

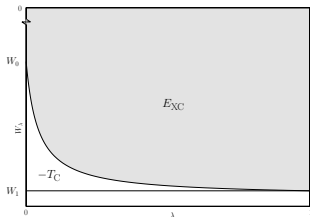
Some challenges in DFT ...

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$E_{XC}[\rho]$

$$\begin{aligned}
 E_{XC} &= V_{ee} - J + T - T_s \\
 &= \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}') h_{XC}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
 &= \int_0^1 d\lambda W_\lambda
 \end{aligned}$$



$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{ee} + \sum_i v_\lambda(\mathbf{r}_i)$$

$$W_\lambda = \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle - J$$

Systematic improvement ... ?

Ab initio DFT, Bartlett *et al.*, JCP **123**, 062205 (2005). DFT: low cost ...

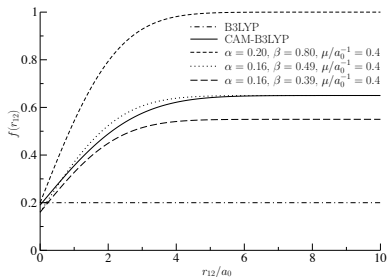
Satisfying exact constraints ... empirical parameters ...

$$E_X^0 = - \sum_{ij} \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})\varphi_i(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$E_X = \int F_X(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) d\mathbf{r}$$

$$E_X = \int F_X(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) d\mathbf{r} + \xi(\mathbf{r}?) E_X^0$$

$$E_X = \text{SR}(\rho) + \text{LR}(\Psi)$$



In practical calculations, what is the best balance between exact & approximate?

Exact exchange \rightarrow 1-e self-interaction free; $-1/r$ behaviour in $v_{XC}(\mathbf{r})$; integer discontinuity.

But, major implications for the associated correlation functional ... static (left-right) correlation not contained in E_X^0 . SR+LR compromise?

Recent progress in XC functionals containing full exact exchange ...

Becke, JCP **122**, 064101 (2005)

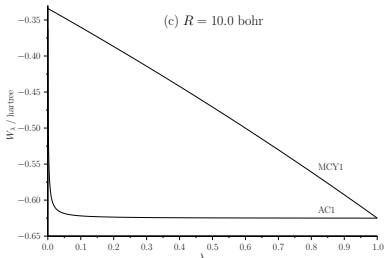
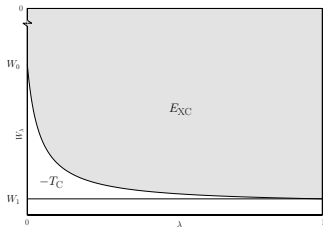
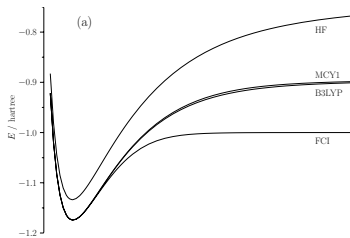
Mori-Sanchez *et al.*, JCP **124** 091102 (2006)

Perdew *et al.*, arXiv:0808.2523v1

Zhao, Truhlar, JPCA **110** 13126 (2006)

But, major challenges remain for the correlation functionals ...

1. Strong static correlation (near degeneracy), eg stretched H_2



Infinite slope arises due to divergence of GL2 energy!

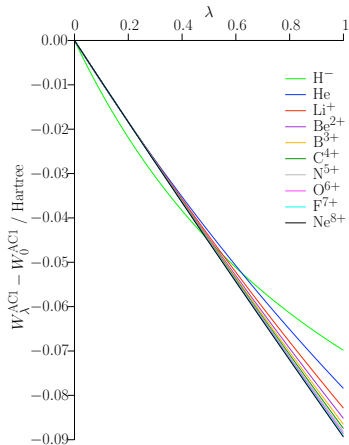
Peach *et al.*, JCP **126** 244104 (2007)

2. High density limit, eg He isoelectronic series for large Z

Exact behaviour of adiabatic connection:

$$\lim_{Z \rightarrow \infty} W_\lambda = E_X^0 + 2E_C^{\text{GL2}} \lambda$$

Error in Ne^{8+} energy from this 'model'
AC approx 10^5 times smaller than for
B3LYP!



Peach *et al.*, JCP **129** 064105 (2008)

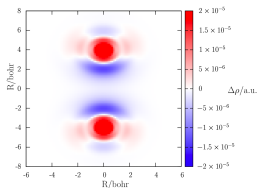
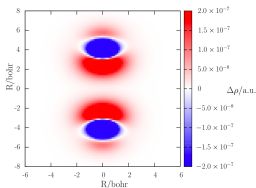
3. Dispersion energies

$$\text{At large } R, \quad E_{\text{disp}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \dots$$

The physics of dispersion is completely absent with conventional GGA/meta-GGA/hybrid functionals

$$F_{\text{disp}} = \frac{6C_6}{R^7} + \frac{8C_8}{R^9} + \dots$$

JCP **117** 11113 (2002)



Pragmatic solution: Add explicit C_6R^{-6} correction

Rigorous solution: Non-local E_C

Dion *et al.*, PRL **92** 246401 (2005)

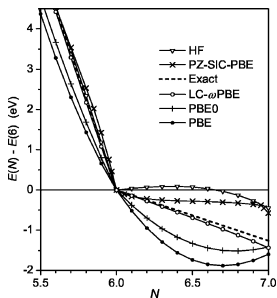
Vydrov *et al.*, JCP **129** 014106 (2008)

DFT for systems with fractional numbers of electrons (locally)

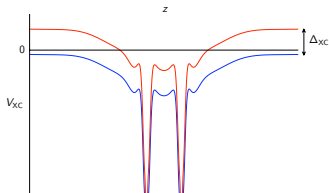
Ruzsinszky *et al.*, JCP **125** 194112 (2006); *ibid* **126** 104102 (2007)

Mori-Sanchez *et al.*, JCP **125** 201102 (2006); Perdew *et al.*, PRL **49** 1691 (1982)

J. Chem. Phys. **126**, 154109 (2007)



- Dissociation of H_2^+
- Underestimated reaction barriers
- Incorrect dissociation to fractionally charged fragments
- Underestimation of CT excitations
- MESIE / Delocalization error ...



JCP **129** 044110 (2008)

"Fractional charges are relevant."

Kohn-Sham equations for orbital-dependent E_{XC}

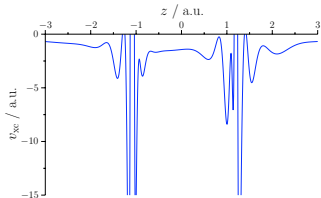
For $E_{XC} = E_{XC}[\{\varphi_i\}]$, conventional implementations derive KS equations by differentiating wrt the *orbitals*. **Not Kohn-Sham theory!**

Instead, need functional derivative wrt *density*

$$v_{XC}(\mathbf{r}) = \frac{\delta E_{XC}}{\delta \rho(\mathbf{r})} = \sum_i \int d\mathbf{r}' \int d\mathbf{r}'' \left[\frac{\delta E_{XC}}{\varphi_i(\mathbf{r}') \delta v_s(\mathbf{r}'')} + cc \right] \frac{\delta v_s(\mathbf{r}'')}{\delta \rho(\mathbf{r})}$$

from which the Optimised Effective Potential (OEP) integral equation is derived.

Expand potential in a basis set. But ...
(Oberwolfach 2006)



Approaches include truncated SVD; penalty function or specific balancing schemes.
Removes black box attraction?

Or use model potential such as ELP, LHF, CEDA (care for virtuals!).

Important issue, given key role of orbital dependent functionals in modern DFT

Current-dependence in E_{XC} ?

In presence of magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$, which induces orbital current,

$$E_{XC} = E_{XC}[\rho_\sigma, \mathbf{j}_{p\sigma}]$$

Vignale *et al.*, PRB **37** 10685 (1988); Skudlarski *et al.* PRB **48** 8547 (1993)

Most functionals in common use have no current-dependence!

To what extent does this degrade molecular properties?

Even for $\mathbf{A} = \mathbf{0}$, still relevant in open shell atoms using complex orbitals.

Johnson *et al.*, JCP **126** 184104 (2007)

Non-local E_{XC}

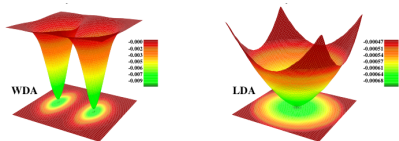
Computationally more expensive, but theoretically appealing ...

Random Phase Approximation (ACFDT)

Langreth and Perdew, Solid State Commun. **17** 1425 (1977)

- Can be used to model dispersion
- Exactly dissociates H_2 and gives high Z limit of He-series, due to GL2.
- Furche, JCP **129** 114105 (2008)

Weighted Density Approximation (WDA)



Choice of pair correlation function?

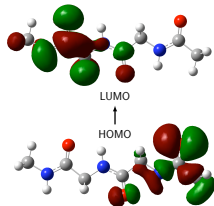
Time-dependent DFT (TDDFT)

Calculation of electronic excitations with TDDFT is one of the most important applications of DFT in chemistry. Use the adiabatic approximation

$$v_{XC}(\mathbf{r}, t) = \tilde{v}_{XC}(\mathbf{r})|_{\rho=\rho(\mathbf{r},t)}$$

and so the kernel exhibits no explicit time dependence.

- Charge-transfer states are too low.
- Excitation energies vanish as H_2 stretches.
- Poor photoabsorption spectra of nonmetallic solids.



Need divergence in the kernel → beyond the adiabatic approximation.

Note: Exact exchange improves CT, Dreuw and Head-Gordon, JCP **119** 2943 (2003)

Eg: Using long-range corrected functionals, Peach *et al.* JCP **128** 044118 (2008)

Also, strong laser fields: High harmonic generation and multiple ionisations ...

Calculation of $\langle S^2 \rangle$ in DFT

Chemists keen to use $\langle S^2 \rangle$ to judge quality of a calculation. Usually evaluate expectation value of the operator with the KS determinant,

$$\langle S^2 \rangle = \langle \Psi_{\text{KS}} | \hat{S}^2 | \Psi_{\text{KS}} \rangle = S(S+1) + N_{\beta} - \sum_{\bar{ij}} S_{ij}^2$$

But, this is not the $\langle S^2 \rangle$ of the *real system*.

Problem:

$$\langle S^2 \rangle = \langle S^2 \rangle [\Gamma_2]$$

How we do evaluate in terms of the one-particle density, $\rho(\mathbf{r})$?

Wang *et al.*, JCP **102** 3477 (1995) proposed an 'LDA' approximation, but still fundamentally linked to a single-determinant wavefunction.

Open question . . .

Using two-particle information ...

The Hamiltonian operator involves just one- and two-particle operators.

Natural to use a two-particle function as the central variable, i.e. the 2RDM $\Gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$ or its diagonal element, the pair density, $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$.

Electron-electron repulsion energy expression now known exactly!

$$V_{ee} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

But, when minimizing energy, how do we know that the function is associated with an N -electron antisymmetric electronic wavefunction?

The N -representability problem ...

Orbital-free DFT

Hohenberg-Kohn theorems tell us

$$E = E[\rho] = T_s[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + J[\rho] + E_{xc}[\rho]$$

where the density is obtained from

$$\mu = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

This direct approach is computationally attractive (linear scaling, no orthonormalization, no Brillouin zone sampling), but is of limited practical use due to errors in $T_s[\rho]$

Much work attempting to develop improved $T_s[\rho]$, often by ensuring correct linear response. Foley and Madden, PRB **53** 10589 (1996); Wang *et al.*, PRB **58** 13465 (1998)

Ongoing ... ISTCP-VI symposium.

Some Challenges for DFT ...

- $E_{XC}[\rho]$ and its systematic improvement
- $E_X[\rho]$; balance of exact and approximate
- $E_C[\rho]$; near-degeneracy; high density; dispersion
- Fractional numbers of electrons; self-interaction; integer discontinuity
- Kohn-Sham equations for orbital-dependent functionals (OEP)
- Current dependence
- Explicit non-locality; high rungs of Jacob's ladder
- Excited states; beyond the adiabatic approximation; strong fields
- $\langle S^2 \rangle$
- Two-particle information; $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$, $\Gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$; N -representability
- Orbital free DFT; $T_s[\rho]$
- More ...