Introduction to Density Functional Theory

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The Big Picture

- DFT improves upon Hartree-Fock by including an approximate treatment of the correlated motions of electrons (these are treated in Hartree-Fock in only an averaged sense)
- Treatment of electron correlation is much cheaper than in correlated wavefunction methods like MP2, CCSD, CCSD(T)
- Although there is a loose ordering of density functionals from “less sophisticated” to “more sophisticated” (e.g., LDA to GGA to hybrid, etc.), in practice there is no reliable way to improve your computation by going to the “next better” functional. By contrast, this is possible with wavefunction methods: one almost always has CCSD(T)>CCSD>MP2>HF.

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 the nuclei is very straightforward to compute; so is the Coulomb interaction of the density with itself (J term)
- Coulomb (J) terms are great, but we also need to account for electron antisymmetry (exchange effects) and electron correlation effects
- Additionally, not clear how to compute kinetic energy as a function of the density

Form of the Density Functional

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee}$$

$$E[\rho] = T[\rho] + E_{eN}[\rho] + E_{ee}[\rho]$$

$$E_{eN}[\rho] = \sum_A \int \frac{Z_A \rho(\vec{r})}{|\vec{R}_A - \vec{r}|} d\vec{r}$$

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

Kohn and Sham (KS)

- Compute the kinetic energy of a density by assuming that the density corresponds to a wavefunction consisting of a single Slater determinant (“non-interacting limit”): 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)

Kohn-Sham Kinetic Energy

$$\begin{aligned} T_s[\rho] &= \sum_{i=1}^{N} \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle, \\ \rho(\vec{r}) &= \sum_{i=1}^{N} |\phi_i(\vec{r})|^2. \end{aligned}$$

$$\begin{aligned} E_{\mathrm{KS-DFT}}[\rho] &= T_s[\rho] + E_{eN}[\rho] + J[\rho] + E_{xc}[\rho], \\ E_{xc}[\rho] &= (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]). \end{aligned}$$

Exchange-Correlation Functional

$$\begin{aligned} E_{\mathrm{KS-DFT}}[\rho] &= T_s[\rho] + E_{eN}[\rho] + J[\rho] + E_{xc}[\rho], \\ E_{xc}[\rho] &= (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]). \end{aligned}$$

- We can compute every piece of a Kohn-Sham DFT energy exactly except for the "exchange-correlation" piece, $E_{xc}[\rho]$.
- Unfortunately the exact exchange-correlation energy functional is not known and is probably so complicated that even if it were known it would not be computationally useful
- Hence, use various *approximate* exchange-correlation functionals (S-VWN, B3LYP, etc.)

Kohn-Sham DFT Self-Consistent-Field Equations

$$
\begin{aligned}
\hat{h}_{KS}(\vec{r})\phi_i(\vec{r}) &= \epsilon_i\phi_i(\vec{r}), \\
\hat{h}_{KS}(\vec{r}) &= -\frac{1}{2}\nabla^2(\vec{r}) + V_{eff}(\vec{r}), \\
V_{eff}(\vec{r}) &= V_{eN}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' + V_{xc}(\vec{r})
\end{aligned}
$$

- Much like Hartree-Fock but there’s an extra “exchange-correlation” piece that adds approximate electron correlation and can handle the exchange term differently

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…)

The Exchange-Correlation Potential

$$V_{xc}(\rho) = \frac{\partial E_{xc}[\rho]}{\partial \rho}$$

Often one breaks up E_{xc} into exchange and correlation parts and writes the in terms of the energy per particle, ε_x and ε_c

$$\begin{aligned} E_{xc}[\rho] &= E_x[\rho] + E_c[\rho], \\ &= \int \rho(\vec{r})\epsilon_x[\rho(\vec{r})]d\vec{r} + \int \rho(\vec{r})\epsilon_c[\rho(\vec{r})]d\vec{r} \end{aligned}$$

$$\begin{aligned} V_{xc}(\rho) &= \epsilon_{xc}[\rho(\vec{r})] + \rho(\vec{r})\frac{\partial \epsilon_{xc}(\vec{r})}{\partial \rho}, \\ &= \epsilon_x[\rho(\vec{r})] + \epsilon_c[\rho(\vec{r})] + \frac{\partial \epsilon_x(\vec{r})}{\partial \rho} + \frac{\partial \epsilon_c(\vec{r})}{\partial \rho} \end{aligned}$$

Hierarchy of DFT Exchange-Correlation Functionals

- 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, B88 exchange functional
- 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 (hybrid GGA). M05-2X and M06-2X are hybrid meta-GGA’s.

Local (Spin) Density Approximation

- Based on results for the uniform electron gas as a model, Dirac introduced this form for the exchange functional (called "Slater" exchange, abbreviated "S"):

$$\begin{aligned} E_x^{\mathrm{LDA}}[\rho] &= -c_x \int \rho^{4/3}(\vec{r})d\vec{r}, \\ \epsilon_x^{\mathrm{LDA}}[\rho] &= -c_x \rho^{1/3}(\vec{r}). \end{aligned}$$

Local (Spin) Density Approximation

- If the α and β densities differ (e.g., open-shell systems), use the local spin density approximation (LSDA)

$$
\begin{aligned}
E_x^{\mathrm{LSDA}}[\rho] &= -2^{1/3} c_x \int \left(\rho_\alpha^{4/3}(\vec{r}) + \rho_\beta^{4/3}(\vec{r}) \right) d\vec{r}, \\
\epsilon_x^{\mathrm{LSDA}}[\rho] &= -2^{1/3} c_x \left[\rho_\alpha^{1/3}(\vec{r}) + \rho_\beta^{1/3}(\vec{r}) \right].
\end{aligned}
$$

Local (Spin) Density Approximation

- For the correlation energy, again use the uniform electron gas as a model. Its correlation energy was determined numerically by Monte Carlo simulations and fit to an analytic form by Vosko, Wilk, and Nusair (VWN), to give ε_c^{VWN}. L(S)DA usually implies VWN correlation
- More technical name for L(S)DA is S-VWN (Slater exchange plus Vosko, Wilk, Nusair correlation)
- Electron correlation can be overestimated by a factor of 2 when using VWN. Bond strengths too large. Need better approximations

Generalized Gradient Approximations (GGA’s)

- The uniform electron gas isn’t such a great model because in molecules, the electron density can vary rapidly over a small region of space
- One way to improve over LSDA is to make the functional depend on both the density and the gradient of the density
- This leads to “gradient corrected” functionals or “generalized gradient approximation” (GGA) functionals
- Also sometimes called “nonlocal” functionals but this is a bad name that is fortunately falling out of favor now: the density and its gradient still supply only *local* information

Examples of GGA’s

- Exchange: PW86, B88 (“B”), PW91
- Correlation: LYP

$$\epsilon_x^{\mathrm{B88}}[\rho] = \epsilon_x^{\mathrm{LDA}}[\rho] - \beta\rho^{1/3}\frac{x^2}{1+6\beta x sinh^{-1}x}, \qquad x = \frac{|\nabla\rho|}{\rho^{4/3}}$$

- GGA’s improve over L(S)DA but are still not necessarily very accurate; one reason is the exchange potential doesn’t necessarily have the correct qualitative behavior
- B88 has the correct -1/r asymptotic behavior of the energy density but not the overall exchange potential

Hybrid Funtionals

- Introduced by Axel Becke in 1993 to provide improved results
- Inspired by the Adiabatic Connection Formula, a formally exact way to get E_{xc}; interpolate between the real (interacting) system and a formal “noninteracting” limit where a single Slater determinant made of KS orbitals exactly solves the Schrödinger equation

$$\begin{array}{rcl} \hat{H}_\lambda & = & \hat{T} + \hat{V}_{ext}(\lambda) + \lambda V_{ee}, \\ \lambda = 1 & \rightarrow & \hat{V}_{ext} = \hat{V}_{eN}, \\ \lambda = 0 & \rightarrow & T[\rho] = T_s[\rho]. \end{array}$$

- For $0 < \lambda < 1$, $V_{ext}(\lambda)$ is adjusted to that the same density is obtained for $\lambda=0$ and $\lambda=1$

Adiabatic Connection Formula

$$E_{xc} = \int_0^1 \langle \Psi_\lambda | \hat{V}_{xc}(\lambda) | \Psi_\lambda \rangle d\lambda$$

- If V_{xc} is linear in λ, can approximate as

$$E_{xc} \approx \frac{1}{2} \langle \Psi_0 | \hat{V}_{xc}(0) | \Psi_0 \rangle + \frac{1}{2} \langle \Psi_1 | \hat{V}_{xc}(1) | \Psi_1 \rangle$$

λ=0: only exchange, no correlation; Ψ_0 is a Slater determinant, can use HF equation for exchange energy

λ=1: Real system, unknown solution. Can approximate with LSDA and add to λ=0 part to give "half and half"

$$E_{xc}^{H+H} = \frac{1}{2} E_x^{\mathrm{HF}} + \frac{1}{2} \left(E_x^{\mathrm{LSDA}} + E_c^{\mathrm{LSDA}} \right)$$

Becke's 3-Parameter Hybrids

- Since GGA's are better than LSDA, could also use a functional form like this (B3):

$$E_{xc}^{\mathrm{B3}} = (1-a)E_x^{\mathrm{LSDA}} + aE_x^{\mathrm{HF}} + b\Delta E_x^{\mathrm{B88}} + (1-c)E_c^{\mathrm{LSDA}} + c\Delta E_c^{\mathrm{GGA}}$$

- B3LYP uses this form, with LYP for ΔE_c^{GGA}
- B3LYP introduced in 1994 by Stephens, Devlin, Chabalowski, and Frisch; their computer code did not match their paper (confusion about VWN-1 vs VWN-5 correlation); led to problems deciding about what is the "real" B3LYP

What you need to specify to run a DFT computation

- Molecule
- Molecular charge
- Spin multiplicity
- 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 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 totally fail for charge-transfer states (fix with “range-separated hybrids” that include HF exchange at long range only)
- Can get wrong energetic ordering of spin states of metals (just like Hartree-Fock)