Basics of DFT

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1. General background
2. DFT
3. Common functionals
4. Tough exact conditions
5. Why exact exchange is mixed in?
6. Miscellaneous
Electronic structure problem

- What atoms, molecules, and solids can exist, and with what properties?

**Figure:** My first ever DFT transparency.
Atomic units

- In atomic units, all energies are in Hartree (1H = 27.2 eV) and all distances in Bohr (1a₀ = 0.529 Å)

- To write formulas in atomic units, set $e^2 = \hbar = m_e = 1$

- In regular units,
  - 1 H = 27.2eV
  - 1 eV = 23.06 kcal/mol
  - 1 kcal = 4.184 kJ/mol = 503K.
Born-Oppenheimer approximation

- Because of difference between proton and electron mass, can separate wavefunction into product to an excellent approximation.

- Because electronic energies are in eV and much greater than 300K, electrons always in ground state.

- Yields

\[
E_{total} = E_{nuc}(\{R_\alpha\}) + E_{elec}(\{R_\alpha\})
\]

where electrons are in ground state.

- Knowing \( E_{total}(\{R_\alpha\}) \) yields structures from minima, vibrations from curvature, all reaction energies from well-depths, all transition states from saddle points, etc.
Hamiltonian

- Hamiltonian for $N$ electrons in the presence of external potential $v(r)$:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V},$$

where the kinetic and elec-elec repulsion energies are

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2,$$
$$\hat{V}_{ee} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

and difference between systems is $N$ and the one-body potential

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i)$$

- Often $v(r)$ is electron-nucleus attraction

$$v(\mathbf{r}) = -\sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}$$

where $\alpha$ runs over all nuclei, plus weak applied $\mathbf{E}$ and $\mathbf{B}$ fields.
Schrödinger equation

- 6\(N\)-dimensional Schrödinger equation for stationary states

\[
\{ \hat{T} + \hat{V}_{ee} + \hat{V} \} \Psi = E \Psi, \quad \Psi \text{ antisym}
\]

- The one-particle density is much simpler than \(\Psi\):

\[
n(r) = N \sum_{\sigma_1} \ldots \sum_{\sigma_N} \int d^3r_2 \ldots d^3r_N |\Psi(r_{\sigma_1}, r_{\sigma_2}, \ldots, r_{\sigma_N})|^2
\]

and \(n(r) \, d^3r\) gives probability of finding any electron in \(d^3r\) around \(r\).

- Wavefunction variational principle:
  - \(E[\Psi] \equiv \langle \Psi | \hat{H} | \Psi \rangle\) is a functional
  - Extrema of \(E[\Psi]\) are stationary states, and ground-state energy is

\[
E = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle
\]

where \(\Psi\) is normalized and antisym.
Outline

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References for ground-state DFT

- *ABC of DFT*, by KB and Rudy Magyar, http://dft.uci.edu/


Brief history of DFT

- **1926**: Old DFT was Thomas-Fermi theory and extensions.
- **50’s and 60’s**: Slater and co-workers develop $X_\alpha$ as crude KS-LDA.
- **1965**: Modern DFT begins with Kohn-Sham equations. By introducing orbitals, get 99% of the kinetic energy right, get accurate $n(r)$, and only need to approximate a small contribution, $E_{XC}[n]$.
- **1965**: KS also suggested local density approximation (LDA) and gradient expansion approximation.
- **1993**: More modern functionals (GGA’s and hybrids) shown to be usefully accurate for thermochemistry.
- **1998**: Kohn and Pople win Nobel prize in chemistry.
- **2010**: DFT in materials science, geology, soil science, astrophysics, protein folding, ...
Hohenberg-Kohn theorem (1964)

1. Rewrite variational principle (Levy 79):

\[ E = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle \]

\[ = \min_{n} \left\{ F[n] + \int d^3 r \, v(r)n(r) \right\} \]

where

\[ F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \]

- The minimum is taken over all positive \( n(r) \) such that \( \int d^3 r \, n(r) = N \)

2. The external potential \( v(r) \) and the hamiltonian \( \hat{H} \) are determined to within an additive constant by \( n(r) \)


Define *fictitious* non-interacting electrons satisfying:

\[
\left\{-\frac{1}{2}\nabla^2 + v_S(r)\right\} \phi_i(r) = \epsilon_i \phi_i(r), \quad \sum_{i=1}^{N} |\phi_i(r)|^2 = n(r).
\]

where \(v_S(r)\) is *defined* to yield \(n(r)\).

Define \(T_S\) as the kinetic energy of the KS electrons, \(U\) as their Hartree energy and

\[
T + V_{ee} = T_S + U + E_{XC}
\]

the remainder is the exchange-correlation energy.

Most important result of exact DFT:

\[
v_S(r) = v_{ext}(r) + \int d^3 r \frac{n(r')}{|r - r'|} + v_{XC}[n](r), \quad v_{XC}(r) = \frac{\delta E_{XC}}{\delta n(r)}
\]
Kohn-Sham energy components

- The KS kinetic energy is the kinetic energy of the KS orbitals

\[ T_s[n] = \frac{1}{2} \sum_{i=1}^{N} \int d^3r \ |\nabla \phi_i(r)|^2 > 0 \]

- The Hartree (aka Coulomb aka electrostatic) repulsive self-energy of a charge density is

\[ U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|} > 0 \]

- The exchange energy is

\[ -\frac{1}{2} \sum_{\sigma} \sum_{i,j}^{\text{occ}} \int d^3r \int d^3r' \ \frac{\phi_{i\sigma}^*(r)\phi_{j\sigma}^*(r')\phi_{i\sigma}(r')\phi_{j\sigma}(r)}{|r-r'|} \]

- \( E_C \) is everything else.
Kohn-Sham elementary facts

- $T$ and $V_{ee}$ are both positive, trying to rip system apart, but overcome by more negative $V$.
- Kinetic energies are positive, and $T > T_S$ by definition.
- $U$ is positive and dominates the electron-electron repulsion.
- $E_X$ only has contributions from same-spin electrons and is negative. This part is given exactly by a HF calculation.
- The electron-electron repulsion of the KS wavefunction is just

$$\langle \Phi[n]|\hat{V}_{ee}|\Phi[n]\rangle = U[n] + E_X[n]$$

- $E_C$ contains both kinetic and potential contributions:

$$E_C = \langle \Psi[n]|\hat{T} + \hat{V}_{ee}|\Psi[n]\rangle - \langle \Phi[n]|\hat{T} + \hat{V}_{ee}|\Phi[n]\rangle$$

$$= (T - T_S) + (V_{ee} - U - E_X) = T_C + U_C$$
KS potential of He atom

Every density has (at most) one KS potential.\(^1\)
Dashed line: \(v_S(r)\) is the exact KS potential.

Energy components of small spherical atoms

<table>
<thead>
<tr>
<th></th>
<th>$T$</th>
<th>$V_{\text{ext}}$</th>
<th>$V_{\text{ee}}$</th>
<th>$T_S$</th>
<th>$U$</th>
<th>$E_X$</th>
<th>$T_C$</th>
<th>$U_C$</th>
<th>$E_C$</th>
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</thead>
<tbody>
<tr>
<td>He</td>
<td>2.904</td>
<td>-6.753</td>
<td>0.946</td>
<td>2.867</td>
<td>2.049</td>
<td>-1.025</td>
<td>.037</td>
<td>-.079</td>
<td>-.042</td>
</tr>
<tr>
<td>Be</td>
<td>14.67</td>
<td>-33.71</td>
<td>4.375</td>
<td>14.59</td>
<td>7.218</td>
<td>-2.674</td>
<td>.073</td>
<td>-.169</td>
<td>-.096</td>
</tr>
<tr>
<td>Ne</td>
<td>128.9</td>
<td>-311.1</td>
<td>53.24</td>
<td>128.6</td>
<td>66.05</td>
<td>-12.09</td>
<td>.33</td>
<td>-.72</td>
<td>-.39</td>
</tr>
</tbody>
</table>

**Table:** Energy components found from the exact densities.

- Thanks to Cyrus Umrigar, Xavier Gonze, and Claudia Filippi.
Important points about KS calculations

- The total energy is not the sum of the orbital energies:
  \[ E \neq \sum_{i=1}^{N} \epsilon_i \]

- If some approximation is used for \( E_{XC} \), then energy can go below the exact ground-state energy.

- Any given formula for \( E_{XC} \), no matter where it came from, produces a non-empirical scheme for all electronic systems.

- The KS scheme, even with the exact functional, yields only \( E \) and \( n(r) \) (and anything that can be deduced from them).

- In principle, from HK, all properties are determined by \( n(r) \), but in reality, we only know one really well.
The KS HOMO-LUMO gap is not the fundamental gap

- **The fundamental gap of any system**
  - $\Delta = I - A$ ($= 24.6 \text{ eV for He}$)

- **The exact Kohn-Sham gap:**
  - $\Delta_S = \epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}$ ($= \epsilon_{1s} - \epsilon_{2s} = 21.16 \text{ eV for He}$)

- These gaps are *not* the same!

- KS gap is typically smaller than $\Delta$

- Most notorious case: bulk Si

- The *exact* ground-state $E_{\text{XC}}[n]$ produces a KS gap different from the fundamental gap.
Spin DFT

- In modern reality, everyone uses *spin*-density functional theory

- Can easily generalize theorems and equations to spin densities, $n_\uparrow(r)$ and $n_\downarrow(r)$, with two different KS potentials.

- No difference for spin-unpolarized systems, but much more accurate otherwise (odd electron number, radicals, etc.)

- Spin-scaling trivial for $E_x$, not so for correlation.

- Can handle collinear $\mathbf{B}$ fields
Lessons about basic DFT

DFT is

- different from all other methods of directly solving the Schrödinger equation.
- in principle exact for $E$ and $n(r)$, knowing only $E_{xc}[n]$.
- approximate in practice.

Exact DFT tells us what we can and cannot expect our functionals to be able to do.

$v_S(r)$ and $\phi_j(r)$ are not real, just logical constructions. The $\phi_j(r)$ can be very useful interpretative tools and follow intuition, but $v_S(r)$ is dangerous.
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Functionals in common use

- Local density approximation (LDA)
  - Uses only $n(r)$ at a point,
  
  $$E_{xc}^{LDA}[n] = \int d^3r \, e_{xc}^{unif}(n(r))$$

- Generalized gradient approx (GGA)
  - Uses both $n(r)$ and $|\nabla n(r)|$
  
  $$E_{xc}^{GGA}[n] = \int d^3r \, e_{xc}(n(r),|\nabla n|)$$
  - Examples are PBE and BLYP

- Hybrid:
  
  $$E_{xc}^{hyb}[n] = a(E_x - E_x^{GGA}) + E_{xc}^{GGA}[n]$$
  - Mixes some fraction of HF, $a$ usually about 25%
  - Examples are B3LYP and PBE0
### Functional Soup

- **Good:** choose one functional of each kind and stick with it (e.g., LDA, PBE, or PBE0).

- **Bad:** Run several functionals, and pick ‘best’ answer.

- **Ugly:** Design your own functional with 2300 parameters.

#### Empirical
- GGA: BLYP
- Hybrid: B3LYP

#### Non-empirical
- GGA: PBE
- Meta-GGA: TPSS
- Hybrid: PBE0

#### Names:
- B=B88 exchange
- LYP = Lee-Yang-Parr correlation
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**Non-empirical**
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Local density approximation (LDA)

- Exchange is trivial (Dirac, 1931)

\[ e_{\text{X}}^{\text{unif}}(n) = A_x n^{4/3}, \quad A_x = -0.738 \]

- Correlation energy known:
  \[ e_{\text{C}}^{\text{unif}}(n) \text{ was accurately calculated by QMC} \]

- Several different accurate parametrizations in use:
  - VWN80, aka S-VWN-5
LDA (or LSDA) general performance

- For total energies, $E_x$ is underestimated by about 10%, $E_C$ is overestimated by about 200%, so $E_{XC}$ is good to about 7% (mysterious cancellation of errors).
- For bond dissociation energies, LDA overbinds by about 1 eV /bond (30 kcal/mol), so no good for thermochemistry.
- Typical bond lengths are underestimated by 1% (unless involving an H atom), so excellent geometries and vibrations. So still used for structure.
- Bulk Fe is non-magnetic, because wrong structure has lowest energy.
- Transitions to unoccupied orbitals in bulk insulators a rough guide to quasiparticle excitations, except for too small gap.
Figure: Exact and LDA radial densities of the Ne atom.
Easy conditions

- **Size-consistency:**

\[ E_{XC}[n_A + n_B] = E_{XC}[n_A] + E_{XC}[n_B], \]

where \( n_A(r) \) and \( n_B(r) \) do not overlap.

- **Uniform limit:** Recover exact XC bulk jellium energy if \( n \) is constant.

- **Linear response of uniform gas:** LDA is almost exact for linear response to perturbation \( \cos(q \cdot r) \) for \( q \leq 2k_F \).

- **Lieb-Oxford bound:** Magnitude of \( E_{XC} \) cannot be greater than \( 2.3 \) \( E_{LDA} \).
Uniform coordinate scaling

Figure: A one-dimensional density (red) being squeezed by $\gamma = 2$ (blue)

- A very handy way to study density functionals, especially in limits:

\[ n_\gamma(r) = \gamma^3 n(\gamma r), \quad 0 \leq \gamma \leq \infty \]

  - For $\gamma > 1$, squeezes up the density, preserving norm; for $\gamma < 1$, stretches it out.

- Exchange: Require $E_x[n_\gamma] = \gamma E_x[n]$

- Correlation: $E_C[n_\gamma] = B[n] + C[n]/\gamma + \ldots$ for high density limit of finite systems. (Violated by LDA!)
History of GGA

- **Gradient expansion approximation (GEA):** Expansion in density gradients that is valid for slowly-varying gas, discussed in KS65.
- **Langreth-Mehl 81:** First modern GGA, but cut-off in wavevector space.
- **PW86:** Early version of Perdew strategy, cutting off gradient-expanded hole in real space. (Phys. Rev. B, 33)
- **B88:** Axel Becke $E_x^{GGA}$, based on energy density of atoms, one parameter (Phys. Rev. A. 38)
- **LYP, 88:** Lee-Yang-Parr turn Colle-Salvetti orbital functional for atoms into an $E_C[n]$ (Phys. Rev. B. 37)
- **PW91:** Parametrization of real-space cut-off procedure
- **PBE, 96:** A re-parametrization and simplification of PW91
- **RPBE, 99:** Danish version, improves surface energetics
- **PBEsol, 08:** Revised PBE for solids
Philosophy of GGA

- If LDA is very reliable using only \( n(r) \), surely can be more accurate if use \( \nabla n(r) \) too.
- Use exact conditions to constrain construction.
- Non-empirical (Perdew):
  - Use known QM limits to fix all parameters.
  - Retains systematic error
  - Controlled extrapolation away from known limits
- Empirical (Becke):
  - Fit parameters to atoms and molecules.
  - Minimizes error on fitted and similar systems
  - Fails badly when applied elsewhere
- Pragmatic (Kieron):
  - Judge a Perdew functional by its derivation, not its numbers
  - Judge a Becke functional by the numbers, not its derivation.
PBE, 1996

- **Correlation:**
  - In slowly varying limit, $E_C \rightarrow E_C^{GEA}$.
  - In rapidly varying limit, $E_C \rightarrow E_C^{LDA}$.
  - In high-density limit, $E_C \rightarrow -\text{const}$.

- **Exchange:**
  - Under uniform scaling, $E_X[n_{\gamma}] = \gamma E_X[n]$.
  - Under spin-scaling, $E_X[n_{\uparrow}, n_{\downarrow}] = (E_X[2n_{\uparrow}] + E_X[2n_{\downarrow}])/2$.
  - Linear response same as LDA.
  - Lieb-Oxford bound: $E_{XC} \geq 2.3 E_{X}^{LDA}$.

Leads to enhancement factor:

$$F_X(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa), \quad \kappa \leq 0.804.$$

- **Performance**
  - Reduces LDA overbinding by 2-3.
  - Overcorrects bond lengths to about $+1\%$. 

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Basics of DFT
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Hybrids

- A hybrid functional replaces some fixed fraction of GGA exchange with exact exchange.

- First proposed by Becke

- Morphed into the infamous B3LYP, now most used functional in DFT.

- The 3 in B3LYP is 3 fitted parameters, but other 2 just modify GGA.

- PBE0 is the derived version, with 1/4 mixing rationalized.
Typical results with functionals

G2 Data Set of small molecules

<table>
<thead>
<tr>
<th>m.a.e.</th>
<th>HF</th>
<th>LDA</th>
<th>PBE</th>
<th>BLYP</th>
<th>Hybrid</th>
</tr>
</thead>
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<tr>
<td>kcal/mol</td>
<td>100</td>
<td>30</td>
<td>10</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

BLYP for uniform gas

<table>
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<tr>
<th>$r_s$</th>
<th>0.1</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>error</td>
<td>-50%</td>
<td>-30%</td>
<td>-40%</td>
<td>-50%</td>
<td>-60%</td>
</tr>
</tbody>
</table>

- Successive improvement (in energetics) at increasing computational cost.
Applications of DFT

- Tens of thousands of papers every year.
- Appearing in every branch of science:
  - Solid-state physics
  - Chemistry
  - Biochemistry
  - Geology
  - Astrophysics
- Traditionally divided into finite systems (molecules) and extended (solids), but distinction is breaking down.
- Codes divided into either using localized basis functions (usually Gaussians) or plane waves.
- Examples:
  - Many throughout week.
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At the edge of all matter...

- Asymptotic decay of the density
  \[ \sqrt{n(r)} \rightarrow Ar^\beta e^{-\sqrt{2}Ir} \]

- leads to severe constraint on XC potential:
  \[ \nu_{\text{XC}}(r) \rightarrow -1/r \quad (r \rightarrow \infty) \]

- and determines KS HOMO:
  \[ \epsilon_{\text{HOMO}} = -l \]
As a function of $N$, the energy is a sequence of straight line segments

\[ \mu = \frac{\partial E}{\partial N} = \begin{cases} I, & N \leq Z \\ A, & N > Z \end{cases} \]

Fig. 2.2. Ground state energy of an atom with nuclear charge $Z$ and $(Z+\omega)$ electrons

The KS potential jumps suddenly as $N$ crosses an integer

- When you add a tiny fraction of an electron to a system, the KS potential shifts uniformly, since before, $\epsilon_{\text{HOMO}}(N) = -I$, but now, $\epsilon_{\text{HOMO}}(N + \delta) = -A$
- Thus $v_S(r)$ must jump by
  $$\Delta_{XC} = (I - A) + (\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}) = -\epsilon_{\text{LUMO}} - A$$

- Very important in DFT calculations of:
  - molecules approaching each other, before they bond covalently.
  - single-molecule transport if molecule is weakly bound to leads.
There are sharp steps in the KS potential between separated systems

**Figure:** Cartoon of step in KS potential between two well-separated open-shell fragments.

Energy as a function of electrons transferred for a stretched bond

**Figure:** Total energy of separated LiH as a function of the number of electrons transferred from Li to H.

Static correlation is not the same as strong correlation

- Effect of small gaps in molecules, if they dissociate into open shells.
- Worsens as bond length increases, producing unbalanced error.
- Called static correlation as there’s no analog in, eg, uniform gas.
- Very slight in total energy, still small in dissociation energy, but causes GGA errors of order 10 kcal/mol.
- Biggest effect in multiple bonds, e.g., N\(_2\).
- Worst cases are Cr\(_2\) at equilibrium, or stretched H\(_2\).
- Can understand how mixing exact exchange improves energetics when static correlation is present.
- Explains accuracy of hybrids for bonds and transition state barriers.
Consider \( H_2 \) as \( R \to \infty \):

- e.g. Yang et al. 8 August 2008 *Science* **321** (5890), 792

\[
E(R) \to 2E(H), \quad R \to \infty
\]

- But \( \Psi \) is *always* a singlet, for large but finite \( R \), have 1/2 electron of each spin on each atom.

- Single-reference wavefunction has one doubly-occupied molecular orbital, but \( \Psi \) becomes Heitler-London wavefunction, which is completely different.

- Any single-reference theory gives spin-unpolarized H atoms that are wrong in energy.

- **Symmetry dilemma**: Can allow spin-symmetry to break, and get right energetics, but then no longer a spin eigenstate.

- Coulson-Fischer point is \( R \) when symmetry spontaneously breaks in approximate treatment
Adiabatic connection and relation to scaling

Write XC energy as integral over coupling constant, \( n(\mathbf{r}) \) fixed:

\[
E_{\text{XC}}^{\lambda}[n] = \lambda^2 E_{\text{XC}}[n_{1/\lambda}], \quad E_{\text{XC}}[n] = \int_0^1 d\lambda \frac{dE_{\text{XC}}^{\lambda}}{d\lambda} = \int_0^1 d\lambda \ U_{\text{XC}}^{\lambda}[n]
\]


**Figure:** Adiabatic connection curve for He in various approximations
Static correlation shows up in adiabatic connection

![Graph showing adiabatic connection in various approximations for H₂ at 5 Å.](image)

**Figure**: Adiabatic connection in various approximations for H₂ at 5 Å.

Adiabatic connection for dissociation energy of $N_2$

**Figure:** Adiabatic decomposition of XC energy difference between $N_2$ and 2 N atoms

You can ‘derive’ the $\frac{1}{4}$ mixing of exact exchange in PBE0.

Orbital dependence

- Much of deficiencies in common functionals are due to their explicit local (or semi-local) density dependence.

- There are many effects due to discrete orbitals that are missed.

- Some of these effects are seriously weird, but are important to know about.
The LDA (or GGA or hybrid) potentials decay too rapidly.

Accurate densities from QMC calculations:

So how come it produces a good density?

FIG. 3: Exact and LDA KS potentials for the He atom. While
With local approximations, each electrons repels itself

- For any one-electron density $n(r)$:
  \[
  E_x[n] = -U[n], \quad E_C[n] = 0 \quad (N = 1)
  \]

- Standard functionals all unable to cancel the self-Hartree energy.

- Real trouble is unbalanced nature of effect.

- Stretched $\text{H}_2^+$ is an extreme case as local-type functionals have huge error as $R \rightarrow \infty$.

- Violated by most semilocal functionals (unless artificially built in).

- Particularly problematic for localized and $f$ electrons in solids.
Perdew-Zunger Self-Interaction Correction, 1981

- Perdew-Zunger found a way to correct for self-interaction:

\[ E_{\text{HXC}}^{\text{SIC}}[n] = E_{\text{HXC}}[n] - \sum_{j=1}^{N} E_{\text{HXC}}[|\phi_j|^2] \]

- Exact for any one electron system, for both X and C
- Improves LDA results, especially those with strong SI error.
- Does not generally improve GGA or hybrid
- Sadly, not invariant under unitary transformation of occupied orbitals, so not a proper functional.
- Very useful for localized electrons, where LDA fails badly, but must choose which orbitals.
- For bulk system, correction vanishes if KS orbitals are used, but generally correct when orbitals are localized.
**Separated LiH with approximations and SIC**

![Graph showing total energy of separated LiH as a function of the number of electrons transferred in various approximations.](image)

**Figure:** Total energy of separated LiH as a function of the number of electrons transferred in various approximations.

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Jacob’s ladder to DFT heaven (or hell?)

Increasingly sophisticated and expensive density functional approximations.

\[ E_{XC} = \int d^3 r \, f(n, \nabla n, \tau, \ldots) \]

JCTC 2009 Vol. 5, Iss. 4.
How to handle orbital-dependence in KS DFT

Use the **Optimized Effective Potential (Method)**

- Way to handle orbital-dependent functionals in KS scheme, i.e., with single multiplicative KS potential
- Still density functionals, since orbitals uniquely determined by density
- Several schemes to implement, all much more expensive than regular KS-DFT
- Improves many properties:
  - No self-interaction error
  - Potentials and orbital energies much better
  - Approximates derivative discontinuity
- But don’t have compatible correlation

▶ Stephan Kümmel and Leeor Kronik, Rev. Mod. Phys. 80, 3 (2008)
What’s the difference between HF and EXX?

- HF minimizes $E_x[\{\phi_j\}]$ over all possible wavefunctions
- EXX includes additional constraint of common potential (i.e., KS)
- Yields almost identical total energies, with HF an eensy bit lower
- Occupied orbital energies very similar, but big difference in unoccupied orbitals
- Reports of good gaps with hybrids use HF scheme mixed with KS (generalized KS scheme), so not getting a ‘good’ KS gap.
Van der Waals forces

- Very important for soft Coulomb matter
- Can show $E \rightarrow -C_6/R^6$ for large $R$ between two fragments
- But GGA’s use $n(r)$ and $|\nabla n|$, so $E$ decays exponentially with $R$.
- Many attempts to include in DFT
  - Add empirical corections to DFT results, eg DFT-D
    - Grimme,LW
  - Langreth and Lundquist: RPA treatment leading to explicit non-local functional.
  - Exchange hole used to get $C_6$.
- LL functional now widely coded and being applied to many systems.
Excitations

- Many ways to do excitations in DFT
  - Ensemble DFT
  - $\Delta$ SCF
  - min-max principle
  - TDDFT linear response

- Many other ways to do excitations

- Quantum transport very difficulty for any method

- Reviews
Semiclassical origins of DFT

- Large ongoing project in our group
- Many implications for DFT
- Basic idea:
  - In a semiclassical limit, LDA is dominant term for *all matter*.
  - Next corrections are usually quantum oscillations, not gradient corrections of slowly varying densities, hence need for *generalization*.
  - Expansion is asymptotic, so sometimes next correction worsens result.
- Short-term results
  - PBEsol: Solves problem of improving lattice constants over LDA, but creates other issues.
  - Orbital-free calculations for atoms.
- Long-term goals
  - Systematic non-empirical functional construction
  - Unification of DFT with Green’s function and wavefunction methods
  - Orbital-free calculations
PBEsol

- **Exchange:**
  - Restore gradient expansion for exchange.
  - In PBE, $\mu = 0.219$, in PBEsol, $\mu = 10/81 = 0.1234$.

- **Correlation**
  - For large neutral jellium clusters, $E_{XC} = e_{XC}^{\text{unif}}(n) V + \sigma_{XC}(n) A + \ldots$.
  - $\beta = 0.046$ gives best energy (PBE had .0667).
  - First proposed by Armiento and Mattsson (2005), whose functional gives almost identical lattice parameters.

- **Performance:**
  - Consistency: $\sigma_X(n)$ almost exact
  - Improves lattice parameters of LDA by 2-3.
  - Means poor atomic energies, so worsens thermochemistry.
  - Improves transition between planar and globular Au$^-$ clusters.
  - Take 5 minutes to implement by modifying PBE
Lessons from second part

- **Standard functionals** should give heirarchy of increasingly accurate results.

- **Non-empirical approach**, championed by Perdew, and few-empirical, by Becke, Parr, Yang, etc.

- Hybrids can be **partially rationalized**.

- Some things are just **not included** in common functionals, e.g., dispersion forces, neutral fragmentation, etc.

- **Excitations formally unavailable** except via other theorems, such as Runge-Gross for TDDFT.

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