XYZ of ground-state DFT

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Outline

1. Self-interaction error
2. Including orbital effects
3. Static correlation
4. Why hybrids work for thermochemistry
5. Present-day developments

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1. Self-interaction error
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With local approximations, each electrons repels itself

- For any one-electron density $n(\mathbf{r})$:

$$E_{\rm X}[n] = -U[n], \qquad E_{\rm C}[n] = 0 \qquad (N = 1)$$

- Standard functionals all unable to cancel the self-Hartree energy.
- Real trouble is unbalanced nature of effect.
- Stretched H_2^+ is an extreme case as local-type functionals have huge error as $R \to \infty$.
- Violated by most semilocal functionals (unless artificially built in).
- Particularly problematic for localized and f electrons in solids.

At the edge of all matter...

To understand asymptotic behavior:

- Each subshell of orbitals decays with characteristic length, depending on binding
- In the tail of a density, most loosely bound electron dominates, so its a one-electron region.
- leads to severe constraint on XC potential:

$$v_{\mathrm{XC}}(\mathbf{r}) \to -v_{\mathrm{H}}^{N=1}(r) = -\frac{1}{r} \qquad (r \to \infty)$$

- Also determines decay of KS potential, since nuclear and Hartree contributions cancel for a neutral system, so

$$v_{\mathrm{S}}(\mathbf{r}) \to v_{\mathrm{XC}}(r) = -\frac{1}{r} \qquad (r \to \infty)$$

The LDA (or GGA or hybrid) potentials decay too rapidly

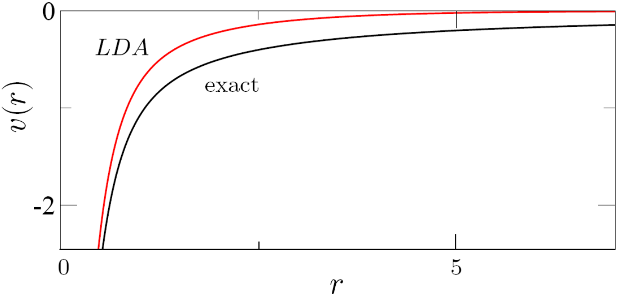


FIG. 3: Exact and LDA KS potentials for the He atom. While

- Accurate densities from QMC calculations:
  - C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).
- So how come it produces a good density?
  - Unambiguous exchange-correlation energy density K. Burke, F.G. Cruz, and K.C. Lam, J. Chem. Phys. 109, 8161 (1998).

Koopmans' theorem is *exact* in KS-DFT

- From many-body wavefunction, can prove aymptotic decay of the density

$$\sqrt{n(\mathbf{r})} \to A r^{\beta} e^{-\sqrt{2I}r}$$

- The KS system must reproduce this behavior exactly, but decay is determined by HOMO.
- So this determines KS HOMO:

$$\epsilon_{\mathrm{HOMO}} = -I$$

As a function of N, the energy is a sequence of straight line segments

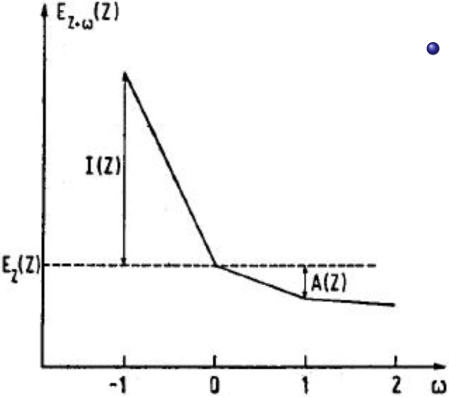


Fig. 2.2. Ground state energy of an atom with nuclear charge Z and $(Z+\omega)$ electrons

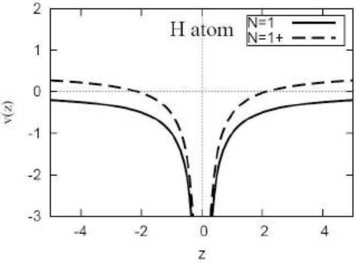
- R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).

$$\begin{aligned} \mu &= \frac{\partial E}{\partial N} \\ &= -\begin{cases} I, & N \leq Z \\ A, & N > Z \end{cases} \end{aligned}$$

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, $\epsilon_{\mathrm{HOMO}}(N) = -I$, but now, $\epsilon_{\mathrm{HOMO}}(N+\delta) = -A$
- Thus $v_{\mathrm{S}}(\mathbf{r})$ must jump by

$$\Delta_{\mathrm{XC}} = (I - A) + (\epsilon_{\mathrm{HOMO}} - \epsilon_{\mathrm{LUMO}}) = -\epsilon_{\mathrm{LUMO}} - A$$



- Very important in DFT calculations of:
  - molecules approaching each other, before they bond covalently.
  - single-molecule transport if molecule is weakly bound to leads.

The KS HOMO-LUMO gap is not the fundamental gap

- The fundamental gap of any system
  - $\Delta = I - A \qquad (= 24.6\,\text{eV for He})$
- The exact Kohn-Sham gap:
  - $\Delta_{\rm S} = \epsilon_{\rm HOMO} - \epsilon_{\rm LUMO} \qquad (= \epsilon_{1s} - \epsilon_{2s} = 21.16\,\text{eV for He})$
- These gaps are *not* the same!
- KS gap is typically smaller than Δ
- Most notorious case: bulk Si
- The *exact* ground-state $E_{\rm XC}[n]$ produces a KS gap different from the fundamental gap.

There are sharp steps in the KS potential between separated systems

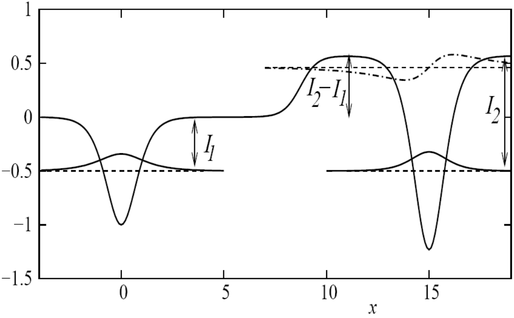


Figure: Cartoon of step in KS potential between two well-separated open-shell fragments.

- N. T. Maitra, J. Chem. Phys. 122, 234104 (2005).

Energy as a function of electrons transferred for a stretched bond

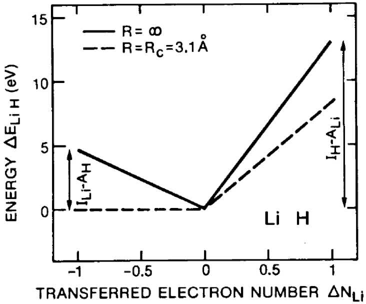


Figure: Total energy of separated LiH as a function of the number of electrons transferred from Li to H.

- *What do the Kohn-Sham orbitals mean? How do atoms dissociate?*, J.P. Perdew, in *Density Functional Methods in Physics*, edited by R.M. Dreizler and J. da Providencia (Plenum, NY, 1985), p. 265.

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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.

Perdew-Zunger Self-Interaction Correction, 1981

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

$$E^{\mathsf{SIC}}_{\mathrm{HXC}}[n] = E_{\mathrm{HXC}}[n] - \sum_{j=1}^{N} E_{\mathrm{HXC}}[|\phi_j|^2]$$

- 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

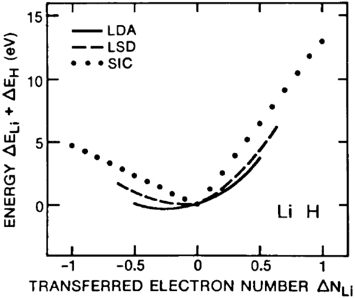

Figure: Total energy of separated LiH as a function of the number of electrons transferred in various approximations.

- *What do the Kohn-Sham orbitals mean? How do atoms dissociate?*, J.P. Perdew, in *Density Functional Methods in Physics*, edited by R.M. Dreizler and J. da Providencia (Plenum, NY, 1985), p. 265.

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Not so weak 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.

Stretched H_2

- Consider H_2 as $R \to \infty$:
    - e.g. Yang et. al, 8 August 2008 *Science* **321** (5890), 792

$$E(R) \to 2E(H), \qquad R \to \infty$$

- But Ψ 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 Ψ 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

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Adiabatic connection and relation to scaling

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

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

- D.C. Langreth and J.P. Perdew, Solid State Commun. 17, 1425 (1975).
- O. Gunnarsson and B.I. Lundqvist, Phys. Rev. B 13, 4274 (1976).

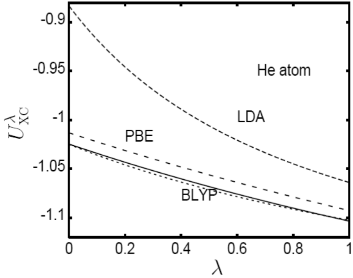


Figure: Adiabatic connection curve for He in various approximations

Static correlation shows up in adiabatic connection

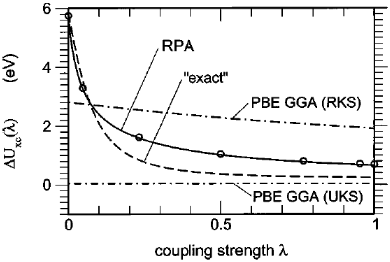


FIG. 3. Same as Fig. 1, but for $R=5$ bohrs, i.e., beyond the Coulson–Fisher point. The RPA results are based on the *total* density of a unrestricted EXX KS calculation. Also shown are the adiabatic connections for the PBE GGA applied in the restricted KS formalism (RKS), yielding poor energetics, and in the unrestricted KS formalism (UKS), yielding better energetics but artifically breaking inversion symmetry.

Figure: Adiabatic connection in various approximations for H_2 at 5Å.

- M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke, J. Chem. Phys. **122**, 094116 (2005)

Adiabatic connection for dissociation energy of N_2

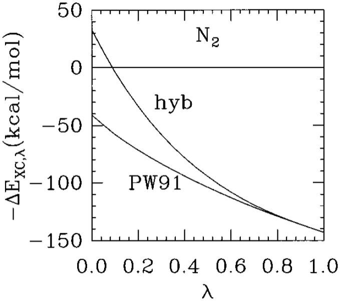


Figure: Adiabatic decomposition of XC energy difference between N_2 and 2 N atoms

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

- J.P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).

Outline

Meta GGA's

- Basic idea: If you are doing KS, you already have an indicator of non-locality, the KS kinetic energy density:
- Formula:

$$E_{\mathrm{XC}} = \int d^3r \; f(n, \nabla n, \tau)$$

where

$$\tau(\mathbf{r}) = \sum_{J}^{\text{occ}} \frac{1}{2} |\nabla \phi_j|^2 = \text{positive KE density}$$

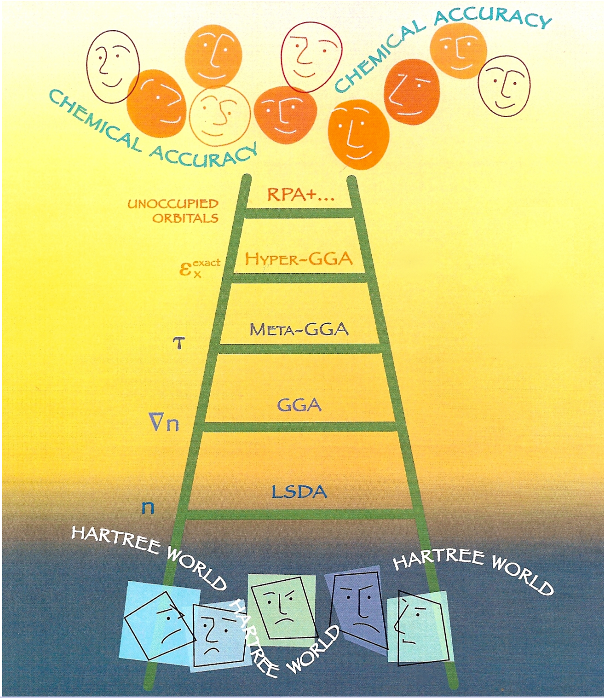
- Attempt to get accuracy of hybrids *without* having to do HF.

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

Increasingly sophisticated and expensive density functional approximations.

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

- 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! (and costs a lot to run...)

- Stephan Kümmel and Leeor Kronik, Rev. Mod. Phys. 80, 3 (2008)

What's the difference between HF and EXX?

- HF minimizes $E_{\rm X}[\{\phi_j\}]$ over all possible wavefunctions
- EXX includes additional constraint of common potential (i.e., KS)
- Yields almost identical total energies, with HF an eensty 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 $E \to -C_6/R^6$ for large R between two fragments
- But GGA's use $n(\mathbf{r})$ 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, J. Comp. Chem. **27**, 1787 (2006).
    - Langreth and Lundquist: RPA treatment leading to explicit non-local functional.
        - ★ M. Dion et al, Phys. Rev. Lett. **92**, 246401 (2004).
    - Exchange hole used to get C_6 .
        - ★ Axel D. Becke and Erin R. Johnson J. Chem. Phys. **127**, 154108 (2007)
- LL functional now widely coded and being applied to many systems.

Lessons from this part

- Self-interaction error is a nebulous error that can be somewhat cured by SIC.
- KS potentials have definite features (steps, decay at large r) related to line-segment nature of $E(N)$.
- Some things are just not included in common functionals, e.g., dispersion forces, neutral fragmentation, etc.
- Good thermochemistry of hyrids can be partially rationalized using adiabatic connection.
- Many things are not correct.