

6.1 Ab Initio Philosophy

- Fundamental assumption of HF theory: that each E sees all of the others as an average field, which allows for tremendous progress in MO calculations
- "ab initio" \Rightarrow from Latin means from the beginning
- HF focused on the long-term approach methodology
- The goal is to reach the HF limit, which is to solve HF equations with the equivalent of an infinite basis set, with no additional approximations

$$E_{\text{corr}} = E - \underbrace{E_{\text{HF}}}_{\text{true } E} \rightarrow \text{System } E \text{ in the HF limit.}$$

- HF energies is useful when the error associated with ignoring the correlation E
- also, HF wave functions made possible the testing of how excited state wave functions to predict of properties other than the E .
- Even if HF wavefunction is not close to being an eigenfunction, it doesn't \Rightarrow a priori preclude it from being closer to eigenfunction for some other quantum mechanical operator.

6.2 Basis Sets

- Basis Set \Rightarrow set of mathematical functions from which the wave function is constructed
- each MO in HF \Rightarrow linear combination of basis functions
- full HF wave function \Rightarrow expressed as a Slater determinant

6.2.1 Functional Forms

- STO's in TTF theory suffers from fairly significant limitation
- AO-like functions chosen to have the form of Gaussian function and that is used as an alternative to the use of STOs

GTO's general form:

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

counting the non-negative integers

width of the GTO

discrete nature of the orbital in Cartesian sense

6.2.2 Contracted Gaussian Functions

GTO's also have issues:

- Shape of the radial portion of the orbital.
 - S type are smooth
 - but real hydrogenic AO's have a cusp
- AO's exponential in r
- GTO's exponential in r^2
- this results in a rapid reduction in amplitude at distance for the GTO's
- To combine the best of GTO's and STO's, most of the first basis sets developed with GTO's used them as building blocks to approximate STO's:
$$\Psi(r, y, z; \{\alpha_i, i, j, k\}) = \sum_{a=1}^{M \leftarrow \# \text{ of GTOs used in the linear combination}} c_a \phi(r, y, z; \alpha_a, i, j, k)$$

↓
coefficient to optimize
the shape of the basis
function sum & enforce
normalization.
- was discovered that for $M=3$, the optimum combination of speed and accuracy was achieved.

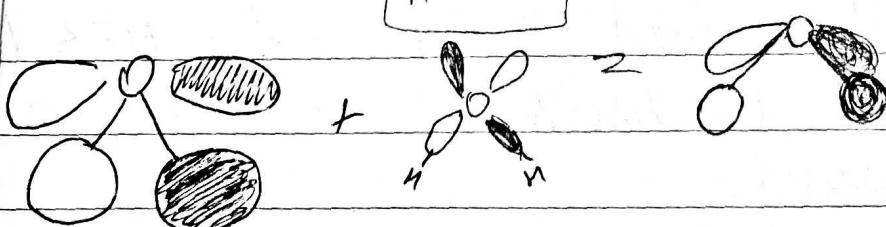
6.2.3 Single- ζ , Multiple- ζ , and Split-Valence

- STD-3G basis set = single- ζ "basis set", or minimal basis set
 - there's 1 and only 1 basis function defined for each type of orbital core through valence
- To ↑ the flexibility of basis set, decompose it.
- If basis set with 2 functions for each AO is called a "double- ζ " basis.
- valence orbitals, vary mildly as a function of elemental bonding

6.2.4 Polarization Functions

- HF calculation can be wrong about the planar geometry of a molecule b/c p and s functions centered on the atoms do not provide sufficient mathematical flexibility.

- MO = expansion of a Bloch's equation



The MO formed by interaction b/w the antisymmetric combination of H's orbitals and the oxygen p_x orbital. Bonding interactions are enhanced by many p_{dxz} character in MO.

6.2.5. Diffuse Functions

- happens when a basis set does not have the flexibility necessary to allow a weakly bound e^- to localize or from the remaining density, significant FEs and other molecular properties can occur.
- presence of diffuse function is shown as "+" in the basis set name
- In the calculations of densities and EAs, diffuse functions are absolutely required.

6.2.6 The HF Limit

Solution of HF equations w/ ∞ basis set.

- never practically possible
- but sometimes you can extrapolate to HF limit w/ confidence
- ~~All~~ ~~diffuse~~ assumptions:
Effect of "orthogonal" increases in basis set size can be considered additive; individual effects can be summed up together to estimate the full basis-set result.
- chemically there're potentially large errors associated with the HF approximation, so HF limit is of more interest from a formal standpoint than from chemical one

6.2.7 Effective Core Potentials

- heavy elements cause distinct challenges to MO theory; large # of es. \Rightarrow have to use large # of basis sets.
- Hellmann proposed resolution:
 - replace the δ with the es and analytical functions that could represent combined nuclear-electron core to the remaining es.
- FCP doesn't account for ~~disturbing the states~~
~~we need to represent in the core.~~
 - represents Coulomb repulsion effects
 - represents behavior of adiabatic core

6.2.8 Sources

- the bigger the basis set, the better. (Rule of thumb)
- but don't forget to account for valence deconstruction and presence of polarization functions.

8. DFT

8.1.1. Philosophy

Wave function is a beast but is essentially uninterpretable

That's why we want to work at something else, which is observable

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

$\downarrow e^-$ $\downarrow e^-$ density

8.1.2. Kohn's Approximation

$= 1$ for Slater's and $\frac{2}{3}$ for Hückel and Piroc

Exchange E :

$$Ex[p(r)] = -\frac{9\alpha}{8} \left(\frac{3}{N}\right)^{\frac{1}{3}} \int p^{\frac{4}{3}}(r) dr$$

"Slater's exchange"

8.2 References: Foundation

- DFT ~~models~~ models were used widespread but had fairly large calculation errors and that caused little impact on chemistry.

8.2.1 The Hohenberg-Kohn Existence theorem

- ground state density is employed, to show it is density that determines the hamiltonian operator.

- Integration of the density gives the # of e^- .

$$E_{0,b} < \int [V_b(r) - V_a(r)] P_0(r) dr + E_{\text{ext}}$$

- non-degenerate ground-state density must determine the external potential, and Hamiltonian, and more bunches.

8.2.2. The Hohenberg-Kohn Variational Principle

- need to predict the density of the system

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

↓
Expected "true" ground-state

- However, DFT don't have mechanism known on how to not randomise the prediction of the density.

8.3 Kohn-Sham Self-consistent Field Methodology

Kohn and Sham suggested that the Hamiltonian operator was considered for a non-interacting system of electrons. The Kohn-Sham L-C operator is defined:

$$h_i^{\text{KS}} = -\frac{1}{2} \nabla_i^2 - \sum_k \frac{Z_k}{|r_i - r_k|} + \int \frac{P(r')}{|r_i - r'|} dr' + V_{xc}$$

$$= \frac{\delta E_{\text{ex}}}{\delta P}$$