Making a chemical bond: simplest molecule

H_2+

Born-Oppenheimer Hamiltonian:

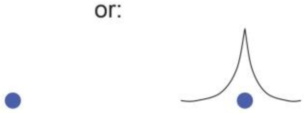
$$H = -\frac{\hbar^2}{2m}\vec{\nabla}_r^2 - \frac{e^2}{\left|\vec{r}-\vec{R}_L\right|} - \frac{e^2}{\left|\vec{r}-\vec{R}_R\right|} + \frac{e^2}{\left|\vec{R}_R-\vec{R}_L\right|}$$

H_2+ wavefunctions

If protons are far away

$$\psi_{1s}\left(\vec{r}-\vec{R}_L\right) = \psi_L$$

or:



$$\psi_{1s}\left(\vec{r}-\vec{R}_R\right) = \psi_R$$

Protons are nearby

Molecular orbital: linear combination of atomic orbitals (LCAO) - Approximation

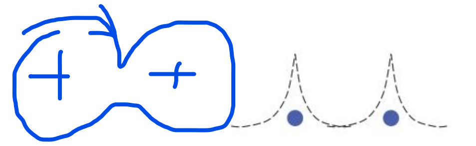
$$\psi_{MO} = a_L\psi_L + a_R\psi_R$$

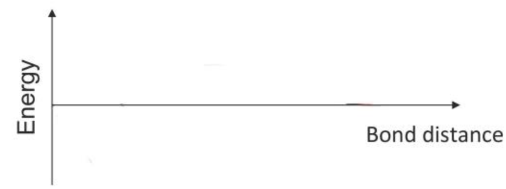
H_2+ intuitive solution

Symmetric:

Potential energy: electrons spend less time at the protons

Kinetic energy: smaller gradients

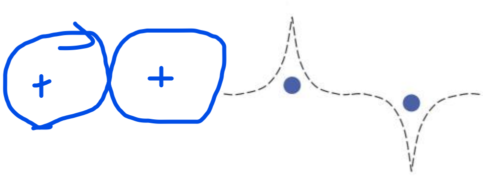




Anti-symmetric:

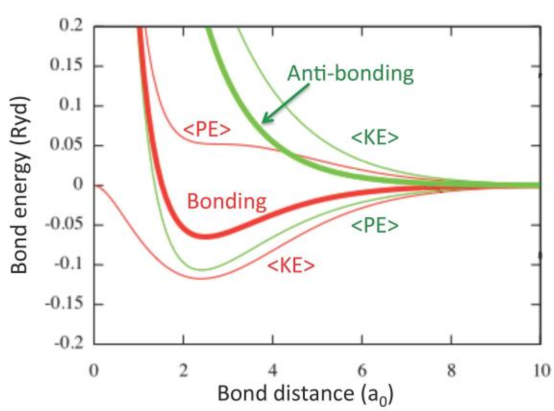
Potential energy: electrons spend more time at the protons

Kinetic energy: larger gradients

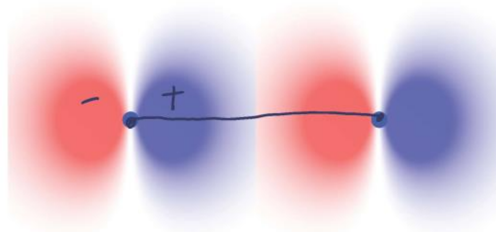


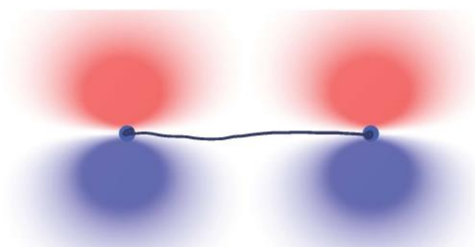
Energy contributions

Analytical solution for H_2+ can be found using 1s hydrogen atomic orbitals



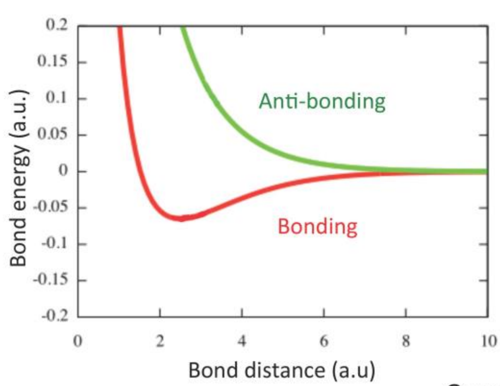
Molecular states with p orbitals





H_2 and He_2 molecules

We can use the H_2+ solution to obtain a qualitative picture of diatomic H and He



H_2 molecule

He_2 molecule

Quantitative predictions require:

- Treating electron-electron interactions
- Exchange interactions (anti-symmetric nature of the wavefunction)