Natalie Williams

✡ 6.1 Ab Initio Philosophy

~~HF~~ Hartree Fock theory is ~~useless~~ useful in ab initio (from the beginning) philosophy because ~~of its~~ it can be used to understand more complicated theories. HF wave functions make it possible for wave functions to be used to test properties that are not energy

$$E_{corr} = E - E_{HF}$$

E_{corr}: correlation energy, used to supplement E_{HF}

E: True energy

E_{HF}: system energy in the HF limit

✡ 6.2.1 Functional Forms

STO = Slater-type orbital

GTO = Gaussian-type orbital

Slater-type orbitals are limited in ab initio HF theory. AO-like functions, ~~are favored~~ in the form of Gaussian functions are used in alternative to STO. The general functional form of a normalized GTO is expressed in atom-centered Cartesian coordinates.

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

- α: exponent controlling width of GTO
- i, j, K: non-negative integers. Dictates
  - All 0 → s-type GTO
  - Index One is 1, p-type GTO
  - Sum = 2, d-type GTO

✱ 6.2.2 Contracted Gaussian Functions

Basis functions φ used for SCF calculations were linear combinations of GTOs used to for the same purpose as (and as accurate) as an STO.

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

M: # of Gaussians; c_a: coefficients

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

"Decontracting" basis sets increase their flexibility. It is ~~Connecting~~ constructing 2 basis functions for each orbital, first is a contraction of the first 2 primative Gaussians, and the second is the normalized primative third.

✱ 6.2.4 Polarization Functions

~~Molecular orbitals~~

Molecular orbitals needs more mathematical flexibility than atoms. AO-like GTOs adds this flexibility in the form of basis functions corresponding to one quantum # of higher angular momentum than the valence orbitals.

☆ 6.2.5 Diffuse Functions

Higher energy MOs are more diffuse. When an electron is unable to delocalize in a basis set, problems arise. To solve this problem, standard basis sets are "augmented" w/ diffuse basis functions. The Pople family + Dunning family of basis sets uses such functions

☆ 6.2.6. The HF Limit

These are
Solutions of Equations w/ an infinite # of basis sets. More commonly, people ~~use~~ extrapolate the HF limit by using similar concepts for somembasis-set incompleteness. There are potentially large errors w/ this approximation, so it is more of a formal standpoint

☆ 6.2.7 Effective Core Potentials

~~Alternay~~ Replacing electrons w/ analytical functions that represents the combined - nuclear - electronic core to remaining electrons is a good way to use basic sets w/ large elements. ECP (effective core potentials) is a nuclear point charge reduced in magnitude by the # of core electrons.

☆ 6.2.8 Sources

Use websites that permits you to download large # of basis sets using different software packages + ~~get~~ their reference information.

8 Density Functional Theory

8.1 Theoretical Motivation

☆ 8.1.1 Philosophy

We can take advantage of our knowledge of quantum mechanics to ask about a particular observable.

# of e → $\mathcal{N} = \int \rho(r)\, dr$

$\rho(r)$: electron density

$\frac{\partial \bar{\rho}(r_A)}{\partial r_A}\Big|_{r_A=0} = -2Z_A\,\rho(r_A)$

$\bar{\rho}(r_A)$: spherically averaged density

r_A: radial distance from A

Z_A: atomic #

$\rho(r_A)$: electron density maximum

$r_A = 0$: nucleus

☆ 8.1.2 Early Approximations

There is both kinetic + potential energy, and they can be found through several equations using several approximations We can calculate exchange energy, E_x using

$$E_x[\rho(r)] = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int \rho^{\frac{4}{3}}(r)\, dr$$

8.2 Rigorous Foundation

✡8.2.1 The Hohenberg-Kohn Existance Theorem

The first Hohenberg-Kohn theorem states that "the grand state of any interacting many particle system w/ a given fixed inner ~~part~~ particle interaction is a unique functional of the electron ~~dens~~ density.

I got over-zealous

$$E_{0,a} + E_{0,b} < \int [v_b(r) - v_a(r)] \rho_0(r)\, dr + \int [v_a(r) - v_b(r)] \rho_0(r)\, dr + E_{0b} + E_{0,a}$$

$E_{0,a}$, $E_{0,b}$: diff e^-

✡8.2.2 The Hohenberg-Kohn Variational Theorem

To establish a dependance of the energy on the density in this theorum, it is employed in the grand-state density, which is sufficient to show that it determines the Hamiltonian operator

✡8.3 Kohn-Sham Self-consistant field Methology

Kohn & Sham realized that things would be ~~so~~ simpler if only the Hamiltonian operator were for a non-interacting system of electrons

The Kohn-Sham one-electron operator is defined as

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

$$V_{XC} = \frac{\delta E_{XC}}{\delta \rho}$$

Function derivative