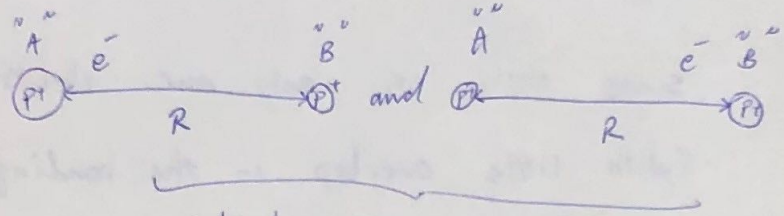
L 12: review

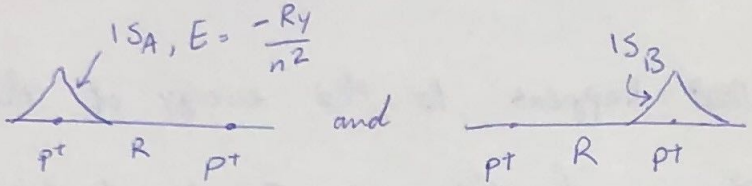
H_2^+, the simplest molecule

when nuclei are far apart,

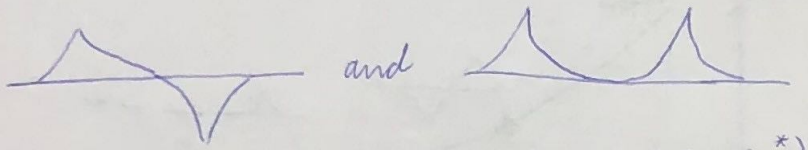
CM:



QM:



Linear combinations are also solutions of Schrödinger equation



$1S_A - 1S_B\ (\sigma)$ $\qquad$ $1S_A + 1S_B (\sigma^*)$

$\Rightarrow$ "Schrödinger cat" states

(QUANTUM SUPERPOSITION)

* in H_2^+, σ orbital $(1S_A + 1S_B)$, the electron occupies a superposition of states, that is, it occupies both nuclei simultaneously.

today: If two wavefunctions for an electron have the same energy, their linear combination also is an eigenstate:

$$\left.\begin{aligned} \hat{H}\,\psi_A(x) &= E\,\psi_A(x) \\ \hat{H}\,\psi_B(x) &= E\,\psi_B(x) \end{aligned}\right\} \Rightarrow$$

(one e^-)

$$\begin{cases} \hat{H}\left(\psi_A(x) + \psi_B(x)\right) = E\left(\psi_A + \psi_B\right) \\ \hat{H}\left(\psi_A(x) - \psi_B(x)\right) = E\left(\psi_A - \psi_B\right) \end{cases}$$

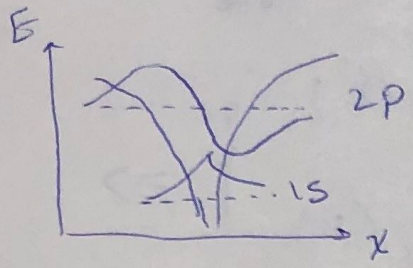
* for an asymmetric H - X bond, the relative localization of the electron around the nuclei can be approximated by a coefficient (α) that is proportional to the electronegativity of X:

$$\sigma = \psi_H + \alpha\,\psi_X$$

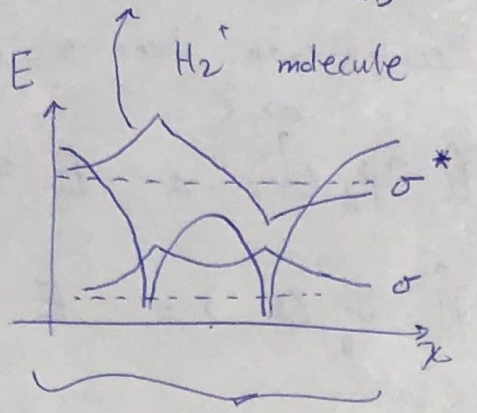
why is bonding explained in QM and not in CM?

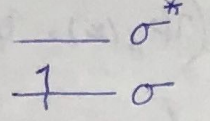
$V(x) \sim -\frac{e^2}{r_{eA}} - \frac{e^2}{r_{eB}}$

H atom

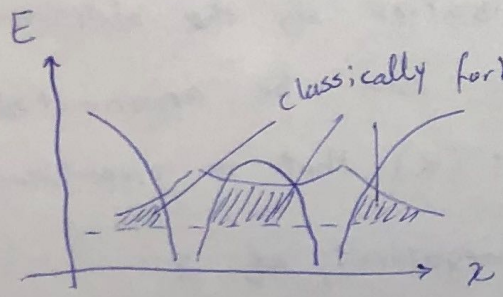


H_2^+ molecule





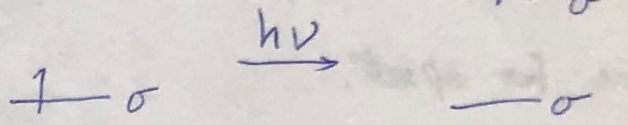
* note the similarity (in number of wiggles) between 1s / 2p orbitals in H atom and σ/σ^* orbitals in H_2^+.



* the bonding region is the tunneling region. ($K < 0$; $E < V$)

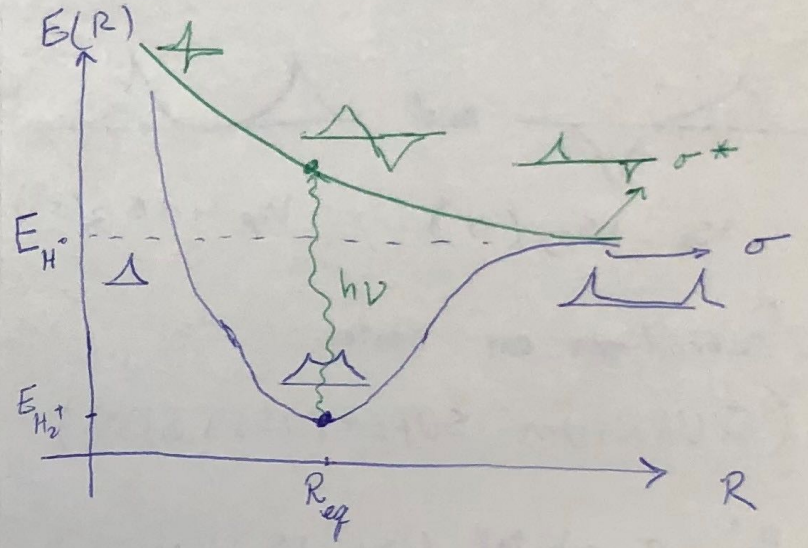
* the wavefunction is the "schrödinger cat" wavefunction

exciting H_2^+ with light...



since there is only one electron in σ^* (with little overlap in the bonding region) the bond will break.

What happens to the energy of the e^- as a function of R (bond distance):



* increasing R from R_{eq}, raises energy due to lower bonding energy (overlap goes down)

* decreasing R from R_{eq} raises the energy due to coulomb repulsion of nuclei

* the energy difference between σ and σ^* is a result of difference between orbital overlap between nuclei. At large R

$E_\sigma \approx E_{\sigma^*}$, but decreasing R causes

$E_\sigma - E_{\sigma^*} = h\nu$ to gradually increase.