Basics of DFT

Kieron Burke and Lucas Wagner

Departments of Physics and Chemistry, University of California, Irvine, CA 92697, USA

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Outline

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Electronic structure problem

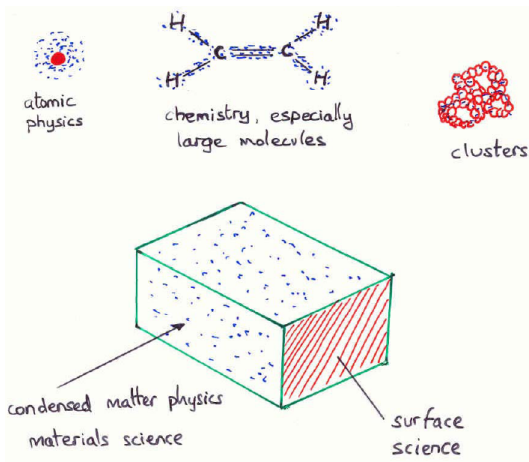- What atoms, molecules, and solids can exist, and with what properties?

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 ($1a_0 = 0.529$ Å)

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

- In regular units,
    - $1\ H = 27.2 eV$
    - $1\ eV = 23.06$ 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

$$E_{total} = E_{nuc}(\{\mathbf{R}_\alpha\}) + E_{elec}(\{\mathbf{R}_\alpha\})$$

  where electrons are in ground state.

- Knowing $E_{total}(\{\mathbf{R}_\alpha\})$ 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 $v(\mathbf{r})$:

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

where the kinetic and elec-elec repulsion energies are

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

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

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

- Often $v(\mathbf{r})$ is electron-nucleus attraction

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

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

Schrödinger equation

- $6N$-dimensional Schrödinger equation for stationary states

$$\{\hat{T} + \hat{V}_{ee} + \hat{V}\}\Psi = E\,\Psi, \qquad \Psi \text{ antisym}$$

- The one-particle density is much simpler than Ψ:

$$n(\mathbf{r}) = N \sum_{\sigma_1} \ldots \sum_{\sigma_N} \int d^3 r_2 \ldots d^3 r_N |\Psi(\mathbf{r}\sigma_1, \mathbf{r}_2\sigma_2, \ldots, \mathbf{r}_N\sigma_N)|^2$$

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

- 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 Ψ is normalized and antisym.

Outline

References for ground-state DFT

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

- *A Primer in Density Functional Theory*, edited by C. Fiolhais et al. (Springer-Verlag, NY, 2003)

- *Density Functional Theory*, Dreizler and Gross, (Springer-Verlag, Berlin, 1990)

- *Density Functional Theory of Atoms and Molecules*, Parr and Yang, (Oxford, New York, 1989)

- *A Chemist's Guide to Density Functional Theory*, Koch and Holthausen (Wiley-VCH, Weinheim, 2000)

- *Which functional should I choose?* Rappoport, Crawford, Furche, and Burke. 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 Xα as crude KS-LDA.

- 1965: Modern DFT begins with Kohn-Sham equations. By introducing orbitals, get 99% of the kinetic energy right, get accurate $n(\mathbf{r})$, and only need to approximate a small contribution, $E_{\mathrm{XC}}[n]$.

- 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):

$$
\begin{aligned}
E &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle \\
&= \min_{n} \left\{ F[n] + \int d^3r \; v(\mathbf{r}) n(\mathbf{r}) \right\}
\end{aligned}
$$

where

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

  ▶ The minimum is taken over all positive $n(\mathbf{r})$ such that $\int d^3r \; n(\mathbf{r}) = N$

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

● P. Hohenberg and W. Kohn, Phys. Rev. **136**, B 864 (1964).

● M. Levy, Proc. Natl. Acad. Sci. (U.S.A.) **76**, 6062 (1979).

Kohn-Sham 1965

- Define *fictitious* non-interacting electrons satisfying:

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\mathrm{S}}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \qquad \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 = n(\mathbf{r}).$$

  where $v_{\mathrm{S}}(\mathbf{r})$ is *defined* to yield $n(\mathbf{r})$.

- Define T_{S} as the kinetic energy of the KS electrons, U as their Hartree energy and

$$T + V_{\mathrm{ee}} = T_{\mathrm{S}} + U + E_{\mathrm{XC}}$$

  the remainder is the exchange-correlation energy.

- Most important result of exact DFT:

$$v_{\mathrm{S}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + \int d^3 r \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\mathrm{XC}}[n](\mathbf{r}), \qquad v_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}}{\delta n(\mathbf{r})}$$

Kohn-Sham energy components

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

$$T_{\mathrm{s}}[n] = \frac{1}{2} \sum_{i=1}^{N} \int d^3r \ |\nabla \phi_i(\mathbf{r})|^2 \quad > 0$$

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

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

- The exchange energy is

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

- 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:

$$
\begin{aligned}
E_C &= \langle \Psi[n]|\hat{T} + \hat{V}_{ee}|\Psi[n]\rangle - \langle \Phi[n]|\hat{T} + \hat{V}_{ee}|\Phi[n]\rangle \\
&= (T - T_S) + (V_{ee} - U - E_X) = T_C + U_C
\end{aligned}
$$

KS potential of He atom
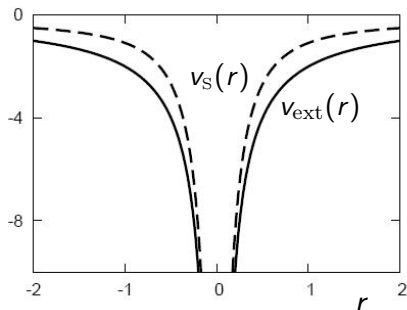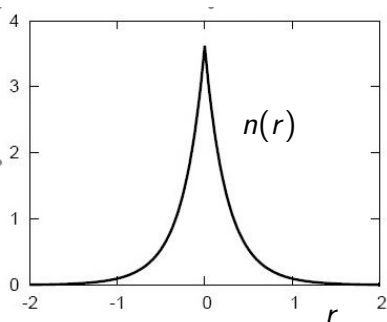
Every density has (at most) one KS potential.[1]
Dashed line: $v_{\mathrm{s}}(r)$ is the *exact* KS potential.

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[1] *Accurate exchange-correlation potentials and total-energy components for the helium isoelectronic series*, C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994)

Energy components of small spherical atoms

	T	V_{ext}	V_{ee}	T_{S}	U	E_{x}	T_{C}	U_{C}	E_{C}
He	2.904	-6.753	0.946	2.867	2.049	-1.025	.037	-.079	-.042
Be	14.67	-33.71	4.375	14.59	7.218	-2.674	.073	-.169	-.096
Ne	128.9	-311.1	53.24	128.6	66.05	-12.09	.33	-.72	-.39

Table: Energy components found from the exact densities.

- Huang and Umrigar, Phys. Rev. A **56**, 290, (1997)

- 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 $n(\mathbf{r})$ (and anything that can be deduced from them).
- In principle, from HK, *all* properties are determined by $n(\mathbf{r})$, 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:
  - $\Delta_{\mathrm{S}} = \epsilon_{\mathrm{HOMO}} - \epsilon_{\mathrm{LUMO}}$ ($= \epsilon_{1s} - \epsilon_{2s} = 21.16\,\text{eV}$ for He)

- These gaps are *not* the same!

- KS gap is typically smaller than Δ

- Most notorious case: bulk Si

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

Spin DFT

- In modern reality, everyone uses *spin*-density functional theory
    - U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

- Can easily generalize theorems and equations to spin densities, $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, 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 **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 $n(\mathbf{r})$, knowing only $E_{\mathrm{xc}}[n]$.
  - approximate in practice.

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

- $v_{\mathrm{S}}(\mathbf{r})$ and $\phi_j(\mathbf{r})$ are *not* real, just logical constructions. The $\phi_j(\mathbf{r})$ can be very useful interpretative tools and follow intuition, but $v_{\mathrm{S}}(\mathbf{r})$ is dangerous.

Outline

Functionals in common use

- Local density approximation (LDA)
  - Uses only $n(\mathbf{r})$ at a point,

$$E_{\text{xc}}^{\text{LDA}}[n] = \int d^3r \; e_{\text{xc}}^{\text{unif}}(n(\mathbf{r}))$$

- Generalized gradient approx (GGA)
  - Uses both $n(\mathbf{r})$ and $|\nabla n(\mathbf{r})|$

$$E_{\text{xc}}^{\text{GGA}}[n] = \int d^3r \; e_{\text{xc}}(n(\mathbf{r}), |\nabla n|)$$

  - Examples are PBE and BLYP
- Hybrid:

$$E_{\text{xc}}^{\text{hyb}}[n] = a(E_{\text{x}} - E_{\text{x}}^{\text{GGA}}) + E_{\text{xc}}^{\text{GGA}}[n]$$

  - 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
- Names:
  - B=B88 exchange
  - LYP = Lee-Yang-Parr correlation

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

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Local density approximation (LDA)

- Exchange is trivial (Dirac, 1931)

$$e_{\mathrm{X}}^{\mathrm{unif}}(n) = A_{\mathrm{X}} \, n^{4/3}, \qquad A_{\mathrm{X}} = -0.738$$

- Correlation energy known:
  $e_{\mathrm{C}}^{\mathrm{unif}}(n)$ was accurately calculated by QMC
  - D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

- Several different accurate parametrizations in use:
  - PW92 – Perdew and Wang, Phys. Rev. B **45**, 13244 (1992)

  - PZ81 – Perdew and Zunger, Phys. Rev. B **23**, 5048 (1981)

  - VWN80, aka S-VWN-5
    S. H. Vosco, L. Wilk, and M. Nusair, Can. J. Phys. **58**(8): 1200 (1980)

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.
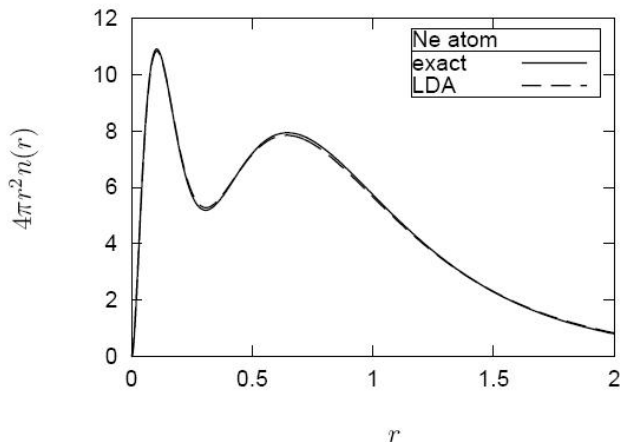
Densities

Figure: Exact and LDA radial densities of the Ne atom.

Easy conditions

- Size-consistency:

$$E_{\mathrm{xc}}[n_A + n_B] = E_{\mathrm{xc}}[n_A] + E_{\mathrm{xc}}[n_B],$$

  where $n_A(\mathbf{r})$ and $n_B(\mathbf{r})$ 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 $\cos(\mathbf{q} \cdot \mathbf{r})$ for $q \leq 2k_{\mathrm{F}}$.

- Lieb-Oxford bound: Magnitude of E_{xc} cannot be greater than 2.3 $E_{\mathrm{x}}^{\mathrm{LDA}}$.

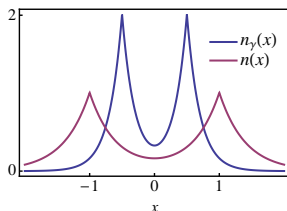# Uniform coordinate scaling

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

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

$$n_\gamma(\mathbf{r}) = \gamma^3 \, n(\gamma \mathbf{r}), \qquad 0 \leq \gamma \leq \infty$$

  - For $\gamma > 1$, squeezes up the density, preserving norm; for $\gamma < 1$, stretches it out.
- Exchange: Require $E_{\mathrm{x}}[n_\gamma] = \gamma \, E_{\mathrm{x}}[n]$
- Correlation: $E_{\mathrm{C}}[n_\gamma] = B[n] + C[n]/\gamma + ...$ 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 $E_{\mathrm{X}}^{\mathrm{GGA}}$, 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 $E_{\mathrm{C}}[n]$ (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 $n(\mathbf{r})$, surely can be more accurate if use $\nabla n(\mathbf{r})$ 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, $E_\mathrm{C} \to E_\mathrm{C}^{\mathrm{GEA}}$.
  - In rapidly varying limit, $E_\mathrm{C} \to E_\mathrm{C}^{\mathrm{LDA}}$.
  - In high-density limit, $E_\mathrm{C} \to -\mathrm{const}$.

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

  Leads to enhancement factor:

  $$F_\mathrm{x}(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa), \qquad \kappa \leq 0.804.$$

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

Hybrids

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

- First proposed by Becke
  - A.D. Becke, J. Chem. Phys. 98, 5648 (1993).

- 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.
  - Burke, Ernzerhof, and Perdew. Chem. Phys. Lett. **265**, 1996

Typical results with functionals

G2 Data Set of small molecules

m.a.e.	HF	LDA	PBE	BLYP	Hybrid
kcal/mol	100	30	10	6	3

BLYP for uniform gas

r_s	0.1	1	2	5	10
error	-50%	-30%	-40%	-50%	-60%

- 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.

Outline

At the edge of all matter...

- Asymptotic decay of the density

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

- leads to severe constraint on XC potential:

$$v_{\mathrm{XC}}(\mathbf{r}) \rightarrow -1/r \quad (r \rightarrow \infty)$$

- and determines KS HOMO: $\quad \epsilon_{\mathrm{HOMO}} = -I$

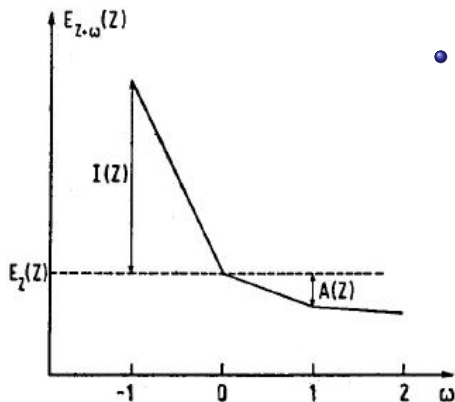# As a function of N, the energy is a sequence of straight line segments

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).

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

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

$$\Delta_{\mathrm{XC}} = (I - A) + (\epsilon_{\mathrm{HOMO}} - \epsilon_{\mathrm{LUMO}}) = -\epsilon_{\mathrm{LUMO}} - A$$
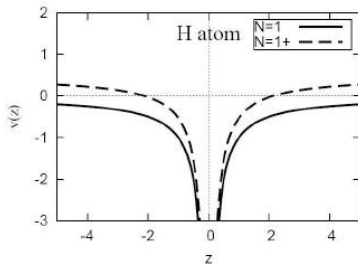
- Very important in DFT calculations of:
  - molecules approaching each other, before they bond covalently.
  - single-molecule transport if molecule is weakly bound to leads.

There are sharp steps in the KS potential between separated systems
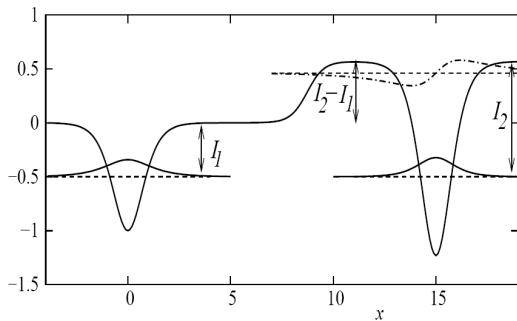

Figure: Cartoon of step in KS potential between two well-separated open-shell fragments.

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

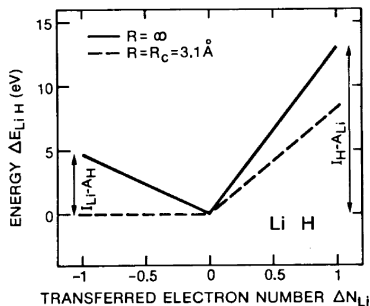# Energy as a function of electrons transferred for a stretched bond

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.

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.

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

Outline

Adiabatic connection and relation to scaling

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

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

- 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).
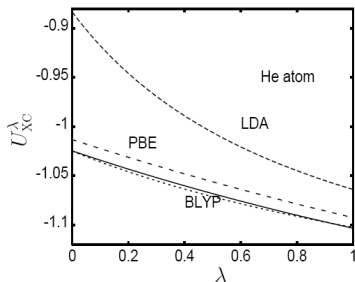

Figure: Adiabatic connection curve for He in various approximations

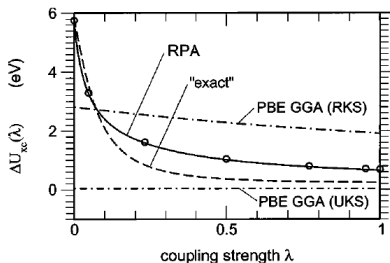# Static correlation shows up in adiabatic connection

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 artificially 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)

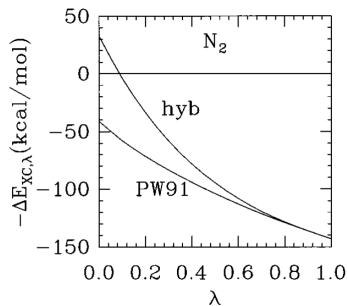# Adiabatic connection for dissociation energy of N_2

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).

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.

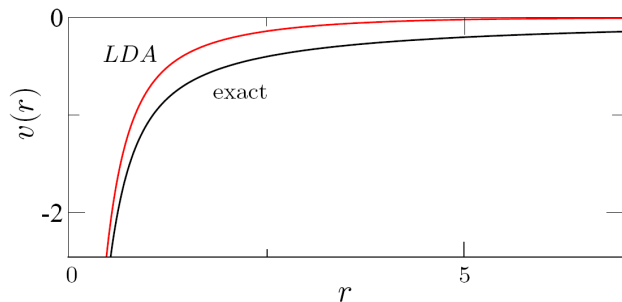# The LDA (or GGA or hybrid) potentials decay too rapidly

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).

With local approximations, each electrons repels itself

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

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

- 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.

Perdew-Zunger Self-Interaction Correction, 1981

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

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

- 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.
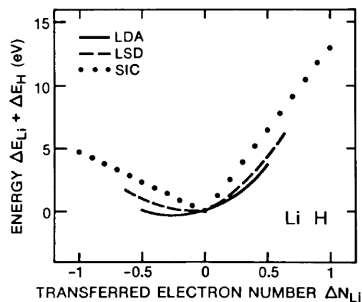
Separated LiH with approximations and SIC

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.
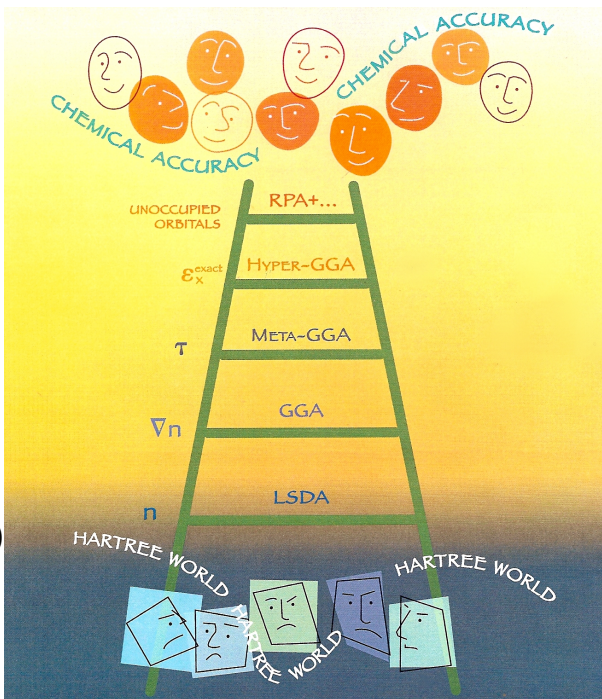
Outline

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.

Labels on ladder (bottom to top):
- n — LSDA
- ∇n — GGA
- τ — META-GGA
- $\varepsilon_{\mathrm{x}}^{\mathrm{exact}}$ — HYPER-GGA
- UNOCCUPIED ORBITALS — RPA+...

CHEMICAL ACCURACY

HARTREE WORLD

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 $E_{\mathrm{x}}[\{\phi_j\}]$ 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,LW
  - 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.

Excitations

- Many ways to do excitations in DFT
  - Ensemble DFT
  - Δ SCF
  - min-max principle
  - TDDFT linear response
- Many other ways to do excitations
- Quantum transport very difficulty for any method

- Reviews
  - TDDFT: K. Burke, J. Werschnik, and E. K. U. Gross, The Journal of Chemical Physics, 123, 062206 (2005).
  - *Density functional calculations of nanoscale conductance* M. Koentopp, C. Chang, K. Burke, and R. Car, J. Phys.: Condens. Matter 20, 083203 (2008).

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, $E_{\mathrm{xc}} = e_{\mathrm{xc}}^{\mathrm{unif}}(n)\, V + \sigma_{\mathrm{xc}}(n)\, A + \dots$.
  - $\beta = 0.046$ gives best energy (PBE had .0667).
  - First proposed by Armiento and Mattsson (2005), whose functional gives almost identical lattice parameters.

- Performance:
  - Consistency : $\sigma_{\mathrm{x}}(n)$ 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.
    - ⋆ Johansson, Lechtken, Schooss, Kappes, and Filipp Furche, Phys. Rev. A 77, 053202 (2008)
  - Take 5 minutes to implement by modifying PBE
  - Perdew, Ruzsinszky, Csonka, Vydrov, Scuseria, Constantin, Zhou, and KB, Phys. Rev. Lett. 100, 136406 (2008)

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.

- Thanks to students and NSF.