A micro-lecture on Density Functional Theory

C. David Sherrill
Georgia Institute of Technology

Hohenberg and Kohn

- First Hohenberg-Kohn theorem: The ground state properties of a many-electron system depend only on the electronic density $n(x,y,z)$
- Second Hohenberg-Kohn theorem: The correct ground state density for a system is the one that minimizes the total energy through the functional $E[n(x,y,z)]$
- A functional is just a function that depends on a function

Form of the Density Functional

- So what's the density functional actually look like? The Coulomb interaction for a given density interacting with itself and the nuclei is easy to compute. This is the "Coulomb" term.

- It is unfortunately not obvious how to compute the exchange or correlation energies. Use an approximate functional for those (the exchange-correlation functional), $E_{xc}[n(x,y,z)]$, often broken up into exchange and correlation functionals

Kohn and Sham (KS)

- The kinetic energy of a density is also not obviously computable, but if we assume that the density corresponds to a wavefunction consisting of a single Slater determinant ("non-interacting limit"), then we can do it because we know how to compute the kinetic energy of a Slater determinant (orbitals) --- looks same as Hartree-Fock Theory

- This procedure is called Kohn-Sham DFT and is the most common approach (although doesn't work well for extremely large systems due to computational cost)

KS DFT Equations Look Like Fancy Versions of HF Equations

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$$

$$V_s(\vec{r}) = V(\vec{r}) + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' + V_{\mathrm{xc}}[n_s(\vec{r})]$$

Where V(r) is the "external potential," i.e., the potential generated by the nuclei

Observations on KS DFT

- Cost is similar to HF (similar equations) but quality can be better because correlation is built in through the correlation functional

- Cost can actually be cheaper than HF if we replace the expensive, long-range exchange integrals (K terms) from HF with a shorter-range exchange potential (which however might not be as accurate...)

Hierarchy of DFT

- Local density approximation (LDA): Functional depends only on the (local) density at a given point. Example: S-VWN

- Gradient-corrected approximation (GGA): Functional depends on local density and its gradient. Examples: PW91 and LYP correlation functionals

- Meta-GGA: Functional depends on density, its gradient, and its second derivative. Example: M06-L

- Hybrid DFT: Mixes in Hartree-Fock exchange. Most popular example: B3LYP

What you need to specify to run a DFT computation

- Basis set

- Exchange functional: S, B, B3, etc.

- Correlation functional: LYP, PW91, etc.

Observations

- DFT good for geometries, often not as good for energies
- B3LYP works really well and is hard to beat (usually)
- Minnesota functionals (M05-2X, M06-2X, M06-L, etc) seem to work well also (but can be sensitive to the numerical integration grid)
- Barrier heights often underestimated
- Totally fails for non-covalent interactions (just like Hartree-Fock); fix with DFT-D or XDM or vdW-DFT
- Can totally fail for charge-transfer states (fix with ???)
- Can have large errors for excitation energies to Rydberg excited states (fix with asymptotically-corrected functionals like CAM-B3LYP) (DFT for excited states is called time-dependent DFT, or TDDFT)
- Can get wrong energetic ordering of spin states of metals (just like Hartree-Fock)