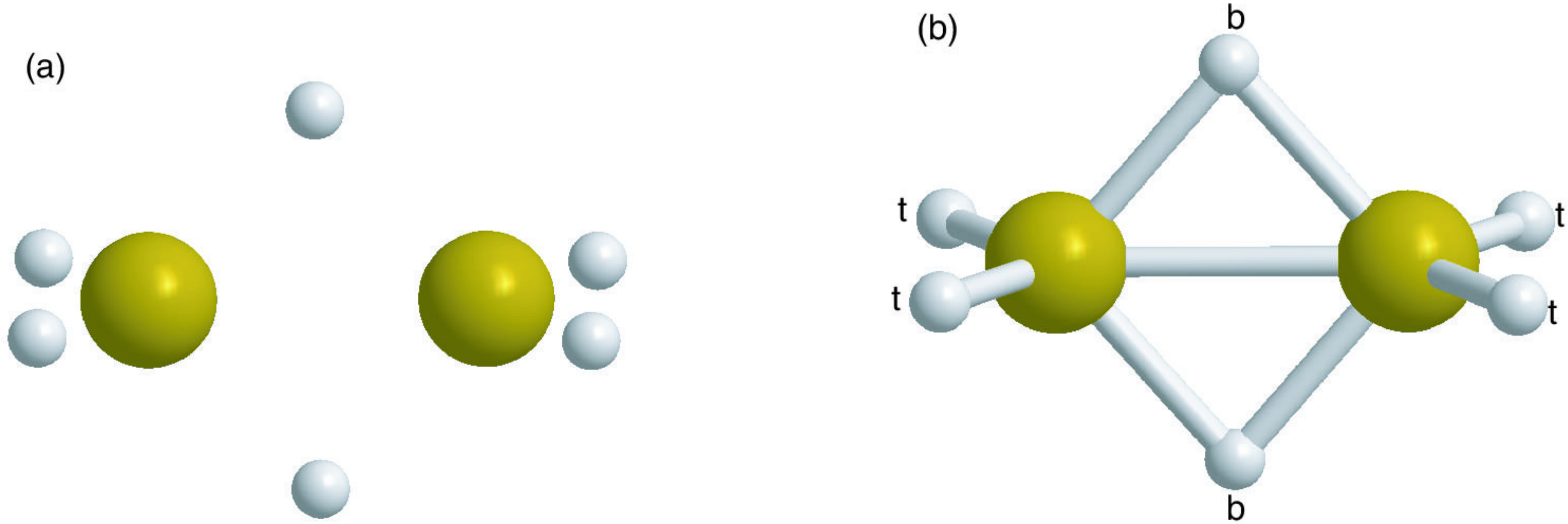
Where are the Bonds?



B-H distances 117 pm and 132 pm; B-B distance 175 pm

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 280]

THE NATURE OF THE CHEMICAL BOND. APPLICATION OF RESULTS OBTAINED FROM THE QUANTUM MECHANICS AND FROM A THEORY OF PARAMAGNETIC SUSCEPTIBILITY TO THE STRUCTURE OF MOLECULES

BY LINUS PAULING

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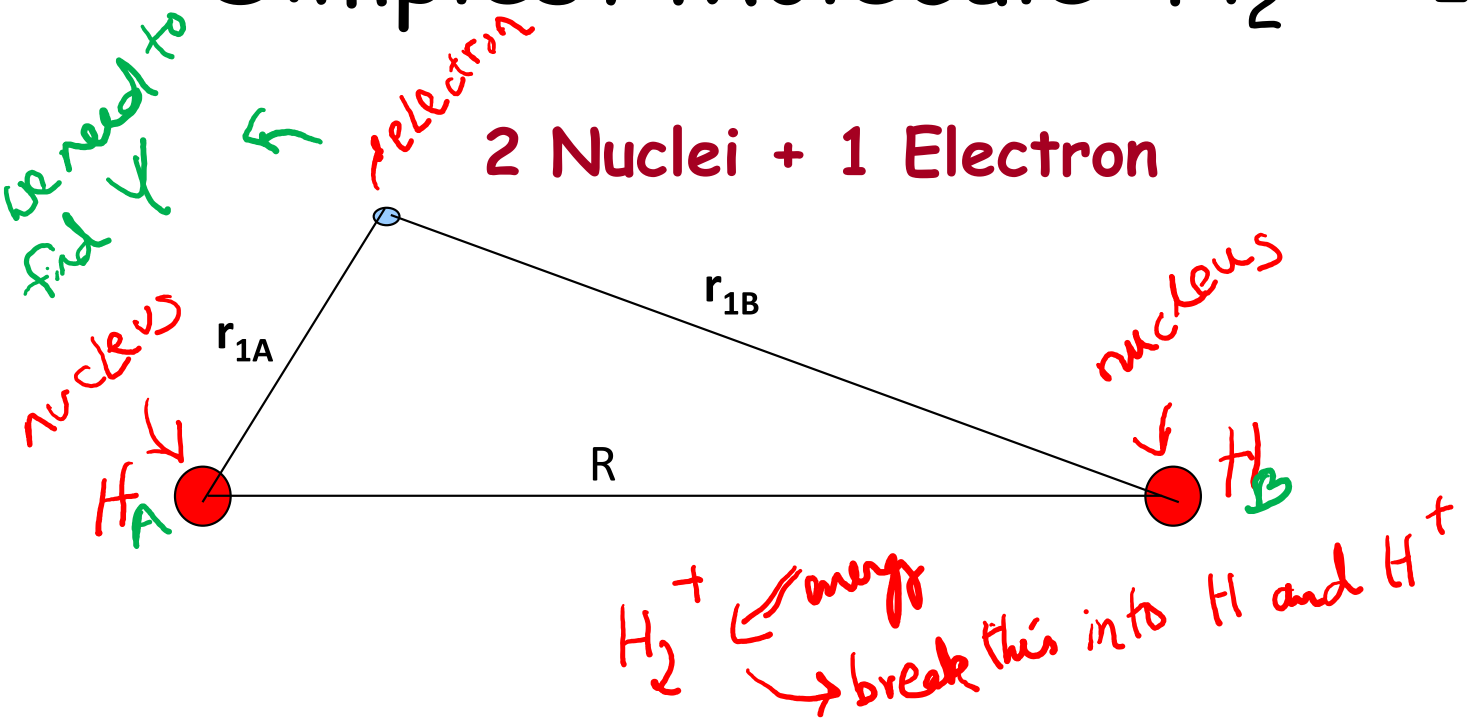
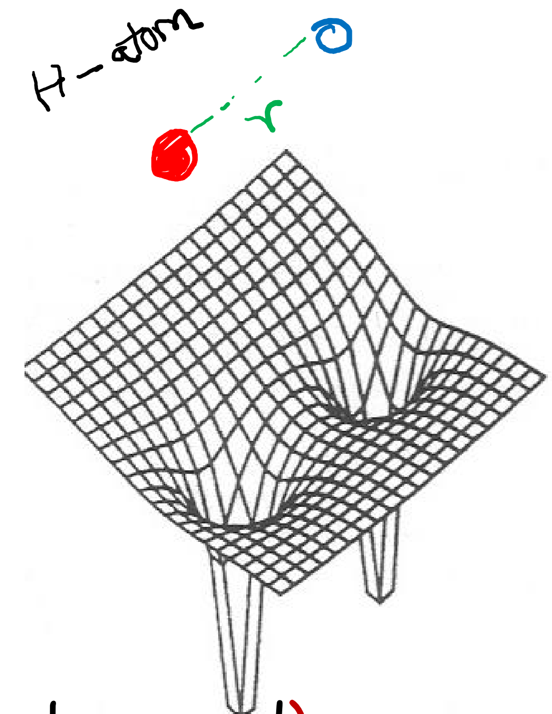
Simplest Molecule: H_2^+ - 1electron





H_2^+ Molecule Ion Exists, Stable (Experimentally observed)
Bond length ~ 1Å ($2a_0$) ; Bond Energy ~ 270 kJ/mole ($0.1E_H$)

One more electron complicate matters to great extent!
Just like many electron atoms – So, we need to build a Model with H_2^+ and get insight into chemical bonding

Then extend model for other multi-electronic molecules

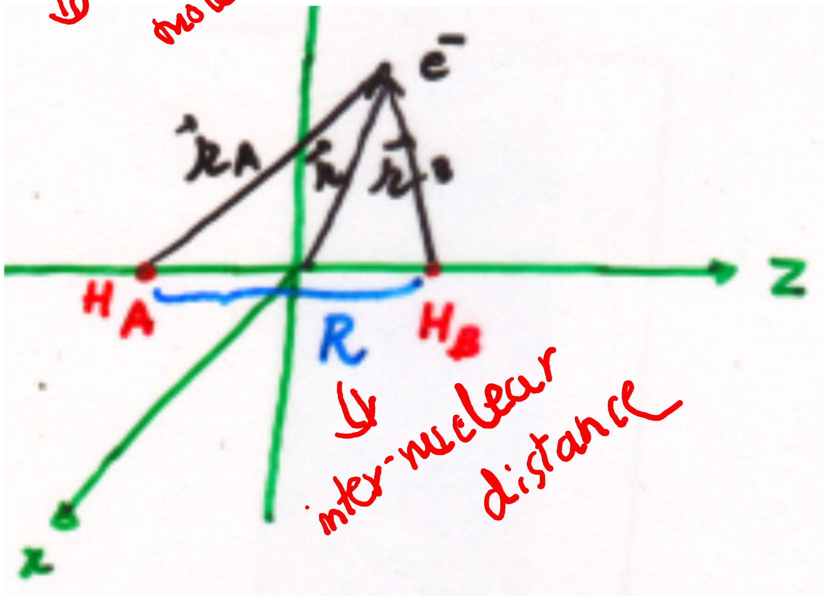
Understanding Chemical Bonding

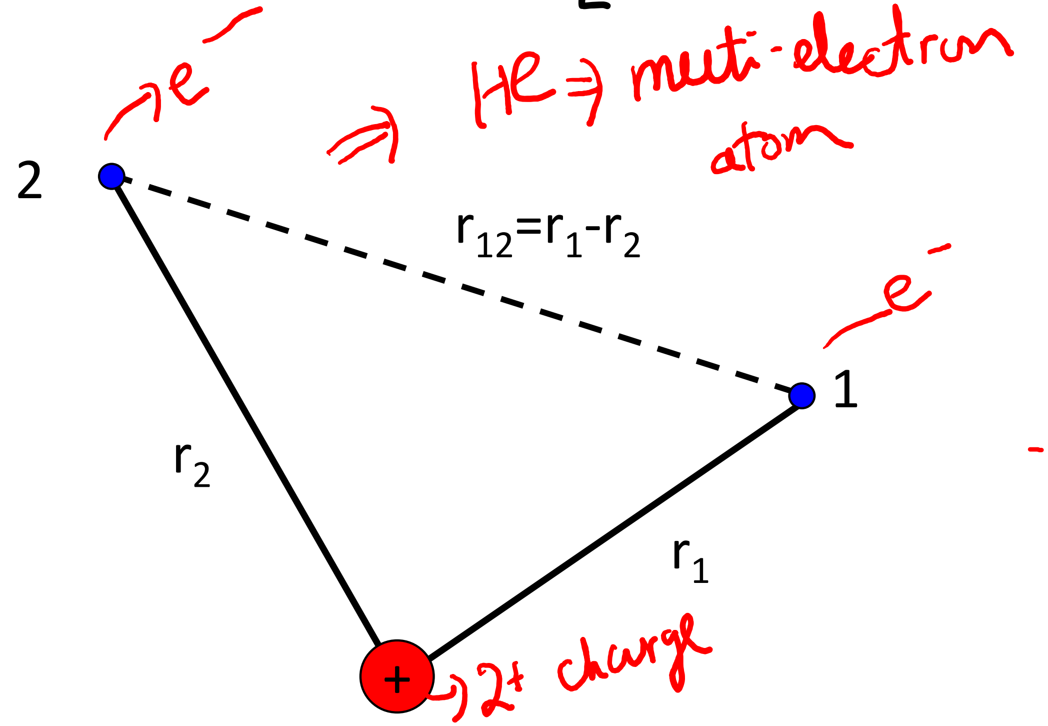
A theory is required which would teach us:

1. Why sharing leads to a lowering of energy
2. Energy of a particular bond is related to the nature of sharing
3. Why sharing might not be equal between atoms

Simplest Molecules: H_2^+

H_2^+: multi-nuclear molecule





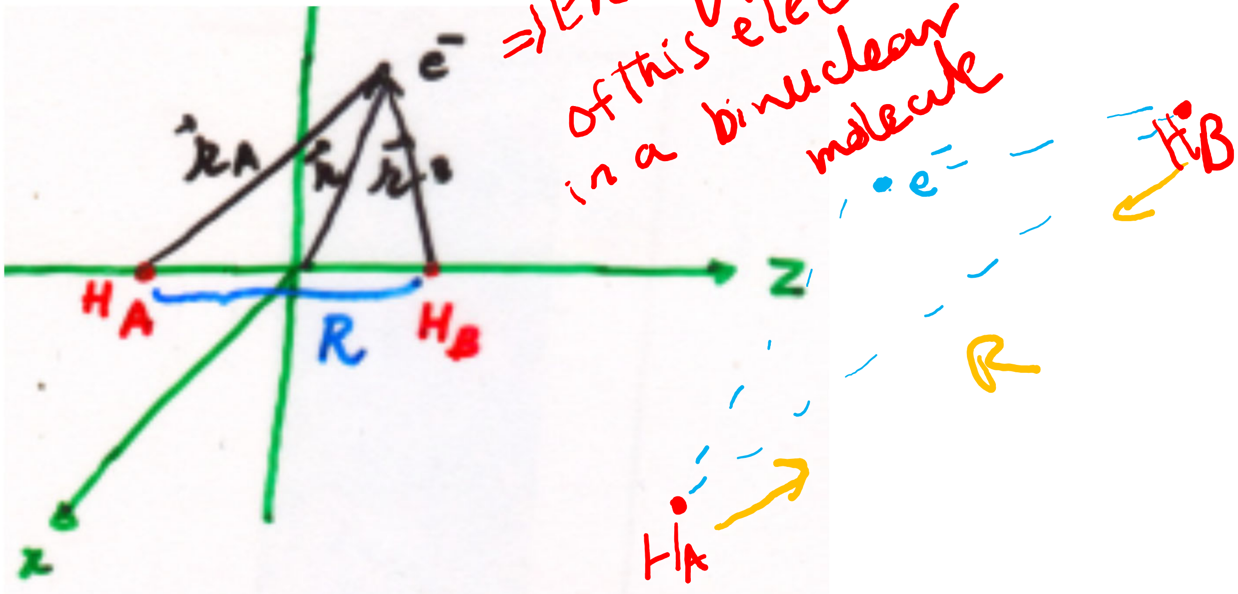
Dissociating this molecule to H and H^+ requires 256 kJ/mol or 61 kcal/mol

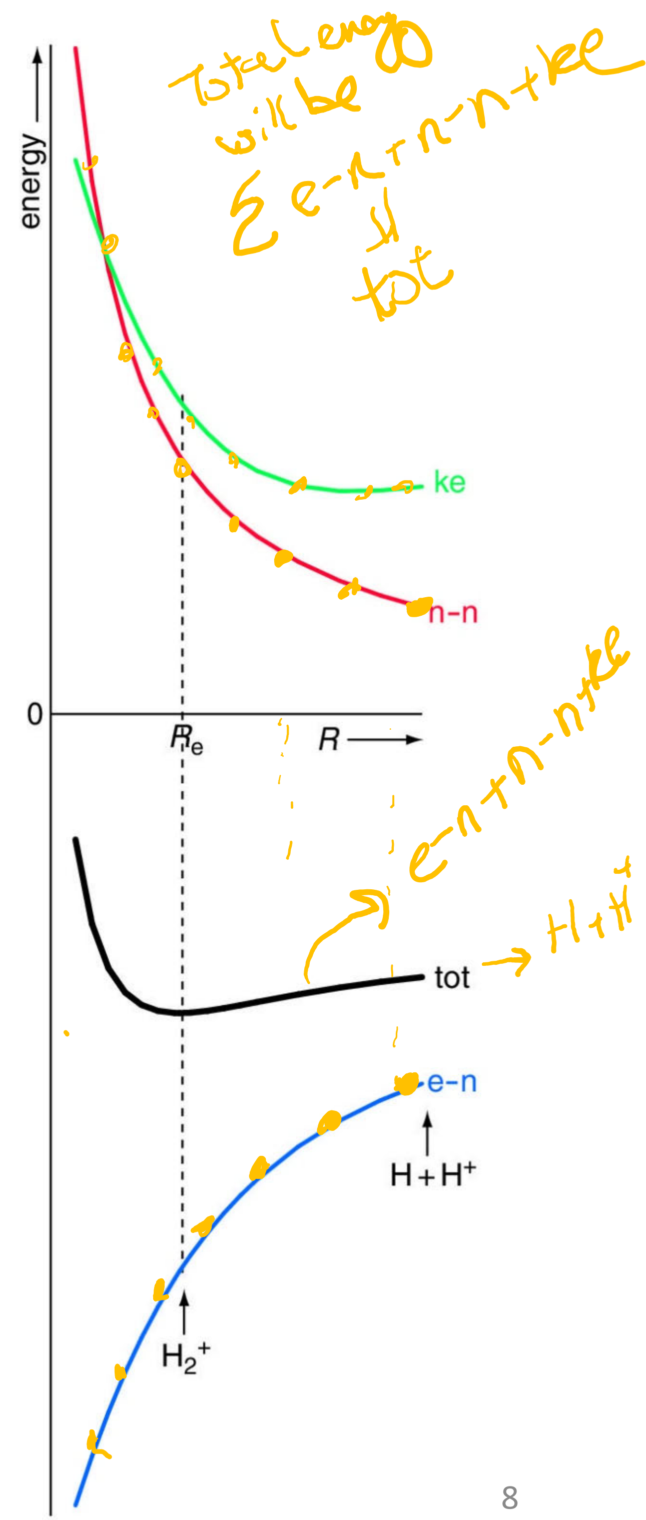
Bond Dissociation energy

$$BDE(H_2^+) = E(H_2^+) - E(H + H^+)$$

Simplest Molecules: H_2^+

=> Energy of this electron in a binuclear molecule





Potential Energy

(i) Favourable interaction of electron and nucleus which is dependent on R

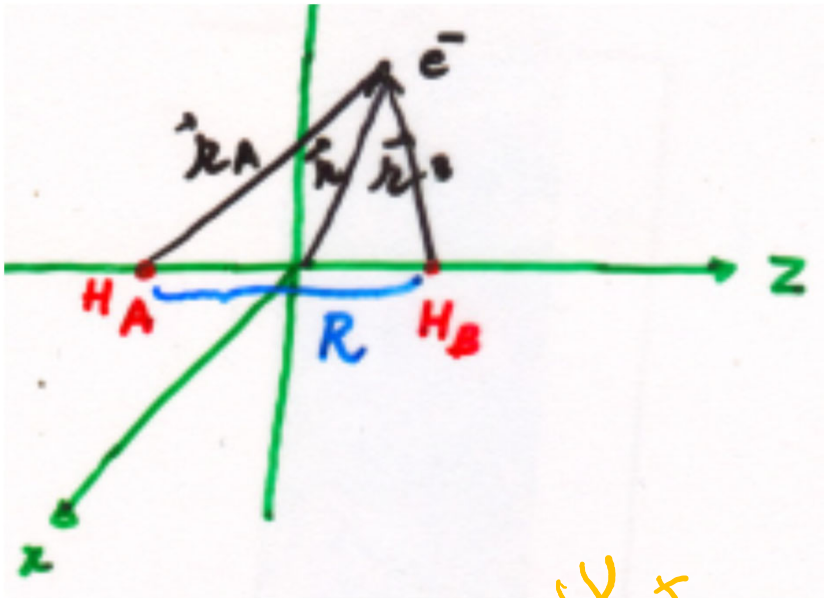
(ii) Unfavourable interaction between nucleus (1/R)

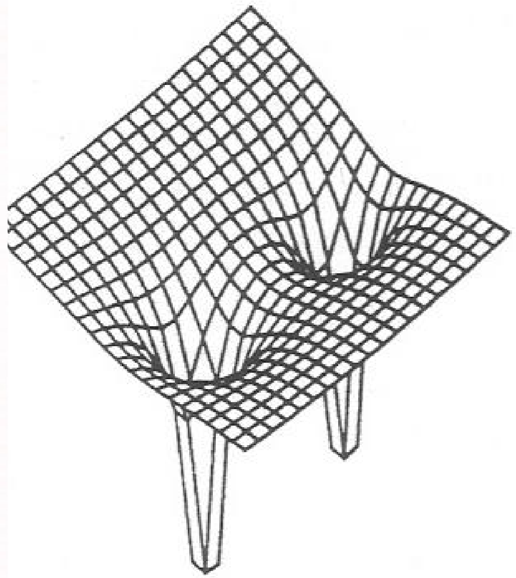
Kinetic Energy

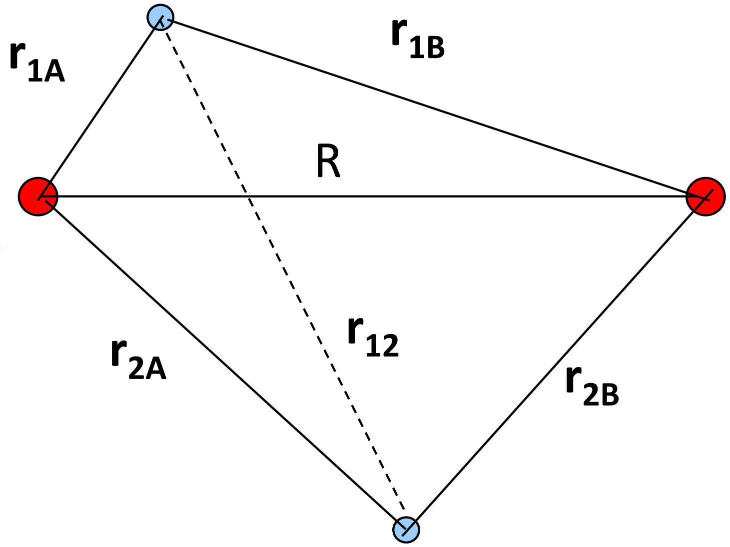
(i) KE of electron associated with its motion about both nucleus

The total energy is summation of these three terms and the minimum at a particular value of R is called equilibrium separator R_e

Simplest Molecules: H_2^+ and H_2







$\Psi_{H_2^+}$

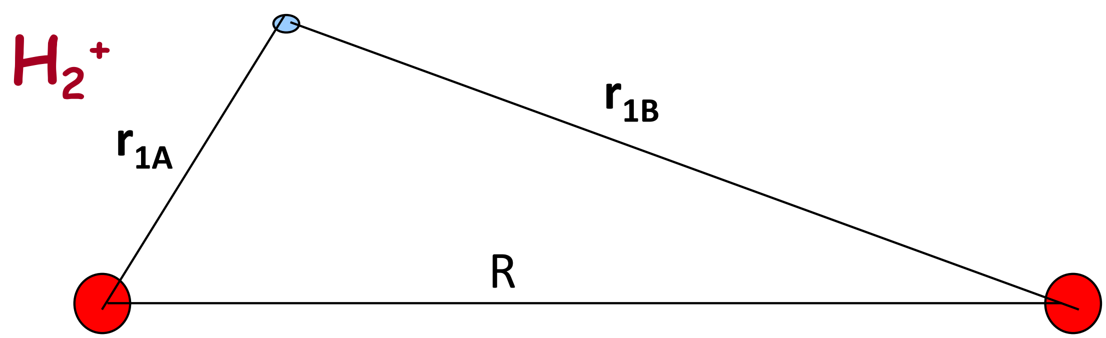
TISE for H_2^+

$$\hat{H}_{H_2^+}(\vec{r},R)\Psi_{H_2^+}(\vec{r},R) = E_{H_2^+}(\vec{r},R)\Psi_{H_2^+}(\vec{r},R)$$

Very difficult, but possible to solve TISE under elliptical polar coordinates at one R. Solve for energy at various R

Molecular Orbital Theory

Analogous to the atomic orbitals, wavefunctions which describe electrons in a molecule are called Molecular Orbital (MO)
MO: Polycentric 1-electron function: spreads through the molecule



One way of constructing the molecular orbitals is to add together atomic orbital wavefunctions which are located at various atoms of the molecule: Linear Combination of Atomic Orbitals (LCAO)