Gherman Group Meeting

Density Functional Theory and Partial Charges

July 16, 2009

Outline

- Density Functional Theory
    - Exchange-Correlation Functionals
    - Comparison to MO (e.g., HF) theory
    - Performance

Part 1: Density Functional Theory

DFT: Background (1)

- Hohenberg-Kohn Existence Theorem
  - ground-state density ρ – distribution of electrons in the molecule
  - external potential – charges and position of the nuclei (i.e., the molecular geometry)

  - theorem: the ground-state density determines the external potential
  - together these determine the Hamiltonian, the wave function, and the energy.

DFT: Background (2)

- Directly from ρ to E

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

- T_{ni} – KE of non-interacting electrons
- V_{ne} – nuclear-electron interaction potential energy
- V_{ee} – classical electron-electron repulsion potential energy
- ΔT – correction to KE from interacting nature of electrons
- ΔV_{ee} – non-classical correction to the electron-electron repulsion energy (exchange and correlation effects)

- Typically combine ΔT and ΔV_{ee} to E_{xc}
- Main question: What is the functional form of E_{xc}?

DFT: Exchange-Correlation Functionals (1)

- Local density approximation (LDA)
  - exchange-correlation value computed exclusively from the value of ρ at that position (“local” value of ρ)

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  - based upon the uniform electron gas
    - infinite # of electrons in an infinite volume in the presence of uniformly distributed positive charge
    - E_{xc} at a position in the molecule is the same as it would be for the uniform electron gas having the same density as at that molecular position.

DFT: Exchange-Correlation Functionals (2)

- Generalized gradient approximation (GGA)
  - E_{xc} depends on local value of ρ **AND** the gradient of ρ (“gradient correction”)
  - constructed as the LDA E_{xc} plus a GGA correction term

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- Meta-GGA
  - include also dependence on kinetic energy density $\sum_{i}^{occupied} \frac{1}{2} \left| \nabla \psi_i(r) \right|^2$
  - e.g., B98, TPSS

DFT: Exchange-Correlation Functionals (3)

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    - e.g., one-parameter methods which only adjust amount of HF exchange
      - mPW1PW91, PBE1PBE
    - e.g., combining mGGA functionals with HF exchange
      - TPSSh

DFT: General Observations

- Exchange and correlation functionals can take on complicated forms and may be difficult to relate to first principles.

- DFT can be viewed as “semi-empirical” in that there are empirically optimized constants and functional forms.

- Improvement from LSDA to GGA to mGGA functionals.
- Best hybrid functionals are as good as best mGGA functionals.

DFT: Shortcomings

- Long-range electron correlation
  - since correlation energy depends on local ρ and gradient
  - leads to failure to model dispersion forces
    - van der Waals complexes, such as noble-gas dimers

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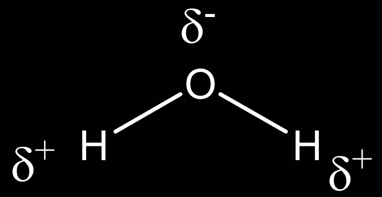
  - In practice, different functionals work best in different systems and choice of functional must be calibrated to experimental data.

Part 2: Partial Charges

Partial Atomic Charges



- Four general classes of partial atomic charges

- Best use: analysis of *changes* in charges in a reaction, from substitution, with geometric change.

- Class I
  - not determined from quantum mechanics

- Class II
  - partition the wave function into atomic contributions based upon orbitals
  - Mulliken, Löwdin, NPA charges…

Partial Atomic Charges – Class II (1)

- Mulliken charges
  - electrons are divided among atoms according to the weight with which basis functions contribute to the molecular wave function
    - electrons associated with a single basis function
      - assigned to the atom associated with the basis function
    - electrons shared between basis functions
      - divided evenly between the 2 atoms associated with the basis functions

- potential problems
  - sensitive to basis-set size
  - does not account well for differing electronegativities of atoms

Partial Atomic Charges – Class II (2)

- Löwdin charges – transform the basis functions before doing Mulliken population analysis
  - more stability with basis sets

- NPA (natural population analysis)
  - most stable with basis set size
  - tend to be larger in magnitude

Partial Atomic Charges – Class III

- Class III charges – reproduce a physical observable that can be calculated from the wave function.

- Example: electrostatic potential (ESP) fit charges
  - partial atomic charges which minimize difference between…
    - the molecular electrostatic potential (from the wave function)
    - the electrostatic potential from the partial atomic charges:

$$V_{ESP}(r) = \sum_{k}^{nuclei} \frac{q_k}{\left| r - r_k \right|}$$

  - advantages
    - intermolecular interactions
  - disadvantages
    - ill-conditioned for atoms not near the surface (big variations have little effect on ESP)
    - intramolecular interactions

Partial Atomic Charges – Class IV

- Class IV: charges to chosen to reproduce an experimentally determined observable
  - start from class II partial atomic charges
  - modify to reproduce experimental observable (e.g. molecular dipole moment)