Phys 425: Lecture 7

Last time:

Micro-interactions $(\phi(r))$ — interatomic potential

↓

Macro-properties (Y, α)

Today: a little bit of micro

Today:

Covalent bonds

Covalent bond special → sharing of electrons

- Share valence electrons
- **Molecular Orbital Theory (MO)** — how orbitals overlap

The standard way of thinking about shared electrons is by looking at how their orbitals combine.

↳ 2 "fixed" nuclei at $\vec{R}_1, \vec{R}_2$

↳ Hamiltonian:

- same kinetic energy H

$$H = K + V_1 + V_2$$

V_1: nucleus 1 potential; V_2: nucleus 2 potential

potential: electrostatic potential

$$V_i = \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}_i|}$$

Coulomb potential due to nucleus

Instead of solving $\Psi(x,t)$, we can rely on the **variational principle**:

↳ Guess a solution / ansatz & minimize energy over some parameter.

Our guess

↳ Linear combination of atomic orbitals (LCAO)

we have an orbital due to 1 nucleus,
guess is a combination of the two.

Atomic Orbital

$|i\rangle$ ← this is the wavefunction for atom i

Ansatz: $|\psi\rangle = c_1|1\rangle + c_2|2\rangle$

where, each is a solution to $K+V_i$

$$\boxed{(K+V_1)|1\rangle = E_0|1\rangle \quad | \quad (K+V_2)|2\rangle = E_0|2\rangle}$$

If we do the inner product, $\cdot$,

$$\langle i|j\rangle = \delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases}$$

The variational energy solution:

$$E \geq \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

↑ this is a bound.

This leads to an eigenvalue problem:

Variational Schrodinger equation:

$$\sum_{m,n} H_{mn} C_m = E C_n \quad \text{where} \quad H_{mn} = \langle m|H|n\rangle$$

↗ expectation value of the Hamiltonian

OR

$$\mathbb{H}\vec{C} = E\vec{C}$$

matrix ↗

In our case, for our Ansatz:

H_{mn} = 2×2 matrix $\quad H = \begin{pmatrix} \langle 1|H|1\rangle & \langle 2|H|1\rangle \\ \langle 1|H|2\rangle & \langle 2|H|2\rangle \end{pmatrix}$

$$\langle 1|H|1\rangle = \langle 1|\, K+V_1+V_2\,|1\rangle$$

$$= \langle 1|\, K+V_1\,|1\rangle + \langle 1|V_2|1\rangle$$

$K+V_1$ acting on $|1\rangle$ gives $E_0|1\rangle$

$$= E_0\langle 1|1\rangle + \langle 1|V_2|1\rangle$$

$$= E_0\underbrace{\langle 1|1\rangle}_{1} + \underbrace{\langle 1|V_2|1\rangle}_{V_{cross}}$$

$$= E_0 + V_{cross}$$

$$H = \begin{pmatrix} E_0+V_{cross} & t \\ -t & E_0+V_{cross} \end{pmatrix}$$

where $\langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle = V_{cross}$

$$t = -\langle 1|V_2|2\rangle = \langle 2|V_1|1\rangle$$

"Exchange energy"

Solve eigenvalue problem to get: the energies

$$E_\pm = E_0 + V_{cross} \pm |t|$$

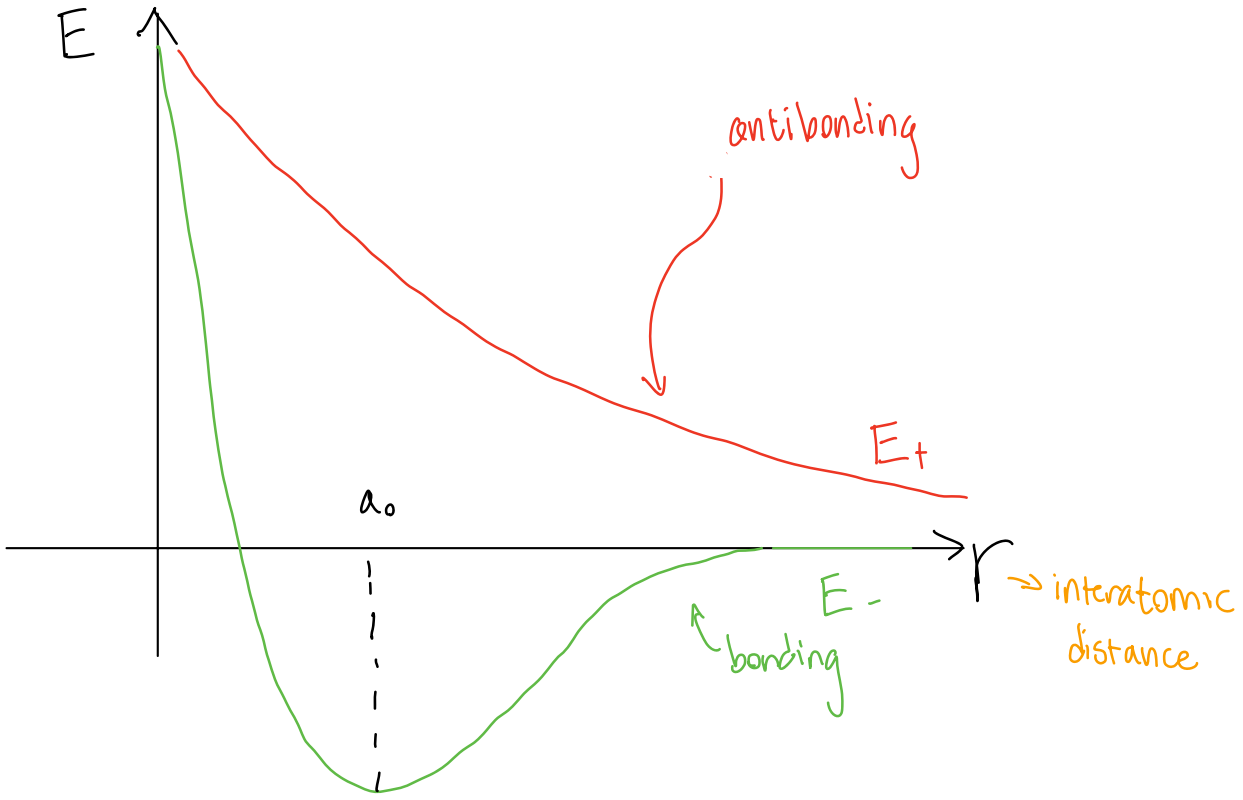
(+ : antibonding, − : bonding)

$$|\psi_{antibonding}\rangle = \frac{1}{\sqrt{2}}(|1\rangle \mp |2\rangle)$$

$$|\psi_{bonding}\rangle = \frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle)$$

$Ax - i = 0$,

plug eigenvalue back in, get the vectors.

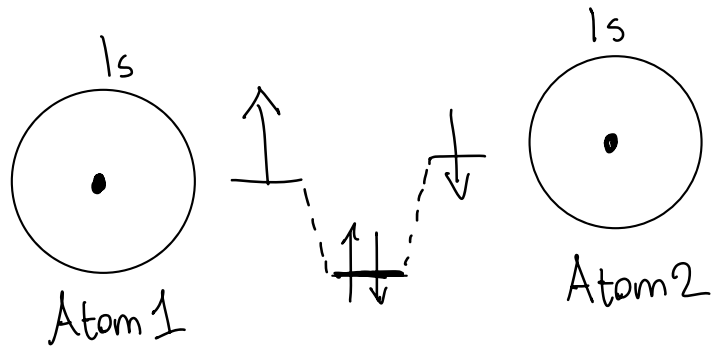


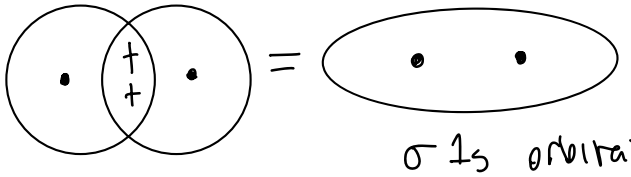
Bonding solution allows for a stable interatomic spacing a_0

Cloud picture:

ex: 2 Hydrogens bonding

H_2





σ 1s orbital

or