

6.1: Ab Initio Philosophy

ab initio: from the beginning

Hartree-Fock used to understand more complicated theories

electron correlation energy

$$E_{\text{corr}} = E - E_{\text{HF}} \quad E: \text{"true" energy}$$

6.2: Basis Sets

6.2.1: Functional Forms

Gaussian-type Orbitals (GTO):

$$\phi(x, y, z; \alpha, i, j, k) = \left(\frac{2\alpha}{\pi} \right)^{3/4} \left[\frac{(8\alpha)^{i+j+k} i! j! k!}{(2i)! (2j)! (2k)!} \right]^{1/2} x^i y^j z^k e^{-\alpha(x^2 + y^2 + z^2)}$$

α : controls width of GTO

i, j, k : non-negative integers that dictate nature of orbitals in cartesian sense.

$i, j, k = 0$: s-type GTO

$i+j+k=1$: p_x, p_y, p_z -type GTO

6.2.2: Contracted Gaussian Functions

linear combinations of GTOs to, accurately as possible, an STO

$$\phi(x, y, z; \{\alpha\}, i, j, k) = \sum_{a=1}^M c_a \phi(x, y, z; \alpha_a, i, j, k)$$

c : contraction coefficients.

6.2.3: Single- ζ , Multiple- ζ , and Split-Valence

decontraction of basis set increases flexibility

create 2 basis function for orbitals

1. contraction of 2 Gaussians

2. 3rd Gaussian.

6.2.4: Polarization Functions



s & p functions centered on atoms do not provide enough flexibility to describe wave function for pyramidal geometry.

molecular orbitals require more flexibility.

added in the form of basis functions corresponding to one quantum # higher angular momentum than valence orbitals.
aka floating Gaussian orbitals (FLOGOs)

6.2.5: Diffuse Functions

Highest energy MOs of anions & highly excited electronic states are more spatially diffuse.

Errors occur when basis set is not flexible enough to localize far electrons.

standard basis sets are "augmented" to accommodate "far-away" electrons

Absolutely required to calculate acidities and electron affinities.

6.2.6: The HF Limit

HF Limit: • Solution of HF equations w/ infinite basis set.
• practically impossible

Use similar concept to correct for basis-set incompleteness

6.2.7: Effective Core Potentials

core electrons can be replaced with previously defined function to reduce # elements.

6.2.8: Sources.

good source has a lot of basis sets with references.

best basis set: the bigger the better.

use results from other simulations and compare them

8: Density Functional Theory

8.1: Theoretical Motivation

8.1.1: Philosophy

$$N = \int \rho(r) dr$$

N : # electrons

ρ : electron density

$$\left. \frac{\partial \bar{\rho}(r_A)}{\partial r_A} \right|_{r_A=0} = -2Z_A \rho(r_A)$$

Z_A : atomic #

r_A : radial distance

$\bar{\rho}$ is spherically averaged density

8.1.2: Early Approximations

Energy is separable into kinetic & potential

$$\text{potential energy} \begin{cases} V_{ne}[\rho(r)] = \sum_K^{\text{nuclei}} \int \frac{Z_K}{|r-r_K|} \rho(r) dr & \text{attraction between nuclei \& electron density} \\ V_{ee}[\rho(r)] = \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|} dr_1 dr_2 & \text{self-repulsion of electron density} \end{cases}$$

$$\text{kinetic energy } T_{\text{ueg}}[\rho(r)] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(r) dr$$

8.2: Rigorous Foundation

8.2.1: The Hohenberg-Kohn Existence Theorem

electrons interact with each other and an external potential
external potential is uniformly distributed positive charge.

ground state of any interacting many particle system with a given fixed inner particle interaction is a unique functional of the electron density.

8.2.2: The Hohenberg-Kohn Variational Theorem

Density obeys a variational principle

$$\langle \Psi_{\text{rand}} | H_{\text{rand}} | \Psi_{\text{rand}} \rangle = E_{\text{rand}} \geq E_0$$

8.3: Kohn-Sham Self-consistent Field Methodology

Simplify system by creating a "fictitious" system of non-interacting electrons and make their overall ground-state density the same as a real system's.

$$E[\rho(r)] = T_{\text{ni}}[\rho(r)] + V_{\text{ne}}[\rho(r)] + V_{\text{ee}}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{\text{ee}}[\rho(r)]$$

Kohn-Sham one electron operators:

$$h_i^{\text{KS}} = -\frac{1}{2} \nabla_i^2 - \sum_K^{\text{nuclei}} \frac{Z_K}{|r_i - r_K|} + \int \frac{\rho(r')}{|r_i - r'|} dr' + V_{\text{xc}}$$

$$V_{\text{xc}} = \frac{\delta E_{\text{xc}}}{\delta \rho}$$