

10.675 LECTURE 8

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1. TODAY

"Basis Sets"

- Linear combination of atomic orbitals (LCAO)
- contraction
- split valence
- polarization functions
- diffuse functions
- basis set super position error (BSSE)

2. BASIS SETS

2 types: local and non-local.

Localized basis sets (what gaussian uses)

Non-localized basis sets (plane waves)

frequencies are much less sensitive to basis sets than the energy

Zero point energy is a destabilizer.

$\frac{3}{2}NkT$ → Rotational

$\frac{3}{2}NkT$ → Vibrational

LCAO → choose a "basis set" for each atom and sum them for the "molecular" basis set.

Example, Slater orbitals. $f(x, y, z)e^{-\alpha r} = \left(\frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}}\right)r^{n-1}e^{-\frac{\zeta r}{a_0}}$

- Numerical

- Gaussians

$s : ce^{-\alpha r^2}$

$p : c'xe^{-\alpha r^2} \dots$ (3 total) x,y,z

$d : c''x^2e^{-\alpha r^2} \dots$ (6 total) xx, yy, zz, xy, yz, xz

Examples of "Basis Sets"

"Minimal basis set" - fewest # of functions needed to treat all electrons.

H-1 Li-2 C-3.

3. STO-3G (SLATER TYPE ORBITAL)

3 Gaussians - Good description, but pain to integrate.

$$\Psi_i = \sum_{\mu=1}^k C_{\mu} \phi_{\mu}$$

$$\phi_{\mu} = \phi_{\mu}^{Slater} = \sum_p dp \cdot g_p$$

dp are the coefficients. g_p are the gaussians. Each gaussian is a primitive functions. dp 's are fixed, a "contraction" of the basis set.

Coefficients, dp 's, and α 's in g_p 's determined ahead of time by fitting to atomic data.

Date: Fall 2004.

$$\epsilon_{nl} = \int (\phi_{nl}^{slaterfunction} - \phi_{nl}^{slaterexpansion})^2 dr$$

minimize ϵ_{nl}

$\Phi_i = \sum_{\mu} C_{\mu} \sum_p dp \cdot g_p$ for H atom.

STO-3G's almost never used as it's HIGHLY INADEQUATE.

Why? Too small, no robust to chem changing environments, and they don't treat anisotropy.

Solution? Better to express orbitals as summation of diffuse and contracted functions.

4. 3-21G, 6-31G SPLIT VALENCE BASIS SET.

$K - K'K''G$ form

K gaussian for each inner shell (non-valence)

K' contracted gaussians for each valence orbital

K'' diffuse gaussians for each valence orbital

$$\phi_{nl} = \sum_{k=1}^{k'k''} d_{nlk} \cdot g_l(\alpha_n, k, \vec{r})$$

coefficients are found by minimization of the total hartree-fock energy of the atoms.

So optimized for hartree-fock, but still is no anisotropy taken into account.

5. POLARIZATION FUNCTIONS (6-31G* AND 6-31G**)

Polarization functions are important for polar molecules

They allow for non-uniform displacement of charge around nucleus

include functions of higher angular momentum

s + p = hybrid sp orbital

term λ used to strike a balance between ratio of s and p.

Examples 6-31G* and 6-31G**

* → add 6 d Gaussians to each "heavy" atom (ie non-hydrogen)

** → 2nd star means p functions to hydrogen and helium. Optimized to HF energy.

6-311B ** → designed for correlation coefficients found by minimizing atomic MP2 energies.

6. DIFFUSE FUNCTIONS (3-21+G*, 6-31+G*, 3-21++G*, 6-31++G*)

Previous basis sets designed for systems w/relatively tight bound electrons (ie not anions) + means adding additional s and p functions optimized for deprotonated hydrides (Li^- and BeH^-).

$K - K'K''K'''$

++, 2nd plus means adding diffuse functions to H, 1st plus means diffuse functions on non-H atoms.

K'' is the diffuse functions, K''' is more diffuse.

Note: Absolute energies are far from conserved, binding energies are much closer to convergence.

6-31++ G** is still not big enough. Additional functions (typically higher order angular momentum functions)

6-31++G(3df,3pd) adds higher orbital angular momentums.