Quantum Mechanics Basics

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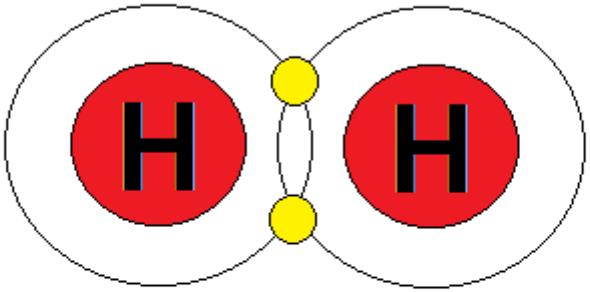
Thank you to George and the MERCURY Consortium!!

Outline

- Some basics of electronic structure
  - Schrödinger equation
  - Hartree-Fock and basis sets
  - Multi-configurational method
  - Electron correlation and methods
  - The “Holy Grail”

Brief introduction to Schrödinger Equation

$$\hat{H}\Psi = E_{Exact}\Psi \qquad \hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee}$$



Assume nuclei are massive compared to electrons (Born-Oppenheimer)

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee} \Rightarrow \hat{H}_{el} = \hat{V}_{Ne} + \hat{T}_e + \hat{V}_{ee}$$

Brief introduction to Schrödinger Equation

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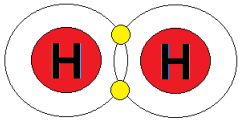
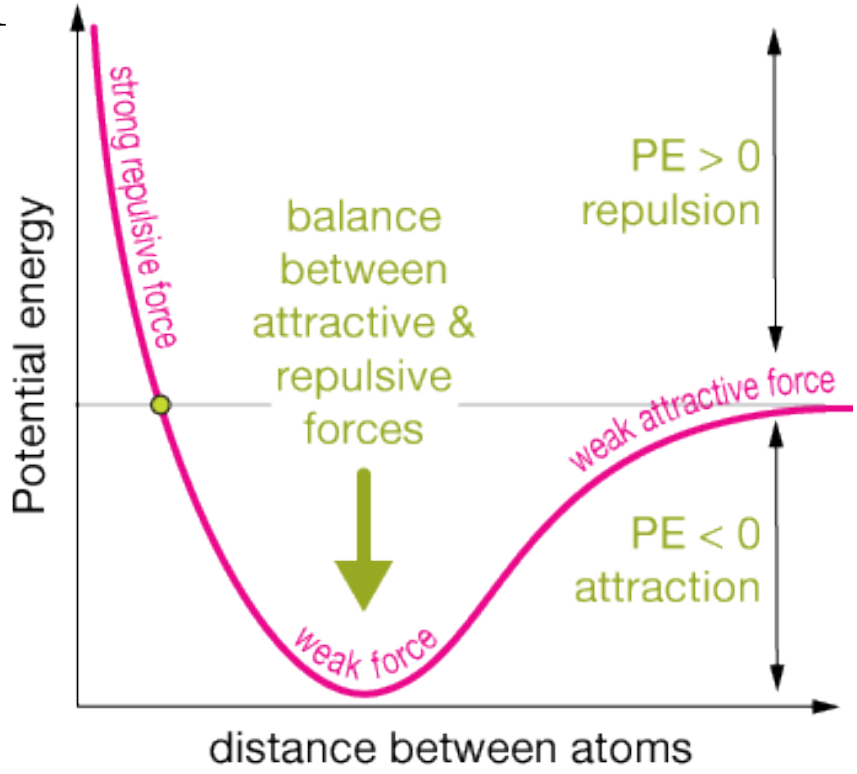




http://xaktly.com/ConservationThermo.html

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee} \Rightarrow \hat{H}_{el} = \hat{V}_{Ne} + \hat{T}_e + \hat{V}_{ee}$$

Brief introduction to Hartree-Fock (HF) or Self Consistent Field (SCF)

$$\hat{H}\Psi = E_{Exact}\Psi \qquad \hat{H}_{el} = \hat{V}_{Ne} + \hat{T}_e + \hat{V}_{ee}$$

Simplest antisymmetric wavefunction is a single determinant

$$|\Psi_0\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}$$

N = number of electrons

For example:

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) \\ \chi_1(x_2) & \chi_2(x_2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left(\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\right)$$

Brief introduction to Hartree-Fock (HF) or Self Consistent Field (SCF)

$$\hat{H}_{el} = \hat{V}_{Ne} + \hat{T}_e + \hat{V}_{ee} \qquad |\Psi_0\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}$$

Use the variational principle to find the lowest energy solution

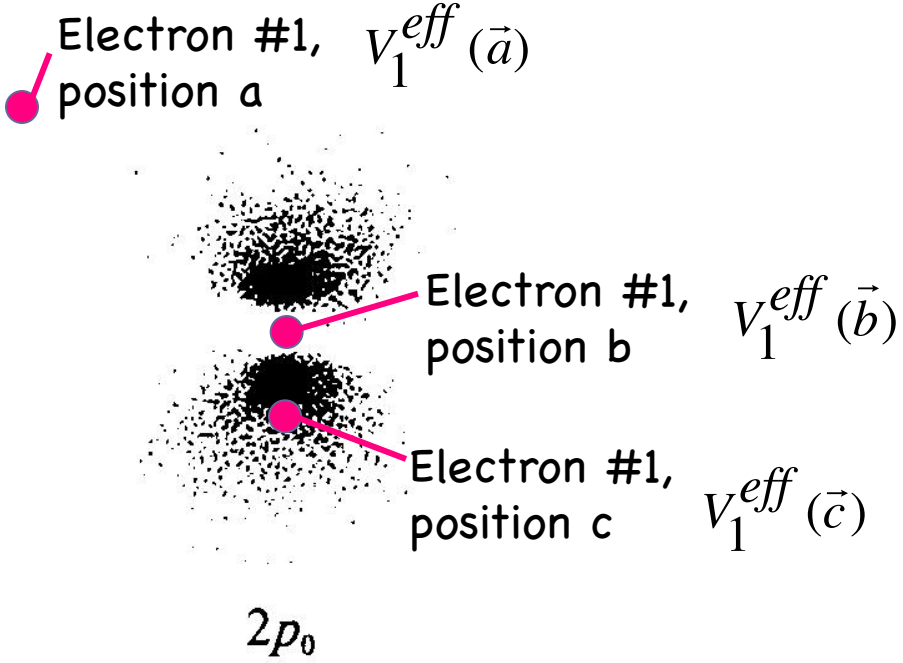
$$E_0 = \langle \Psi_0 | \hat{H}_{el} | \Psi_0 \rangle = \int \Psi_0^* \hat{H}_{el} \Psi_0 d\tau$$

This leads to the Hartree-Fock equations:

$$\hat{f}(x_1)\chi_i(x_1) = \varepsilon_i \chi_i(x_1)$$

$$FC = SC\varepsilon \quad \Longrightarrow \quad E_{HF}$$

Effective potential



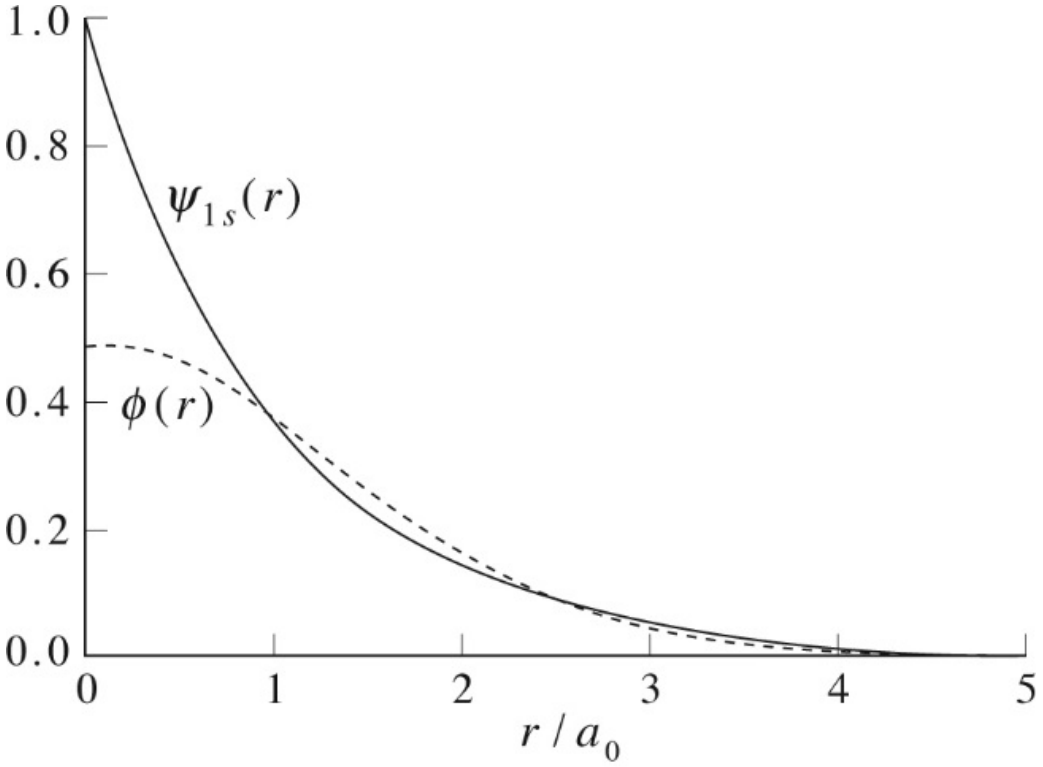
Probability (charge) density of electron #2 is the cloudy stuff in black

At a position from the nucleus given by r_1, electron #1 has a potential energy due to its Coulombic interaction with electron #2. This potential energy can be ***approximated*** from the ***average*** electric field set up by electron #2. It's only an approximation because both electrons are actually moving simultaneously, and their motion is *correlated*.

Basis sets

$$\phi(r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$



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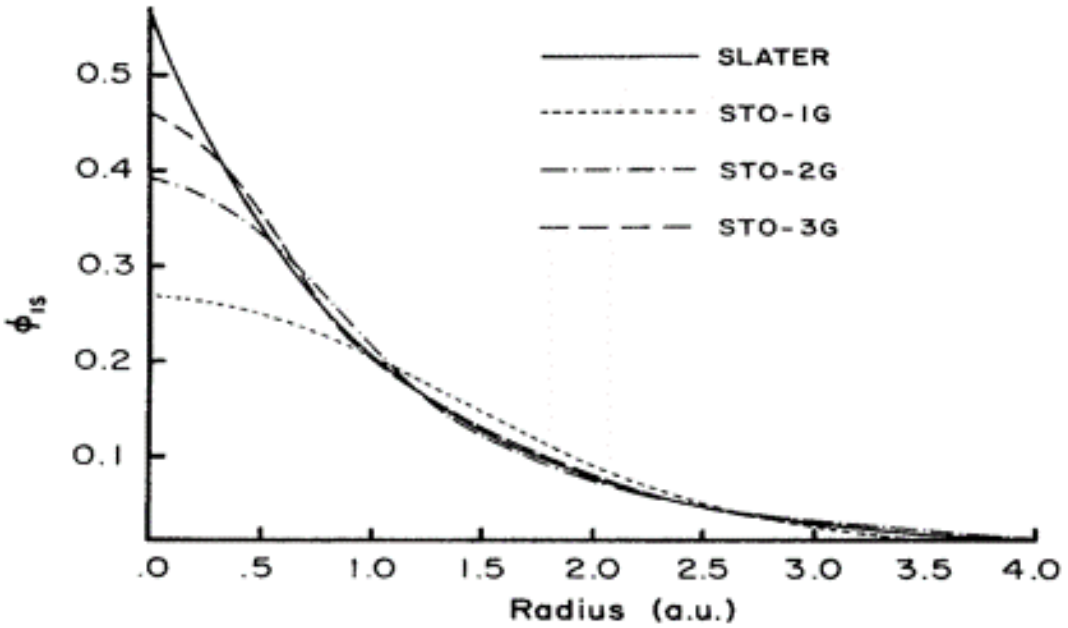


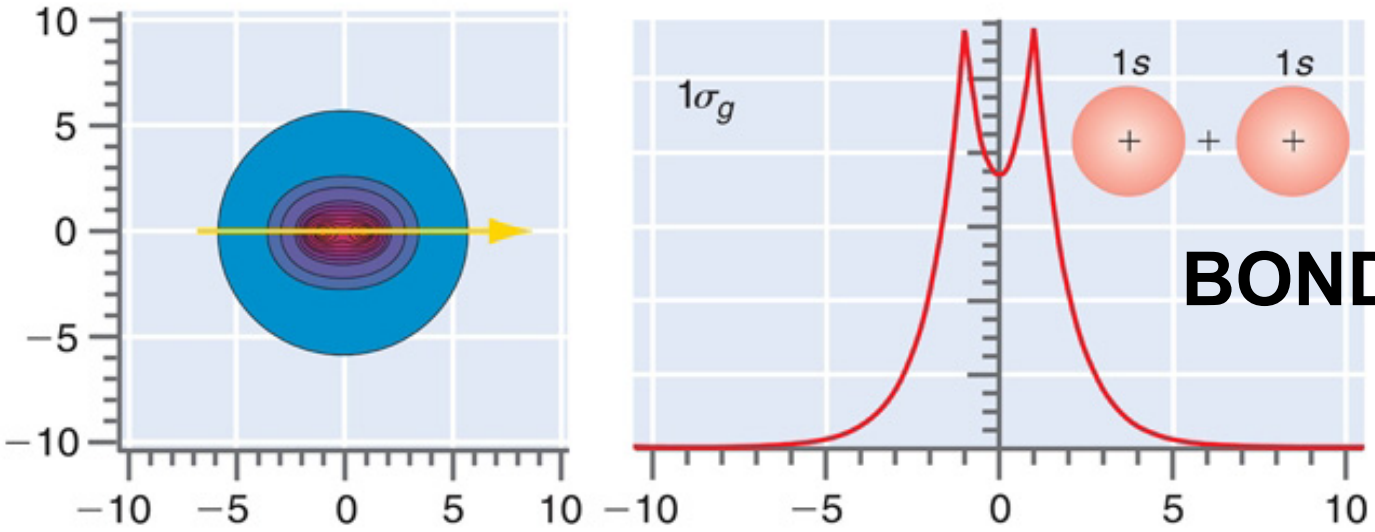
Szabo and Ostlund, Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory

Pople:
3-21G(d)
6-31G(d)
6-311++G(d,p)

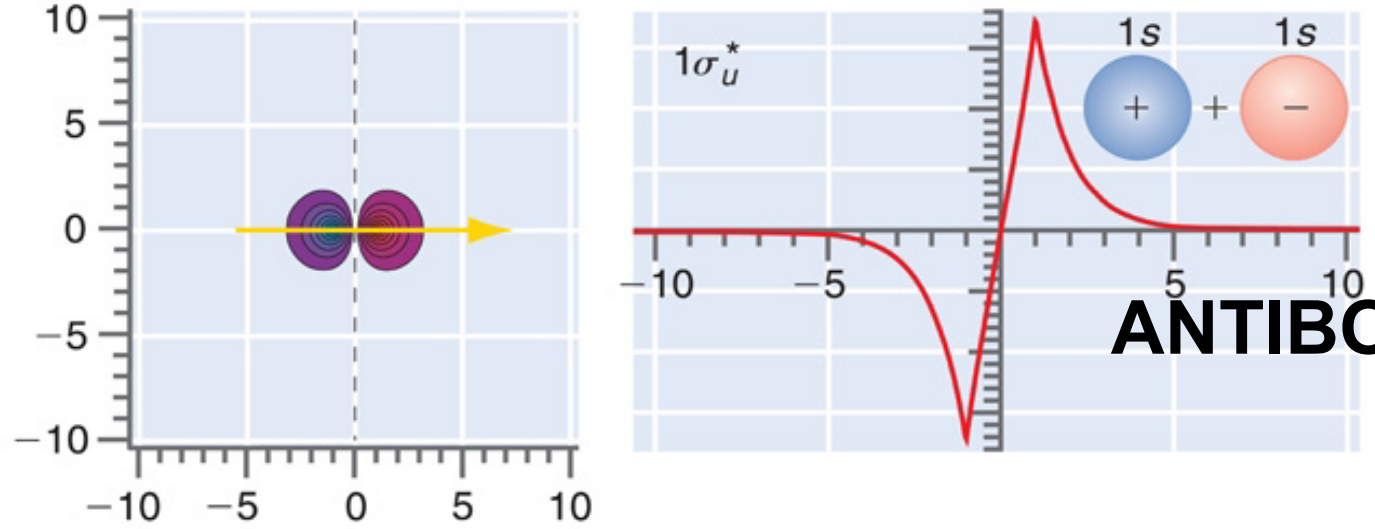
Dunning:
cc-pVDZ
cc-pVTZ
aug-cc-pVTZ

https://www.basissetexchange.org/

Linear Combination of Atomic Orbitals for Molecular Orbitals (LCAO-MO)

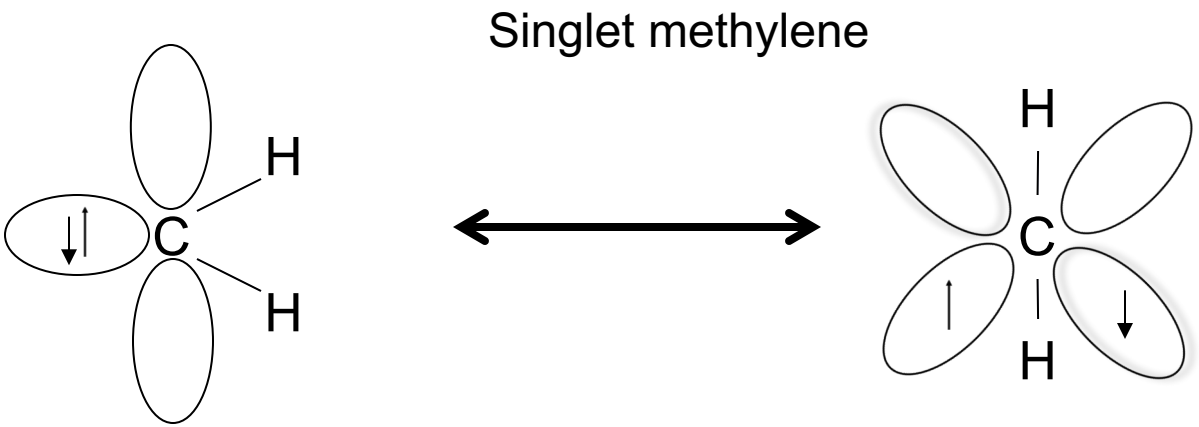


BONDING



ANTIBONDING

Brief introduction to Multi-configurational Self Consistent Field (MCSCF)



$$\left|\Psi_{MCSCF}\right\rangle = \sum_{I} c_I \left|\Psi_I\right\rangle$$

"The Construction and Interpretation of MCSCF Wavefunctions", M.W. Schmidt and M.S. Gordon, *Annu. Rev. Phys. Chem.* 1998, **49**, 233-266

Problem with HF and MCSCF

Misses what we call correlation energy

$$E_{corr} = E_{exact} - E_{HF/MCSCF}$$

Brief introduction to Configuration Interaction (CI)

$$\left|\Psi\right\rangle = c_0\left|\Psi_0\right\rangle + \sum_{i,a} c_i^a \left|\Psi_i^a\right\rangle + \sum_{\substack{i<j \\ a<b}} c_{ij}^{ab} \left|\Psi_{ij}^{ab}\right\rangle$$

HF or MCSCF CIS CISD

$$+ \sum_{\substack{i<j<k \\ a<b<c}} c_{ijk}^{abc} \left|\Psi_{ijk}^{abc}\right\rangle + \cdots$$

CISDT

Full-CI

$$\binom{M}{N} = \frac{M!}{N!(M-N)!}$$

$$\binom{N}{n}\binom{M-N}{n}$$

M = # of orbitals
N = number of electrons
n = level of excitation

Brief introduction to Coupled Cluster (CC)

$$\left|\Psi_{CC}\right\rangle = e^{\hat{T}}\left|\Psi_0\right\rangle,$$

$$= \left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots\right)\left|\Psi_0\right\rangle$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$$

$$\hat{T}_1\left|\Psi_0\right\rangle = \sum_{i,a} t_i^a \Psi_i^a, \quad \longleftarrow \text{CCS}$$

$$\hat{T}_2\left|\Psi_0\right\rangle = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} \Psi_{ij}^{ab} \quad \longleftarrow \text{CCSD}$$

Scales as N^5, N^6, ..

Brief introduction to Density Functional Theory (DFT)

HF: $E_0 = \langle \Psi_0 | \hat{H}_{el} | \Psi_0 \rangle = \int \Psi_0^* \hat{H}_{el} \Psi_0 d\tau \qquad \hat{H}_{el} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee}$

DFT: $E[\rho] = E_{Ne}[\rho] + T_e[\rho] + E_{ee}[\rho] = \int \rho(\vec{r}) \hat{V}_{Ne}(\vec{r}) d\vec{r} + F_{HK}[\rho]$

$$F_{HK}[\rho] = T_e[\rho] + E_{ee}[\rho]$$

All of the work goes here!!

https://tddft.org/programs/libxc/

Scales as N^3

The Holy Grail

Thank you!

Questions?