

internuclear distance

Four ingredients so far to calculate electronic potential energy surface $V(R_i)$ of molecules:

1) ϕ_i , the one-electron MO or VB basis functions = linear combinations of atomic orbitals φ_i :

$$\phi_i(\vec{r}_i) = \sum_m c_m \varphi_m(\vec{r}_i)$$

2) Ψ_n , the many-electron basis functions = antisymmetric products of the ϕ_i :

$$\Psi_n(\vec{r}_1, \vec{r}_2 \dots) = \hat{A}_n \prod_{i=1}^N \phi_i(\vec{r}_i)$$

3) The electronic Hamiltonian :

$$\hat{H} = \sum_j \left(\frac{\vec{p}_j^2}{2m_e} - \sum_n \frac{e^2 Z_n}{4\pi\epsilon_0 r_{jn}} \right) + \sum_{i,j>i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{i,j>i} \frac{e^2 Z_n Z_m}{4\pi\epsilon_0 R_{nm}}$$

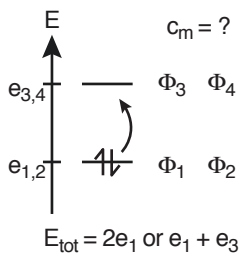
$$= \sum_j \hat{h}_j + \sum_{i,j>i} \hat{V}_{ij} + V_{nuc}$$

1-electron energy, e-e repulsion, nuclear repulsion

4) Variational principle: systematically vary c_m to get lowest energy, called...

The Hartree Fock energy

What do you get when you calculate the matrix element of the big messy antisymmetric multi-electron wavefunction with the Hamiltonian, or $\langle \Psi_n | H | \Psi_n \rangle = ?$



Orbital energy vs. total energy

One electron orbitals ϕ or φ vs. total (multielectron) wavefunction Ψ

For 2 electrons,

$$E_{HF} = h_1 + h_2 + J_{12} - K_{12}$$

For N electrons,

$$E_{HF} = \sum_{i=1}^N h_i + \sum_{i,j \neq i}^N J_{ij} - \sum_{i,j \neq i}^N K_{ij}$$

antimmetry = Pauli exclusion

exchange force } only in attractive QM