Wed. Sept. 25

* Today we will discuss the covalent bond

- Associated with insulators and semiconductors

- electrons are said to be "shared" between atoms which lowers energy state of electrons

- Simplistically, think of the atom as a "box" - electron has larger volume in which to move with two atoms

- analogy 1D box: (of length 'a')

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

- two H-atoms each donate 1 electron to bond

- for 1 electron, box is now ~2a

$$E_n = \frac{\hbar^2 \pi^2}{2m(2a)^2}$$ grand state

which is 1/4 the energy in 1 atom

- of course there are two electrons; if they have opposite spin, they both fall into the grand state

$$E_{bond} = \frac{\hbar^2 \pi^2}{2m(2a)^2}$$

- if electrons have opposite spin, one must be in the first excited state

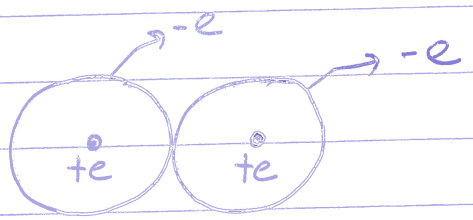
$$E_{anti\text{-}bond} = \frac{\hbar^2 \pi^2 2^2}{2m(2a)^2} \rightarrow \text{ex. state}$$

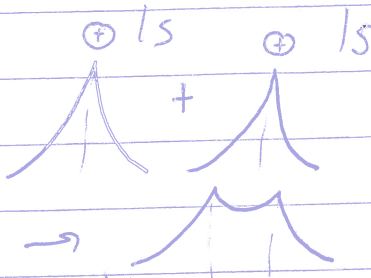
$$= \frac{\hbar^2 \pi^2}{2ma^2} \quad \text{(same as ground state in 1-atom)}$$

- we have ignored repulsion of protons & electrons via Coulomb force

- we will briefly discuss the "tight-binding" model → tight means orbitals are approximately atomic orbitals

- bring two H-atoms together so the orbitals begin to overlap





- for a single electron, the Hamiltonian

$$H = K + V_1 + V_2$$

where the e^- feels potential from the 2 protons

$$K = \frac{\vec{p}^2}{2m} \qquad + V_i \equiv \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}_i|}$$

where $\vec{R}_i \equiv$ location of protons

- One approach is the "linear combination of atomic orbitals" (LCAO)

- We choose a trial function

$$|\Psi\rangle = \phi_1 |1\rangle + \phi_2 |2\rangle$$

where $|1\rangle$ & $|2\rangle$ are tight-binding orbitals (atomic orbitals)

→

- the ground state energy is the same for independent atoms

$$(K + V_1)|1\rangle = \epsilon_0 |1\rangle$$

$$(K + V_2)|2\rangle = \epsilon_0 |2\rangle$$

where ϵ_0 is the ground state (for atomic orbital)

- for the molecule, the approximate S.E.

$$\sum_j H_{ij} \phi_j = E \phi_i$$

where $$H_{ij} = \langle i | H | j \rangle$$

- for our case, $i, j = 1, 2$ & our S.E

$$\begin{pmatrix} \epsilon_0 + V_{cross} & -t \\ -t^* & \epsilon_0 + V_{cross} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

$$= E \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

- which gives us $E_\pm = \epsilon_0 + V_{cross} \pm t$

- E_- is the bonding energy while E_+ is anti-bonding

- What is the interpretation?

- the energy of an electron is shifted by V_{cross} when 2nd proton is added

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

$$= \langle 2|V_1|2\rangle$$

i.e. the potential felt by orbital 1 by effects of proton 2 & vice versa

- We also have off-diagonal terms which allows one orbital to "hop" to the other as described by the time-dep. S.E.

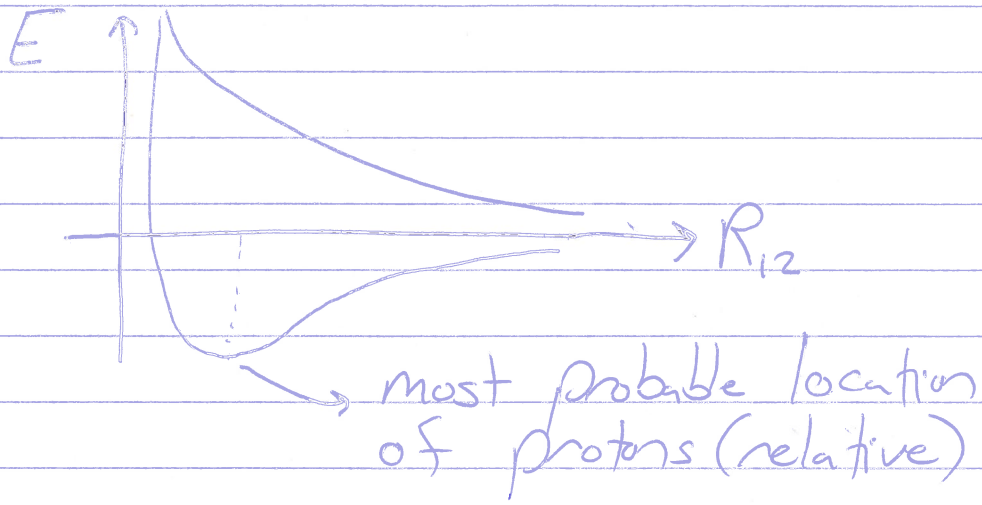
- the "hopping term"

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

$$\text{Note } t^* = -\langle 2|V_1|1\rangle$$

→

- although we have not derived this function, we plot what the actual energy vs. distance looks like



- thermal fluctuations around energy minimum are biased toward longer separation (well is steep toward short separation & shallow toward longer)

- this is the origin of thermal expansion

- Some notes about covalently bonded solids:

(1) bonds are strong - making material strong but brittle
(2) not usually conductors
(3) lower density - atoms do not fill space like metals (not close packed)