Ab initio methods: The e-e cusp and DFT

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Density-Functional Theory I

Hohenberg & Kohn (Phys. Rev. B, **136**, 864 (1964)):

Theorem

H–K Theorem 1 There is a one-to-one mapping between the electronic density and the external potential, and hence, the Hamiltonian:

$$\rho(\mathrm{r}) \iff \mathcal{H}$$

Proof is by *reductio ad absurdum*.

Density-Functional Theory II

Consider the Hamiltonian with the electron–nuclear potential v_{ext} (this is sometimes called the *external* potential):

$$\mathcal{H} = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_{i<j}^N \frac{1}{r_{ij}} + \sum_i^N v_{\text{ext}}(r_i) \tag{1}$$

- Let v_{ext}^1 and v_{ext}^2 arise from the same density.
- We therefore have two Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$ with the same ground state density but with *different* ground state wavefunctions, Ψ_1 and Ψ_2.

Density-Functional Theory III

- Consider $\mathcal{H}_1$: The variational principle states that

$$
\begin{aligned}
E_1^0 &< \langle \Psi_2 | \mathcal{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \mathcal{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \mathcal{H}_1 - \mathcal{H}_2 | \Psi_2 \rangle \\
&= E_2^0 + \langle \Psi_2 | v_{\text{ext}}^1 - v_{\text{ext}}^2 | \Psi_2 \rangle \\
&= E_2^0 + \int \rho(\text{r}) \left[v_{\text{ext}}^1(\text{r}) - v_{\text{ext}}^2(\text{r}) \right] d\text{r}
\end{aligned}
$$

- Similarly $E_2^0 < E_1^0 + \int \rho(\text{r}) \left[v_{\text{ext}}^2(\text{r}) - v_{\text{ext}}^1(\text{r}) \right] d\text{r}$
- Adding the inequalities:

$$
E_1^0 + E_2^0 < E_2^0 + E_1^0 \quad \rightarrow\leftarrow
$$

- Hence $\rho(\text{r}) \iff \mathcal{H}$

Density-Functional Theory IV

E. Bright Wilson's observation: To know the Hamiltonian we need to know the number of electrons and position and charge of the nuclei. These can be obtained from the density:

- $N = \int \rho(\mathrm{r})\mathrm{dr}$
- Position and charge of nuclei can be obtained from the cusps:

$$\frac{\partial}{\partial r}\langle \rho(r)\rangle_{\mathrm{sph}}\bigg|_{r=0} = -2Z\langle \rho(0)\rangle_{\mathrm{sph}}$$

So ρ completely determines the Hamiltonian and therefore the ground-state energy (and also all excited state energies!).

Density-Functional Theory V

What the Hohenberg–Kohn theorem allows us to do is (formally) write the energy as a *functional* of the density.

$$E = E[\rho] = T[\rho] + V_{\mathrm{ee}}[\rho] + V_{\mathrm{en}}[\rho]$$
$$= F[\rho] + \int \rho(\mathrm{r})v_{\mathrm{ext}}(\mathrm{r})\mathrm{dr}$$

This leads to the second Hohenberg–Kohn theorem:

Theorem

H–K Theorem 2 If $\tilde{\rho}$ is an approximate density then

$$E[\rho] \leq E[\tilde{\rho}]$$

Density-Functional Theory VI

It's easy to see how this theorem arises:

- $\tilde{\rho}$ gives rise to a unique potential $v_{\tilde{\text{ext}}}$, and hence a Hamiltonian $\tilde{\mathcal{H}}$ and therefore to a ground state wavefunction $\tilde{\Psi}$.

- Using the variational principle

$$E^0 = E[\rho] \leq \langle \tilde{\Psi} | \mathcal{H} | \tilde{\Psi} \rangle = F[\tilde{\rho}] + \int \tilde{\rho}(\mathrm{r}) v_{\text{ext}}(\mathrm{r}) \mathrm{dr} = \mathrm{E}[\tilde{\rho}]$$

So *in principle* we can search over all N-electron densities to find the one that leads to the lowest energy.

Density-Functional Theory VII

In practice searching over all N-electron densities is next to impossible. How do we do this? If we are given a trial N-electron density $\tilde{\rho}$, how can we obtain the corresponding external potential $v_{\widetilde{\mathrm{ext}}}$? This can be done for a one or two electron system (Ex. How?) but not in general.

All this would have been a curiosity had it not been for a paper by Kohn & Sham published in 1965 (Phys. Rev. A **140**, 1133) which gave us what we now know as Kohn–Sham DFT.

Hartree–Fock again I

Before getting on with DFT, let's have another look at Hartree–Fock, but this time, from a slightly different angle. The HF energy can be written as

$$E_{\mathrm{HF}} = \min_{|\Psi_{\mathrm{SD}}\rangle \to N} \langle \Psi_{\mathrm{SD}}| \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{ee}}|\Psi_{\mathrm{SD}}\rangle$$

$$= \min_{|\Psi_{\mathrm{SD}}\rangle \to N} \langle \Psi_{\mathrm{SD}}| \hat{T} + v_{\mathrm{ext}} + \hat{V}_{\mathrm{ee}}|\Psi_{\mathrm{SD}}\rangle$$

Here $|\Psi_{\mathrm{SD}}\rangle$ is our Slater determinant that yields an N electron density. In the second line I have used our notation for the electron–nuclear potential: the external potential.

Hartree–Fock again II

This minimization procedure gives rise to an effective Hamiltonian — the Fock operator:

$$f^{\mathrm{HF}}(i) = -\frac{1}{2}\nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + v^{\mathrm{HF}}(i) \tag{2}$$

The HF potential is an effective potential that contains the effective electron–electron Coulomb and exchange interactions (no correlation!). To get us ready for Kohn–Sham theory, we will make a few changes to the above equation.

Hartree–Fock again III

- First of all recognise that the second term in the Fock operator is just the external potential: v_{ext}
- Next, split the HF operator into its Coulomb and Exchange parts. These are usually labeled by 'J' and 'X', respectively:

$$v^{\mathrm{HF}} = v_{\mathrm{J}} + v_{\mathrm{X}}$$

So our Fock operator is now written as

$$f^{\mathrm{HF}}(i) = -\frac{1}{2}\nabla_i^2 + v_{\mathrm{ext}}(i) + v_{\mathrm{J}}(i) + v_{\mathrm{X}}(i) \qquad (3)$$

Hartree–Fock again IV

In some sense we can say that the HF ground state energy is a functional of the density and can be written as

$$E_{\mathrm{HF}}[\rho^{\mathrm{HF}}] = T_{\mathrm{S}}[\rho^{\mathrm{HF}}] + J[\rho^{\mathrm{HF}}] + E_{\mathrm{x}}^{\mathrm{HF}}[\rho^{\mathrm{HF}}] + \int \rho^{\mathrm{HF}}(\mathrm{r}) v_{\mathrm{ext}}(\mathrm{r}) \mathrm{dr} \quad (4)$$

where the *non-interacting* Kinetic energy functional is

$$T_{\mathrm{S}}[\rho^{\mathrm{HF}}] = -\frac{1}{2} \sum_{i=1}^{N} \langle \chi_i | \nabla_i^2 | \chi_i \rangle \quad (5)$$

which is not strictly a functional of the density, but since the density is implicitly a functional of the orbitals we can still think of the KE functional as a density functional.

Hartree–Fock again V

The Coulomb energy functional is defined as

$$J[\rho^{\mathrm{HF}}] = \frac{1}{2} \iint \frac{\rho^{\mathrm{HF}}(\mathrm{r}_1)\rho^{\mathrm{HF}}(\mathrm{r}_2)}{r_{12}} d\mathrm{r}_1 d\mathrm{r}_2 \qquad (6)$$

The exchange energy functional is non-local and is, like the KE functional, dependent on the HF orbitals:

$$E_{\mathrm{x}}^{\mathrm{HF}}[\rho^{\mathrm{HF}}] = -\sum_{a\in\mathrm{occ}}\sum_{b\in\mathrm{occ}} \iint dx_1 dx_2 \chi_a^*(1) \frac{\chi_b^*(2)\mathcal{P}_{12}\chi_b(2)}{r_{12}} \chi_a(1)$$

$$(7)$$

where $\mathcal{P}_{12}$ is the permutation operator.

Hartree–Fock again VI

Looked at in this way HF theory is a kind of density functional theory, but one that is not, even in principle, exact (except for 1-electron systems).

In this formulation of HF theory, we define the HF energy as

$$E^{\mathrm{HF}} = \min_{\rho \to |\Psi_{\mathrm{SD}}\rangle, N} E_{\mathrm{HF}}[\rho]$$

That is, we minimize the functional $E_{\mathrm{HF}}[\rho]$ over all N-electron densities that arise from a Slater determinant. We need to impose the N-electron constraint and this is done using Lagrange multipliers. We minimize the functional:

$$\Omega[\rho] = E_{\mathrm{HF}}[\rho] - \sum_{i,j}^{N} \epsilon_{ij}(\langle \chi_i | \chi_j \rangle - \delta_{ij})$$

Hartree–Fock again VII

Since $\Omega[\rho]$ really is a functional of the orbitals, we need to perform the variation over the orbitals and use the chain rule:

$$\frac{\delta}{\delta\chi_i(\mathrm{r})} = \frac{\delta}{\delta\rho(\mathrm{r})}\frac{\delta\rho(\mathrm{r})}{\delta\chi_i(\mathrm{r})} \qquad (8)$$

I do not want to get is bogged down with functional derivatives, but one example of how its done could be illuminating:
First of all, since $\rho(\mathrm{r}) = \sum_{i=1}^{N} \chi_i^*(\mathrm{r})\chi_i(\mathrm{r})$ we get

$$\frac{\delta\rho(\mathrm{r})}{\delta\chi_i^*(\mathrm{r})} = \chi_i(\mathrm{r})$$

Hartree–Fock again VIII

Now consider the functional derivative of $J[\rho]$:

$$
\begin{aligned}
\frac{\delta J[\rho]}{\delta \chi_i^*(\mathrm{r})} &= \frac{\delta J[\rho]}{\delta \rho(\mathrm{r})} \frac{\delta \rho(\mathrm{r})}{\delta \chi_i^*(\mathrm{r})} \\
&= \frac{\delta}{\delta \rho(\mathrm{r})} \left[\frac{1}{2} \iint \frac{\rho(\mathrm{r})\rho(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|} d\mathrm{r}d\mathrm{r}' \right] \times \chi_i(\mathrm{r}) \\
&= \int \frac{\rho(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|} d\mathrm{r}' \chi_i(\mathrm{r}) \\
&= v_J(\mathrm{r}) \chi_i(\mathrm{r})
\end{aligned}
$$

Do this for all terms and we get back our Fock equation (in a generalised form).

Kohn–Sham DFT I

In 1965 Walter Kohn & Lu Sham put DFT on a practical footing through what is now known as Kohn–Sham DFT. The begain by *postulating* the existence of a non-interacting system with external potential v_S that yields the *exact density*. That is

$$\mathcal{H} = \sum_i \left(-\frac{1}{2} \nabla_i^2 + v_S(i) \right)$$

has a ground state single determinant solution with density ρ.

Kohn–Sham DFT II

We know how to write the kinetic energy of this system:

$$T_S[\rho] = \sum_i^N -\frac{1}{2}\langle\chi_i|\nabla^2|\chi_i\rangle$$

Now write the Hohenberg–Kohn functional as

$$F[\rho] = T[\rho] + V_{ee}[\rho]$$
$$= T_S[\rho] + J[\rho] + E_{xc}[\rho]$$

where this eXchange-Correlation functional is defined as

$$E_{xc}[\rho] = (T[\rho] - T_S[\rho]) - (V_{ee}[\rho] - J[\rho])$$

Kohn–Sham DFT III

In analogy with the Hartree–Fock functional, we find the ground state energy by minimizing the Kohn–Sham energy functional defined as:

$$E[\rho] = T_{\mathrm{S}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho] + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr} \qquad (9)$$

subject to the orthonormality constraints

$$\langle \chi_i | \chi_j \rangle = \delta_{ij}.$$

As before, we include these constraints using Lagrange multipliers and minimize

$$\Omega[\rho] = E[\rho] - \sum_{i,j}^{N} \epsilon_{ij}(\langle \chi_i | \chi_j \rangle - \delta_{ij})$$

Kohn–Sham DFT IV

This gives us the Kohn–Sham equations (no proof, but it is a reasonably straightforward exercise in functional differentiation):

$$\left(-\frac{1}{2}\nabla_i^2 + v_{\mathrm{S}}(\mathrm{r})\right)\chi_i = \epsilon_i\chi_i$$

where the effective potential is defined as

$$v_{\mathrm{S}}(\mathrm{r}) = v_{\mathrm{J}}(\mathrm{r}) + v_{\mathrm{ext}}(\mathrm{r}) + v_{\mathrm{xc}}(\mathrm{r})$$

The various potentials that enter this expression are:

- v_{J}: The Coulomb potential defined as:

$$v_{\mathrm{J}}(\mathrm{r}) = \int \frac{\rho(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|}\mathrm{d}\mathrm{r}'$$

Kohn–Sham DFT V

- v_{ext}: The external potential, i.e., the electron-nuclear potential:

$$v_{\mathrm{ext}}(\mathrm{r}) = -\sum_{\alpha} \frac{\mathrm{Z}_{\alpha}}{|\mathrm{r} - \mathrm{R}_{\alpha}|}$$

- v_{xc}: The exchange-correlation potential which is defined through the exchange-correlation energy $E_{\mathrm{xc}}[\rho]$ as:

$$v_{\mathrm{xc}}(\mathrm{r}) = \frac{\delta \mathrm{E}_{\mathrm{xc}}[\rho]}{\delta \rho}$$

Kohn–Sham DFT VI

- In a sense, what Kohn & Sham did was to sweep all the unknowns under the rug. But they did this intelligently as they had a good idea of how to approximate the unknown bits: the exchange-correlation energy and its functional derivative.

- Also, they knew that their formalism was *in principle* exact as they had proved various theorems to that effect.

- It turned out that their proofs were not mathematically sound, but this was fixed by others.

- The rest of the DFT story is how we find the exchange-correlation functional $E_{\mathrm{xc}}[\rho]$.

Density Functionals I

Exchange correlation functionals are usually written in the form

$$E_{xc}[\rho] = \int \rho(r) \epsilon_{xc}(\rho(r), \nabla \rho(r), \cdots) dr \qquad (10)$$

where $\epsilon_{xc}(\rho(r), \nabla \rho(r), \cdots)$ can be regarded as the exchange-correlation density.

We usually split the exchange-correlation density into its exchange and correlation parts:

$$\epsilon_{xc}(\rho(r), \nabla \rho(r), \cdots) = \epsilon_{x}(\rho(r), \nabla \rho(r), \cdots) + \epsilon_{c}(\rho(r), \nabla \rho(r), \cdots) \qquad (11)$$

This separation is convenient for we can then think of using well-understood approximations for each of these.

LDA I

The first of the many functionals is the local density approximation or LDA. In this approximation the exchange-correlation density depends on the electron density alone (no dependence on gradients etc.):

$$E_{\text{xc}}[\rho] = \int \rho(\text{r}) \epsilon_{\text{xc}}^{\text{LDA}}(\rho(\text{r})) \text{dr} \tag{12}$$

The Slater approximation is used for the exchange-energy density:

$$\epsilon_{\text{x}}^{\text{S}}(\rho(\text{r})) = -\frac{3}{4} \left(\frac{3\rho(\text{r})}{\pi} \right)^{3/2}$$

Using this we get the Slater exchange functional:

$$E_{\text{x}}^{\text{S}}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{3/2} \int \rho^{4/3}(\text{r}) \text{dr} = -C_{\text{x}} \int \rho^{4/3}(\text{r}) \text{dr}$$

LDA II

Paired with this is a correlation functional parameterized on very accurate quantum Monte-Carlo (QMC) calculations of the energy of the homogeneous free electron gas as a function of density. There are a variety of correlation parameterizations. These differ by the choice of QMC energies used or by the interpolation scheme used in the parameterization (the QMC energies are calculated at a set of densities so some scheme is required to interpolate to all densities).

Common choices of the correlation functional are:

- PW91c The Perdew–Wang (1992) parameterization (called `pw91lda` in NWChem.
- VWN The Voski–Wilk–Nusair (1980) parameterization.

So what is called the LDA translates into a combination of the Slater exchange functional and one of these correlation functionals. The actual choice will vary with program.
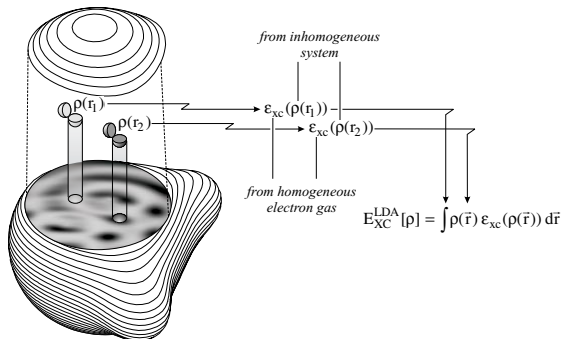
LDA III

Figure 6-2. The local density approximation.

From Koch & Holthausen *A Chemist's Guide to density Functional Theory* (2001).

LDA IV

Generalization to open-shell systems (local spin-density approximation (LSD)): the exchange-correlation density depends on the spin-up and spin-down densities:

$$E_{\mathrm{xc}}[\rho_\alpha, \rho_\beta] = \int \rho(\mathrm{r}) \epsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\rho_\alpha(\mathrm{r}), \rho_\beta(\mathrm{r})) \mathrm{dr} \qquad (13)$$

- GOOD LDA is better than HF. Good equilibrium geometries, harmonic frequencies.
- BAD Energetics very poor. Errors in atomization energies 36 kcal/mol. (HF has errors of 78 kcal/mol on same set of molecules)

GGA I

In the generalized gradient approximations the exchange-correlation density is dependent on the density and its gradient.

$$E_{\mathrm{xc}}[\rho] = \int \rho(\mathrm{r}) \epsilon_{\mathrm{xc}}^{\mathrm{GGA}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r}))\mathrm{dr}$$

As before, we split the exchange-correlation density into its exchange and correlation parts:

$$\epsilon_{\mathrm{xc}}^{\mathrm{GGA}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r})) = \epsilon_{\mathrm{x}}^{\mathrm{GGA}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r})) + \epsilon_{\mathrm{c}}^{\mathrm{GGA}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r}))$$

The exchange part of all GGAs takes the form

$$E_{\mathrm{x}}^{\mathrm{GGA}}[\rho] = \int \rho(\mathrm{r}) \epsilon_{\mathrm{x}}^{\mathrm{LDA}}(\rho(\mathrm{r})) \mathrm{F_x(s)dr}$$

GGA II

$F_X(s)$ is sometimes called the enhancement factor and is written as a function of the reduced density gradient defined as

$$s(r) = \frac{|\nabla \rho(r)|}{2(3\pi^2)^{1/3}\rho^{4/3}(r)}.$$

Note that in general all quantities will depend on spin.

This definition is used so as to make s dimensionless (Q: Show this!) and means that s will be large when the gradient of the density is large (where the LDA should fail) and also where the density is small (in the region of the density tails).

Two of the common exchange enhancement factors are

GGA III

- Becke, 1988 (B88)

$$F_x^{\mathrm{B88}}(s) = 1 - \frac{\beta s^2}{1 + 6\beta s \sinh^{-1} s}$$

Becke fitted the parameter $\beta = 0.0042$ to reproduce known exchange energies of rare gas atoms. This particular form for the enhancement factor was chosen to obey a few exact relations.

- Perdew, Burke & Ernzerhof, 1996 (PBE)

$$F_x^{\mathrm{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1 - \mu s^2/\kappa}$$

In this functional all parameters were obtained theoretically. $\kappa = 0.804$. Most physcists use this exchange functional.

Hybrid Functionals I

The exchange contribution to the energy is much larger than the correlation energy (which is why HF is not too bad!). So why not use the best exchange energy we have — from HF, usually termed *exact* exchange in this context — and combine it with the best correlation funtional available:

$$E_{\mathrm{xc}}[\rho] = E_{\mathrm{x}}^{\mathrm{HF}}[\rho] + E_{\mathrm{c}}[\rho]$$

This turns out to be better than HF, but much worse than the GGAs.

The precise reason for this somewhat poor behaviour has to do with the nature of the exchange hole. The exact x-hole is local, but the HF x-hole is non-local. So it must be corrected by a non-local correlation hole, but the DFT correlation hole is also local and so cannot correct the HF x-hole. This is all very interesting but also very technical.

Hybrid Functionals II

In 1993, Becke proposed a three-parameter semi-empirical functional that cured this problem. The general idea is to mix some fraction of HF exchange with DFT exchange:

$$E_{xc}^{\text{hybrid}} = aE_x^{\text{HF}} + (1-a)E_x^{\text{GGA}} + E_c^{\text{GGA}}$$

The B3LYP is the most widely used of these and is a slight modification of Becke's 1993 proposal made the following year by Stephens and others:

$$E_{xc}^{\text{B3LYP}} = E_{xc}^{\text{SVWN}} + a_0(E_x^{\text{HF}} - E_x^{\text{S}}) + a_x(E_x^{\text{B88}} - E_x^{\text{S}}) + a_c(E_c^{\text{LYP}} - E_c^{\text{VWN}})$$

A better choice (in my opinion) is the PBE0 functional (sometimes called PBE1PBE) which mixes PBE with 20% HF exchange.

Jacob's Ladder I

John Perdew has summarised the state of DFT using the Biblical
picture of Jacob's Ladder: At the base we have the LDA and at
the top, in the heaven of chemical accuracy (interesting concept -
what is Physical Accuracy?) we have some unknown functional.
Here's the whole Ladder...

Jacob's Ladder II

CHEMICAL HEAVEN

1. corr-hyper-GGA: Modifies the hyper-GGAs by including correlation through range-separation. This is currently done at the RPA level.

2. hyper-GGA: Adds exact exchange using range-separation. Leads to functionals that can fix (part of) the charge-transfer problem of most DFT functionals. CamB3LYP

3. meta-GGA: $\rho, \nabla\rho, \nabla^2\rho, \tau$, here $\tau = \frac{1}{2}\sum_{a\in\text{occ}}|\nabla\chi_a|^2$ is the Kohn–Sham orbital kinetic energy density. TPSS

4. GGA: $\rho, \nabla\rho$. PBE

5. LDA,LSD: ρ

INACCURATE HELL

Meaning of the KS orbital energies I

- The Kohn–Sham non-interacting system was initially regarded as no more than a device to facilitate the solution of the Schrödinger equation.

- The orbitals and orbital eigenvalues were not taken to mean anything with one exception:

- $\epsilon_{HOMO} = -I$: Perdew, Parr, Levy and Balduz (Phys. Rev. Lett. **49**. 1691 (1982)) had shown that the energy of the highest occupied molecular orbital was exactly equal to the negative of the vertical Ionization energy.

- However, there was a lot of empirical evidence that the Kohn–Sham orbital energies were closely related to the experimental ionization energies.

- But they were generally shifted w.r.t. the experimental values.

Meaning of the KS orbital energies II

- In 2001, Chong, Gritsenko and Baerends (J. Chem. Phys. **116**, 1760) showed that for the exact XC potential (they used a method called SAOP that had many of the properties of the exact XC potential):

$$I_k \approx -\epsilon_k$$

 With the relation being exact for the HOMO.

- In practice this means that we can use the KS orbital energies as a good approximation to the experimental excitation levels of our system, but with a constant, and possibly large, shift.

- Q: Why are the orbital energies shifted?

First, some evidence for the statements made above.
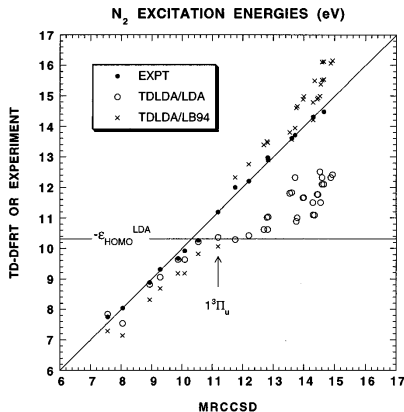
Meaning of the KS orbital energies III

N₂ EXCITATION ENERGIES (eV)

Casida, Jamorski,
Casida & Salahub,
J. Chem. Phys.
108, 4439 (1998).

FIG. 1. Correlation plot comparing TD-DFRT results with the multirefer-
ence coupled cluster singles and doubles (MRCCSD) results of Ref. 53 for
the first 35 vertical excitation energies (not counting degeneracies) of N₂.
Experimental values taken from Ref. 53 are also shown.

Meaning of the KS orbital energies IV

CO EXCITATION ENERGIES (eV)

Casida, Jamorski,
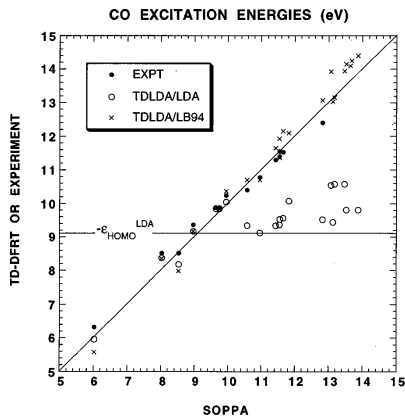Casida & Salahub,
J. Chem. Phys.
108, 4439 (1998).

FIG. 2. Correlation plot comparing TD-DFRT results with second-order polarization propagator (SOPPA) ($S \neq 1$ results from Table II of Ref. 54) for the first 23 vertical excitation energies (not counting degeneracies) of CO. Experimental values taken from Ref. 54 are also shown.

Meaning of the KS orbital energies V

Also in 1998, Savin, Umrigar & Gonze published a superb set of results, this time using exact XC potentials. They obtained these exact, or very accurate XC potentials using a method of inversion:

- Calculate a very very accurate density, say using QMC.
- From the first Hohenberg–Kohn theorem there is a one-to-one mapping between this density and the Kohn–Sham potential for a non-interacting system that produces this density.
- Use a convenient method to obtain this potential. Q: How do you do this for the Helium atom density?
- Solve the Kohn–Sham equations using this potential.
- The resulting orbitals and orbital energies are the most accurate you can get.

Here are two sets of tables from their paper in Chem. Phys. Lett. **288**, 391 (1998):

Meaning of the KS orbital energies VI

Table 1
Excitation energies of He in hartree atomic units

Transition	Final state	Experiment	Drake	$\Delta \epsilon_{KS}$
$1s \rightarrow 2s$	$2\,^3S$	0.72833	0.72850	0.7460
	$2\,^1S$	0.75759	0.75775	
$1s \rightarrow 2p$	$1\,^3P$	0.77039	0.77056	0.7772
	$1\,^1P$	0.77972	0.77988	
$1s \rightarrow 3s$	$3\,^3S$	0.83486	0.83504	0.8392
	$3\,^1S$	0.84228	0.84245	
$1s \rightarrow 3p$	$2\,^3P$	0.84547	0.84564	0.8476
	$2\,^1P$	0.84841	0.84858	
$1s \rightarrow 3d$	$1\,^3D$	0.84792	0.84809	0.8481
	$1\,^1D$	0.84793	0.84809	
$1s \rightarrow 4s$	$4\,^3S$	0.86704	0.86721	0.8688
	$4\,^1S$	0.86997	0.87014	

The theoretical energies of Drake and coworkers [14,15] and the eigenvalue differences are for infinite nuclear mass and neglect relativity. The experimental energies are from Ref. [17].

Meaning of the KS orbital energies VII

Table 2
Excitation energies of Be in hartree atomic units

Transition	Final state	Experiment	$\Delta \epsilon_{\mathrm{KS}}$
$2s \rightarrow 2p$	$1\,^3P$	0.100153	0.1327
	$1\,^1P$	0.193941	
$2s \rightarrow 3s$	$2\,^3S$	0.237304	0.2444
	$2\,^1S$	0.249127	
$2s \rightarrow 3p$	$2\,^3P$	0.267877	0.2694
	$2\,^1P$	0.274233	
$2s \rightarrow 3d$	$1\,^3D$	0.282744	0.2833
	$1\,^1D$	0.293556	
$2s \rightarrow 4s$	$3\,^3S$	0.293921	0.2959
	$3\,^1S$	0.297279	
$2s \rightarrow 4p$	$3\,^3P$	0.300487	0.3046
	$3\,^1P$	0.306314	
$2s \rightarrow 4d$	$2\,^3D$	0.309577	0.3098
	$2\,^1D$	0.313390	
$2s \rightarrow 5s$	$4\,^3S$	0.314429	0.3153
	$4\,^1S$	0.315855	

The eigenvalue differences are for infinite nuclear mass and neglect relativity. The experimental energies are from Ref. [17].

Self-Interaction I

Q: What are the problems with using an approximate XC functional?

Q: What is the origin of the constant shift of energies mentioned above?

To understand this we will work out how v_{xc} should behave for the hyrdogen atom.

- What is the form of the exact Kohn–Sham potential v_S for large r?

$$\left(-\frac{1}{2}\nabla^2 + v_S(r)\right)\chi_k(r) = \epsilon_k\chi_k(r)$$

This is equivalent to asking what the potential felt by an electron will be as we pull it off the atom/molecule. It will see

Self-Interaction II

a hole and hence experience a $-1/r$ potential. Therefore we must have

$$v_S \to -\frac{1}{r}$$

as $r \to \infty$.

- We know that $v_S = v_J + v_{\text{ext}} + v_{\text{xc}}$. We also know the long-range (asymptotic) forms of v_J and v_{ext}:

$$v_J(r) = \int \frac{\rho(r')}{|r - r'|} dr' \to +\frac{1}{r}$$

$$v_{\text{ext}}(r) = -\frac{1}{|r - R|} \to -\frac{1}{r}$$

Therefore these two cancel out asymptotically.

Self-Interaction III

- Hence we must have

$$v_{\mathrm{xc}}(\mathrm{r}) \to -\frac{1}{\mathrm{r}}$$

- How do common XC potentials behave at asymptotically? Best to use the simplest XC functional: the Slater exchange functional (the VWN correlation part does not change the picture very much). The Slater functional is

$$E_{\mathrm{x}}^{\mathrm{S}}[\rho] = -C_{\mathrm{x}} \int \rho^{4/3}(\mathrm{r})\mathrm{dr}$$

Self-Interaction IV

This gives us an XC potential:

$$
\begin{aligned}
v_{\mathrm{xc}}(\mathrm{r}) &= \frac{\delta E_{\mathrm{xc}}^{\mathrm{S}}[\rho]}{\delta \rho} \\
&= -\frac{4}{3} C_{\mathrm{x}} \rho^{1/3}(\mathrm{r}) \\
&\rightarrow -e^{-\frac{2}{3}r}
\end{aligned}
$$

It has the wrong asymptotic form. It decays too quickly with distance.

- This is what leads to a small band-gap in DFT: the unoccupied levels are all shifted down with respect to the occupied orbitals.
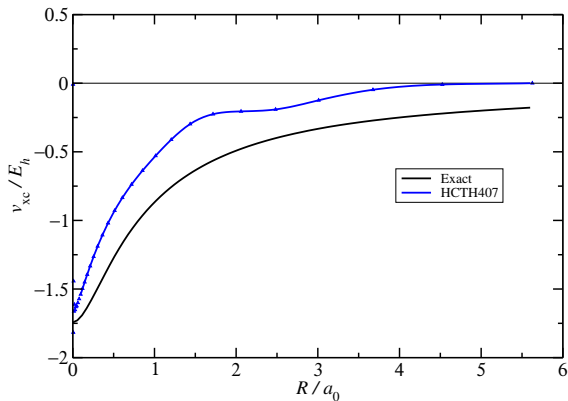
Self-Interaction V

- Self-Interaction: Another way of looking at this problem is to realise that the too rapid decay of v_{xc} with distance is equivalent to the electron 'seeing' itself. I.e., rather than see a hole with charge $+1$, it sees a hole with charge $+re^{-\frac{2}{3}r}$. This is the self-interaction problem. exponentially fast to zero, eventually the electron will see no attraction.

- Any molecular property that depends on the unoccupied levels will there be effected. Examples are: polarizabilities, hyperpolarizabilities, excitations, in particular charge-transfer excitations, NMR shifts.

It is best to see this pictorially. In the next few images we will look at the XC potential for Helium calculated using the HCTH407 functional compared with a (nearly) exact XC potential (this was obtained by calculating a very accurate He density and *inverting* it to obtain the potential).
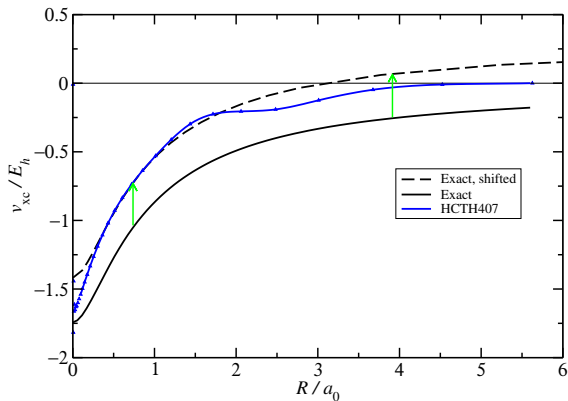
Self-Interaction VI

He: eXchange-Correlation potential

Self-Interaction VII

He: eXchange-Correlation potential

Figure axes: v_{xc} / E_h versus R / a_0

Legend:
- Exact, shifted
- Exact
- HCTH407

Asymptotic-correction I

Since we know what the asymptotic form of v_{xc} should be we can enforce it through an empirical fix known as the asymptotic correction. We need to account for the shift. Tozer and Handy worked all this out in 1998:

$$v_{xc}(r) \rightarrow -\frac{1}{r} + I + \epsilon_{HOMO}$$

So if know (or calculate) I, calculate ϵ_{HOMO} from a standard DFT calculation, then we will be able to work out the shift and apply this correction. This is known as the asymptotic correction.

Asymptotic-correction II

He: eXchange-Correlation potential
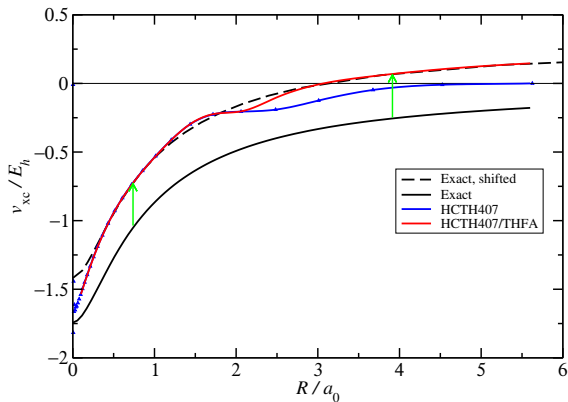
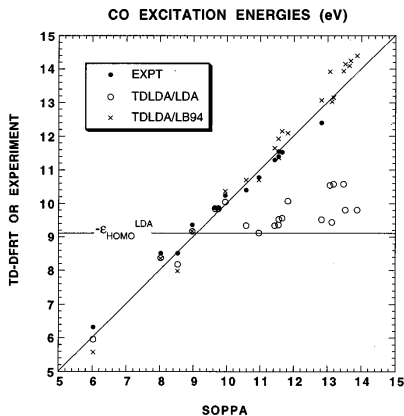## Asymptotic-correction III

CO EXCITATION ENERGIES (eV)

FIG. 2. Correlation plot comparing TD-DFRT results with second-order polarization propagator (SOPPA) ($S \neq 1$ results from Table II of Ref. 54) for the first 23 vertical excitation energies (not counting degeneracies) of CO. Experimental values taken from Ref. 54 are also shown.

The LB94 functional is one route to imposing an asymptotic correction. The effect of this on the excitation energies is quite dramatic. Casida, Jamorski, Casida & Salahub, J. Chem. Phys. **108**, 4439 (1998).

Asymptotic-correction IV

The asymptotic correction does fix what is called the one-electron
self-interaction error, but self-interaction is a nasty beast and it
takes more than this to correct for it. Besides, there is no clear
way to apply an asymptotic correction in the bulk phase. And the
self-interaction error manifests itself there too. We will see
examples of this in the next lecture.

Performance I

Assessing XC functionals is a continually evolving field as more functionals are developed and more kinds of tests are devised. Here are a few results collated by Koch & Holthausen.
As Physicists we will be mainly interested in band structures (excitation energies), polarizabilities, densities (i.e., moments), magnetic properties and binding energies. So I've selected examples of this sort of assessment.

Performance II

Excitation energies
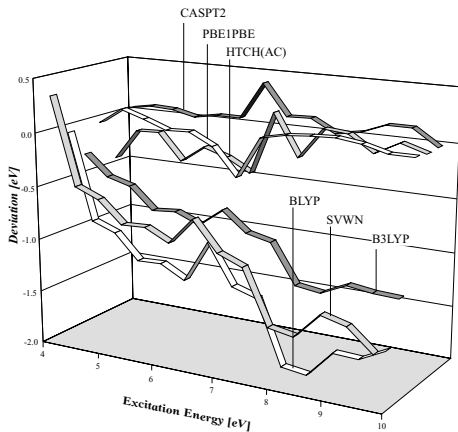
Figure 9-2. Performance of various functionals in the framework of time-dependent DFT for excitation energies of ethylene.

Performance III

Polarizabilities

5 molecules,TZVP+FIP basis set, Calaminici, Jug and Köster, 1998			
HF	1.29	BLYP	0.41
LDA	0.33	CCSD(T)	0.31
12 molecules, POL basis set, Adamo et al., 1999			
MP2	0.25	B97	0.42
MP4	0.28	B3LYP	0.39
BD(T)	0.23	HCTH	0.29
PBE1PBE	0.20		
20 molecules, POL basis set, Cohen and Tozer, 1999			
HF	1.76	HCTH	1.38
MP2	0.95	B3LYP	1.79
BD	1.29	B97	1.50
BLYP	2.25	B97-1	1.53