#### Lecture 11 DFT: Kohn-Sham and LDA Functionals

Kohn-Sham approach; functional derivative; comparison to Hartree-Fock; Local Density Approximation

Prof. David A. Kofke CE 500 – Modeling Potential-Energy Surfaces Department of Chemical & Biological Engineering University at Buffalo



© 2024 David Kofke

#### DFT is founded on the existence of a groundstate energy functional of the electron density

- First HK theorem: Any given  $\rho(\mathbf{r})$  corresponds to a unique external field  $V_{\text{ext}}(\mathbf{r})$ . What does this mean?
  - $V_{\text{ext}}(\mathbf{r})$  defines a Hamiltonian:  $\hat{H} = -\frac{1}{2}\nabla^2 + V_{\text{ee}} + V_{\text{ext}}$
  - This Hamiltonian specifies a ground-state wavefunction  $\psi$ :  $\hat{H}\Psi = E\Psi$
  - This  $\psi$  yields an electron density:  $\rho(\mathbf{r}) = \sum_{s} N^{s} \int \dots \int |\Psi(\{\mathbf{r},s\},\tau_{2},\dots,\tau_{N})|^{2} d\tau_{2} \dots d\tau_{N}$
  - No other  $V_{\text{ext}}(\mathbf{r})$  would yield this  $\rho(\mathbf{r})$  if put through this process
  - The ground-state energy  $E_0$  is specified uniquely as well:  $\langle \Psi | \hat{H} | \Psi \rangle$
  - In sum, there exists a functional  $E_0[\rho]$

Caveat: ground state must be nondegenerate

to the interaction

with atomic nuclei

## An exact variational principle guides the identification of a $\rho(r)$ for a given $V_{ext}$

- $V_{\text{ext}}$  is input to the definition of the functional  $E_0[\rho]$
- Second HK theorem: Given  $E_0[\rho; V_{ext}]$ , the electron density that corresponds to the given  $V_{ext}$  is the one that minimizes  $E_0$
- The difficulty in applying this frameworks is that we do not know the functional  $E_0[\rho; V_{ext}]$

electron

nuclear

• As a start to addressing this problem, we separate it into components:  $E_0[\rho] = T[\rho] + E_{ee}[\rho] + E_{Ne}[\rho]$ 

energy

## Kohn and Sham presented an approach to treating the kinetic-energy functional

- The QM kinetic energy has no clear connection to  $\rho(\mathbf{r})$ - Contrast with connection to wavefunction:  $KE = \hat{T}\Psi = -\frac{1}{2}\nabla^2\Psi$
- Introduce a *reference system* of non-interacting electrons that have the same electron density as the target ρ(r)
- The wavefunction for these noninteracting fermions can be represented exactly as a Slater determinant of orbitals  $\varphi_i$
- Kinetic energy and electron densities are given in terms of  $\varphi_i$  $T = -\frac{1}{2} \sum_{i}^{N} \langle \varphi_i | \nabla^2 | \varphi_i \rangle \qquad \rho(\mathbf{r}) = \sum_{i}^{N} \sum_{s} |\varphi_i(\mathbf{r}, s)|^2$ How do we get the  $\varphi_i$ ? ...

#### Minimization of $E_0[\rho(\mathbf{r})]$ turns to minimization with respect to the orbitals

• Energy functional is expressed in terms of the orbitals



classical electron-electron, [i i | j j]

$$ho({f r}) = \sum_i^N \sum_s |arphi_i({f r},s)|^2$$

5

'exchange-correlation functional' encapsulates everything that's wrong with the other terms

## Minimization of $E_0[\rho(\mathbf{r})]$ yields a 1-electron KS eigenvalue equation very similar to the HF formula



#### Aside: Intuition for the functional derivative gained by considering a multivariate partial derivative

For example  

$$\mathcal{F}[f] \equiv \int_{0}^{1} (f(x))^{2} dx \rightarrow \sum_{i} f_{i}^{2} \rightarrow \frac{\partial \mathcal{F}}{\partial f_{i}} = 2f_{i} \rightarrow \frac{\delta \mathcal{F}}{\delta f(x)} = \frac{2f(x)}{\delta f(x)}$$

### Aside: Intuition for the functional derivative gained by considering a multivariate partial derivative

For example

$${\cal F}[f]\equiv \int_0^1 (f(x))^2 dx o \sum_i f_i^2 o {\partial {\cal F}\over\partial f_i}=2f_i o {\delta {\cal F}\over\delta f(x)}=2f(x)$$

Try these:

$${\cal F}[f] \qquad \int_0^1 f(x) dx \qquad \int_{-\infty}^\infty e^{-f(x)} dx \qquad f(2) \qquad \int_{-1}^1 \int_{-1}^1 (1+f(x,y)+f(x,y)^2) dx dy$$

$$rac{\delta \mathcal{F}}{\delta f(x)}$$
 (°°)  $-e^{-f(x)}$   $\delta(x)^{\circ} (x)^{\circ} (x) = 2$ )  $rac{\delta \mathcal{F}}{\delta f(x,y)} = 1 + 2f(x,y)$ 

## While superficially very similar to HF treatment, DFT offers some advantages

• 4-center integrals can be avoided,  $N^3$  scaling instead of  $N^4$ 

$$rac{1}{2}\sum_{i,j}([ii|jj]-[ij|ji]) \implies rac{1}{2}\sum_{i}^{N} ig\langle arphi_{i}|\int rac{
ho({f r})}{|r_{i}-r'|}dr'|arphi_{i}ig
angle + E_{
m xc}[
ho({f r})]$$

- HF is inherently incorrect, as it has no accommodation for electron correlation (apart from effects of Pauli exclusion)
- DFT is exact in principle
  - Although this is accomplished by lumping all the inaccuracies into a term ( $E_{\rm XC}[\rho]$ ,  $V_{\rm XC}(\mathbf{r})$ ) that is not specified in detail
- Machinery developed for HF is readily adapted to DFT calculations

### The exchange-correlation functional collects a variety of inaccuracies from the other terms

- Difference in kinetic energy between true system and reference system of non-interacting electrons
- Correction of classical e-e electrostatic interaction to include correlation, and to remove the self interaction
- Exchange contribution to the energy
- Development of DFT methods is focused on this term

# A Local Density Approximation (LDA) estimates $E_{XC}[\rho]$ by its value in a uniform electron gas

• Electron gas

11

- *N* electrons in a volume *V*, both → ∞, defining uniform singlet density:  $\rho(\mathbf{r}_1) = \rho = N/V = \text{constant}$
- Electrons may or may not interact with each other
- A uniform background field of positive charge maintains electroneutrality
- Not a bad model for some metals, but very different from electronic structure of a molecule
- LDA methods define  $E[\rho]$  in terms of a function of the density evaluated at **r**:  $E_{\rm XC}^{\rm LDA}[\rho] = \int \rho(1)\varepsilon_{\rm XC}(\rho(1))d1$

#### A simple toy LDA example

• Functional 
$$\mathcal{F}[\rho] = \int_{-5}^{5} \rho(x)\epsilon(\rho, x)dx$$
  
with  $\epsilon(\rho, x) = \int_{-1}^{1} \rho(x+t)dt$ 

• Local density approximation? uniform density reference

#### A simple toy LDA example

• Functional 
$$\mathcal{F}[\rho] = \int_{-5}^{5} \rho(x)\epsilon(\rho, x)dx$$
  
with  $\epsilon(\rho, x) = \int_{-1}^{1} \rho(x+t)dt$ 

• Local density approximation, uniform density reference constant w.r.t. t

$$\epsilon^{ ext{LDA}}(
ho,x) = \int_{-1}^{1} 
ho(x) dt = 2
ho(x) 
onumber \ \mathcal{F}^{ ext{LDA}}[
ho] = \int_{-5}^{5} 2
ho(x)^2$$

**Example applications** 

<b>ρ(x)</b>	F	FLDA
$x^2$	2555	2500
x	166.67	166.67
exp(-x)	25,885	22,026

#### The exchange contribution to $E_{XC}$ can be approached via the exchange hole concept

$$E_{
m X}[
ho] = rac{1}{2} \int \int rac{
ho(1)h_{
m X}(1,2)}{r_{12}} d1d2 \qquad h_{
m XC}(1,2) = rac{
ho_2(1,2)}{
ho(1)} - 
ho(2)$$

- An early approach to the exchange hole viewed it as an zerodensity region around an electron in a uniform electron gas
  - $-\rho(1) = \rho(2) = \rho = \text{constant}$  (uniform electron gas)
  - −  $\rho(1,2) = 0$  in hole →  $h_{\rm XC} = -\rho$  in hole
  - Given that  $\int h_{\rm XC}(1,2)d2 = -1$

$$(-
ho)rac{4}{3}\pi r_{
m c}^{3} = -1 ext{ } 
ightarrow r_{c} = \left(rac{3}{4\pi}
ight)^{lash 2}
ho({f r}_{1})^{-rac{1}{3}} 
onumber E_{
m X}[
ho] = -rac{9}{8}\left(rac{3}{\pi}
ight)^{1/3}lpha\int
ightarrow 
ho(1)^{4/3}d1 ext{ } V_{
m T}$$



 $V_{
m X}({f r}_1) \! lpha \, 
ho({f r}_1)^{1/3}$ 

# A treatment for the correlation contribution to $E_{xc}$ was developed from simulations

- No explicit form for  $E_{\rm C}[\rho]$  can be developed in a similar way
- Ceperly & Alder (1980) performed accurate quantum Monte Carlo simulation of the homogeneous interacting-electron gas at different densities
- Various authors presented analytical expressions for  $\varepsilon_{\rm C}$  via interpolation schemes, for use in  $E_{\rm C}[\rho] = \int \rho(1)\varepsilon_{\rm C}(1)d1$
- Most widely used variants were developed by Vosco, Wilk, & Nusair (1980) (VWNn)
- More accurate now is due to Perdew & Wang (1992) (PW)

## Nomenclature for DFT methods usually references the choice of the XC functionals

- No strict rule, but a convention exists
- General form 'XC'
  - X is the exchange part, C is the correlation part
- Initial letters of authors are the indicators (C: VWN, PW)
  - E.g., Becke + Lee-Yang-Parr (BLYP)
  - Supplemented by year if they provided more than one
- If same authors do both X and C, letters used only once
  - E.g., Perdew-Burke-Ernzerhof (PBE)

## Sometimes DFT is used in *unrestricted* form, with separate densities for each spin

- In principle, this is completely unnecessary
  - If working with the exact XC functional
- In practice, sometimes this approach provides advantages
  - Open-shell systems in particular
  - $-\rho^{\alpha} \neq \rho^{\beta}$ , "spin-polarized" case



• We won't consider this detail any further

#### **Suggested Reading/Viewing**

- Wolfram Koch and Max C. Holthausen, A Chemist's Guide to Density Functional Theory, 2<sup>nd</sup> ed., Wiley (2001)
  - Chapter 5, Secs. 6.1-6.4
  - On digital reserve at the UB library <u>https://search.lib.buffalo.edu/permalink/01SUNY\_BUF/9qhqtp/alma9</u> <u>90021458730204803</u>
- Cramer
  - Video 5.04: <u>https://www.youtube.com/watch?v=vvRS8SHjAFw</u>
  - Video 5.05: <u>https://www.youtube.com/watch?v=gk6HAl-7OmU</u>