

Lecture 23 - 11/29

Remember: Final presentations!

Timeline: → suggestion of topic (in person or via email): Wednesday

→ first draft (in person or via email):
in next week

→ Presentation: Thu, Dec 7,
10am - 2pm
will provide lunch
Science Center 309

Topics today:

- Group theory: crystal field splitting
selection rules
- Artificial atoms & molecules:

Basis fct: in group tables:

linear + quadratic, combinations

$x, y, z, x^2, \dots, x^2 + y^2, \dots, xy, \dots$

R_x, R_y, R_z + comb's : axial, i.e. even under i (inversion)

(see table previous page)

e) Crystal field splitting:

What is the effect of lowering symmetry?

Example: O : proper rotations of  ($h=24$)

Hint: calculate characters of irred. reps. of high-symmetry for actions allowed under low symmetry and use orthogonality:

e.g.
$$D_{low}^{(l)} = \sum_i a_i \Gamma_{low}^{(l_i)} \quad a_i = \dots$$

(Tables here...)

Trikham:

| O | | E | 8C ₃ | 3C ₂ | 6C ₂ | 6C ₄ |
|---------------------------|----------------|---|-----------------|-----------------|-----------------|-----------------|
| Γ₁ | α | 1 | 1 | 1 | 1 | 1 |
| Γ₂ | β' | 1 | 1 | 1 | -1 | -1 |
| Γ₁₂ | γ | 2 | -1 | 2 | 0 | 0 |
| Γ₁₅ | δ' | 3 | 0 | -1 | -1 | 1 |
| Γ₂₅ | ε | 3 | 0 | -1 | 1 | -1 |
| | A ₁ | 1 | 1 | 1 | 1 | 1 |
| | A ₂ | 1 | 1 | 1 | -1 | -1 |
| | E | 2 | -1 | 2 | 0 | 0 |
| | T ₁ | 3 | 0 | -1 | -1 | 1 |
| | T ₂ | 3 | 0 | -1 | 1 | -1 |

$$\chi(C_2) = \chi(\pi) = (-1)^L$$

$$L = 0, 3, \dots$$

$$\chi(C_3) = \chi\left(\frac{2\pi}{3}\right) = \begin{cases} 1 \\ 0 \\ -1 \end{cases}$$

$$L = 1, 4, \dots$$

$$L = 2, 5, \dots$$

$$L = 0, 1, 4, 5, \dots$$

$$\chi(C_4) = \chi\left(\frac{\pi}{2}\right) = \begin{cases} 1 \\ -1 \end{cases}$$

$$L = 2, 3, 6, 7, \dots$$

Crystal field splitting \rightarrow spherically symm \rightarrow cubic

| O | E | $8C_3$ | $3C_2$ | $6C_2$ | $6C_4$ |
|-------|-----|--------|--------|--------|--------|
| D_0 | 1 | 1 | 1 | 1 | 1 |
| D_1 | 3 | 0 | -1 | -1 | 1 |
| D_2 | 5 | -1 | 1 | 1 | -1 |
| D_3 | 7 | 1 | -1 | -1 | -1 |
| D_4 | 9 | 0 | 1 | 1 | 1 |

$$D_L = \sum a_i \Gamma_i$$

where $a_i = (24)^{-1} \sum N_k \chi_i(\mathcal{C}_k) \chi_L(\mathcal{C}_k)$

$D_0 = A_1$ cannot split since it is only one-dimensional.

$D_1 = T_1$, by comparison of the characters. Since D_1 remains a single irreducible representation, a P state ($L = 1$) is not split by a cubic field.

$D_2 = E + T_2$. D_2 must split, since there are no five-dimensional irreducible representations of O . The actual decomposition shows that a D state ($L = 2$) is split into a twofold and a threefold degenerate level in a cubic field.

$D_3 = A_2 + T_1 + T_2$. Thus an F state is split into a nondegenerate and two threefold degenerate states.

$D_4 = A_1 + E + T_1 + T_2$. Thus a G state splits into a nondegenerate state, a doubly degenerate state, and two triply degenerate states.

compare characters of classes

Example:

Consider, for example, the group C_{2v} . Its character table is:

| C_{2v} | | | E | C_2 | σ_v | σ'_v |
|-----------------|----------|-------|-----|-------|------------|-------------|
| x^2, y^2, z^2 | z | A_1 | 1 | 1 | 1 | 1 |
| xy | R_z | A_2 | 1 | 1 | -1 | -1 |
| xz | R_y, x | B_1 | 1 | -1 | 1 | -1 |
| yz | R_x, y | B_2 | 1 | -1 | -1 | 1 |

Our notation here is such that σ_v is reflection in the xz plane and σ'_v is reflection in the yz plane. Then we can write out symbolically the effect of each of these operations (or its inverse, which is the same in this example) on the three coordinate functions as follows:

$$P_E \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad P_{C_2} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix} \quad P_{\sigma_v} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix} \quad P_{\sigma'_v} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$$

Comparing the results with the character table, and using the fact that $\chi^{(i)}(R) = \Gamma^{(i)}(R)$ for a one-dimensional representation, we have, for example,

$$P_{C_2}x = \Gamma^{(B_1)}(C_2)x$$

or more generally

$$P_Rx = \Gamma^{(B_1)}(R)x$$

Similarly,

$$P_Ry = \Gamma^{(B_2)}(R)y$$

and

$$P_Rz = \Gamma^{(A_1)}(R)z$$

We summarize these results by saying that, under the group C_{2v} , x transforms according to B_1 , y according to B_2 , and z according to A_1 . From these results it follows that xy transforms according to $B_1 \times B_2 = A_2$, etc.

c) Matrix elements & selection rules

- H invariant under all $g \in G$, where G is group of Solv. Eq.

$\Rightarrow H$ belongs to A ,

for φ_n, φ_m belonging to $\Gamma^{(n)}, \Gamma^{(m)}$
 $= E_{nn} |\varphi_n^{(n)}\rangle$

$$\Rightarrow \langle \varphi_n^{(n)} | H | \varphi_m^{(m)} \rangle \propto \delta_{nm}$$

- When $\langle \varphi_n^{(n)} | V | \varphi_m^{(m)} \rangle \neq 0$?

V belongs to Γ_V

$V | \varphi_m^{(m)} \rangle$ belongs to $\Gamma_V \otimes \Gamma^{(m)}$

$$\Gamma_V \otimes \Gamma^{(m)} = \sum_k a_{V, mk} \Gamma^{(k)}$$

$$\langle \varphi_n^{(n)} | V | \varphi_m^{(m)} \rangle = 0 \text{ if } a_{V, mn} = 0$$

Most general formulation of selection rules!

$$\otimes \Gamma_A \otimes \Gamma_B \rightarrow \Gamma_A \cdot \Gamma_B \dots \Gamma_A \Gamma_B \Gamma_A \Gamma_B \Rightarrow \chi(\Gamma_A \otimes \Gamma_B) = \chi_A \cdot \chi_B$$

10) Atom-like particles

Why atoms?

controllable + coherent + all the same

- qubits
- engineered quantum-level material response
- metrology

What other systems?

- molecules
- artificial atoms (quantum dots, color centers...)
- (- nanocircuits (e.g. superconducting qubits)
→ LC circuits)

a) 'Artificial atoms'

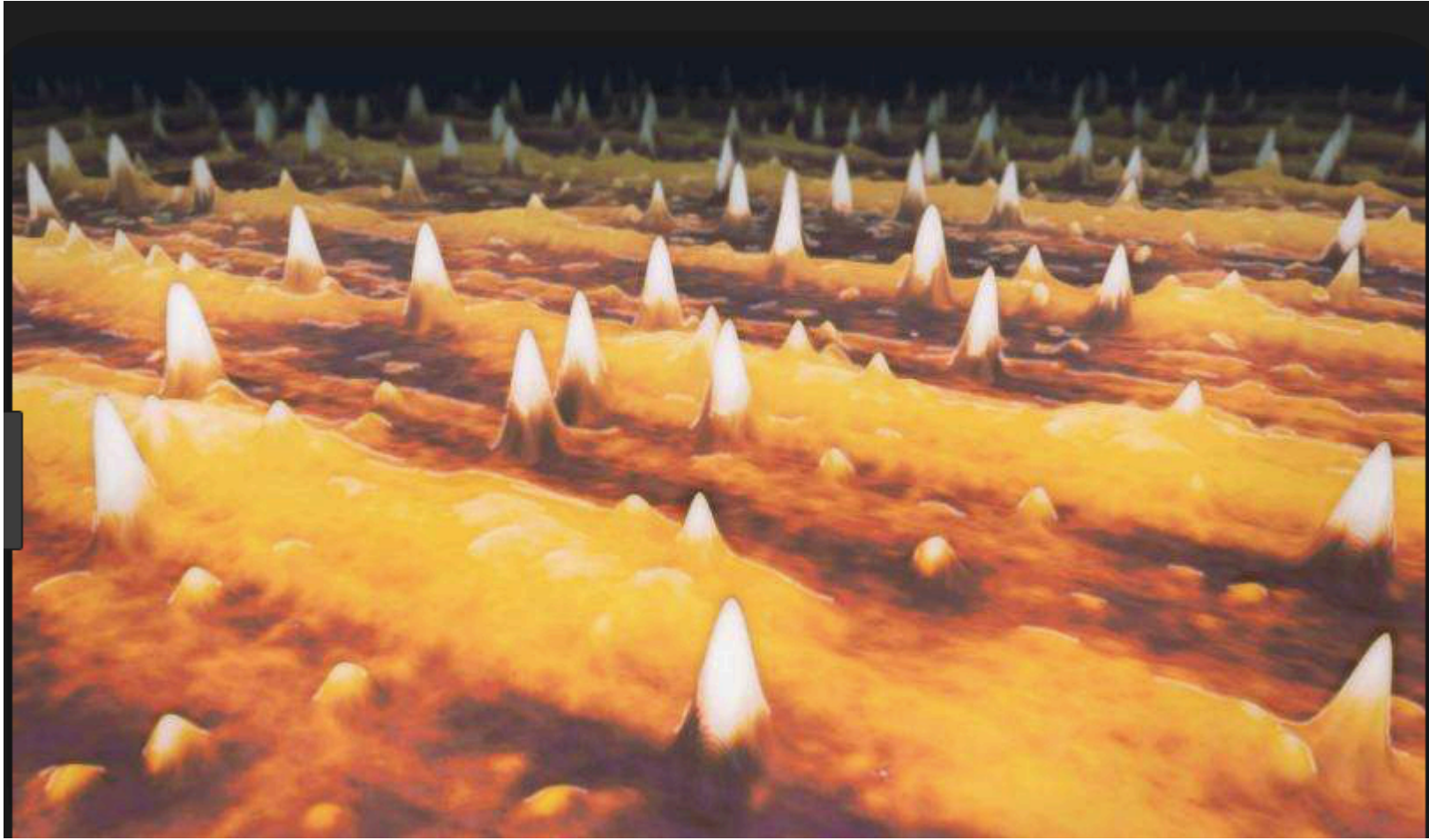
- * any quantum object with similar properties as atoms:
 - discrete energy levels
 - TLS can be coupled by light
- + is constructed / engineered

Why?

Properties (frequencies, size, ...) can be engineered on chip

Basically two types

1) Confined e^- \Rightarrow discrete levels (quantum dots)

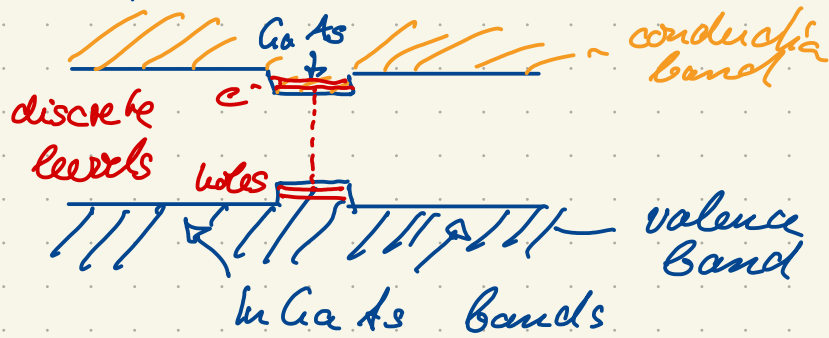


phys.org

spatially confined, with different material
OD \square in 3D crystal
(on surface)

→ confinement (e.g. 0D "dot" of GaAs in 3D

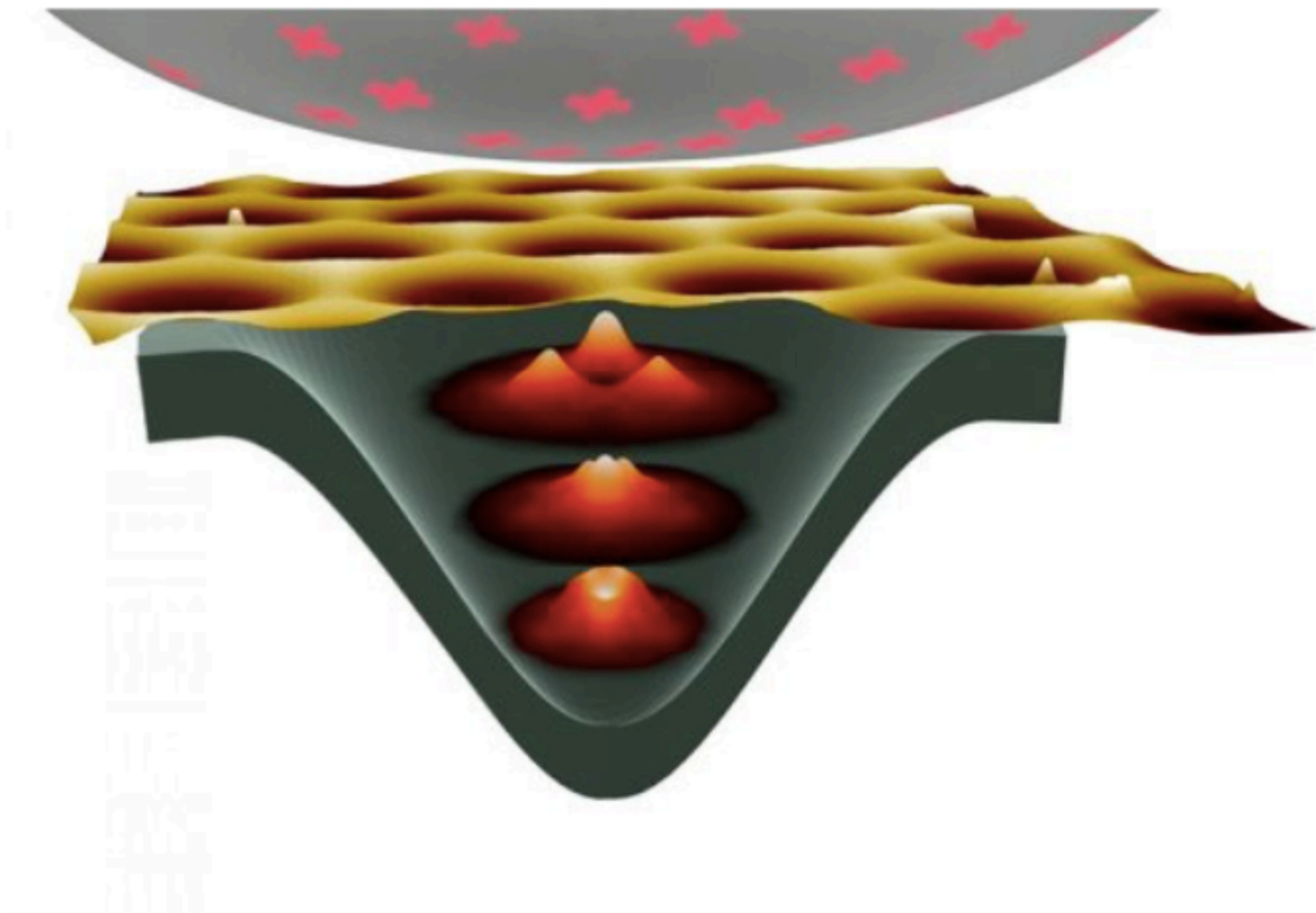
crystal of InGaAs:



How will they like atoms?

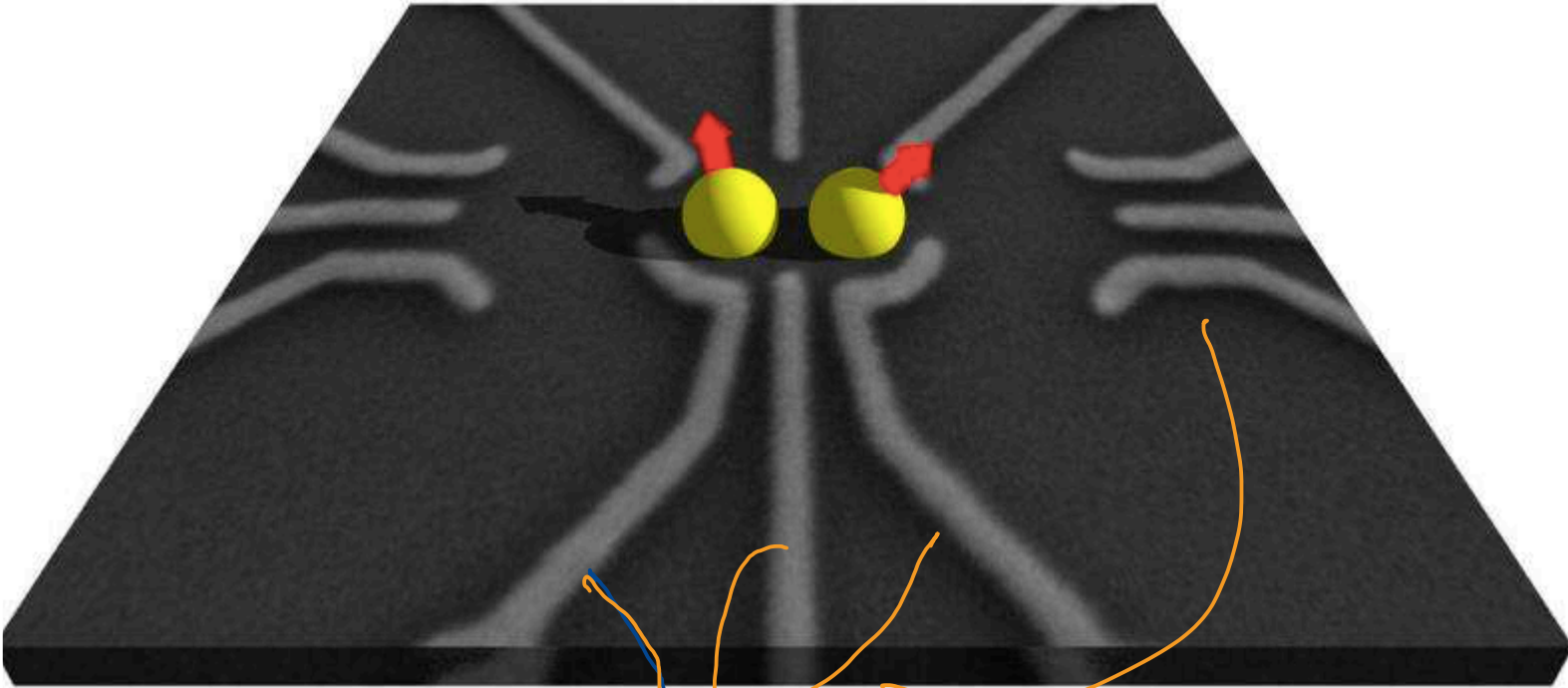
- homogeneity of levels - works, but no great
- symmetry: degeneracy & coupling depends on symm. - usually cannot distinguish between polarizations

| | Natural atoms | Artificial atoms | |
|------------|----------------|------------------|---------------------|
| | Atoms and ions | Quantum dots | Josephson junctions |
| $E = 0$ | | | |
| $E \neq 0$ | | | |

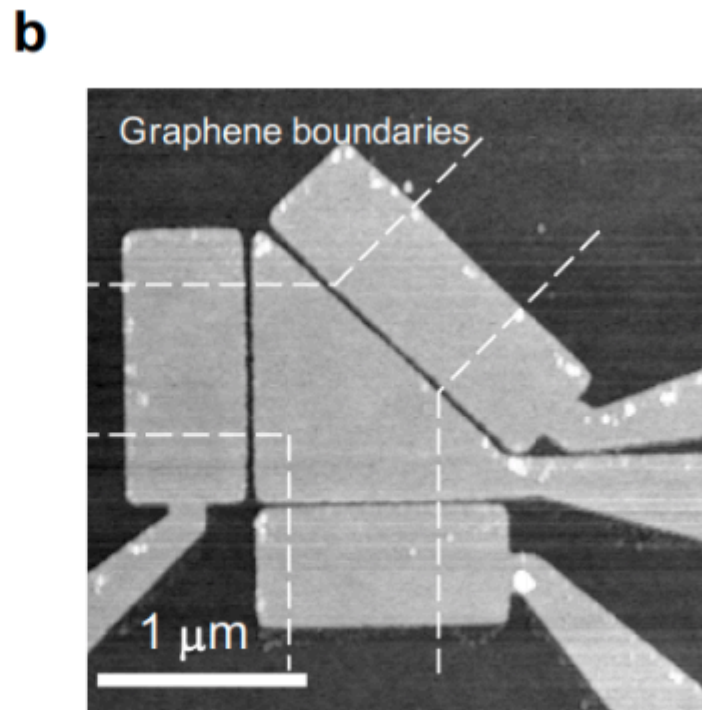
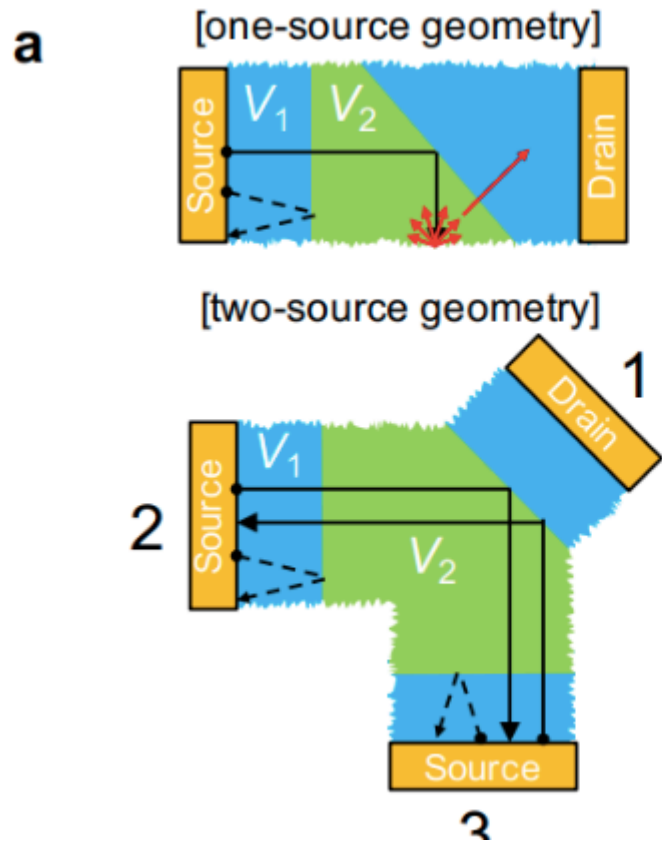


The charged tip of a scanning tunneling microscope and an additional magnetic field lead to localized stable electron states in graphene.

Credit: Nils Freitag, RWTH Aachen



electrodes



Philip Kim - graphene quantum dots

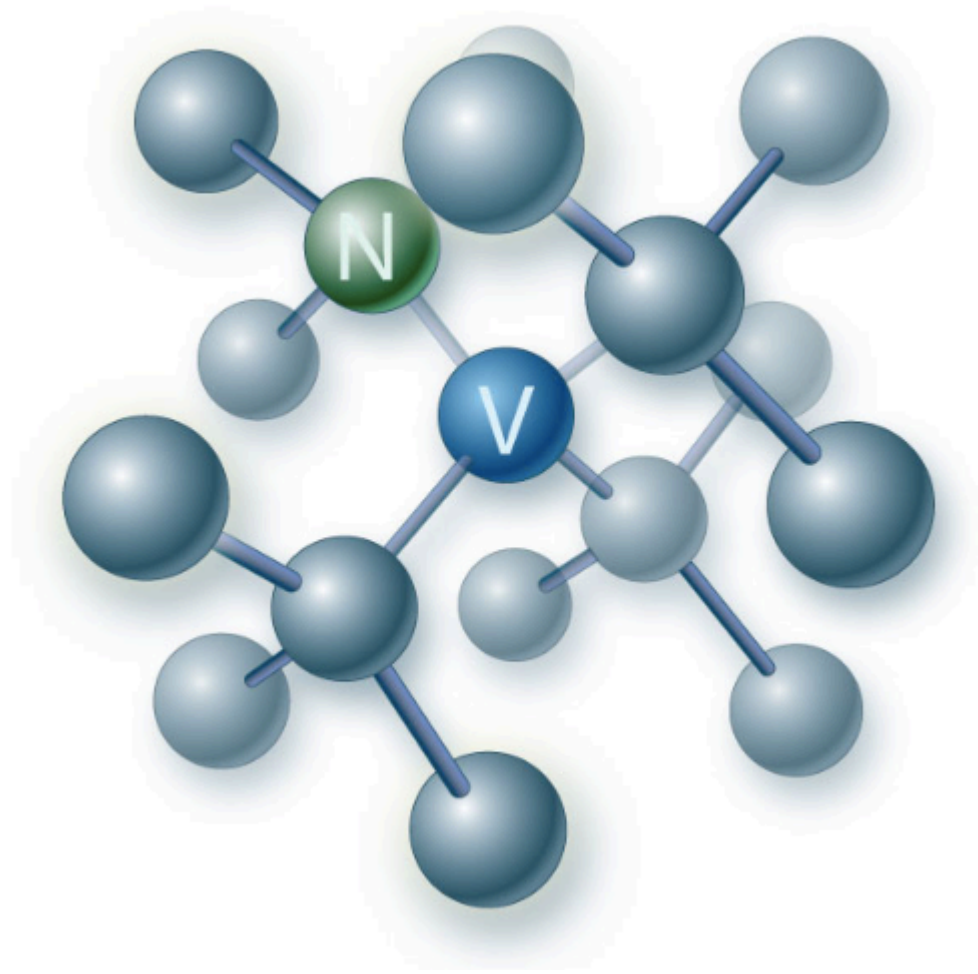
b) Color centers

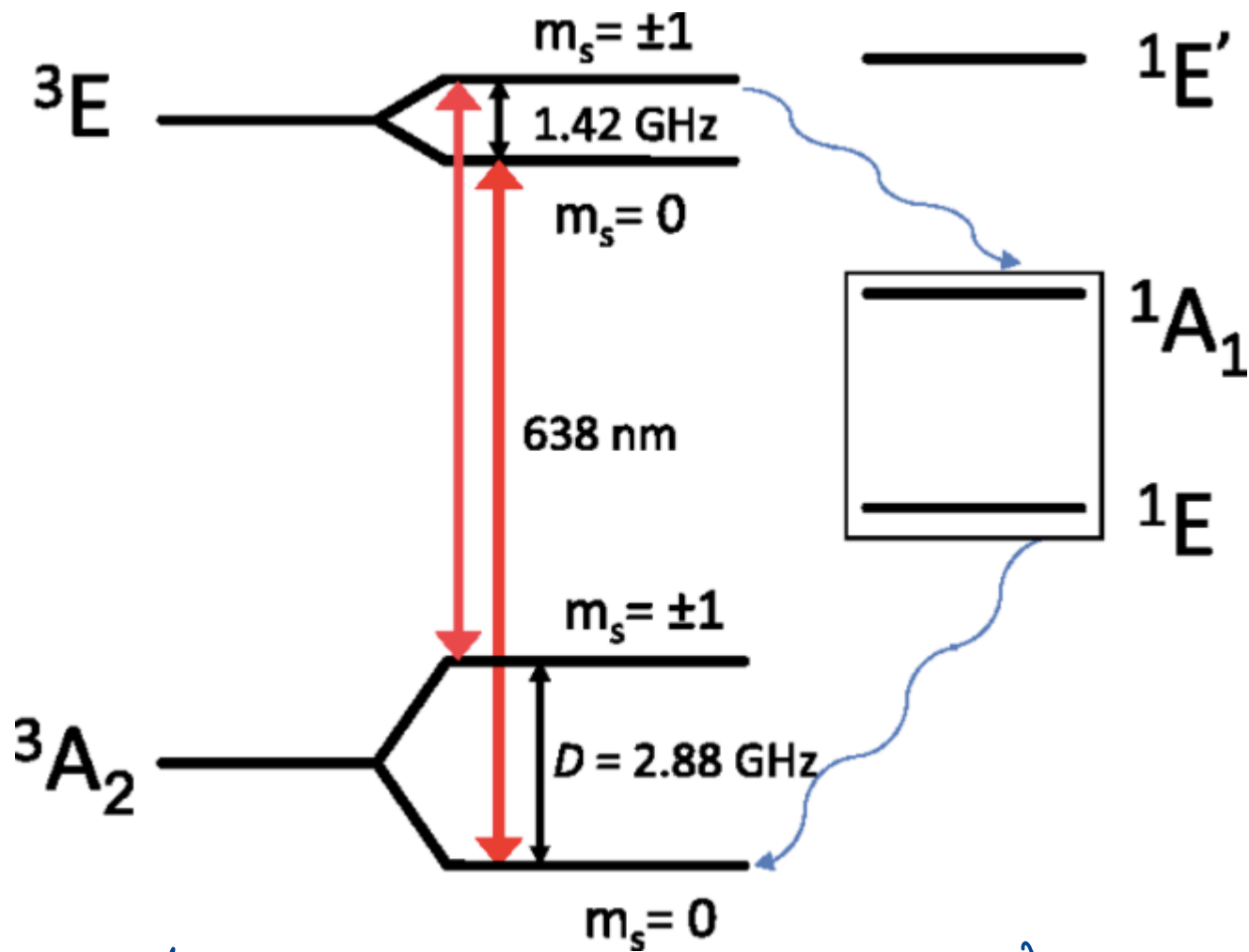
Most : NV centers } in diamond
famous SiV centers }

- Basically like atom / e^- into crystal symmetry
=> crystal defects that leave (typically unpaired) e^- / hole confined, with symm. of lattice

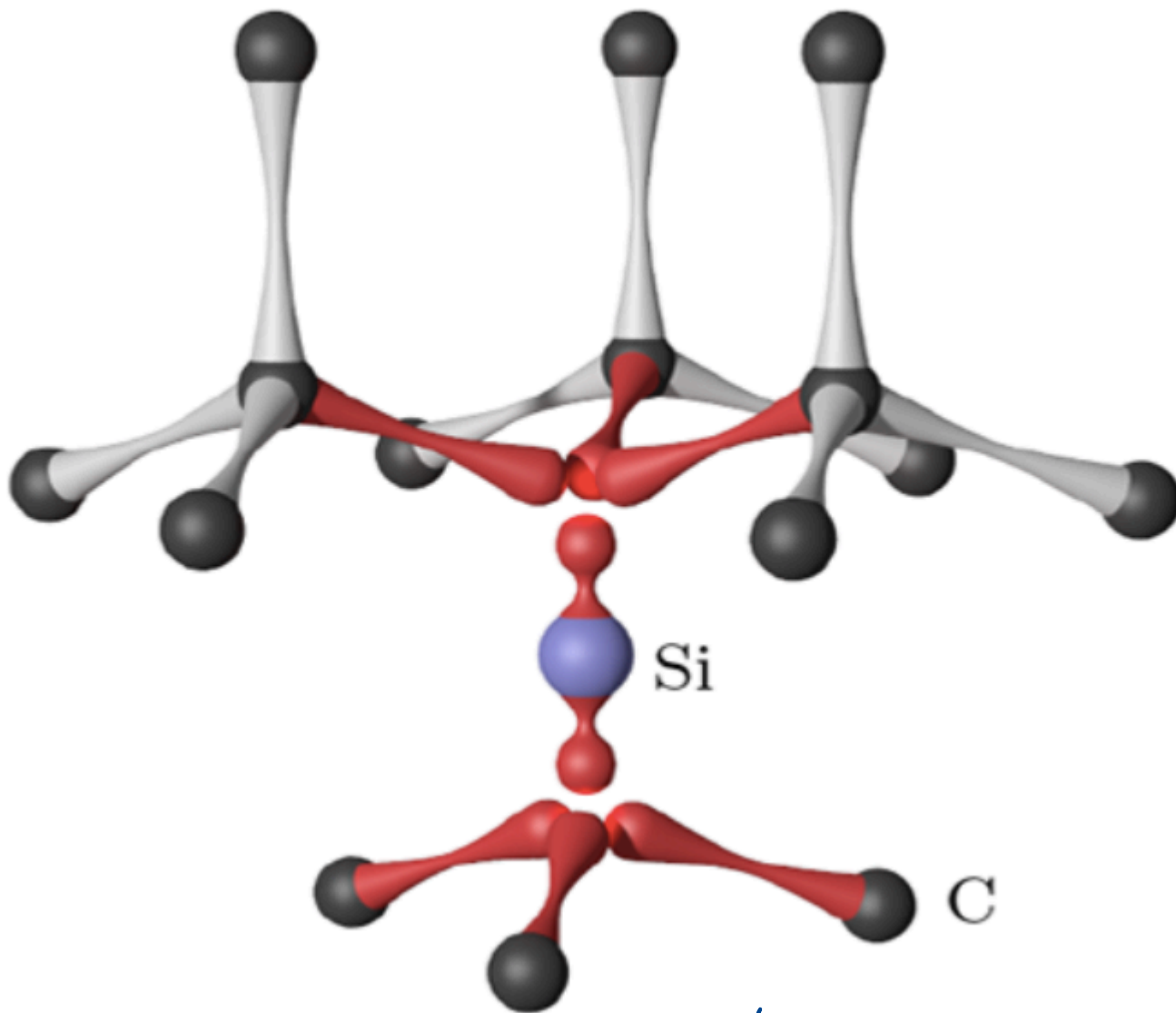
Why "color centers" ?

discrete level structure => "color"





symmetry of diamond (T) +
 "N-V axis" (\hat{z} E-field) treated as
 perturbation



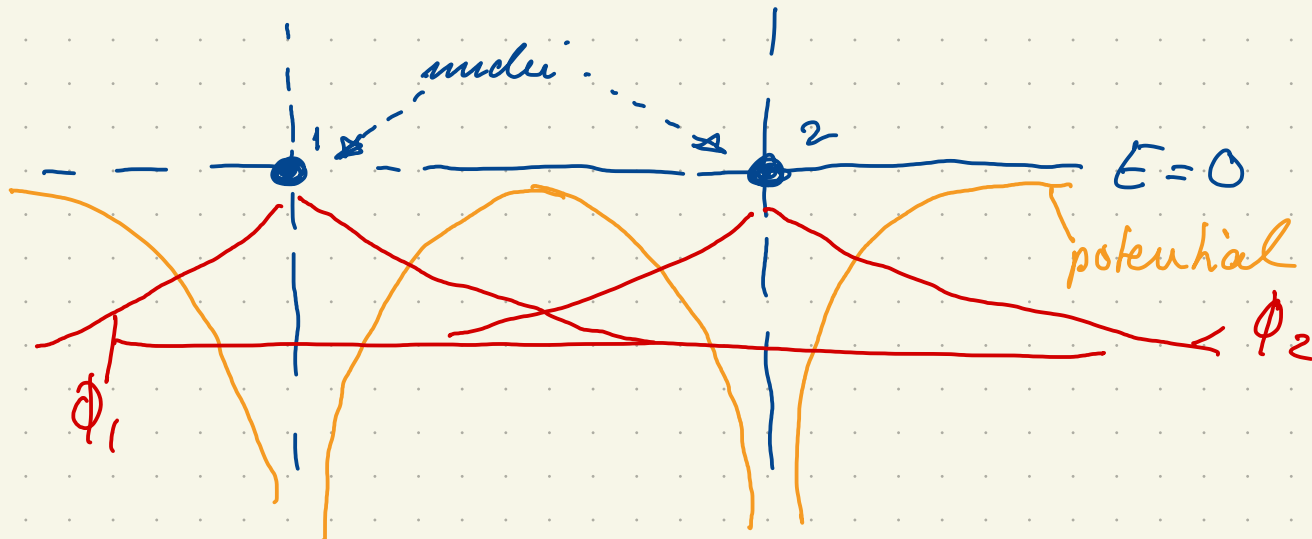
slightly higher symm. than Si
 \Rightarrow better properties

c) Brief introduction: Molecules

- Basic principles

Why do molecules exist? (ex: H_2)

two charge centers



R (distance)

H_2^+ : wavefunction?

approx: linear combination of atomic orbitals (LCAO):

trial wavefunction: $\Phi = c_1 \phi_1 + c_2 \phi_2$

ϕ_i : atomic (H-like) wavefunction of atom/nucleus i

Variational ansatz: ("Hartree-Fock")

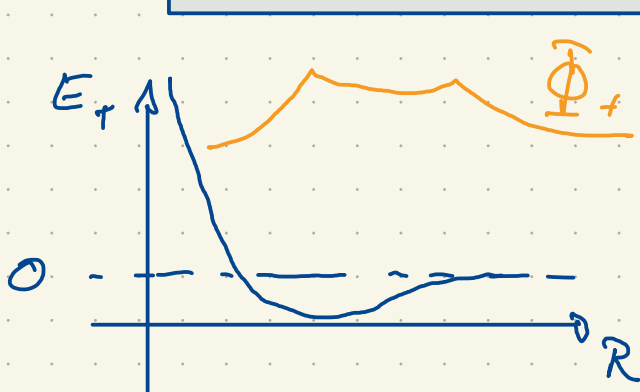
$$E = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} \stackrel{!}{=} \text{min as function of } R$$

$$\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$$

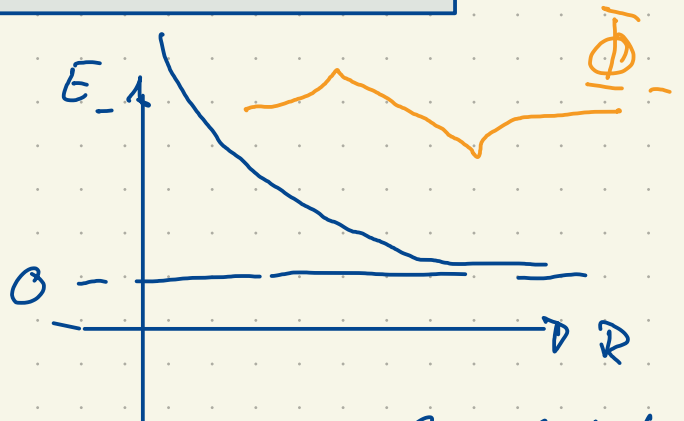
$$\begin{vmatrix} H_{11} - E & H_{12} - E s \\ H_{21} - E s & H_{22} - E \end{vmatrix} = 0 \quad \text{where}$$

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle, \quad s = \langle \phi_1 | \phi_2 \rangle$$

$$\Rightarrow E_{\pm} = \frac{H_{11} \pm H_{12}}{1 \pm s} \Rightarrow \bar{\phi}_{\pm} = \frac{\phi_1 \pm \phi_2}{\sqrt{2(1 \pm s)}}$$



\Rightarrow has bound states



\Rightarrow no bound states!

($\bar{\phi}_-$ has 0-density region)

- 1) e^- (density) between nuclei lowers energy
- 2) total wavefunction more spread out than single-atom wavefunction.

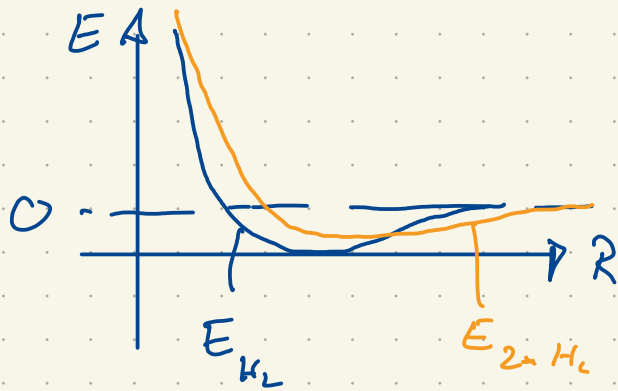
H₂: (two e^-) - cf. He

For both e^- in g. s.

$$\bar{\Psi}^{\text{spun}} = \bar{\Psi}_A^{\text{spun}} = \frac{1}{\sqrt{2}} (1\uparrow\downarrow - 1\downarrow\uparrow) \quad \text{in bound state}$$

cf. Helium: split between 2^3S and 2^1S : $\sim 0.5 \text{ eV}$

\Rightarrow somewhat different energy for H₂ than for $2 \times \text{H}_2^+$ (similar to He vs $2 \times \text{H}$)
 \rightarrow similar order of magnitude of splitting



In general: How do molecular orbitals look?

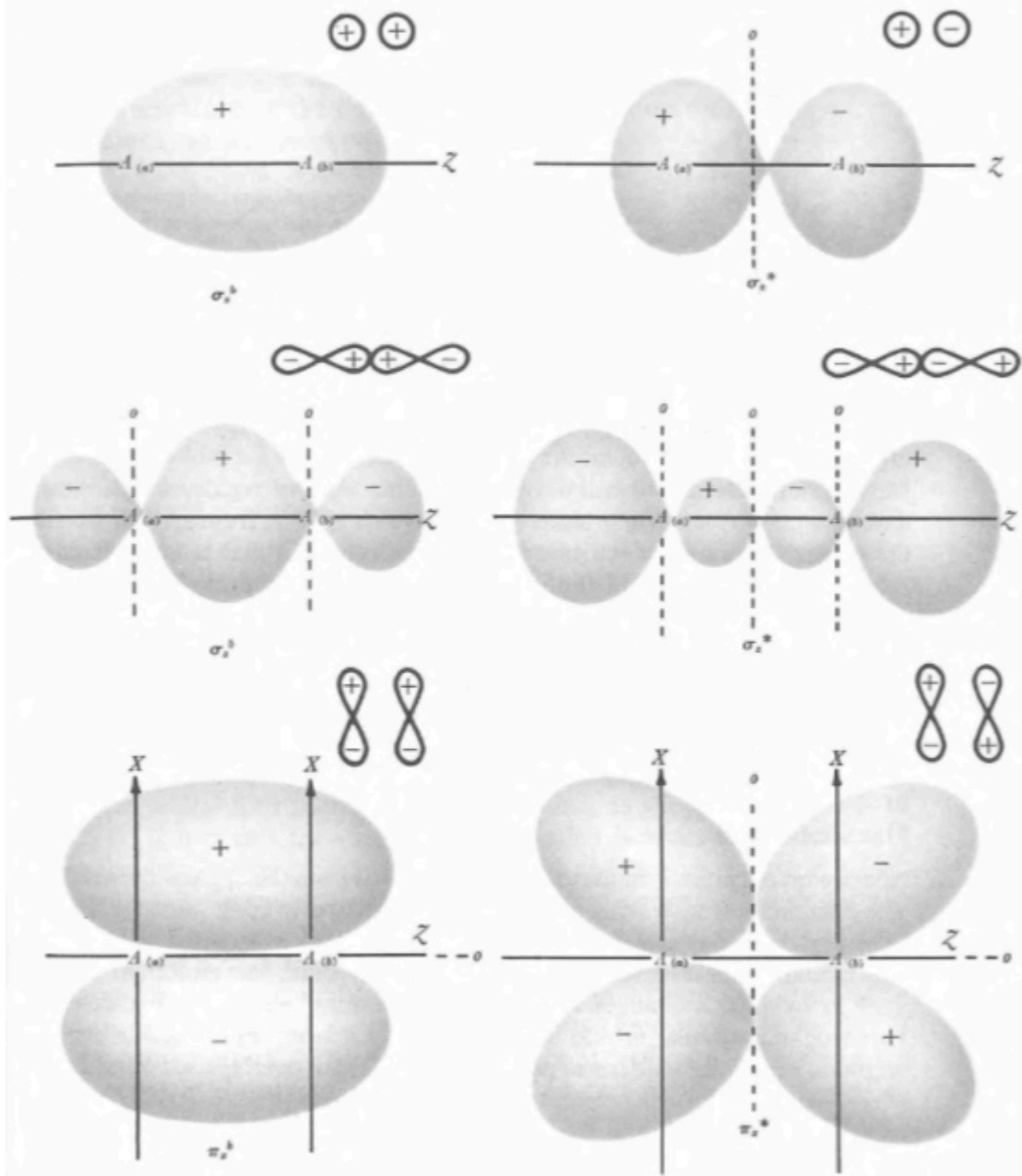
$\hat{z} \parallel$ molecule axis

(bound states only; also cf Gray pic.)

- 1) $(s) + (s) \rightarrow \sigma_s$
- 2) $(p) + (p) \rightarrow \sigma_z$
- 3) $(p) + (p) \rightarrow \pi_x \text{ or } \pi_y$
- 4) $(s) + (p) \rightarrow \text{hybrid}$

Bound

Unbound



from Gray, "Chemical bonds"