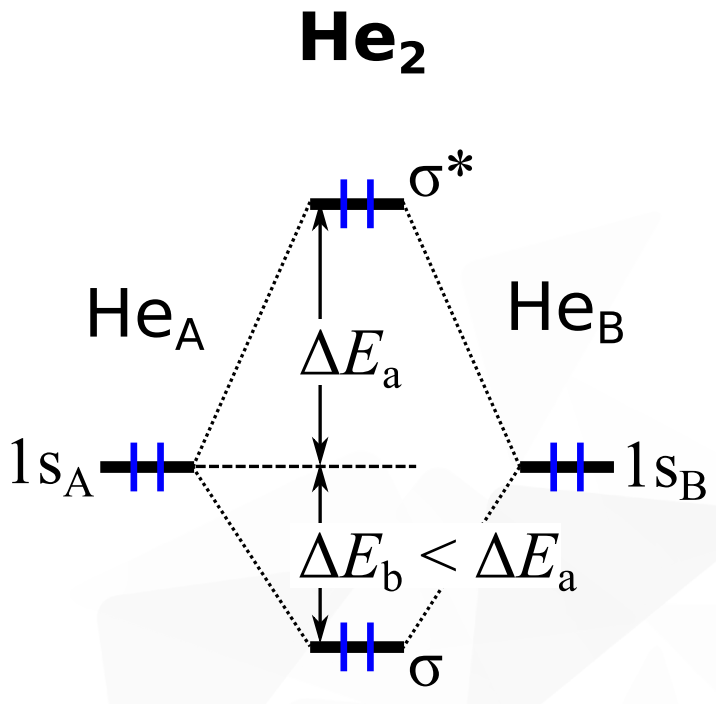


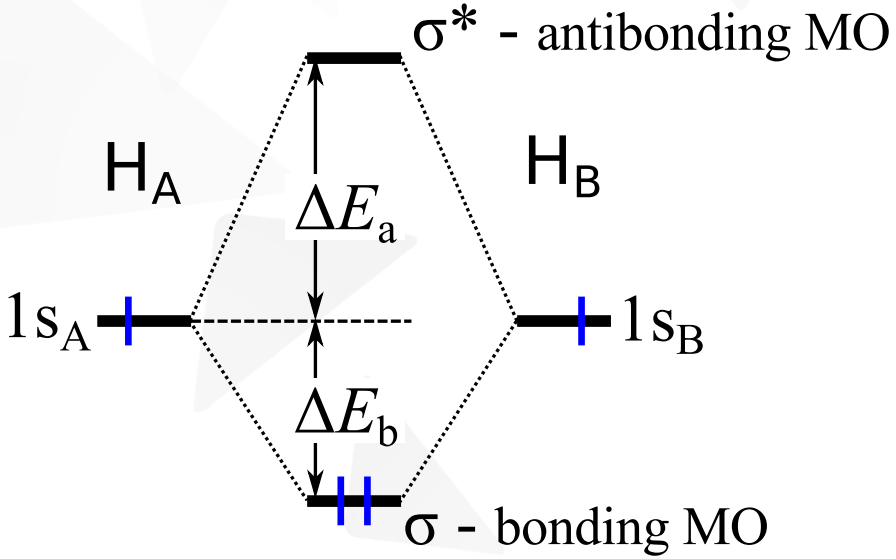
net repulsion

(two-orbital four-electron interaction)

A chemist's view of bonding

- molecular orbital (MO) diagram

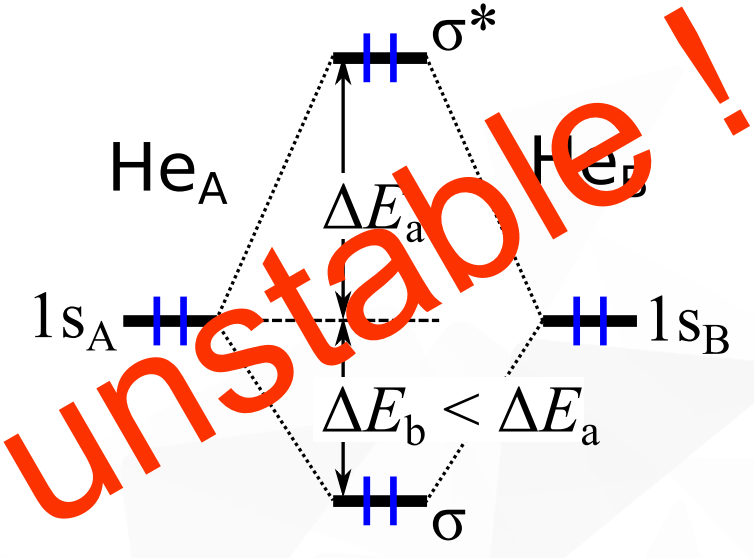
H_2



net attraction

(two-orbital two-electron interaction)

He_2



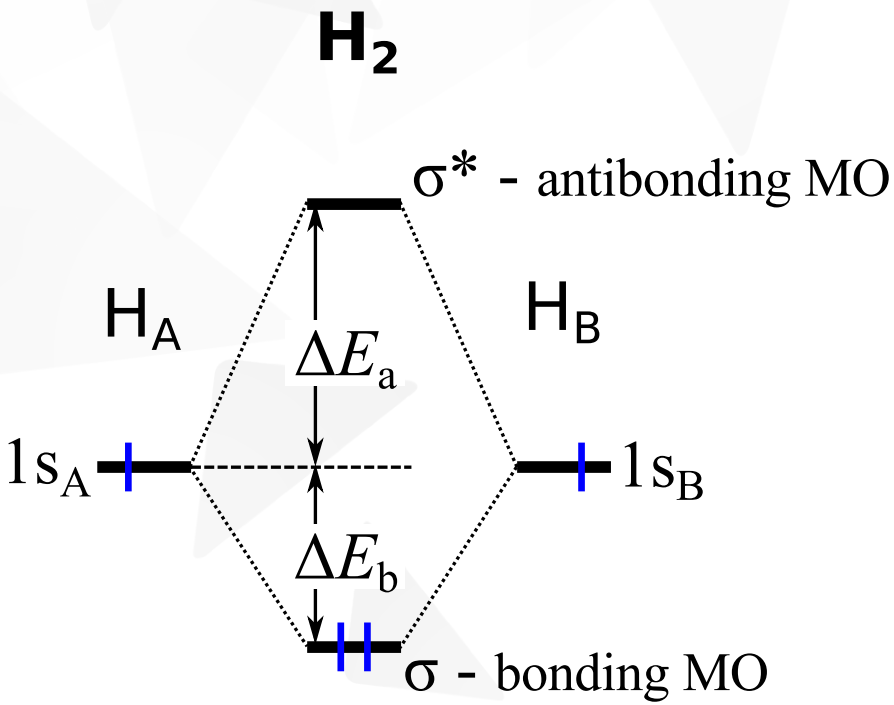
unstable !

net repulsion

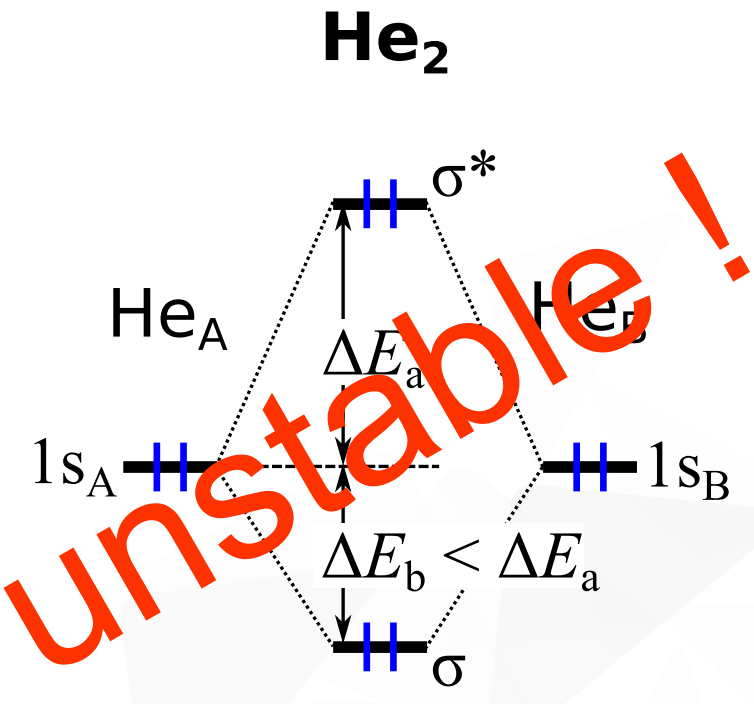
(two-orbital four-electron interaction)

A chemist's view of bonding

- molecular orbital (MO) diagram



net attraction



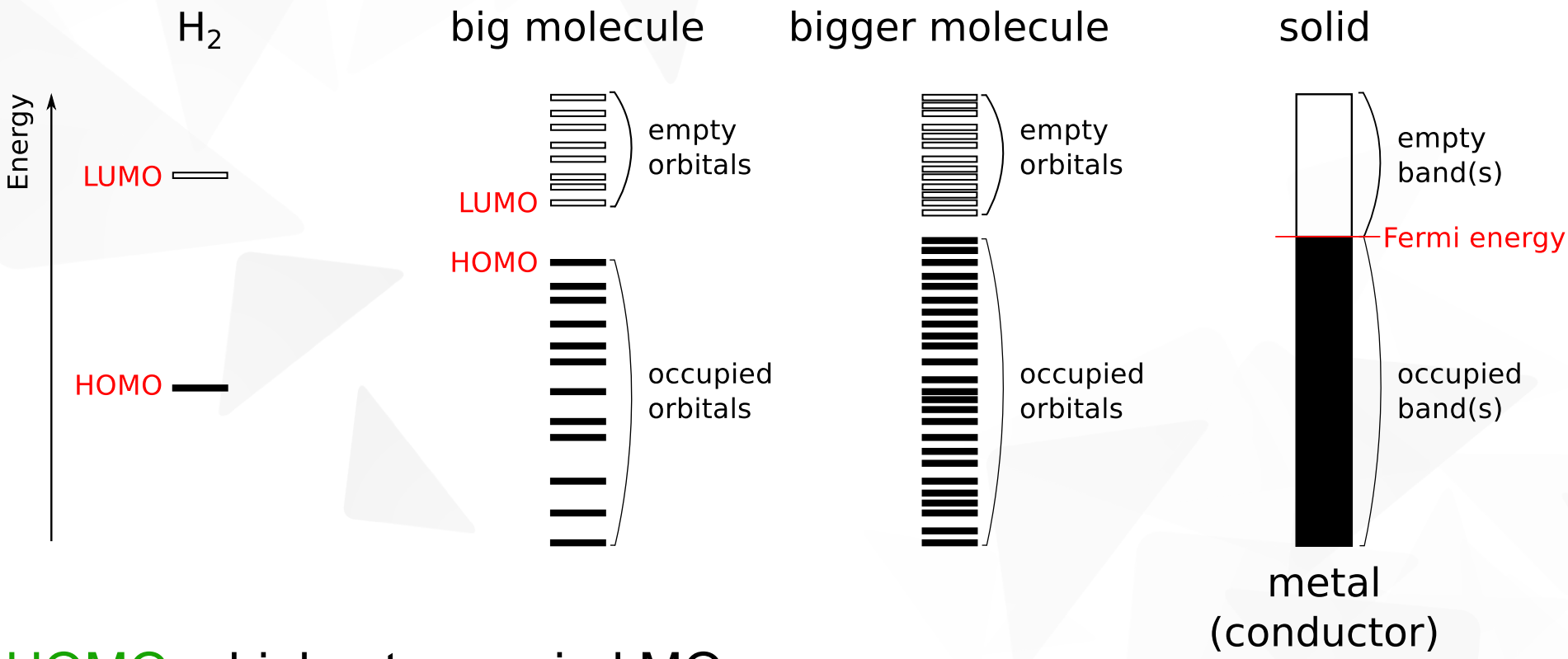
net repulsion

(two-orbital tw

keep antibonding states empty

A chemist's view of bonding

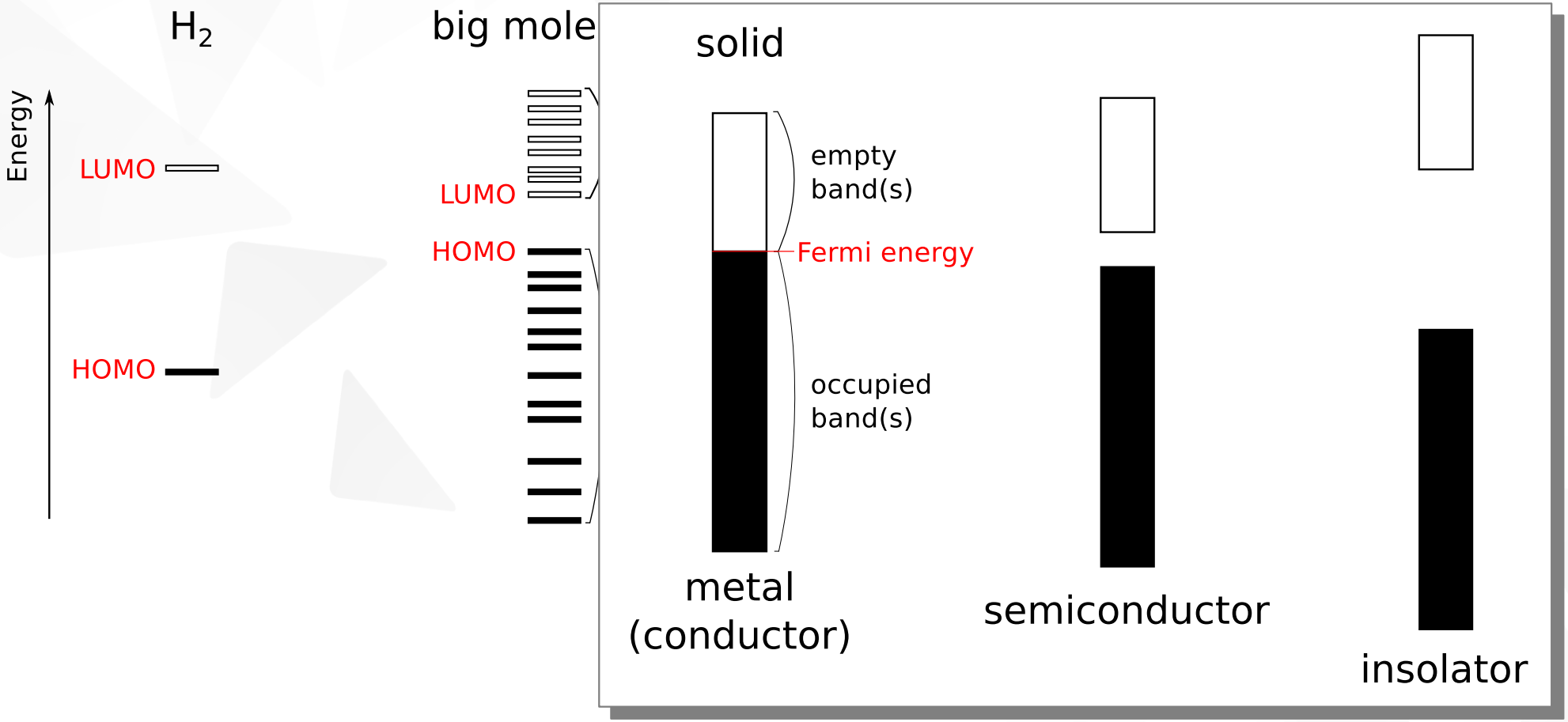
- from H_2 to solid



HOMO – highest occupied MO
LUMO – lowest unoccupied MO

A chemist's view of bonding

- from H_2 to solid



A chemist's view of bonding

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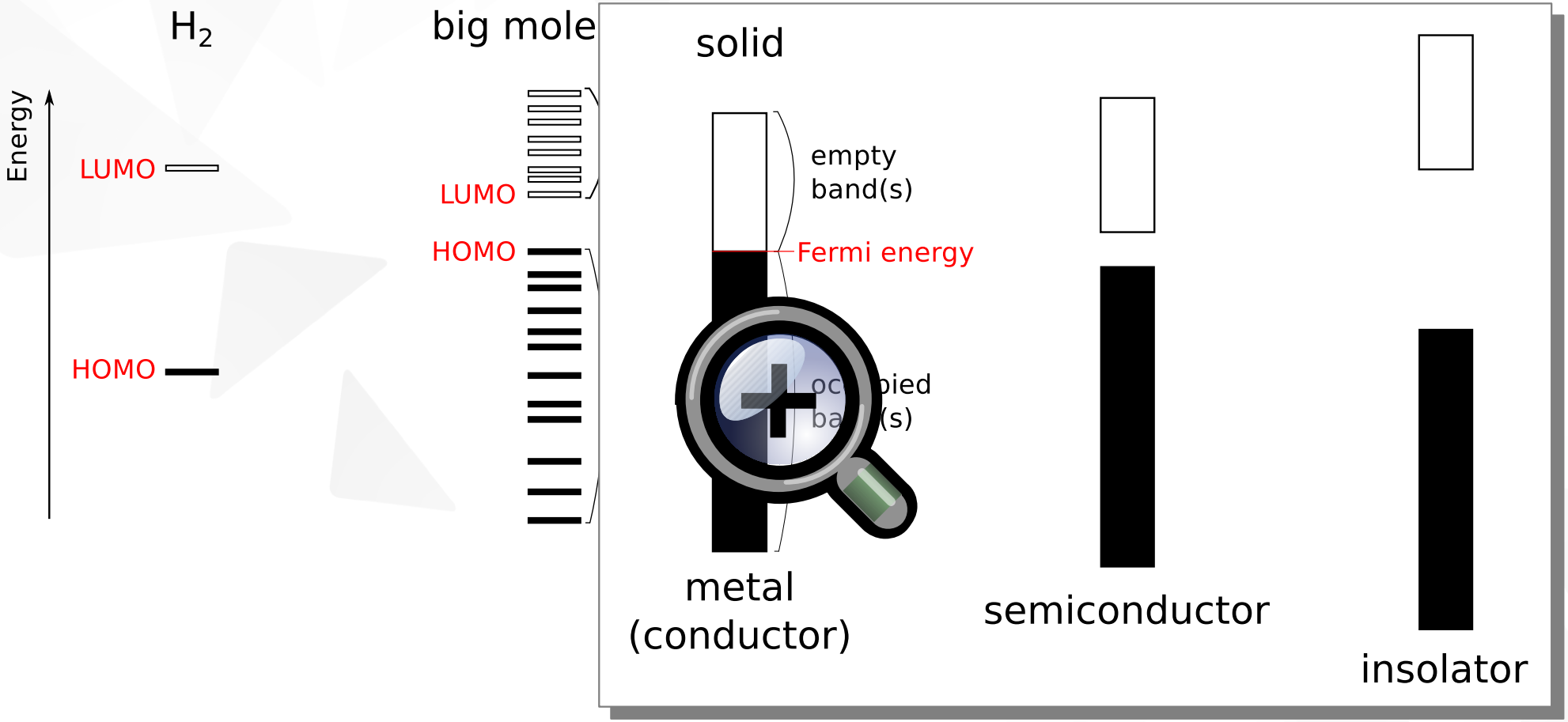
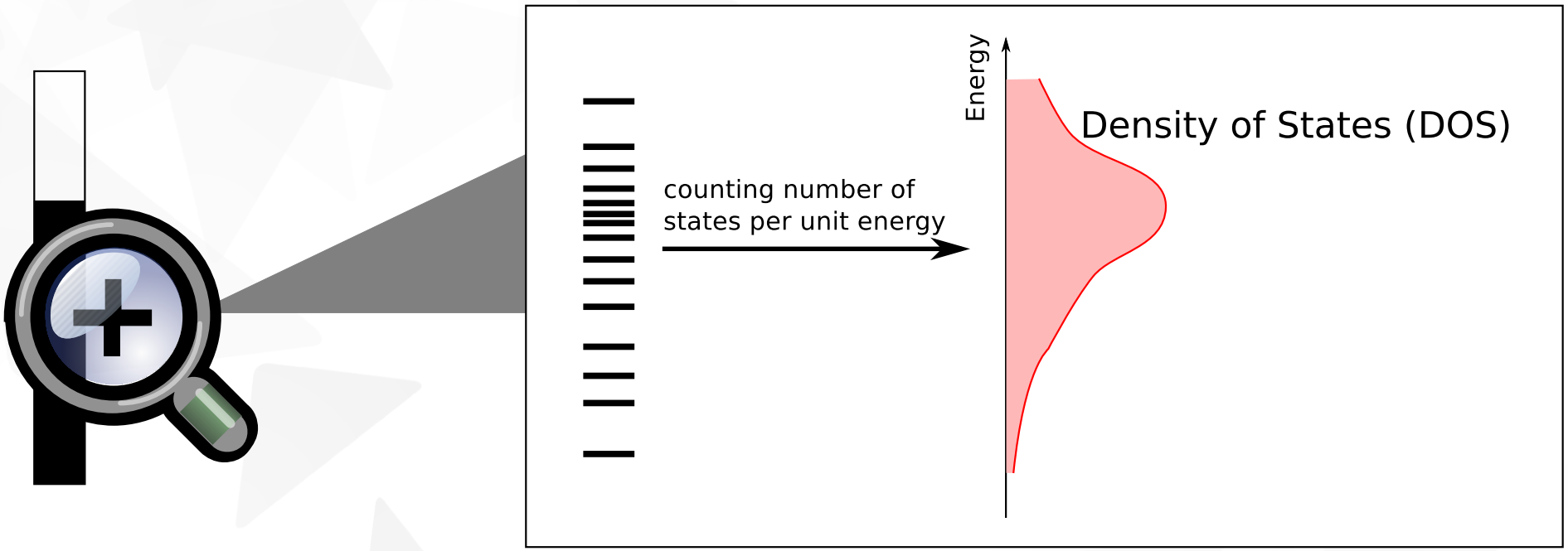


Density of states (DOS)



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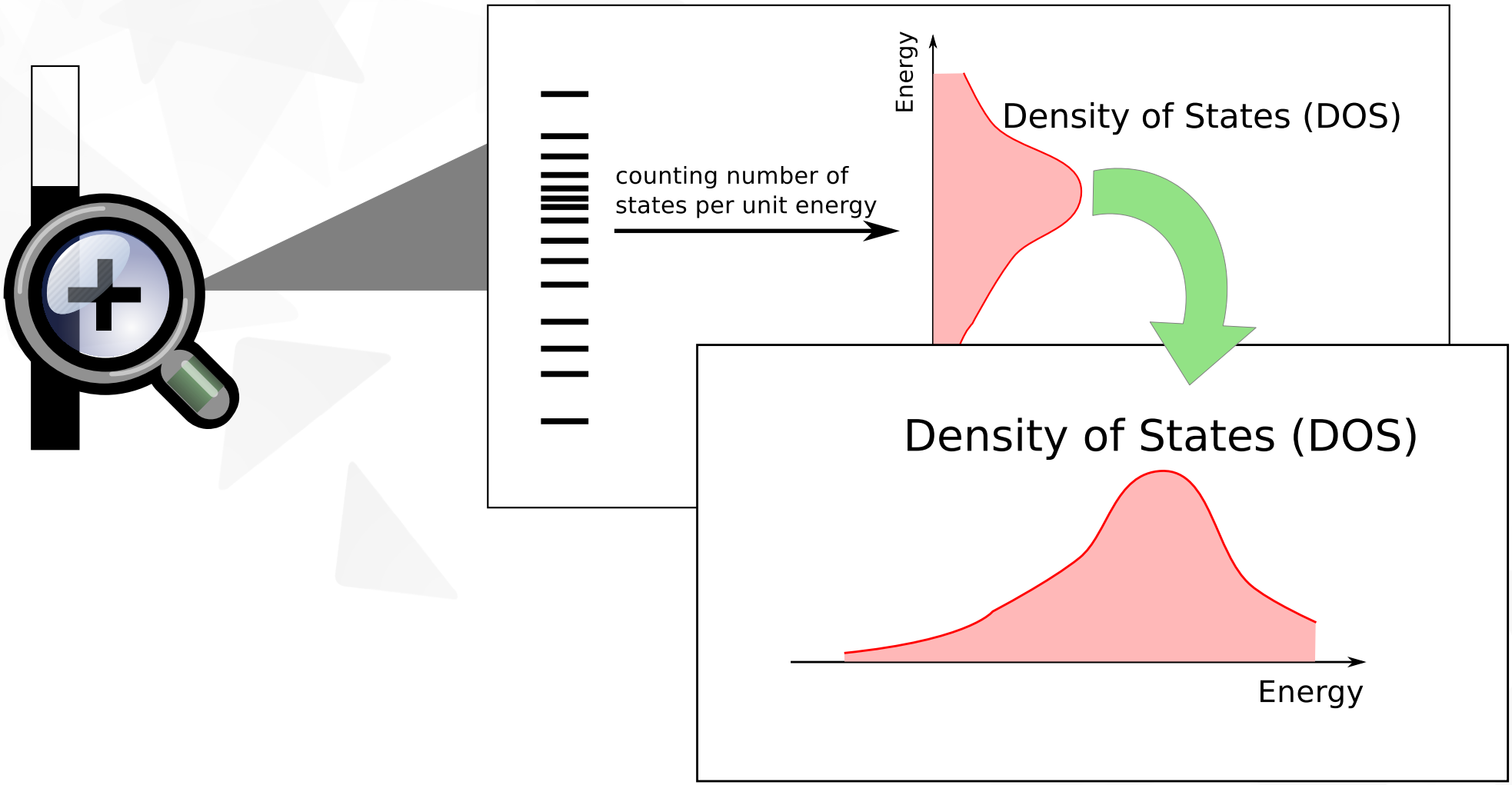
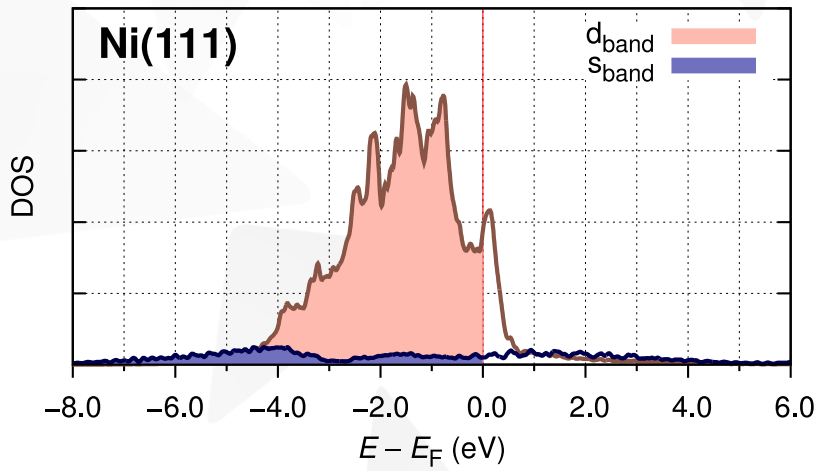
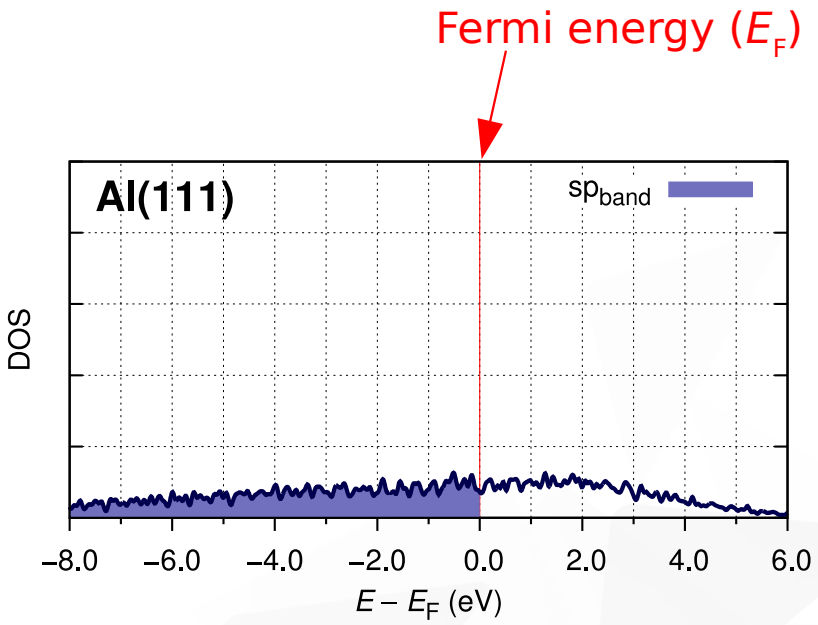


Electronic structure of metals

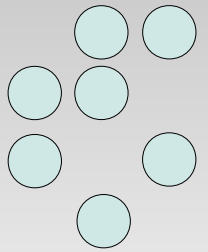
- two types of bands:
  - delocalized (broad) sp-bands
  - localized (narrow) d-bands



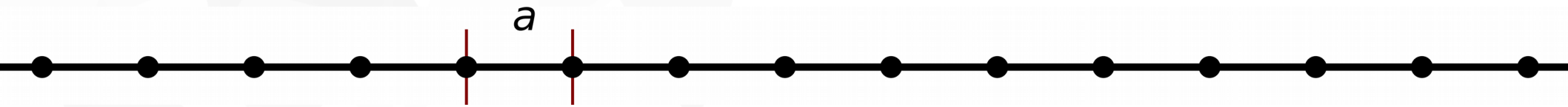


- Transition metals (TM):
  - s-band is half filled for all TMs (similar bonding for all)
  - variation in bonding comes from d-band

From H_2 to solids … only 1D for simplicity



- lets' consider a simple 1D system: an infinite chain of H atoms



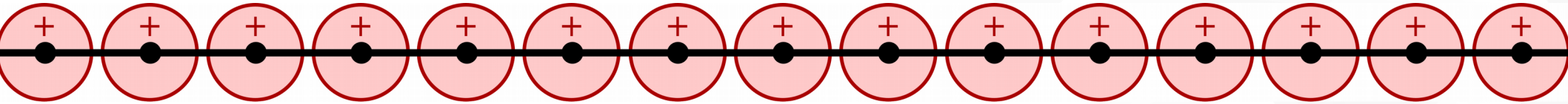
- due to translational symmetry:

$$\rho(x) = \rho(x + R), \text{ where } R = na$$

$$V(x) = V(x + R)$$

- what about wave-function? Let's try:

$$\psi(x) \stackrel{?}{=} \psi(x + R)$$



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- what about wave-function? Let's try:

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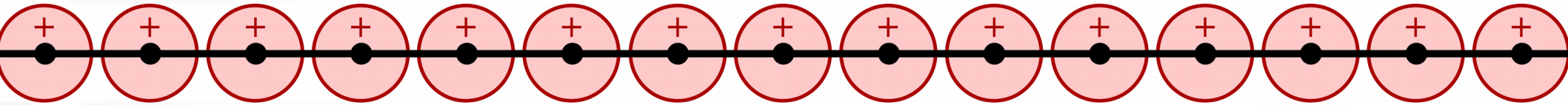
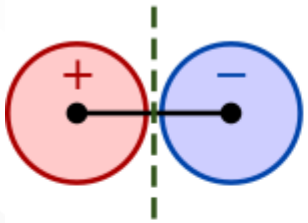


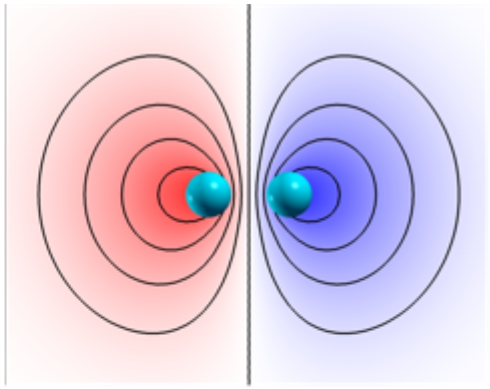
I can only put 2 electrons in this state …

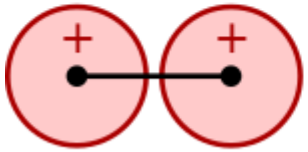
I need to form linear combinations!

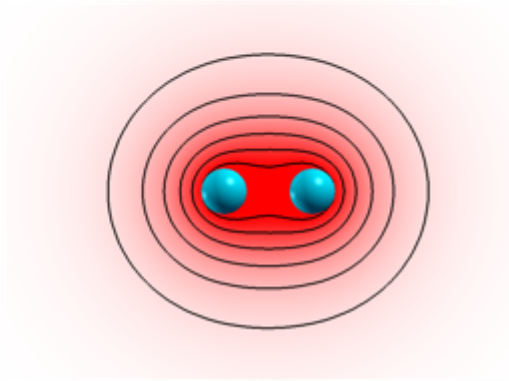
From H_2 to H_∞ ...

- H_2



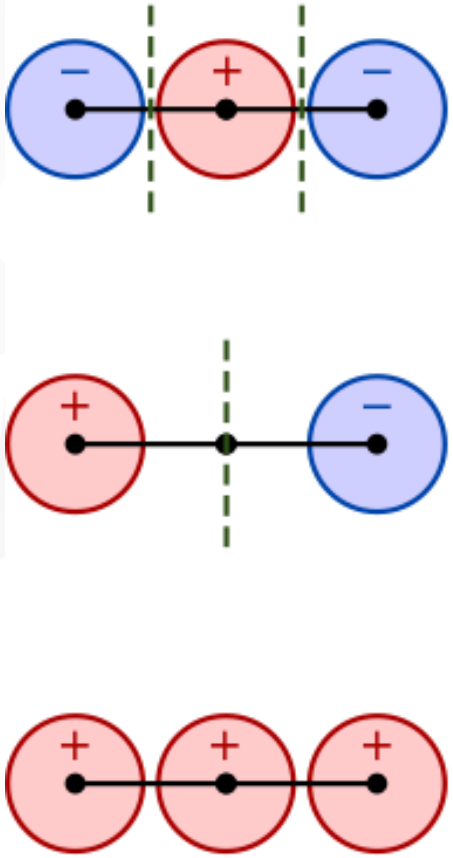


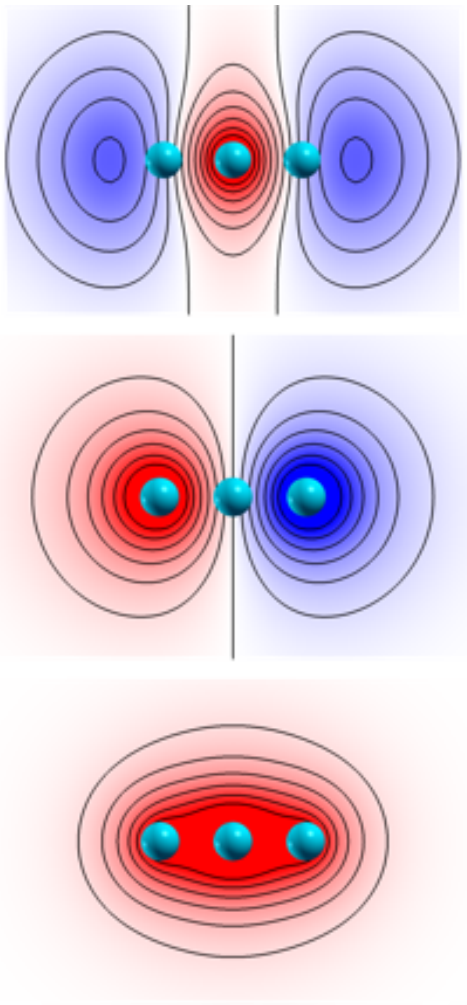




From H_2 to H_∞ ...

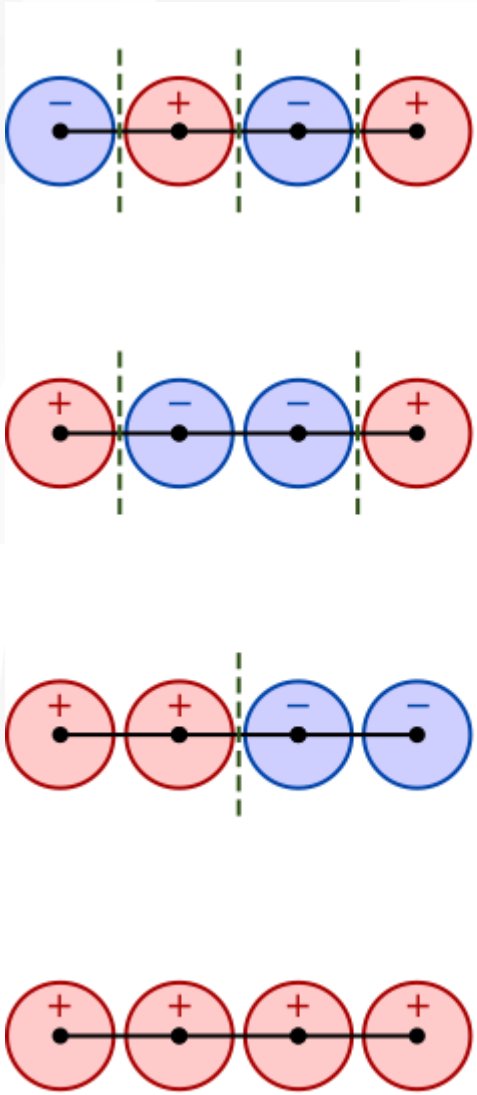
- H_3

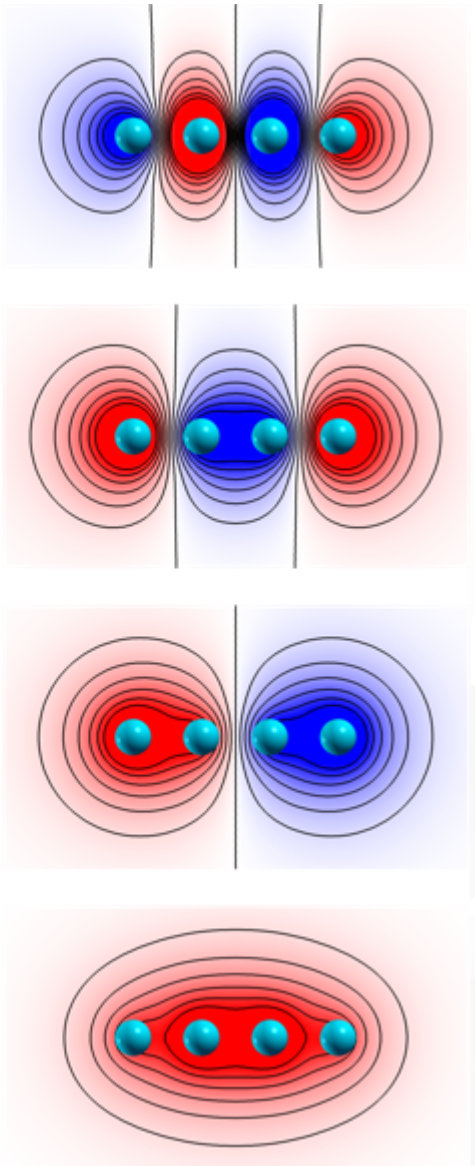




From H_2 to H_∞ ...

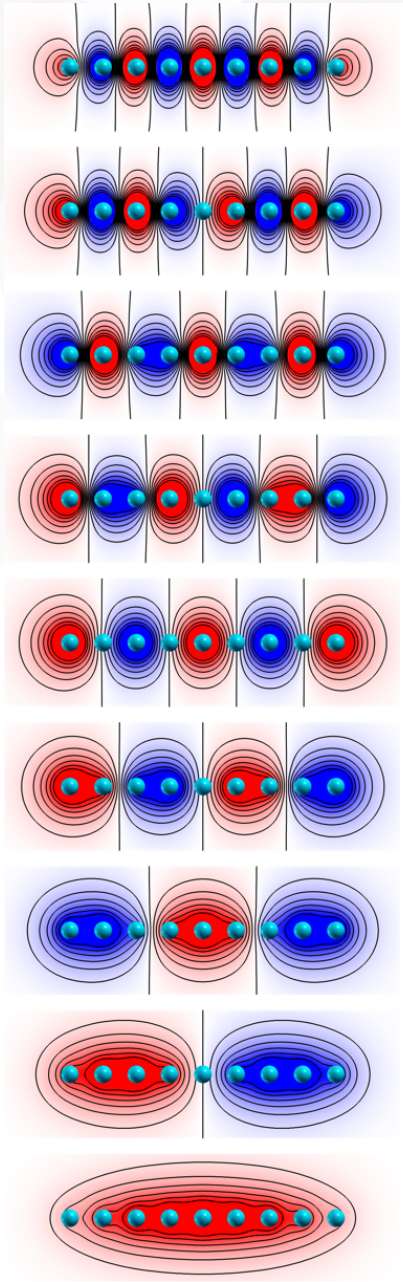
- H_4

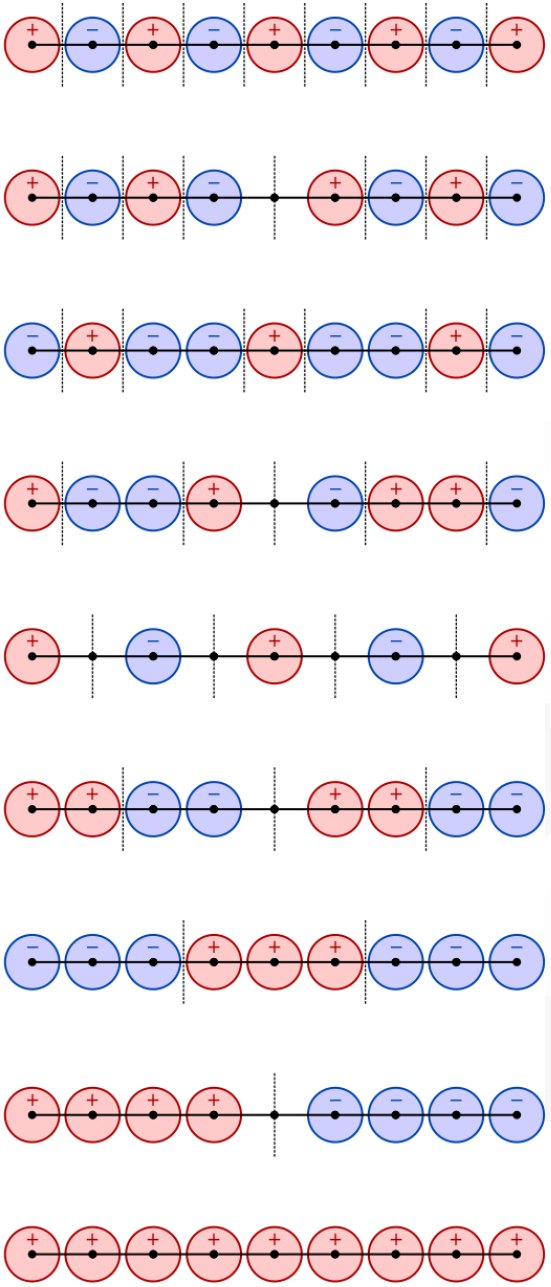




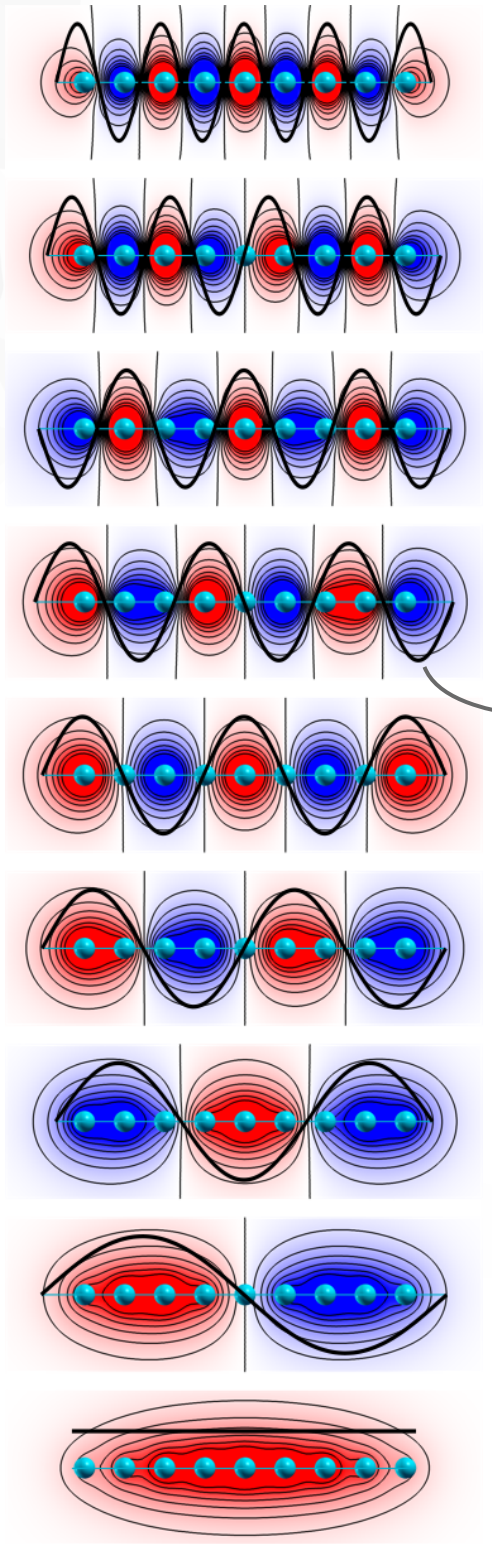
From H_2 to H_∞ ...

- H_9





- H_9

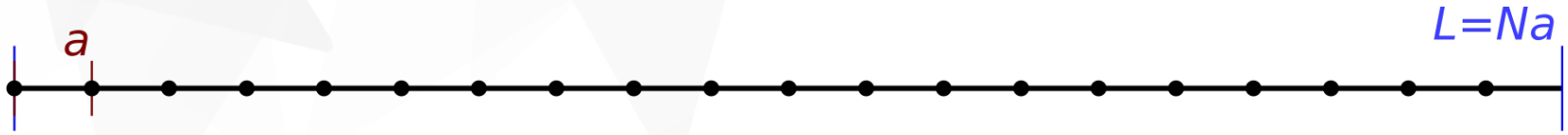


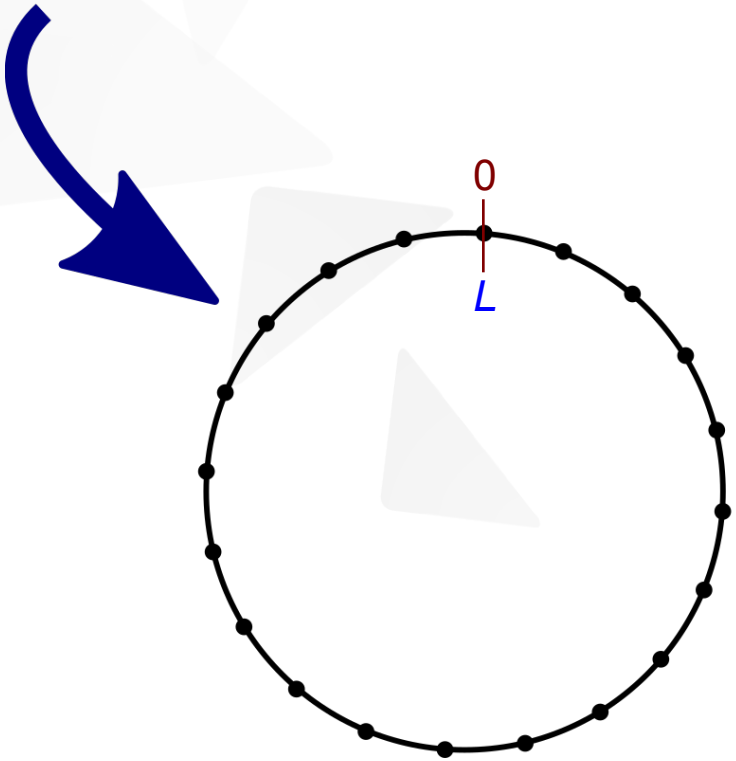
$\sin(kx)$

more general:
$\exp(ikx)$

From H_2 to H_∞ ...

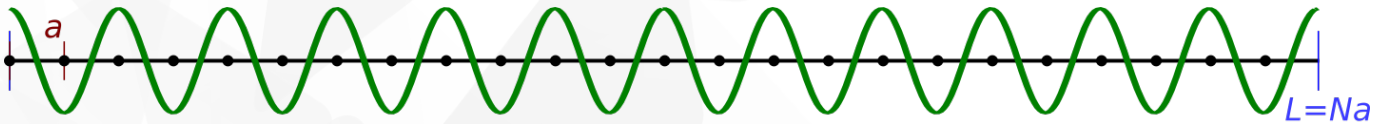
- H_N (suppose N is very large)



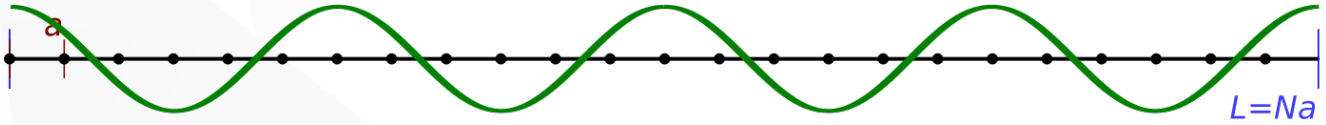


$$\psi(0) = \psi(L)$$
$$\psi(x) = \psi(x + L)$$

Born−von Karman boundary conditions

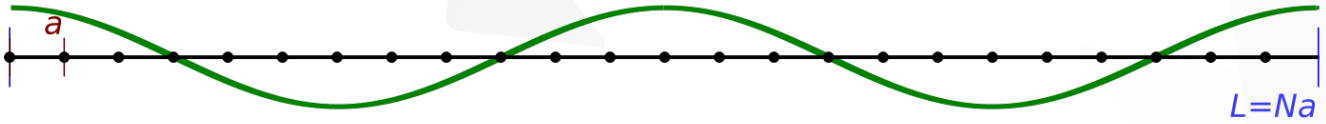


$\cos(2\pi/L \cdot Nx/2) = \cos(\pi/a \cdot x)$

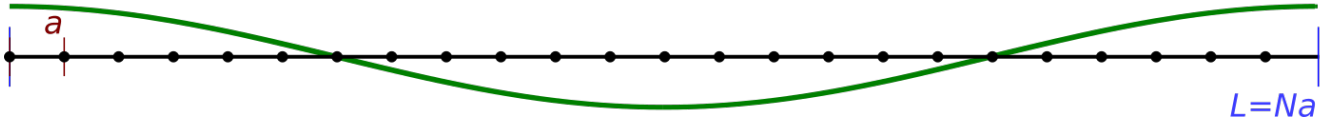


$\cos(2\pi/L \cdot 4x)$

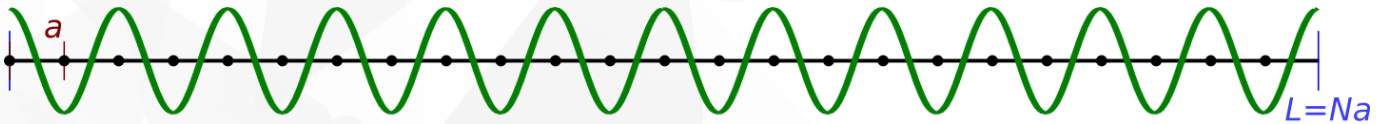
$\cos(2\pi/L \cdot 3x)$



$\cos(2\pi/L \cdot 2x)$

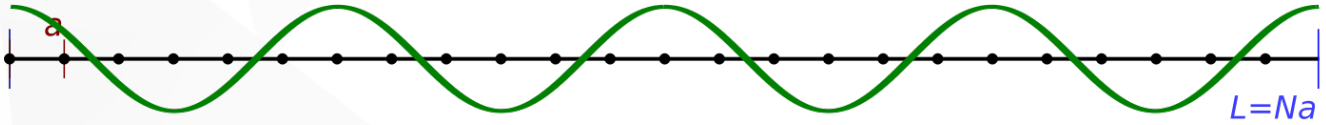


$\cos(2\pi/L \cdot x)$



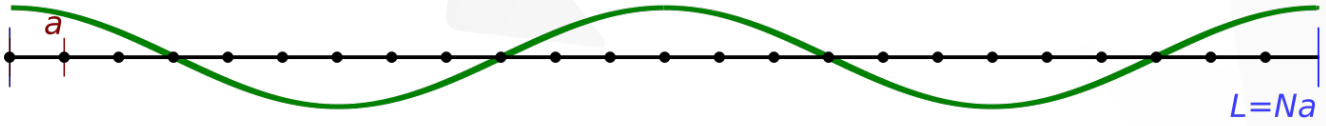
$\cos(2\pi/\mathrm{L}\cdot Nx/2) = \cos(\pi/\mathrm{a}\cdot x)$

- *more general:*
- $\exp(ikx)$, where $k = 2\pi\kappa/(Na)$ and $\kappa \in (-N/2, N/2]$
- (if κ is outside this range it *folds back* due to periodicity)

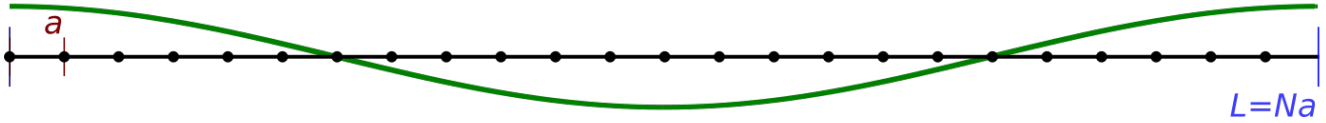


$\cos(2\pi/L\cdot 4x)$

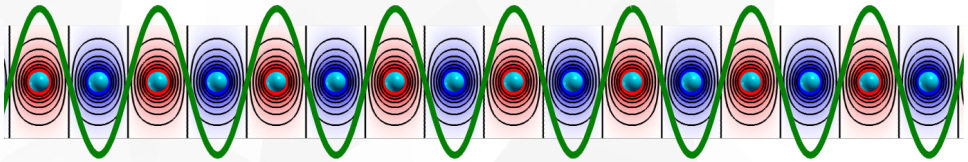
$\cos(2\pi/L\cdot 3x)$



$\cos(2\pi/L\cdot 2x)$



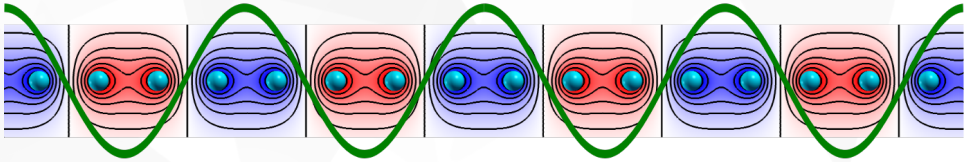
$\cos(2\pi/L\cdot x)$



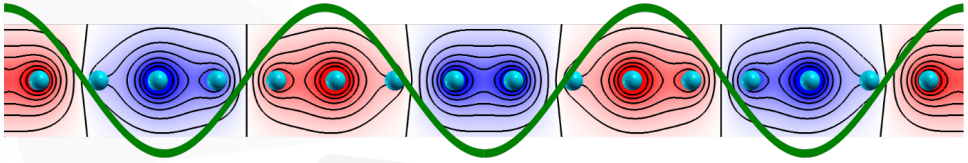
$\cos(2\pi/\mathrm{L}\cdot Nx/2) = \cos(\pi/\mathrm{a}\cdot x)$

more general:

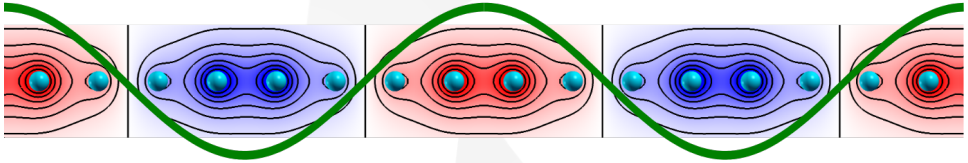
$\exp(ikx)$, where $k = 2\pi\kappa/(Na)$ and $\kappa \in (-N/2, N/2]$



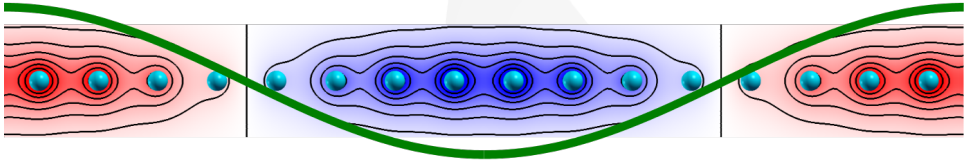
$\cos(2\pi/L\cdot 4x)$



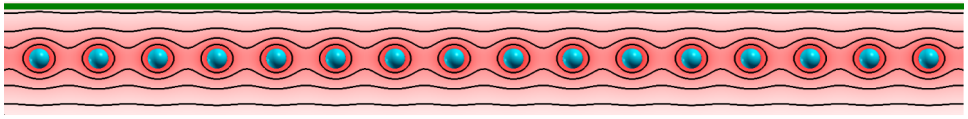
$\cos(2\pi/L\cdot 3x)$



$\cos(2\pi/L\cdot 2x)$



$\cos(2\pi/L\cdot 1x)$



$\cos(2\pi/L\cdot 0x) = 1$

$\psi_\kappa(x) = \exp(ikx)\, u(x)$

Bloch theorem (still 1D chain of H atoms)

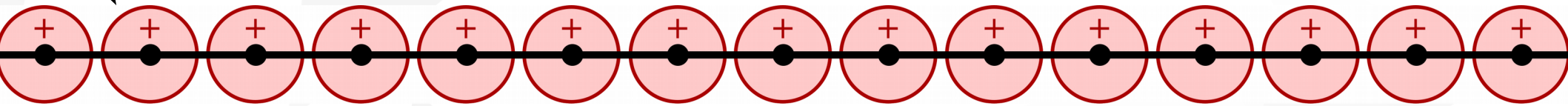
- $\psi_k(x) = \exp(ikx)\, u_k(x)$

notice:

$$\psi_k(x+R) = \exp(ikR)\, \psi_k(x)$$

where R is any lattice translation

cell function has periodicity of lattice $u_k(x+R) = u_k(x)$



sum „all“ 1s orbitals

$$u(x) = \mathcal{N} \sum_R s(x+R)$$

sum over lattice vectors
($\boldsymbol{R} = n\boldsymbol{a}$, $n \in (-\infty,\infty)$)

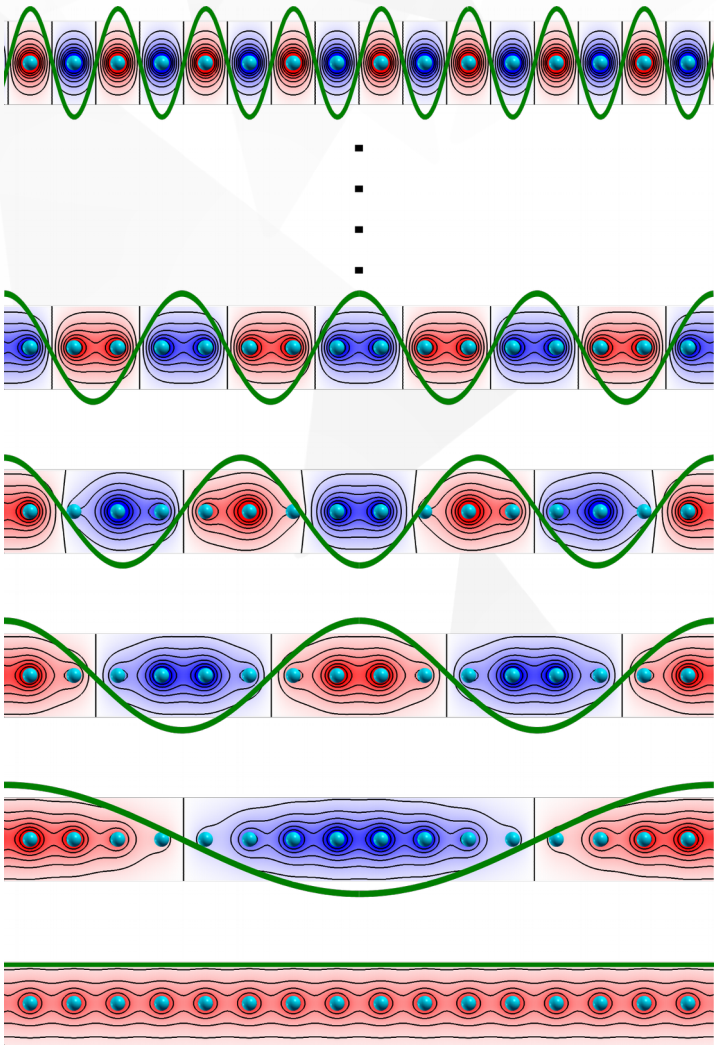
plane-waves

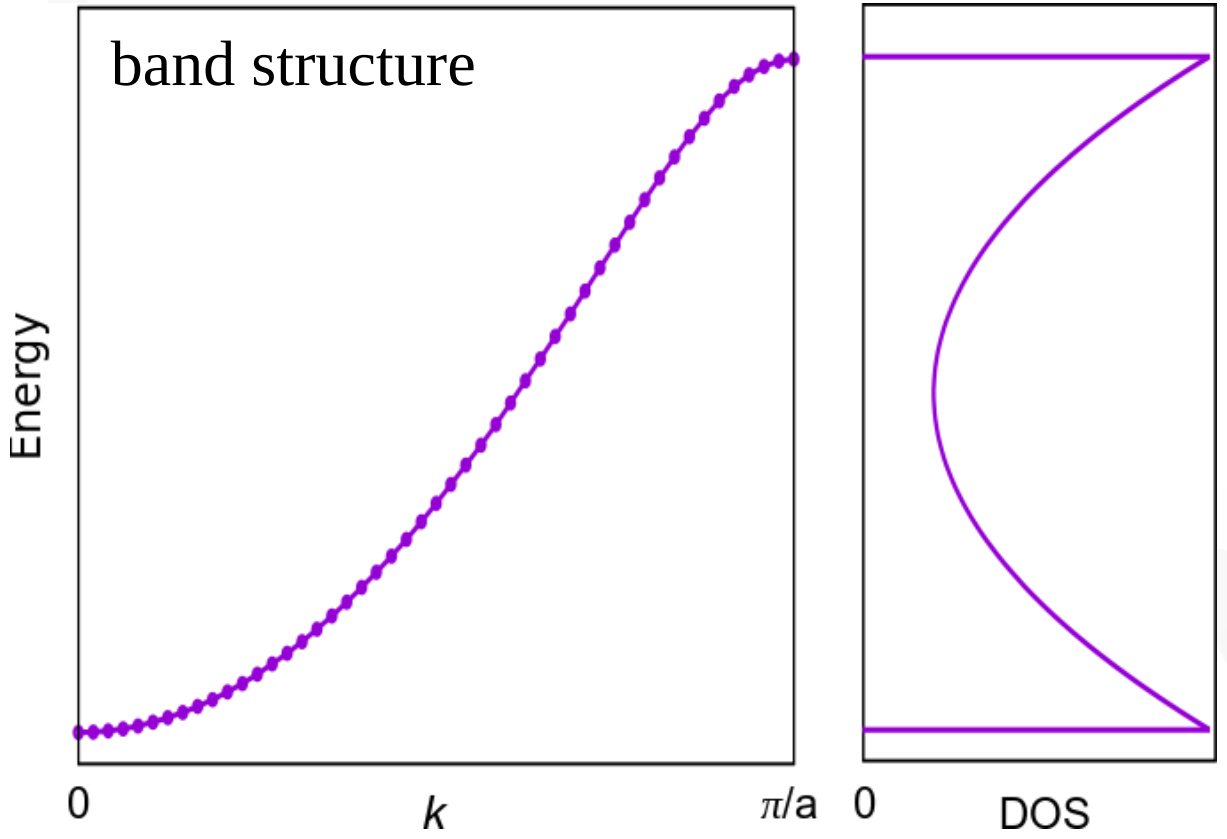
$$u(x) = \sum_G c_G \exp(\mathrm{i}Gx)$$

sum over „reciprocal“ lattice vectors
($\boldsymbol{G} = n/\boldsymbol{a}$, $n \in (-\infty,\infty)$)

K-points

- $\psi_k(x) = \exp(ikx)\, u_k(x)$ where $\boldsymbol{k} = 2\pi\kappa/(Na)$ and $\kappa \in (-N/2, N/2]$

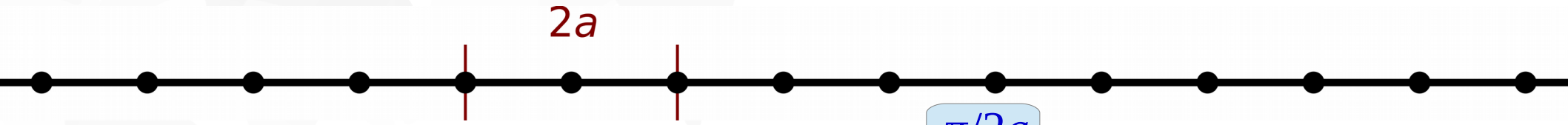




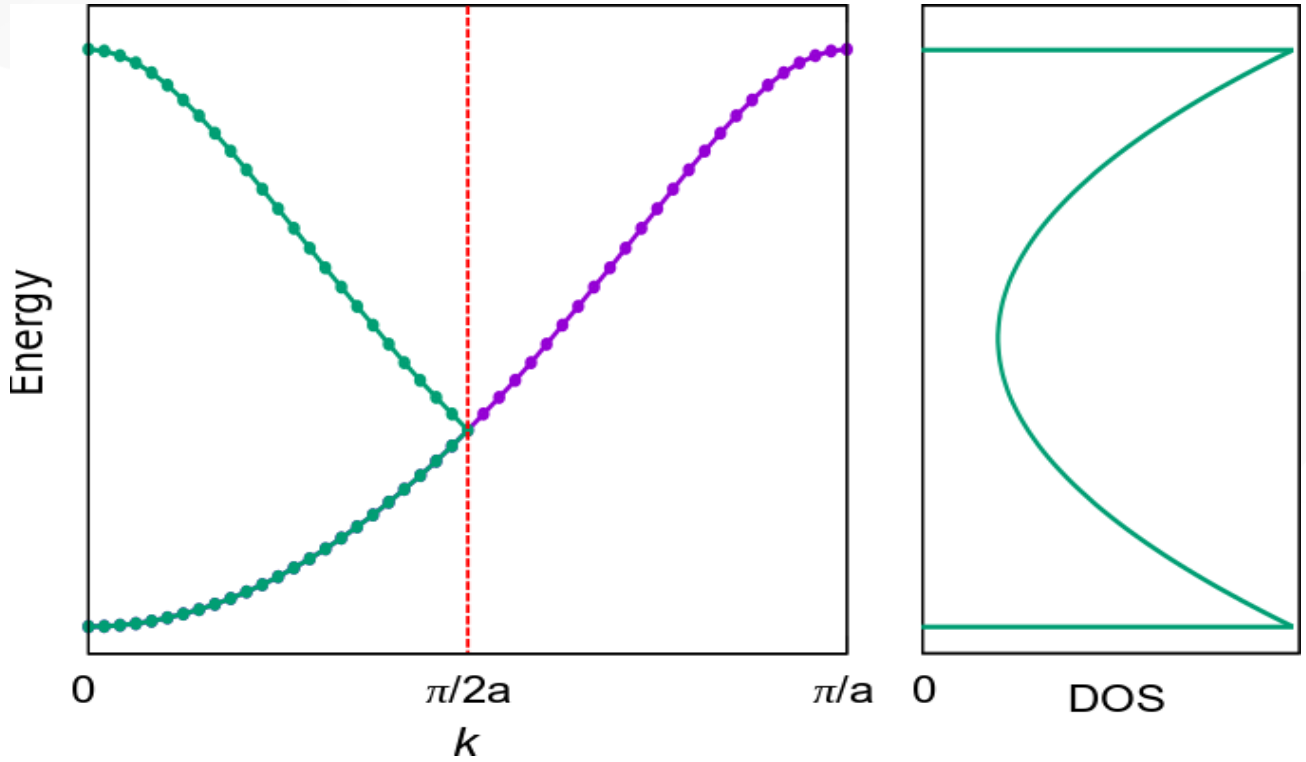
note that $\varepsilon(k) = \varepsilon(-k)$

Supercell

- Let's double the unit cell: $a_{new} = 2a$



- **but:** $k \propto 1/a$, *hence* $k_{new} \in [0, \pi/a_{new}]$ while $k \in [0, \pi/a]$



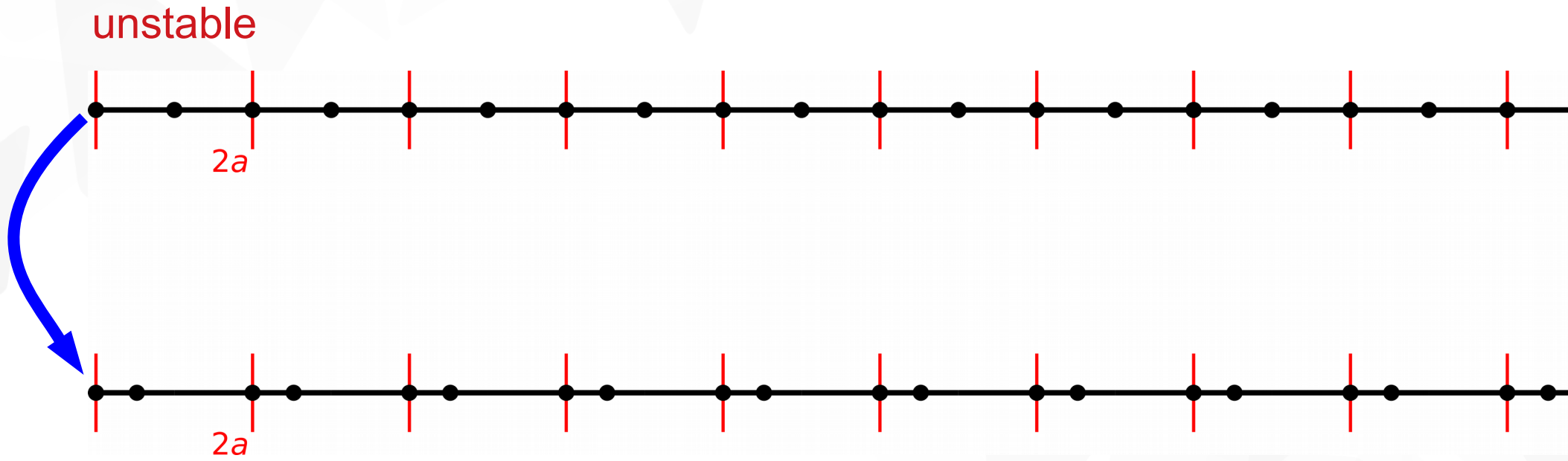
Remember !

when **supercell** increases:

# of k-points decreases
# of bands increases

Supercell & symmetry lowering

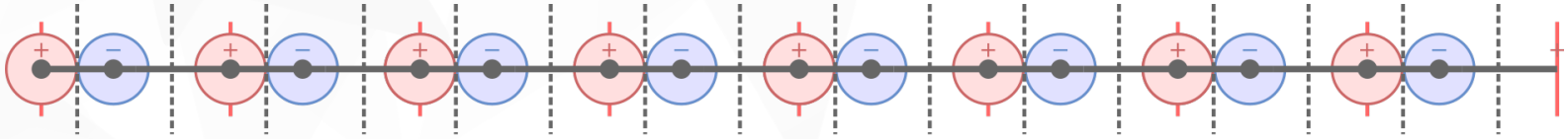
- uniform chain of H-atoms is not stable !



Jahn-Teller or Peierls distortion

Supercell & symmetry lowering

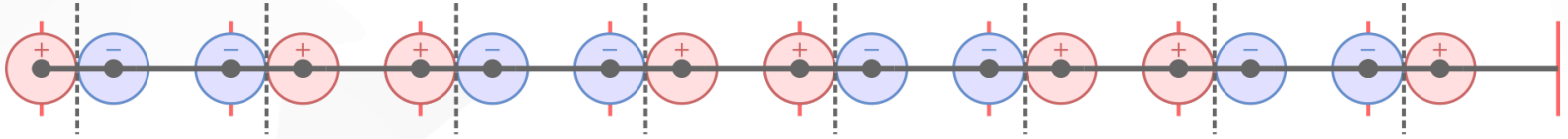
- uniform chain of H_2 pairs



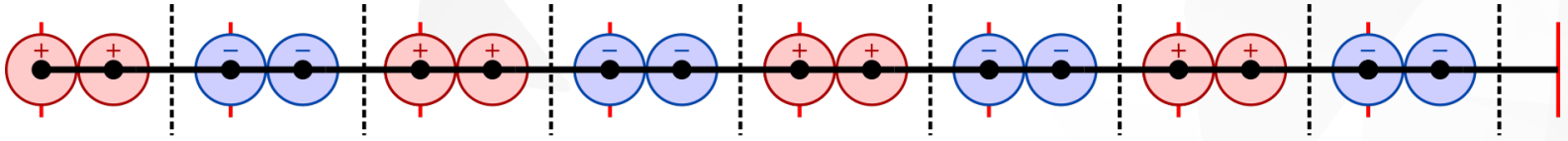
HUMO

combinations of σ-antibonding orbitals*

***U**noccupied*



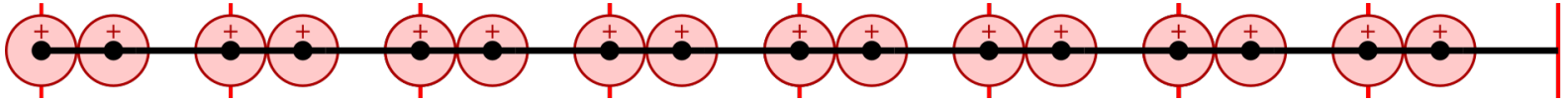
LUMO



HOMO

combinations of σ-bonding orbitals

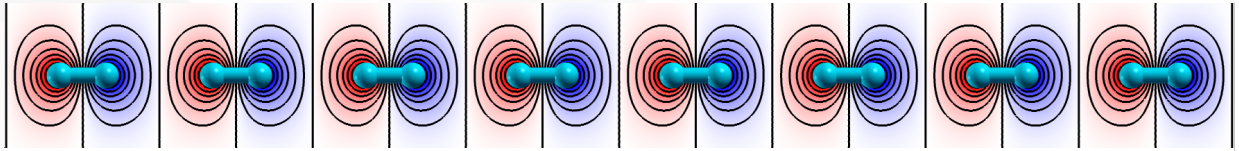
***O**ccupied*



LOMO

Supercell & symmetry lowering

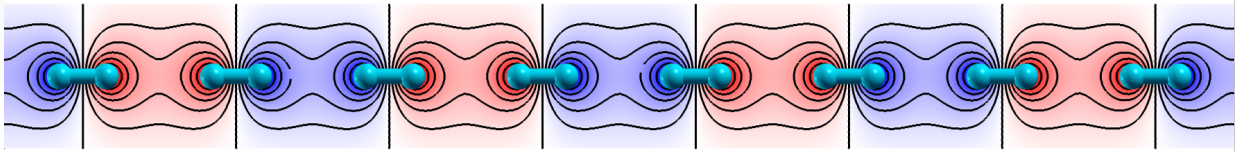
- uniform chain of H_2 pairs



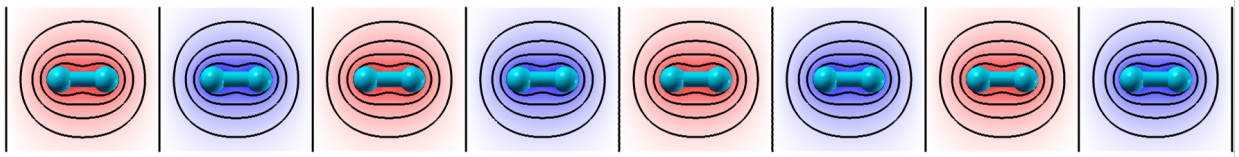
HUMO

combinations of σ-antibonding orbitals*

***U**noccupied*



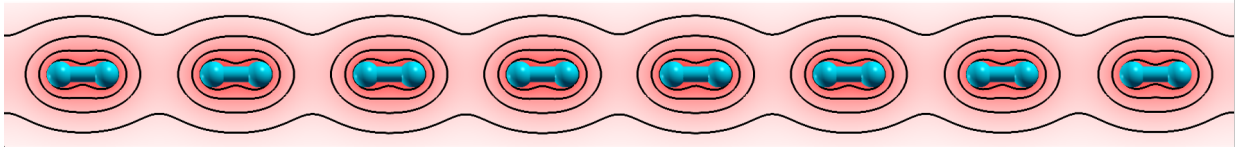
LUMO



HOMO

combinations of σ-bonding orbitals

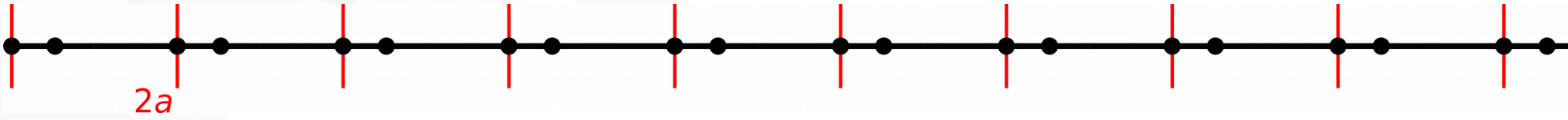
***O**ccupied*

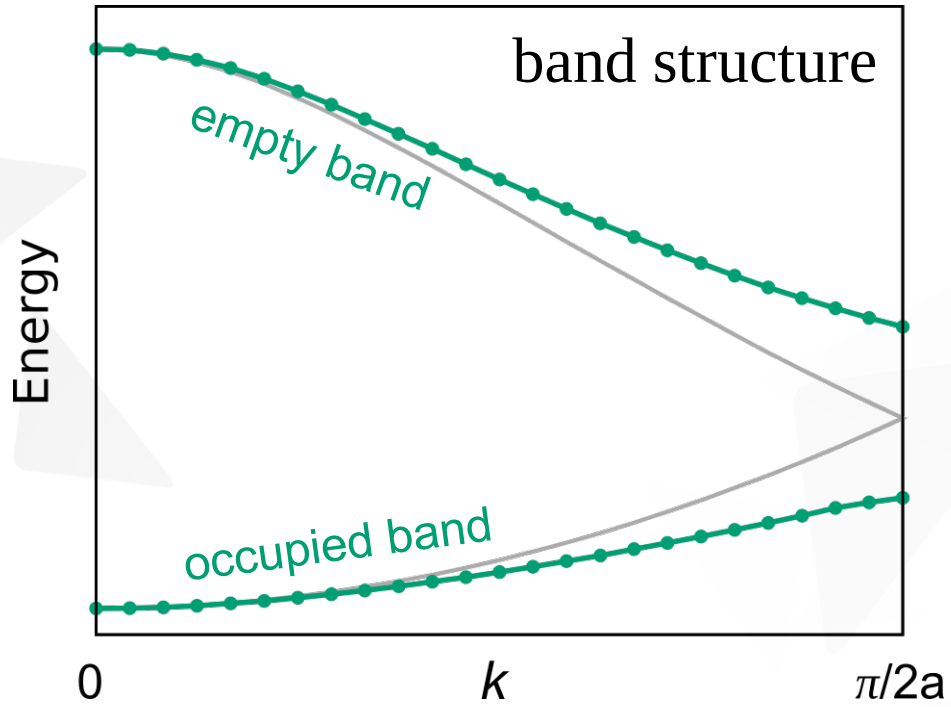


LOMO

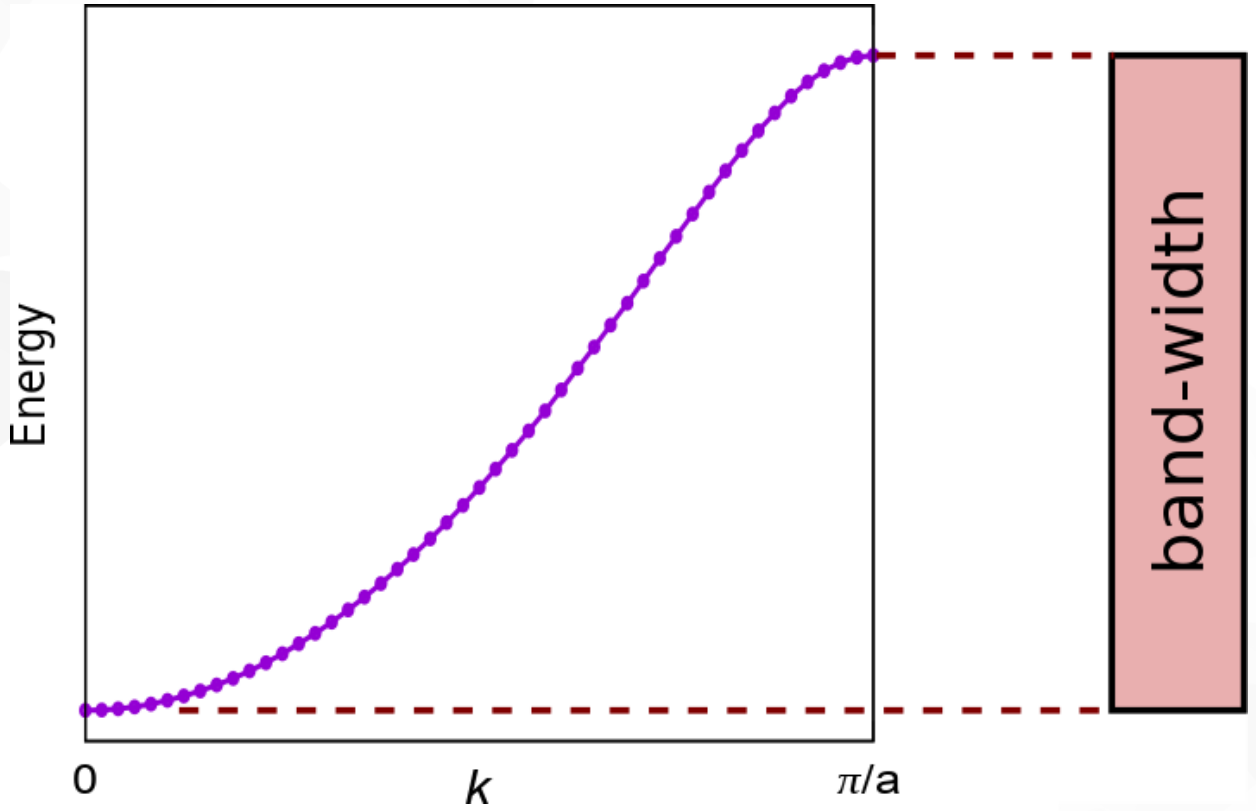
Supercell & symmetry lowering

- uniform chain of H_2 pairs: **band-gap opening**



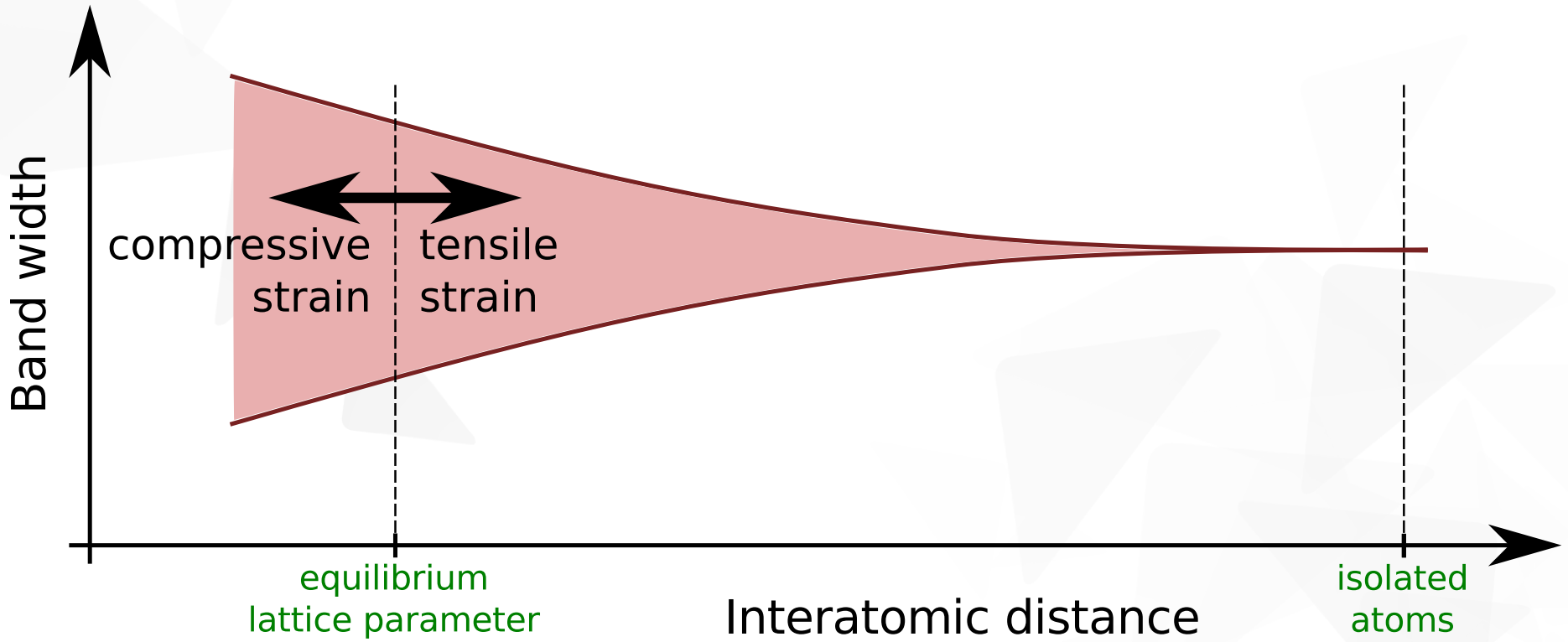


What determines the band-width ?



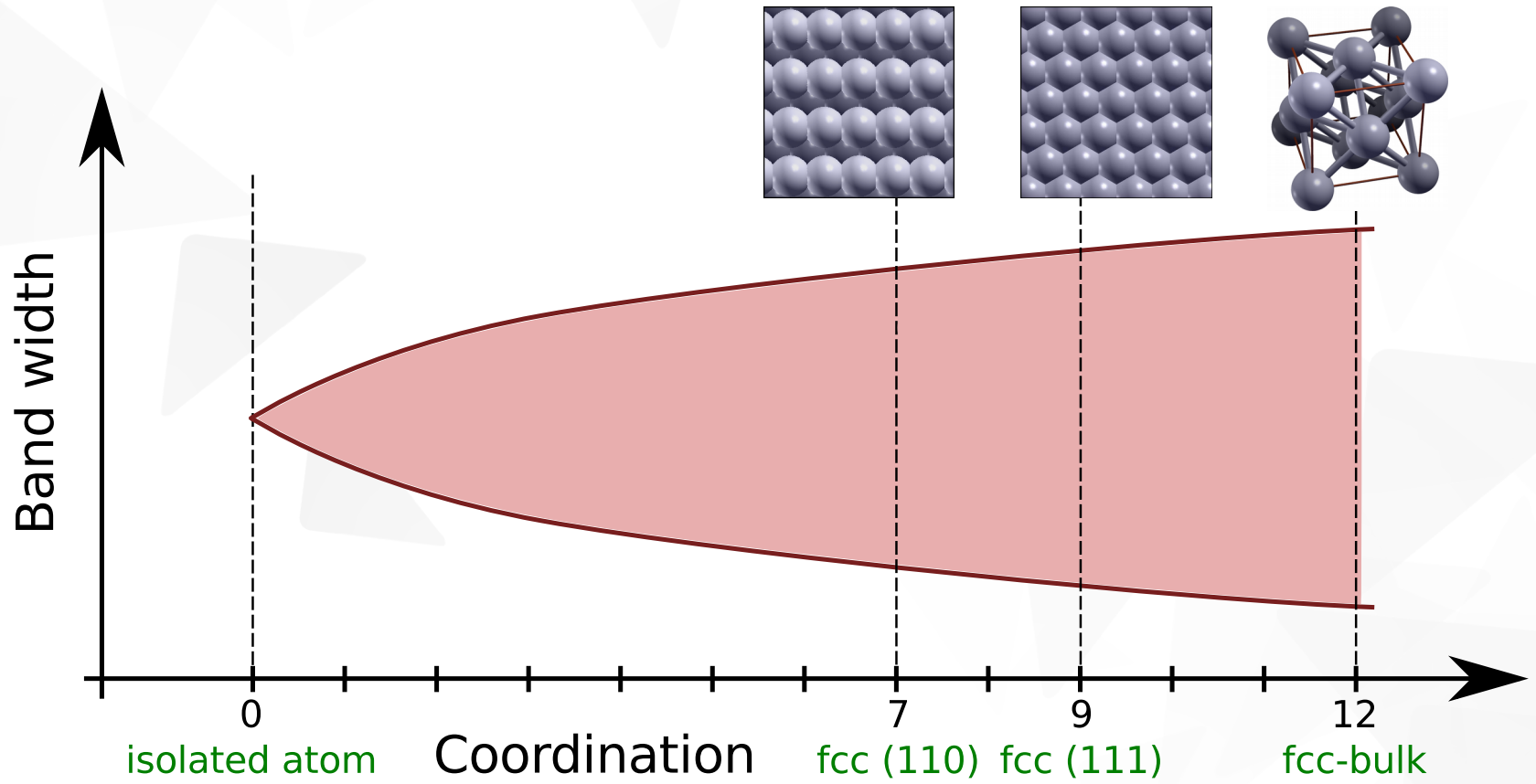
What determines the band-width ?

- **overlap** !
- Effect of strain on band-width



What determines the band-width ?

- **overlap** !
- Effect of coordination on band-width

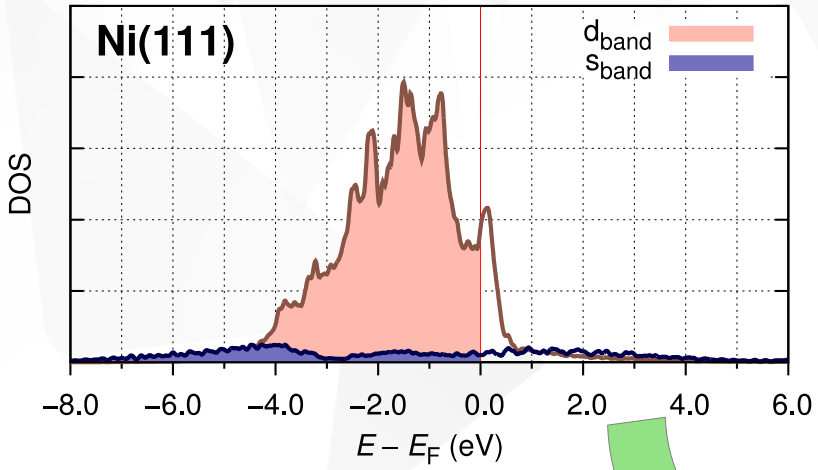


From molecules to solids:
interaction of a molecule with a surface

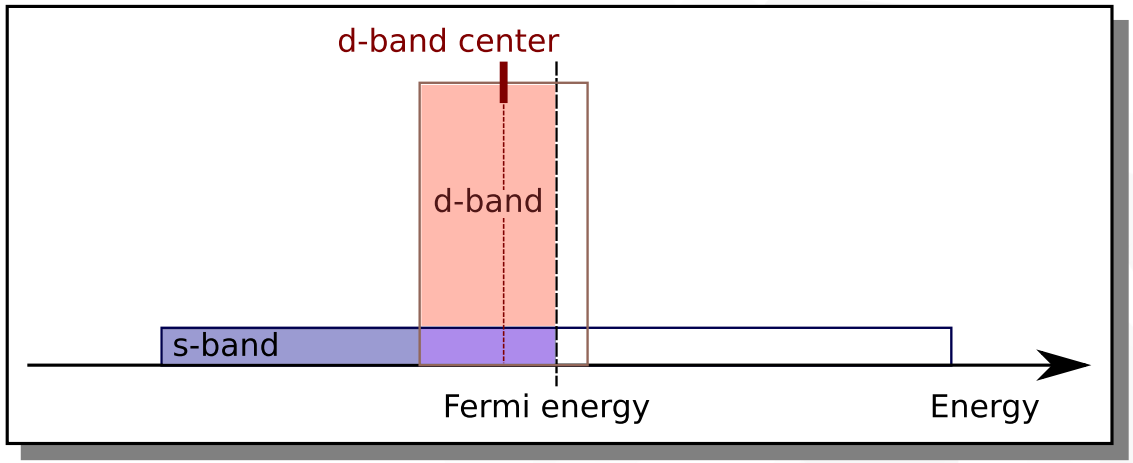
concept of
charge donation and **back-donation**

Electronic structure of transition metals (TM)

- Hammer-Nørskov chemisorption model → d-band center (ε_d)

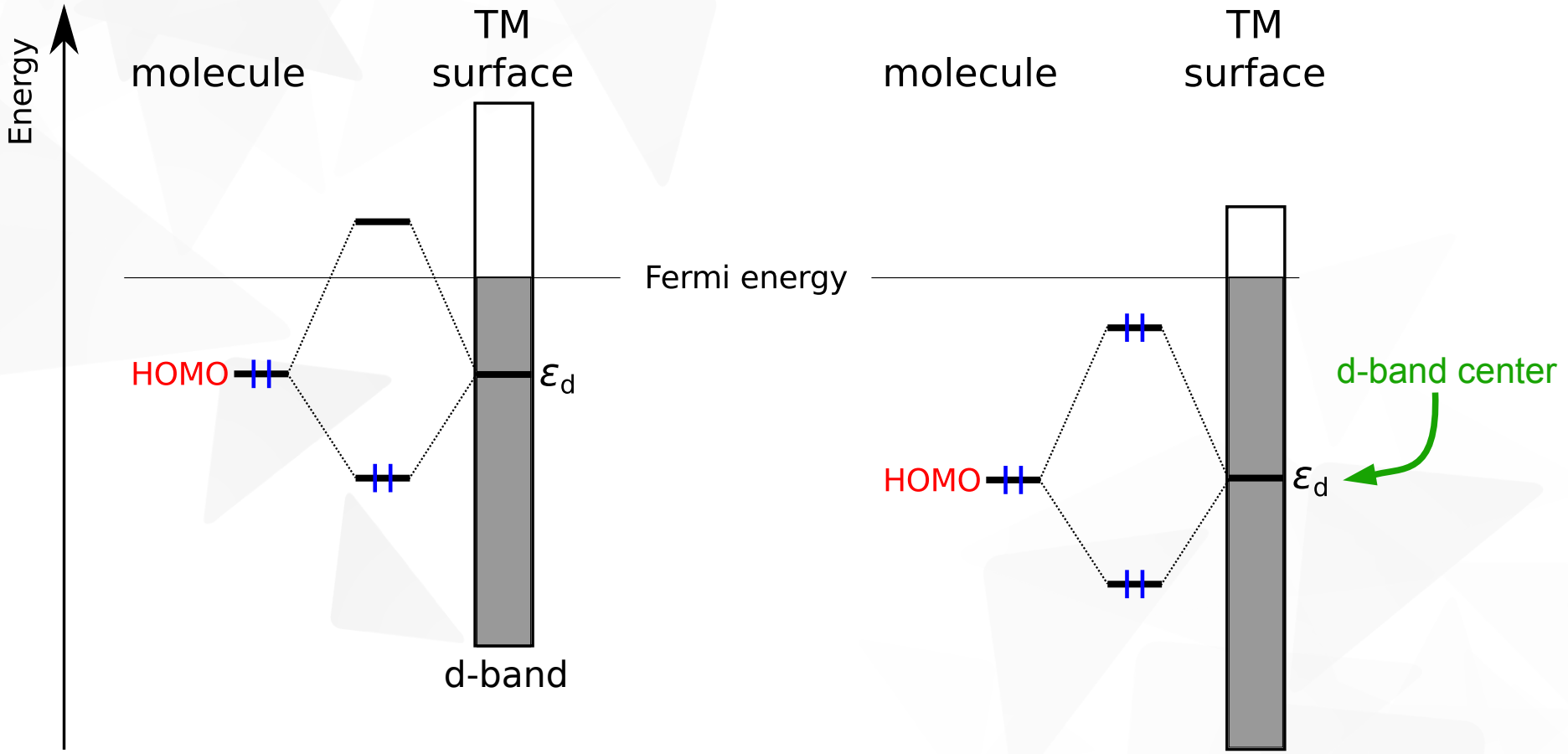


$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} \varepsilon \, \mathrm{DOS_d}(\varepsilon) \mathrm{d}\varepsilon}{\int_{-\infty}^{+\infty} \mathrm{DOS_d}(\varepsilon) \mathrm{d}\varepsilon}$$



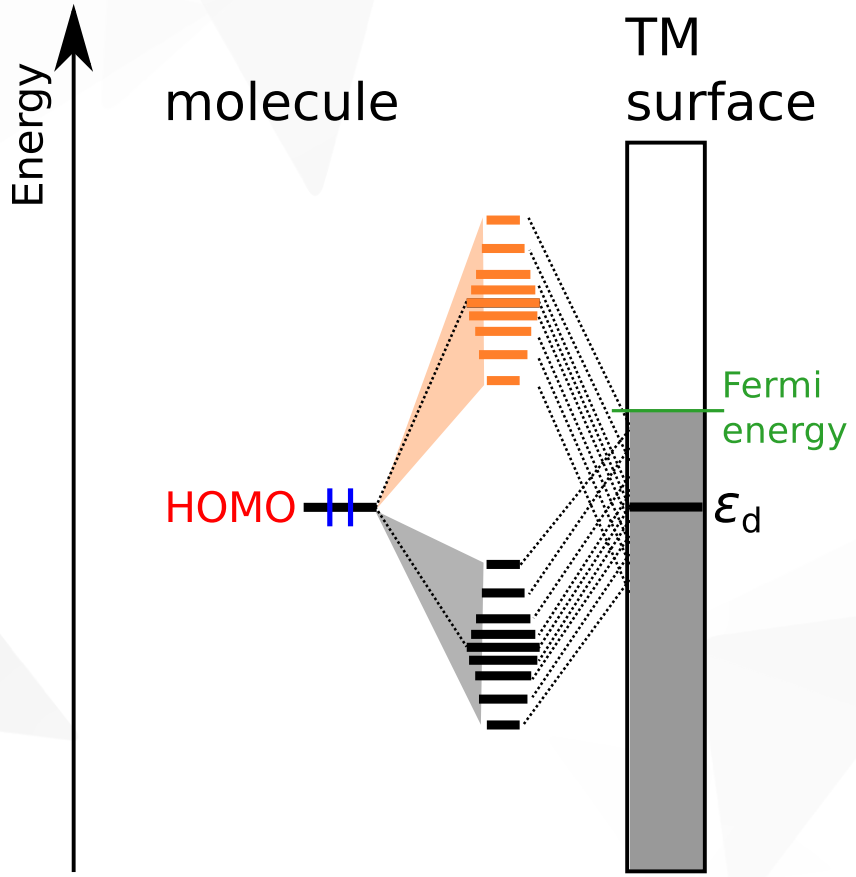
Molecule – TM-surface interaction

TM ≡ transition metal



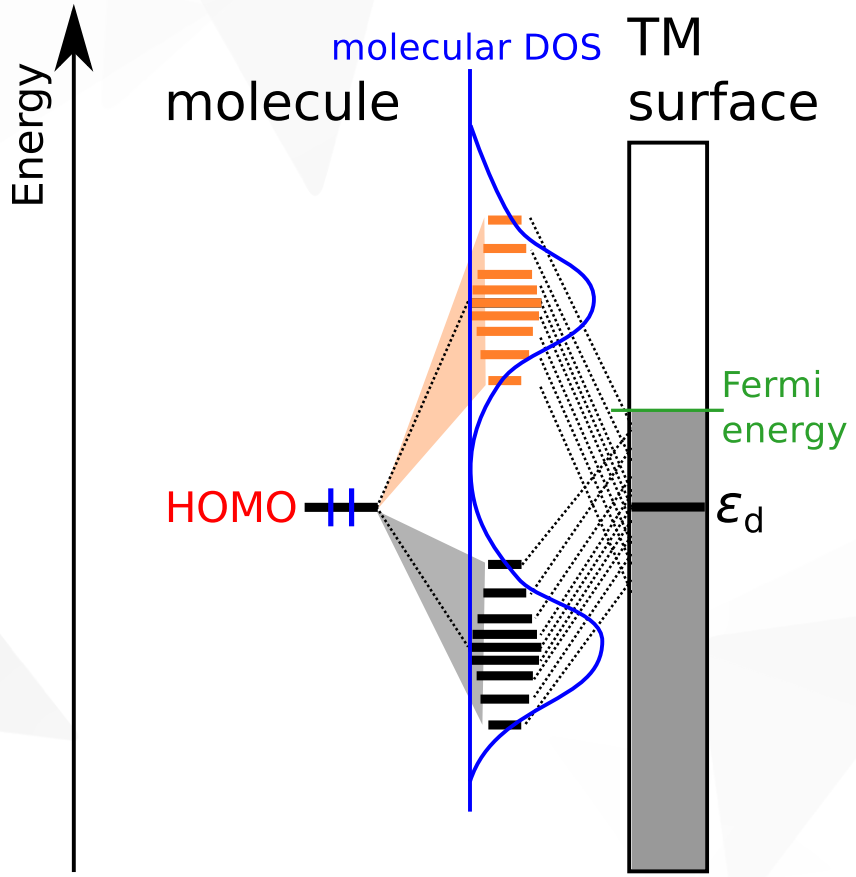
Molecule – TM-surface interaction

TM ≡ transition metal



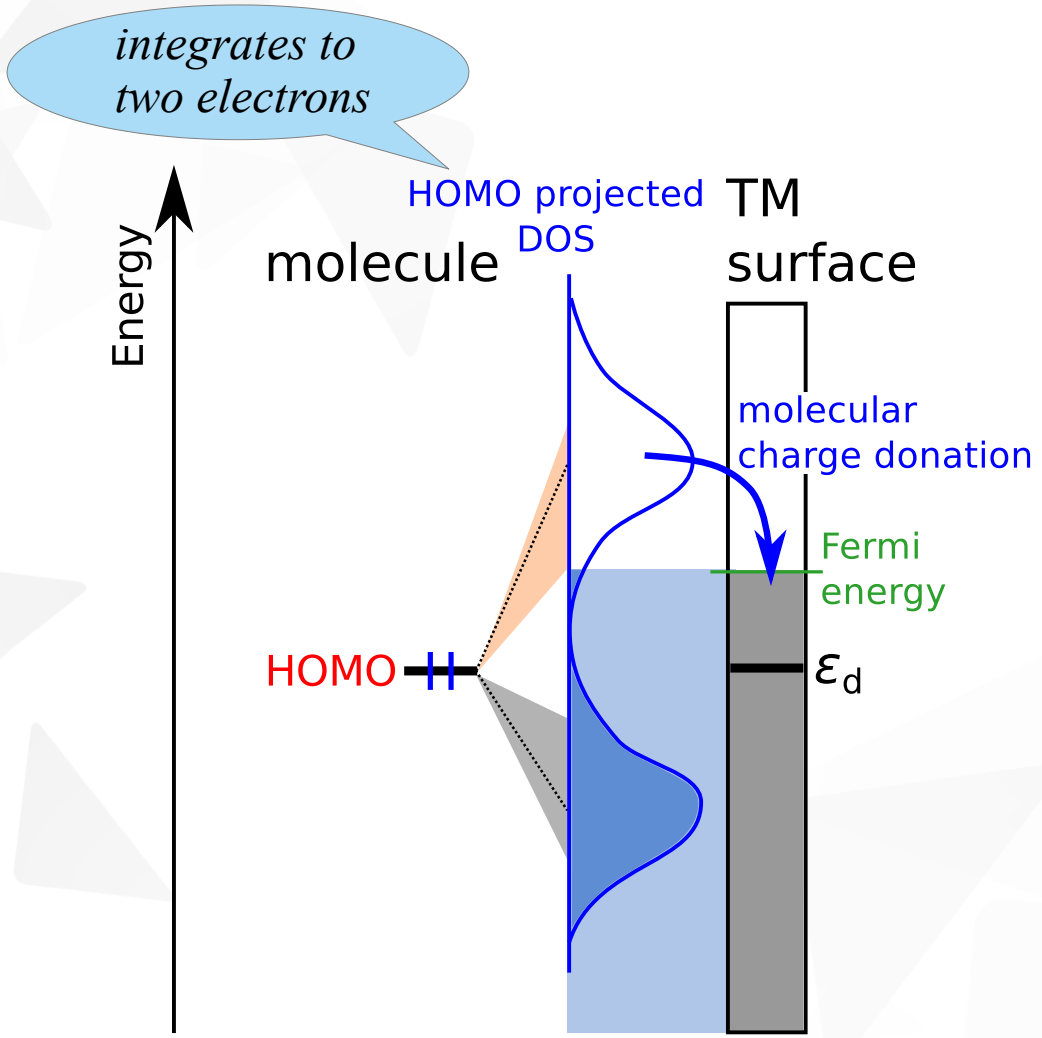
Molecule – TM-surface interaction

TM ≡ transition metal



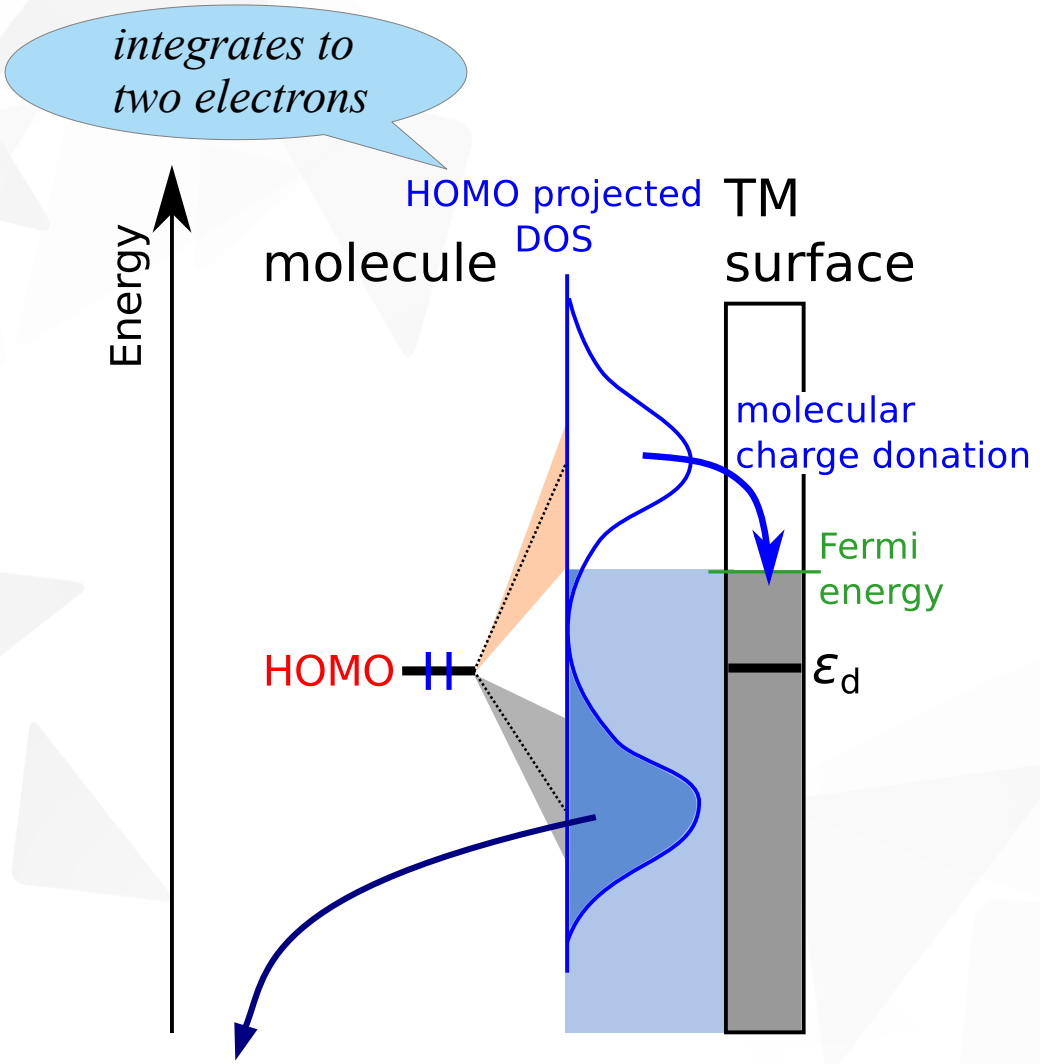
Molecule – TM-surface interaction

TM ≡ transition metal



Molecule – TM-surface interaction

TM ≡ transition metal

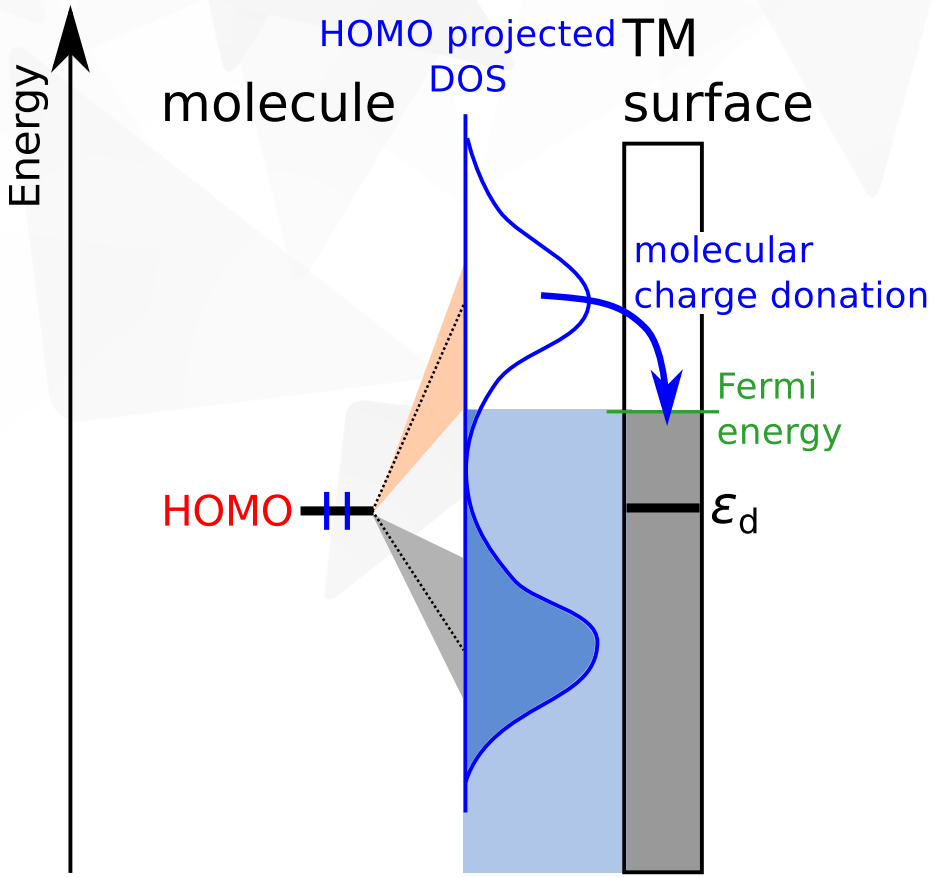


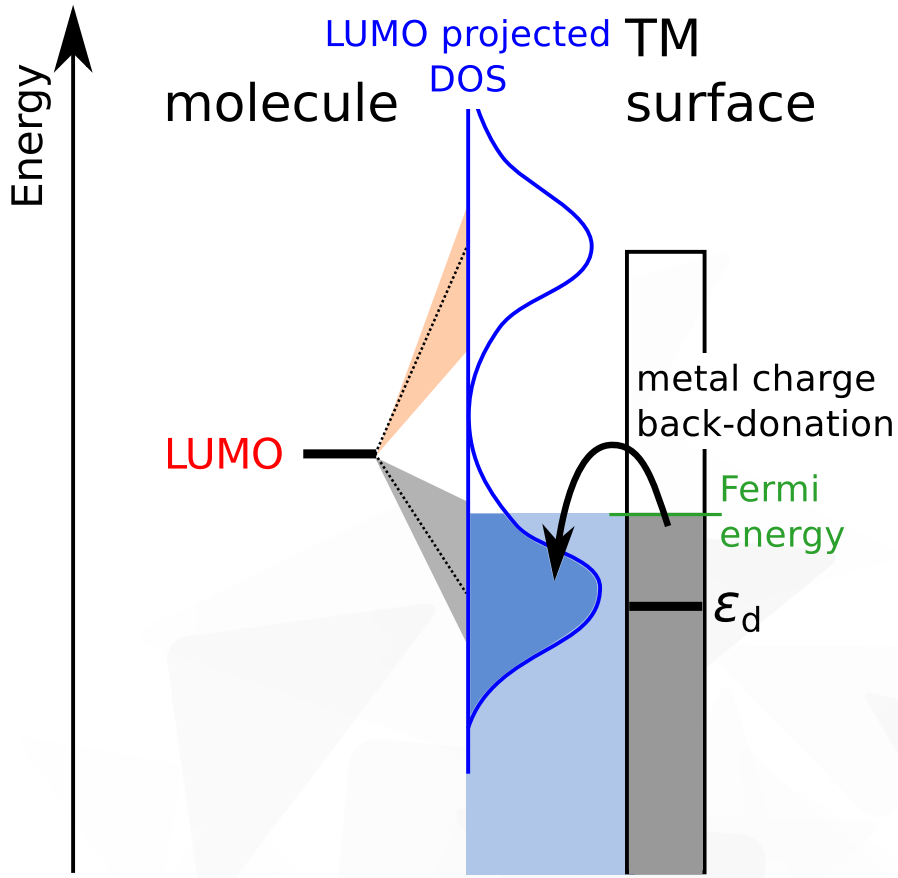
projwfc.x
moleculardpos.x

hands-on excercise on Tue: CO@Rh(100)

Molecule – TM-surface interaction

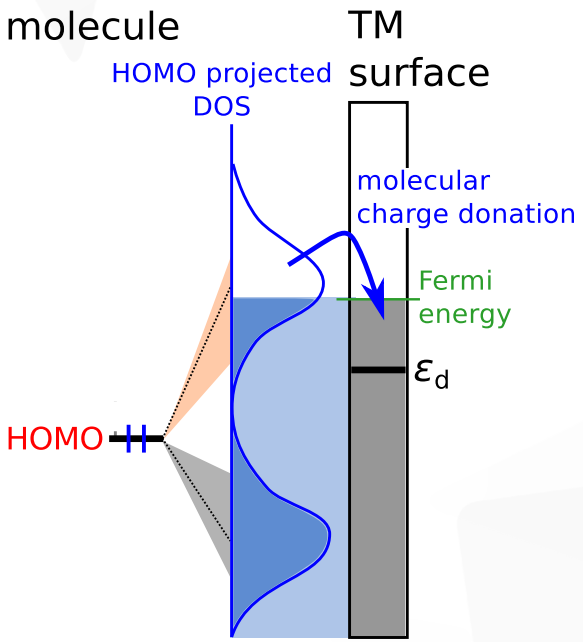
TM ≡ transition metal





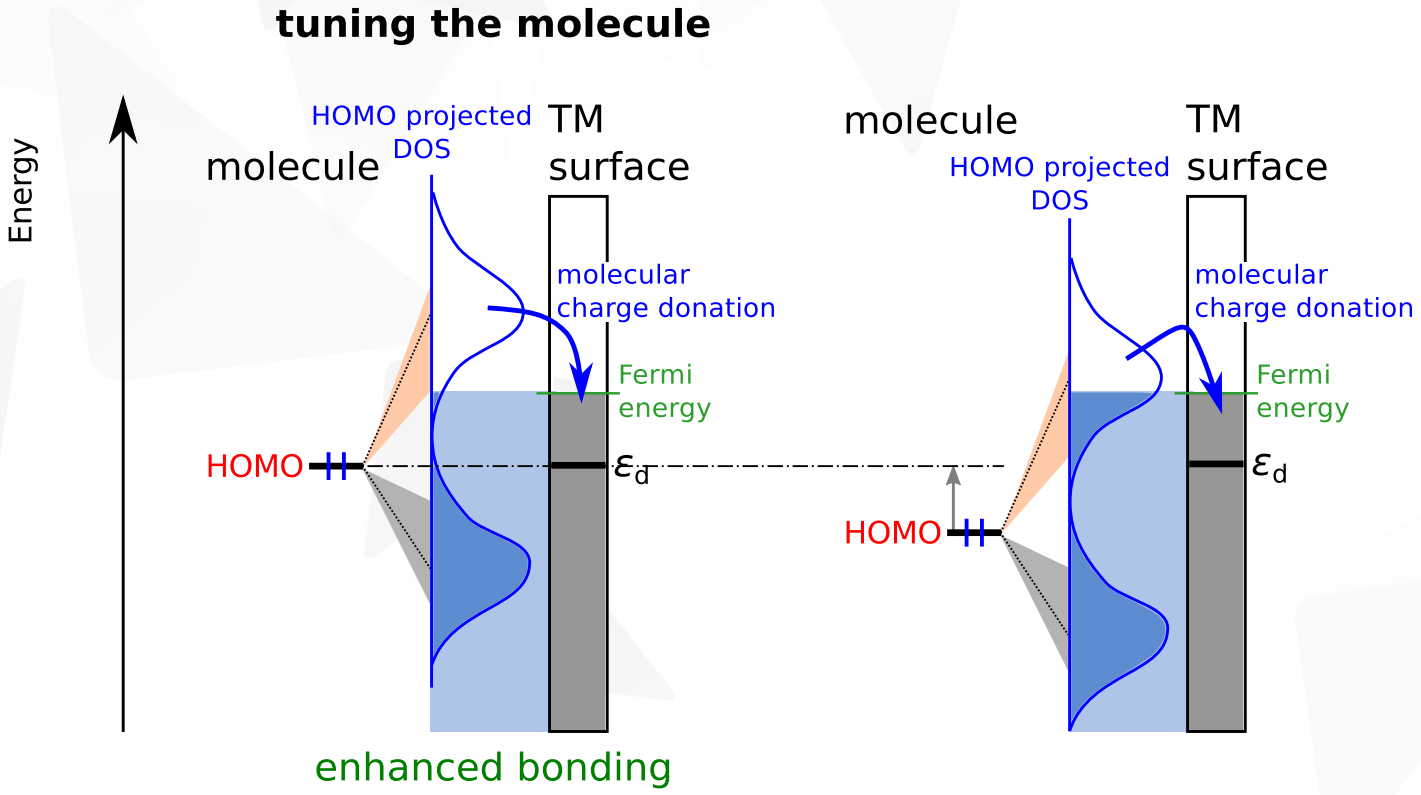
Tuning the molecule – TM-surface interaction

TM ≡ transition metal



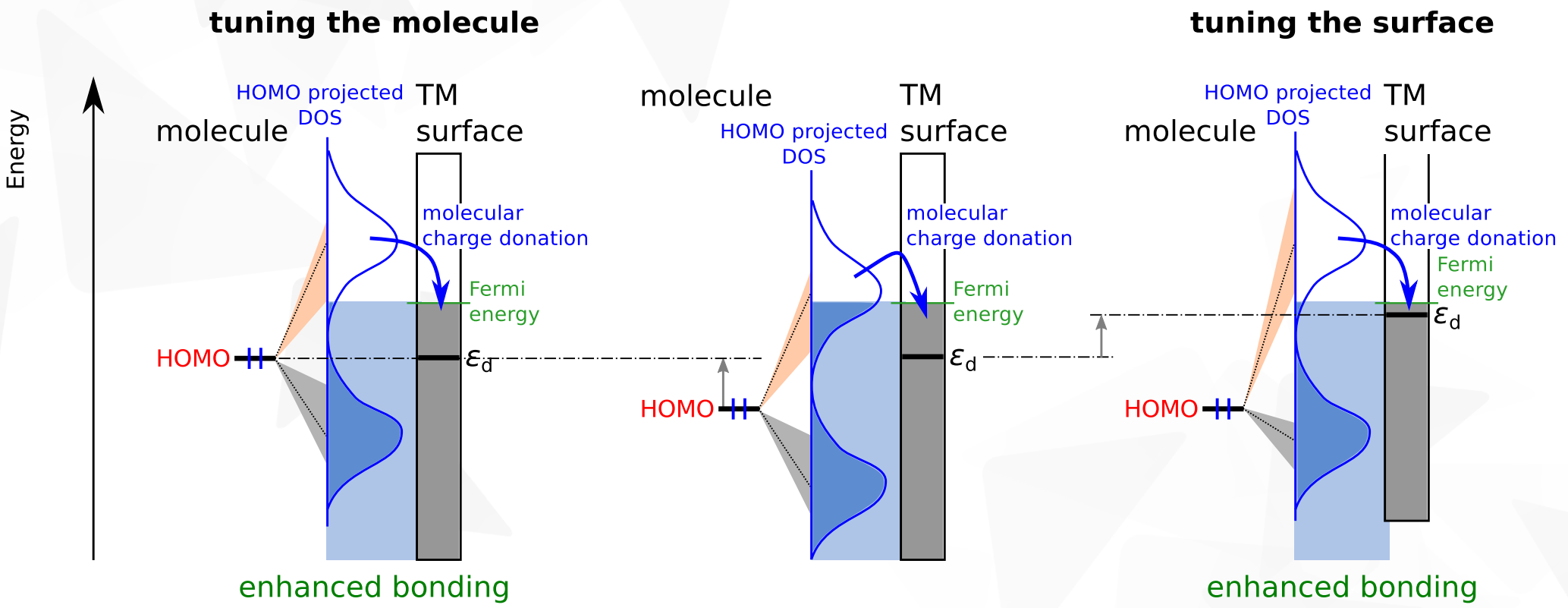
Tuning the molecule – TM-surface interaction

TM ≡ transition metal

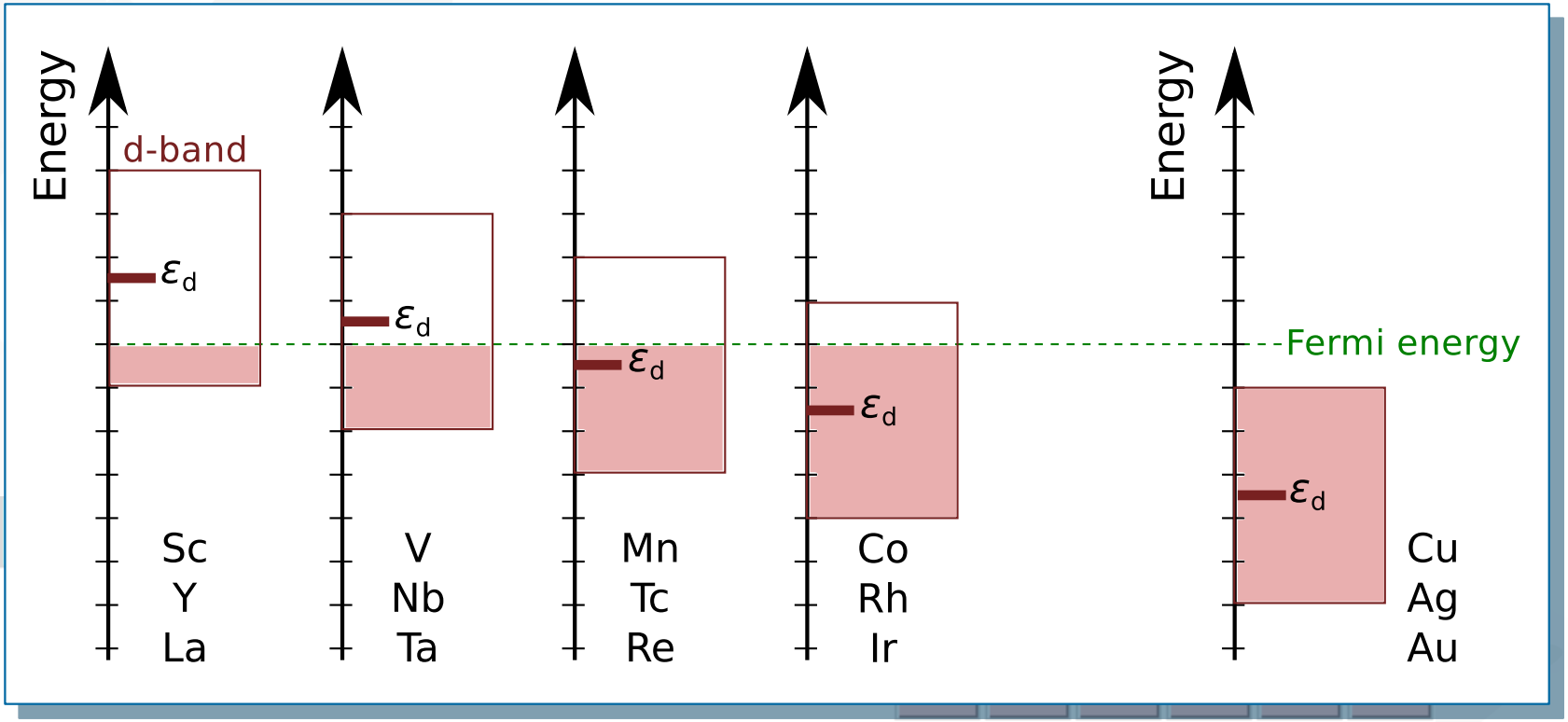


Tuning the molecule – TM-surface interaction

TM ≡ transition metal

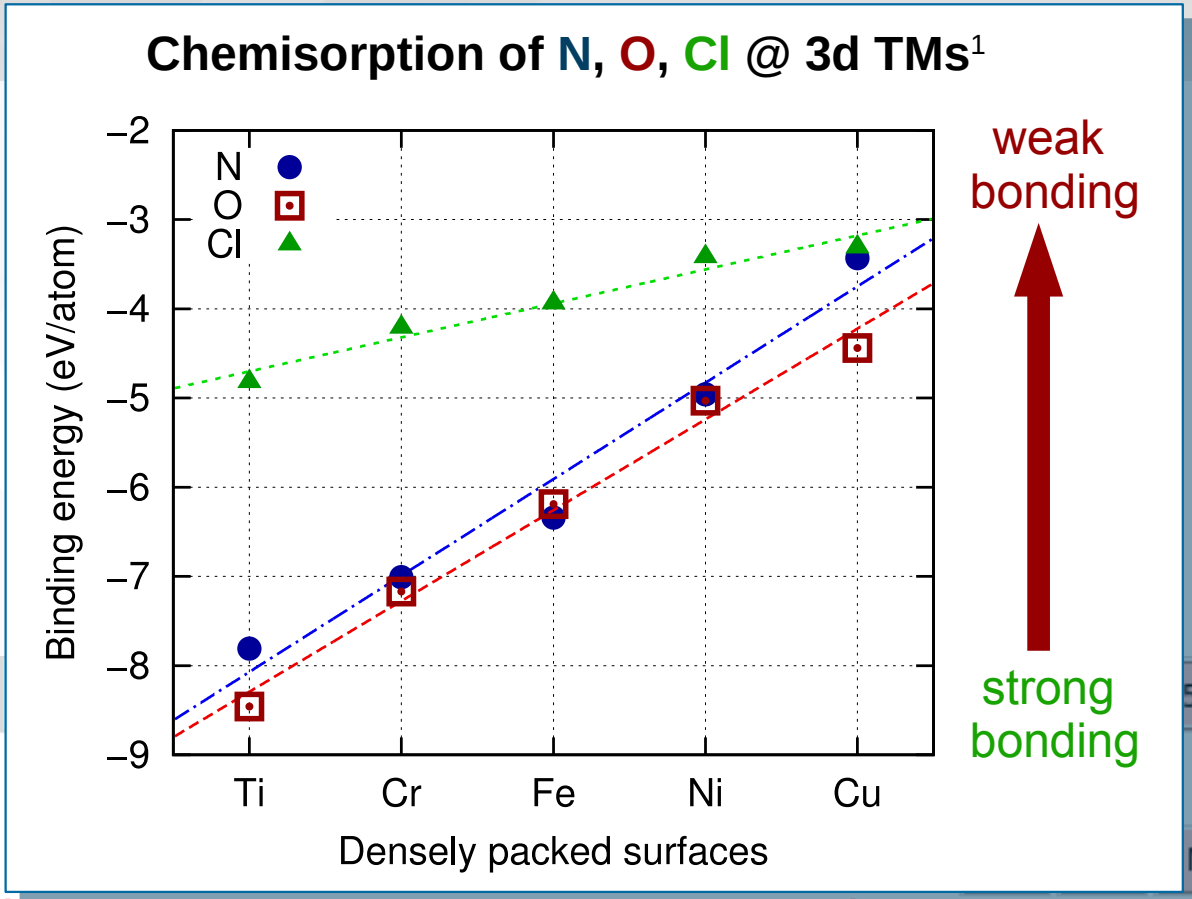


Position of d-band



	1a	2a																
I	H																	
II	Li	Be																
III	Na	Mg											Al	Si	P	S	Cl	Ar
IV	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
V	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
VI	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
VII	Fr	Ra	Ac	Rf	Ha	Sg	Ns	Hs	Mt									

TM: bonding decreases from left to right



	1a	2a											5a	6a	7a	8a
I	H															He
II	Li	Be											N	O	F	Ne
III	Na	Mg											Al	Si	P	S	Cl	Ar
IV	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
V	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
VI	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
VII	Fr	Ra	Ac	Rf	Ha	Sg	Ns	Hs	Mt									

[1]Kokalj, Chem. Phys. **393** (2012) 1–12

Take home message

- recipe for bonding: keep antibonding states empty

- $\psi_k(x) = \exp(ikx)\, u_k(x)$ where $k = 2\pi\kappa/(Na)$ and $\kappa \in (-N/2, N/2]$

or $k \in 2\pi(-1/(2a), 1/(2a)] = 2\pi(-a^*/2, a^*/2]$ (for 1D)

Brillouin zone

a^* = reciprocal lattice vector

- when **supercell** increases:

# of k-points decreases

# of bands increases

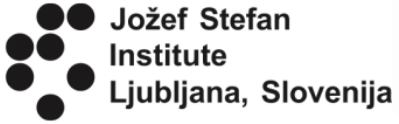
Literature

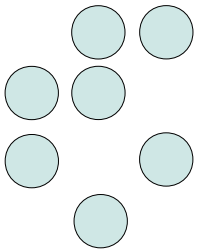
- Roald Hoffmann, *“SOLIDS and SURFACES: A Chemist’s View of Bonding in Extended Structures”* (Wiley-VCH)

- Roald Hoffmann, “*A chemical and theoretical way to look at bonding on surfaces*”, Rev. Mod. Phys. **60**, 601–628

Acknowledgment

- *to my daughter Katarina for calculating and plotting all pictures of orbitals*





Thank you very much for your attention