
بسم الله الرحمن الرحيم

Density Functional Theory

Lecture # 04

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Key Concepts

- In this lecture we ‘ll learn:
- Electron correlation methods
- Density Functional Theory
- Hybrid functionals
- Dispersion correction
- Integration Grids

Electron Correlation Methods

- Electronic correlation is the interaction between electrons in the electronic structure of a quantum system.
- The ***correlation energy*** is a measure of how much the movement of one electron is influenced by the presence of all other electrons.
- Electron correlation is calculated in Hartree-Fock (HF) and Post HF methods.
- In Hartree–Fock method the molecular orbitals are optimized by evaluating the energy of an electron in each molecular orbital moving in the mean field of all other electrons, rather than including the instantaneous repulsion between electrons.

Electron Correlation Methods

- Post Hartree-Fock methods include the following:
- Configuration Interaction (CI)
- Møller–Plesset perturbation theory (MP2, MP3, MP4, etc.)
- Multi-Configurational Self-Consistent Field (MCSCF)
- Coupled Cluster Methods (CCSD, CCSD(T) etc.)

Density Functional Theory

- Electron correlation methods can lead to highly accurate energies. However, this accuracy comes at significant computational cost, limiting the application of these methods to relatively small molecules.
- If we want to answer questions that can only be addressed by modeling large numbers of atoms, another approach will need to be taken.
- Density Functional Theory (DFT) provides this alternative.
- It was not until the 1990s that DFT became widely used.
- Although the theory itself is quite precise and even elegant, its implementation has not been.

Density Functional Theory

- Researchers continue to work to refine and improve the models, and each year many new density functional approximations (DFAs) are offered to the computational chemistry community.
- The basic premise behind DFT is that the energy and associated properties of any system containing electrons are calculable from the probability distribution that is the total electron density, $\rho(r)$.
- Using an orbital basis set, this quantity can be easily obtained as:

$$\rho(\vec{r}_g) = \sum_{i}^{\text{occupied}} \phi_i^2(\vec{r}_g)$$

Density Functional Theory

$$\rho(\vec{r}_g) = \sum_{i}^{\text{occupied}} \phi_i^2(\vec{r}_g)$$

- Here the position vector, $\vec{r}_g$, represents all space coordinates for the system as defined by a grid g.
- The probability of observing an electron in the volume element at $\vec{r}_g$ is $\rho(\vec{r}_g)$.
- While it may be intuitively useful to picture the volume surrounding a molecule as divided into a three-dimensional rectangular grid of small cubic elements, the grids typically used in calculations employ spherical and radial coordinates centered on each atom.

Density Functional Theory

- Although it generally produces much more accurate results, typical DFT implementations use much of the same computational infrastructure as Hartree-Fock, which accounts for its speed and efficiency.
- In its “pure” form, DFT uses the following expression for the energy as a functional of the density:

$$E_{\mathrm{DFT}}[\rho(\vec{r})] = T[\rho(\vec{r})] + V_{\mathrm{NE}} + J[\rho(\vec{r})] + E_{\mathrm{XC}}[\rho(\vec{r})]$$

- The first three terms similar to Hartree-Fock theory. The final term is known as the exchange-correlation term. It models the parts of the electron-electron interactions that are neglected by Hartree-Fock theory.

Density Functional Theory

- What is missing from this formulation (shown on previous slide) is any term corresponding to Hartree-Fock exchange (*K*).
- Pure DFT functionals eliminate it entirely; hybrid functionals include some portion of it in the energy expression.
- Exchange energy is basically associated with identical particles (say electrons) exchanging their signs or remain symmetric.
- The preceding equation yields a modified Fock matrix:

$$\mathbf{F}_{\mu\nu}^{\mathrm{DFT}} = \mathbf{H}_{\mu\nu}^{\mathrm{core}} + \mathbf{J}_{\mu\nu}\left(\mathbf{P}_{\lambda\sigma}\right) + \sum_{g} w_g \, \mathbf{F}_{\mu\nu}^{\mathrm{XC}}\left[\rho(\vec{\mathrm{r}}_g)\right]$$

Density Functional Theory

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- $\mathbf{H}^{\mathrm{core}}$ is obtained from the one-electron integrals (kinetic plus nuclear-electronic attraction) just as before.
- The second term ($\mathbf{J}_{\mu\nu}$) can be found by considering the classical electron-electron repulsions and depends on the molecular orbitals through the density matrix $\mathbf{P}_{\lambda\sigma}$ which will again require the calculation of two-electron integrals.
- The final term is the new quantity introduced by DFT that accounts for all electron correlations: both exchange and correlation.

Density Functional Theory

- Unlike the coulombic repulsions, which are evaluated using integrals involving basis functions, this new quantity is evaluated by summing over a grid of points, with each volume element multiplied by a weighting factor, w_g .
- This technique was suggested by Kohn and Sham in 1965.
- The additional work required scales more or less the same as a Hartree-Fock calculation, allowing DFT models to study a wide range of systems, including ones with very large numbers of atoms.

Density Functional Theory

- Unfortunately, the exact specification of $\mathbf{F}^{XC}$ is not known.
- Its form has been postulated from the equations describing a uniform electron gas, from the exact solution of the hydrogen atom, by parameterization with experiment, and in other fashions, giving rise to a multitude of DFAs.
- These different DFAs or so called Density Functionals are available in different software packages.

Hybrid Functionals

- While the early application of pure DFT functionals showed promise, their results were nevertheless decidedly mixed, and many significant failures accompanied the successes.
- In the early 1990s, ***Axel Becke*** demonstrated that more accurate energies could be obtained if some part of the Hartree-Fock exchange was included within the functional.
- This crucial insight is what made DFT methods accurate and consistent and enabled them to be applied to the full range of chemical problems, resulting in the widespread use they see today.

Hybrid Functionals

- Functionals that mix exchange-correlation functionals with Hartree-Fock exchange are termed ***hybrid functionals***.
- Conceptually, a hybrid functional defines the DFT exchange-correlation term as a sum of Hartree-Fock exchange and pure DFT exchange-correlation, mixed in some fixed percentages.
- For example the hybrid functional B3LYP contains 20 % Hartree-Fock exchange and 80 % pure DFT exchange-correlation.

Hybrid Functionals

- The table on the right presents the results for the proton affinity of methyl anion as well as the optimized C-H bond length in methane for some hybrid functionals and the Hartree-Fock and MP2 methods.

- Hartree-Fock theory greatly overestimates the proton affinity of methyl anion, and all the DFA methods correct it in the direction of the accepted value.

METHOD	PA (kJ/mol)	R (Å)
HF	1814	1.0832
pure functionals:		
BLYP	1761	1.0963
BRxBRc	1759	1.0960
TPSSTPSS	1786	1.0925
PBEPBE	1765	1.0972
hybrid functionals:		
BRxBRc, c_1=0.307	1785	1.0879
B1B95	1787	1.0871
PBE1PBE	1785	1.0901
TPSSh	1792	1.0904
B3LYP	1778	1.0896
BMk	1788	1.0908
B98	1786	1.0908
MP2	1780	1.0888
accepted value	1785[a]	1.0859[b]

[a]Estimated from W1BD calculations [b][Landolt76]

Hybrid Functionals

- In general, pure DFA models slightly underestimate it (with the exception of TPSS) while overestimating the C-H bond length of methane.
- The use of hybrid DFAs improves both quantities, and their results are in line with MP2 for this problem.
- The performance of a given DFA will depend on basis set. However, increased accuracy does not always follow by increasing the basis set.

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BRxBRc, c_1=0.307	1785	1.0879
B1B95	1787	1.0871
PBE1PBE	1785	1.0901
TPSSh	1792	1.0904
B3LYP	1778	1.0896
BMk	1788	1.0908
B98	1786	1.0908
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accepted value	1785[a]	1.0859[b]

[a]Estimated from W1BD calculations [b][Landolt76]

Dispersion

- Dispersion refers to the weak interaction arising from the fact that the charge distribution around a molecular system isn't constant; rather, it fluctuates due to the movement of electrons.
- Dispersion forces—both intra- and intermolecular—are present in any chemical system.
- They are often dwarfed by the other covalent and dipole-dipole type interactions, which are of much larger magnitude.
- However, dispersion forces dominate in the absence of other types of intermolecular forces, and they can be important in other situations when highly accurate energies are desired.

Dispersion

- Both pure and hybrid DFA models fail to describe dispersion adequately.
- Most functionals exhibit spurious long-range repulsion or short range attraction.
- For instance, if you were to use B3LYP to study the attraction of two noble gas atoms (or even two methane molecules), you would find that the theory predicts repulsion at all distances.
- MP2 theory can recover some of the effects of dispersion, but it often underestimates them.

Dispersion Correction

- Since approximate density functionals already have parameterization built into them, it seems reasonable to add one more empirical term, $\mathbf{E}_{disp}$, to account for dispersion.
- Prof. Grimme devised the dispersion correction for density functionals that can be used from within the software package we are using.

Integration Grids and DFT Calculations

- DFT calculations evaluate the terms added to Hartree-Fock theory via numerical integration.
- Such calculations employ a grid of points in space in order to perform the numerical integration.
- Grids are specified as a number of radial shells around each atom, each of which contains a set number of integration points.
- For example, in the (75,302) grid, there are 75 radial shells each containing 302 points, resulting in a total of 22,650 integration points per atom.

Integration Grids and DFT Calculations

- Uniform and pruned versions of many grids have been defined.
- Uniform grids contain the same number of angular points at each radial distance, while pruned grids are reduced from their full form so that fewer points are used on the shells near the core and far from the nucleus, where less density is needed for a given level of computational accuracy.
- Put another way, pruned grids are designed to be densest in the region of the atom where its properties are changing most rapidly.
- For example, the pruned (75,302) grid, denoted “(75,302)p,” contains about 7,500 integration points per atom. In general, pruning reduces the size of a uniform grid by about 66%.

Integration Grids and DFT Calculations

- In addition to producing more accurate results, larger grids also have better rotational invariance properties and are thus much more suitable for molecular systems involving transition metals and calculations using pseudopotentials.
- As of this writing, (75,302)p—known as FineGrid—is the default grid in Gaussian 09 software.
- The SGl grid, a pruned (50,194) grid containing about 3,600 points per atom is used for lower accuracy single point calculations.
- However, it is recommend to use the larger UltraFine grid, (99,590)p for all production calculations, to produce more accurate results and to increase the stability of all numerical computation process.

Integration Grids and DFT Calculations

- In Gaussian software the following choices of grids are present:

  - **Integral=SG1**: (50,194)p
  - **Integral=FineGrid**: (75,302)p
  - **Integral=UltraFine**: (99,590)p
  - **Integral=SuperFine**: (150,974)p for the first two rows of the periodic table, (225,974)p for the third row and beyond.

References

- James B. Foresman, Aeleen Frisch, "*Exploring Chemistry with Electronic Structure Methods*" (2015)