

# Basics of DFT

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# Outline

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

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# Electronic structure problem

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

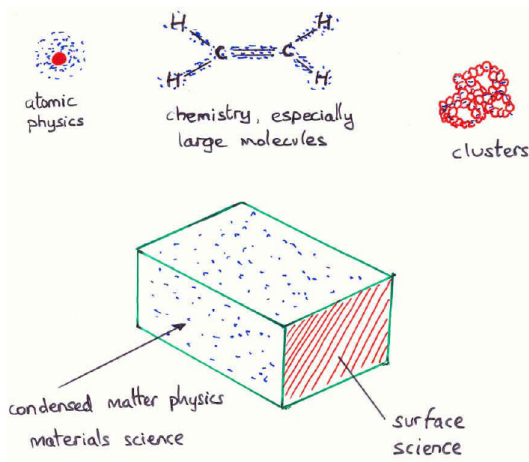


Figure: My first ever DFT transparency

# Atomic units

- In atomic units, all energies are in Hartree ( $1H = 27.2 \text{ eV}$ ) and all distances in Bohr ( $1a_0 = 0.529 \text{ \AA}$ )
- To write formulas in atomic units, set  $e^2 = \hbar = m_e = 1$
- In regular units,
  - ▶  $1 H = 27.2 \text{ eV}$
  - ▶  $1 \text{ eV} = 23.06 \text{ kcal/mol}$
  - ▶  $1 \text{ kcal} = 4.184 \text{ kJ/mol} = 503 \text{ K}$ .

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- 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  $v(\mathbf{r})$ :

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

where the kinetic and elec-elec repulsion energies are

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

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- Often  $v(\mathbf{r})$  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

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

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

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and  $n(\mathbf{r}) d^3 r$  gives probability of finding any electron in  $d^3 r$  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  $\Psi$  is normalized and antisym.

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- 2 **DFT**
- 3 Common functionals
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# 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  $X\alpha$  as crude KS-LDA.
- **1965:** Modern DFT begins with Kohn-Sham equations. By introducing orbitals, get 99% of the kinetic energy right, get accurate  $n(\mathbf{r})$ , 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):

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

where

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

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

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- ▶ 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).

- Define *fictitious* non-interacting electrons satisfying:

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

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$$T + V_{ee} = T_s + U + E_{xc}$$

the remainder is the exchange-correlation energy.

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$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}), \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

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# Kohn-Sham energy components

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- $E_C$  is everything else.

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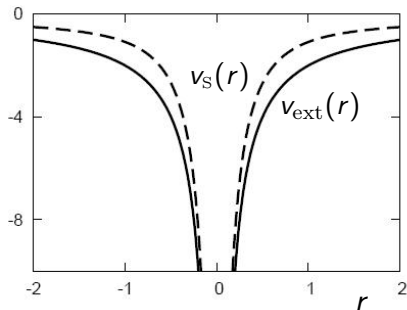
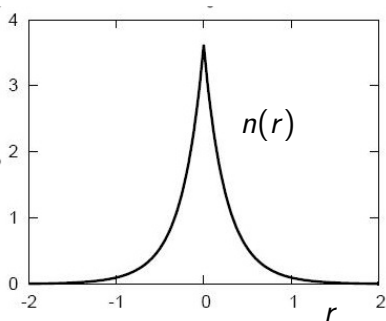
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$$\langle \Phi[n] | \hat{V}_{ee} | \Phi[n] \rangle = U[n] + E_x[n]$$

- $E_C$  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.<sup>1</sup>

Dashed line:  $v_S(r)$  is the *exact* KS potential.

<sup>1</sup> *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

	$T$	$V_{\text{ext}}$	$V_{\text{ee}}$	$T_{\text{S}}$	$U$	$E_{\text{X}}$	$T_{\text{C}}$	$U_{\text{C}}$	$E_{\text{C}}$
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:

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- 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.



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- 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.

- 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

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  - ▶ approximate in practice.
- Exact DFT tells us what we can and cannot expect our functionals to be able to do.
- $v_{\text{s}}(\mathbf{r})$  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  $v_{\text{s}}(\mathbf{r})$  is dangerous.

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# Functionals in common use

- Local density approximation (LDA)

- ▶ Uses only  $n(\mathbf{r})$  at a point,

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- Generalized gradient approx (GGA)

- ▶ Uses both  $n(\mathbf{r})$  and  $|\nabla n(\mathbf{r})|$

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- 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).



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- 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).

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- Transitions to unoccupied orbitals in bulk insulators a rough guide to **quasiparticle excitations**, except for too small gap.

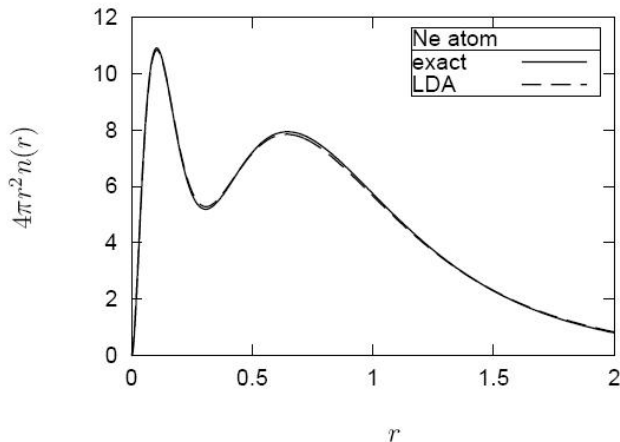


Figure: Exact and LDA radial densities of the Ne atom.

# Easy conditions

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# Uniform coordinate scaling

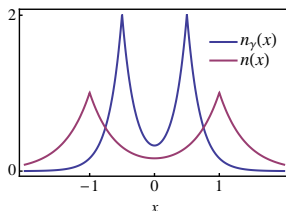


Figure: A one-dimensional density (red) being squeezed by  $\gamma = 2$  (blue)

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

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

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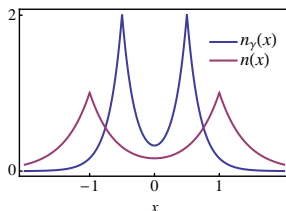


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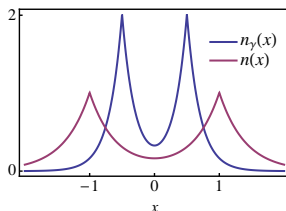


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- Performance

- ▶ 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. (Jacobsen, Tues).

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- Examples:
  - ▶ Phase diagrams of solids (Gillan, Fri)
  - ▶ Surfaces (Norskov, Mon, and Mavrikakis and Kitchin, Tues).
  - ▶ Electrochemistry (Rossmeisl, Thu).



[http://dcwww.fys.dtu.dk/~bligaard/School2010/CAMDSchool\\_2010\\_KBurke.pdf](http://dcwww.fys.dtu.dk/~bligaard/School2010/CAMDSchool_2010_KBurke.pdf)

# Outline

- 1 General background
- 2 DFT
- 3 Common functionals
- 4 Tough exact conditions**
- 5 Why exact exchange is mixed in?
- 6 Miscellaneous

# At the edge of all matter...

- Asymptotic decay of the density

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

- leads to severe constraint on XC potential:

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

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

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

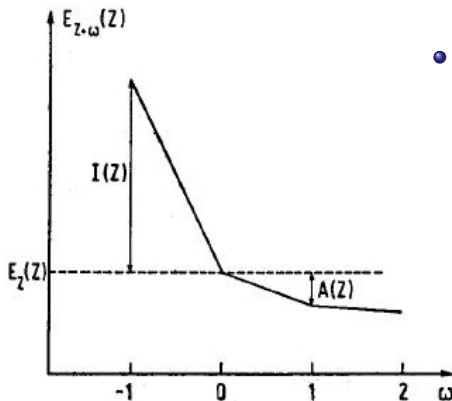


Fig. 2.2. Ground state energy of an atom with nuclear charge  $Z$  and  $(Z+\omega)$  electrons

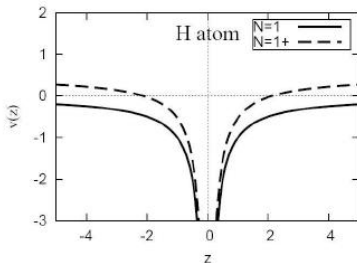
- R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).

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

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

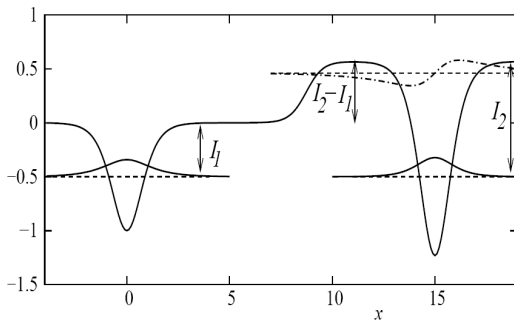
- When you add a tiny fraction of an electron to a system, the KS potential shifts uniformly, since before,  $\epsilon_{\text{HOMO}}(N) = -I$ , but now,  $\epsilon_{\text{HOMO}}(N + \delta) = -A$
- Thus  $v_{\text{S}}(\mathbf{r})$  must jump by

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



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

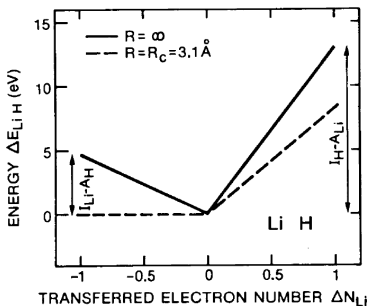
There are sharp steps in the KS potential between separated systems



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

- 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  $R \rightarrow \infty$ :

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

$$E(R) \rightarrow 2E(H), \quad R \rightarrow \infty$$

- 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

# Outline

- 1 General background
- 2 DFT
- 3 Common functionals
- 4 Tough exact conditions
- 5 Why exact exchange is mixed in?**
- 6 Miscellaneous

# 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).

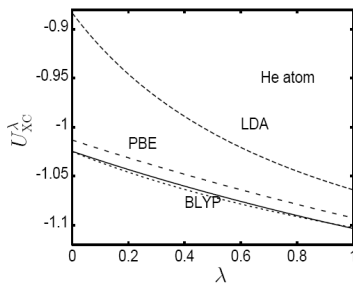


Figure: Adiabatic connection curve for He in various approximations

# Static correlation shows up in adiabatic connection

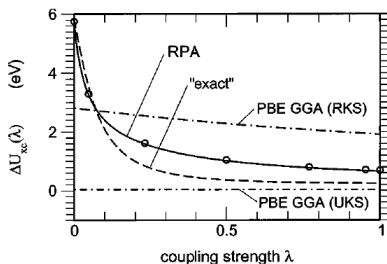
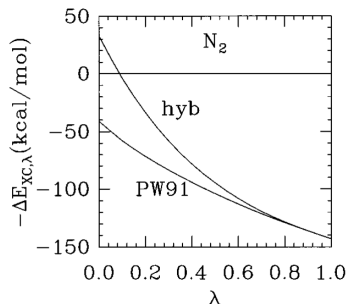


FIG. 3. Same as Fig. 1, but for  $R=5$  bohrs, i.e., beyond the Coulson–Fisher point. The RPA results are based on the *total* density of a unrestricted EXX KS calculation. Also shown are the adiabatic connections for the PBE GGA applied in the restricted KS formalism (RKS), yielding poor energetics,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

- 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.

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- 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

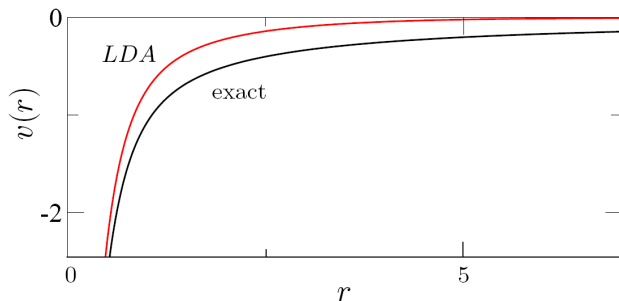


FIG. 3: Exact and LDA KS potentials for the He atom. While

- 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  $n(\mathbf{r})$ :

$$E_x[n] = -U[n], \quad E_c[n] = 0 \quad (N = 1)$$

- 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.

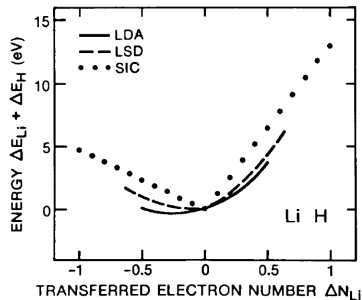
# Perdew-Zunger Self-Interaction Correction, 1981

- 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



**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

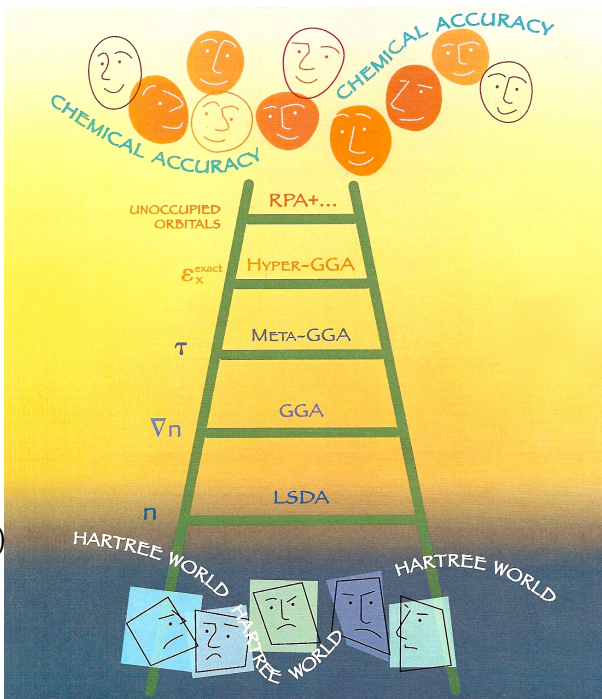
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# Jacob's ladder to DFT heaven (or hell?)

Increasingly sophisticated  
and expensive density  
functional approximations  
(Head-Gordon, **Tues**).

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

- 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 Leor 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 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  $E \rightarrow -C_6/R^6$  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 (sunday): 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.

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- 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).

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- Long-term goals
  - ▶ Systematic non-empirical functional construction
  - ▶ Unification of DFT with Green's function and wavefunction methods
  - ▶ Orbital-free calculations

- **Exchange:**

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

- **Correlation**

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

- **Performance:**

- ▶ Consistency :  $\sigma_{\text{X}}(n)$  almost exact
- ▶ Improves lattice parameters of LDA by 2-3.
- ▶ Means poor atomic energies, so worsens thermochemistry.
- ▶ Improves transition between planar and globular  $\text{Au}^-$  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 hierarchy 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.