DFT: Analysis and Failures

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Kohn–Sham DFT I

$$\boxed{E[\rho] = T_{\mathrm{S}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho] + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr} \qquad (1)}$$

must be minimized subject to the orthonormality constraints

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

This gives us the Kohn–Sham equations after the usual occupied orbital rotation to make the eigenvalue matrix ϵ_{ij} diagonal:

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

Kohn–Sham DFT II

where the effective potential is defined as

$$
\begin{aligned}
v_{\mathrm{S}}(\mathrm{r}) &= v_{\mathrm{J}}(\mathrm{r}) + \mathrm{v}_{\mathrm{ext}}(\mathrm{r}) + \mathrm{v}_{\mathrm{xc}}(\mathrm{r}) \\
&= \int \frac{\rho(\mathrm{r}')}{|\mathrm{r}-\mathrm{r}'|} d\mathrm{r}' - \sum_{\alpha} \frac{\mathrm{Z}_{\alpha}}{|\mathrm{r}-\mathrm{R}_{\alpha}|} + \frac{\delta \mathrm{E}_{\mathrm{xc}}[\rho]}{\delta \rho}
\end{aligned}
$$

Kohn–Sham DFT III

We solve the 1-electron Kohn–Sham equations self-consistently:

$$\boxed{k(1)\chi_i(1) = \left(-\frac{1}{2}\nabla_1^2 + v_{\mathrm{S}}(1)\right)\chi_i(1) = \epsilon_i\chi_i(1)}$$

where we have defined the Kohn–Sham operator $k(1)$.

Kohn–Sham DFT IV

Once we have the orbitals χ_i, we can evaluate the energy using

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

or, equivalently,

$$\begin{aligned} E[\rho] &= T_{\mathrm{S}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho] + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr} \\ &= \sum_i \epsilon_i - J[\rho] + E_{\mathrm{xc}}[\rho] - \int v_{\mathrm{xc}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr} \end{aligned}$$

Kohn–Sham DFT V

Exchange correlation functionals are usually written in the form

$$E_{\mathrm{xc}}[\rho] = \int \rho(\mathrm{r})\epsilon_{\mathrm{xc}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r}), \cdots)\mathrm{dr} \tag{2}$$

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

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

$$\epsilon_{\mathrm{xc}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r}), \cdots) = \epsilon_{\mathrm{x}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r}), \cdots) + \epsilon_{\mathrm{c}}(\rho(\mathrm{r}), \nabla\rho(\mathrm{r}), \cdots) \tag{3}$$

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

Kohn–Sham DFT VI

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.):

$$E_{\rm xc}[\rho] = \int \rho(\mathrm{r})\epsilon_{\rm xc}^{\rm LDA}(\rho(\mathrm{r}))\mathrm{dr} \tag{4}$$

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

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

Using this we get the Slater exchange functional:

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

Kohn–Sham DFT VII

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.

Kohn–Sham DFT VIII

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

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

Kohn–Sham DFT IX

$F\mathrm{x}(s)$ is sometimes called the enhancement factor and is written as a function of the reduced density gradient defined as

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

Two of the common exchange enhancement factors are

- Becke, 1988 (B88)

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

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.

Kohn–Sham DFT X

- Perdew, Burke & Ernzerhof, 1996 (PBE)

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

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

Kohn–Sham DFT XI

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:

$$E_{\mathrm{xc}}^{\mathrm{hybrid}} = aE_{\mathrm{x}}^{\mathrm{HF}} + (1-a)E_{\mathrm{x}}^{\mathrm{GGA}} + E_{\mathrm{c}}^{\mathrm{GGA}}$$

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:

$$\begin{aligned} E_{\mathrm{xc}}^{\mathrm{B3LYP}} = & E_{\mathrm{xc}}^{\mathrm{SVWN}} + a_0(E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{S}}) + a_x(E_{\mathrm{x}}^{\mathrm{B88}} - E_{\mathrm{x}}^{\mathrm{S}}) \\ & + a_c(E_{\mathrm{c}}^{\mathrm{LYP}} - E_{\mathrm{c}}^{\mathrm{VWN}}) \end{aligned}$$

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

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

Before seeing evidence for the above, here's a problem:

Meaning of the KS orbital energies III

To prove that $\epsilon_{\rm HOMO} = -I$ we follow the steps:

- In principle, the DFT density is the exact density. So we can use the result we have proved earlier (lecture 2):

$$\rho(r) \rightarrow e^{-2\sqrt{2E_I}r}$$

- In Kohn–Sham DFT the density is written as the sum of orbital densities:

Q:

$$\rho(\mathrm{r}) = \sum_{i}^{N} |\chi_i(\mathrm{r})|^2 = \sum_{\mathrm{i}}^{\mathrm{N}} \rho_{\mathrm{i}}(\mathrm{r})$$

- Now determine the asymptotic form of the orbital densities $\rho_i(\mathrm{r})$.

continued...

Meaning of the KS orbital energies IV

To prove that $\epsilon_{\rm HOMO} = -I$ continued....

- The asymptotic form of $\rho_i(\rm r)$ is found using techniques we developed in lecture 2. The Kohn–Sham Hamiltonian for orbital χ_i is

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

Q:

- This is a one-electron Hamiltonian. We will soon show that $v_{\rm S} \rightarrow \frac{1}{r}$, so you can write the large-r form of this Hamiltonian exactly as we did in lecture 2. Do this and show than

$$\chi_i(r) \rightarrow e^{-\sqrt{-2\epsilon_i}r}$$

Hence $\rho_i(r) \rightarrow e^{-2\sqrt{-2\epsilon_i}r}$.

Meaning of the KS orbital energies V

To prove that $\epsilon_{\mathrm{HOMO}} = -I$ continued....

Q:

- Now realise that because $\rho(\mathrm{r})$ is the sum of the ρ_i, so the asymptotic form of ρ will be determined by the (occupied) orbital with the largest (least negative) energy. This will be the HOMO. Hence we should have, in KS-DFT,

$$\rho(r) \rightarrow e^{-2\sqrt{-2\epsilon_{\mathrm{HOMO}}}r}$$

- Hence show that $\epsilon_{\mathrm{HOMO}} = -I$.

Meaning of the KS orbital energies VI

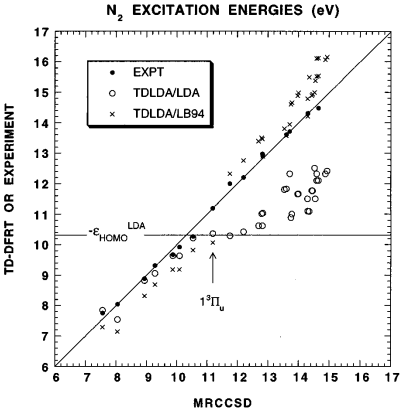


FIG. 1. Correlation plot comparing TD-DFRT results with the multireference coupled cluster singles and doubles (MRCCSD) results of Ref. 53 for the first 35 vertical excitation energies (not counting degeneracies) of N_2. Experimental values taken from Ref. 53 are also shown.

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

Meaning of the KS orbital energies VII

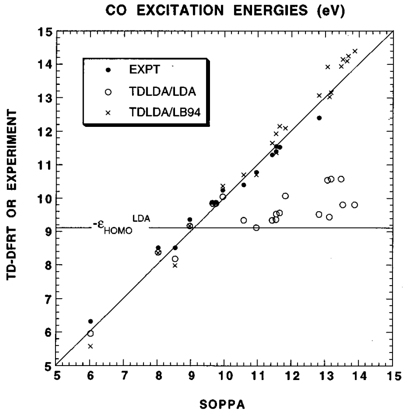


FIG. 2. Correlation plot comparing TD-DFRT results with second-order polarization propagator (SOPPA) ($S \neq 1$ results from Table II of Ref. 54) for the first 23 vertical excitation energies (not counting degeneracies) of CO. Experimental values taken from Ref. 54 are also shown.

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

Meaning of the KS orbital energies VIII

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 IX

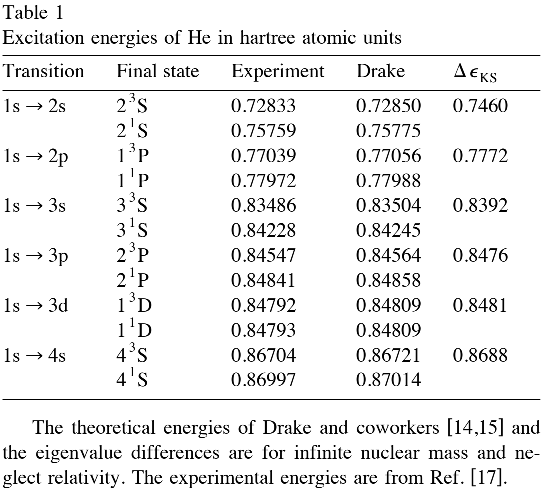


Table 1
Excitation energies of He in hartree atomic units

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

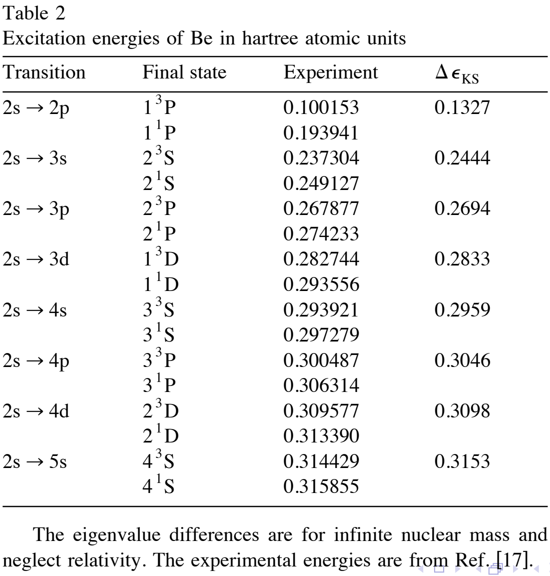


Table 2

Excitation energies of Be in hartree atomic units

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

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{S}}(\mathrm{r})\right)\chi_k(\mathrm{r}) = \epsilon_{\mathrm{k}}\chi_{\mathrm{k}}(\mathrm{r})$$

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

$$v_{\mathrm{S}} \to -\frac{1}{r}$$

as $r \to \infty$.

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

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

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

Therefore these two cancel out asymptotically.

Self-Interaction III

- Hence we must have

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

- 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

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

Self-Interaction IV

This gives us an XC potential:

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

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

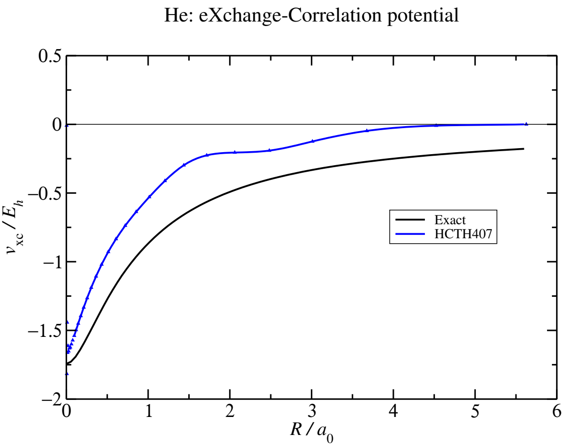
- This is what leads to a small band-gap in DFT: the unoccupied levels are all shifted down with respect to the occupied orbitals.

Self-Interaction V

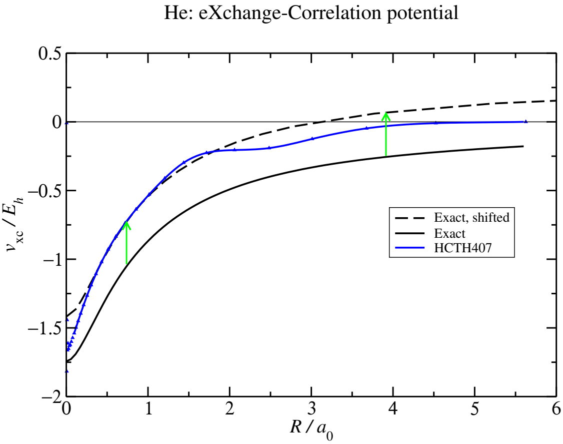
- Self-Interaction: Another way of looking at this problem is to realise that the too rapid decay of $v_{\rm xc}$ with distance is equivalent to the electron 'seeing' itself. I.e., rather than see a hole with charge $+1$, it sees a hole with charge $+re^{-\frac{2}{3}r}$. This is the self-interaction 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



Self-Interaction VII



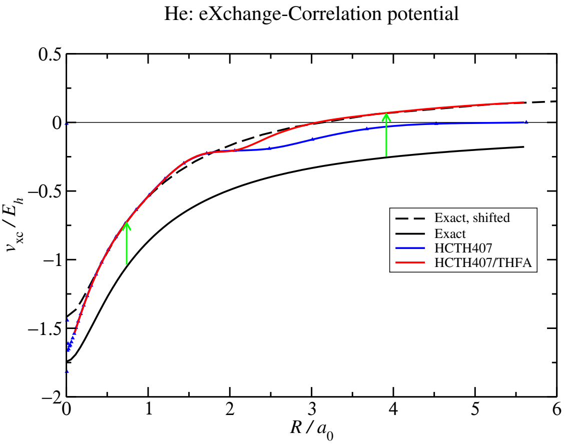
Asymptotic-correction I

Since we know what the asymptotic form of $v_{\rm xc}$ 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:

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

So if know (or calculate) I, calculate $\epsilon_{\rm HOMO}$ 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



Asymptotic-correction III

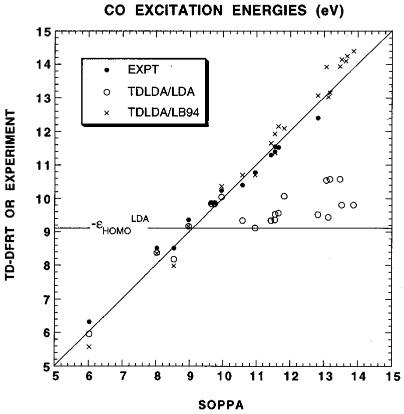


FIG. 2. Correlation plot comparing TD-DFRT results with second-order polarization propagator (SOPPA) ($S \neq 1$ results from Table II of Ref. 54) for the first 23 vertical excitation energies (not counting degeneracies) of CO. Experimental values taken from Ref. 54 are also shown.

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

Excitation energies

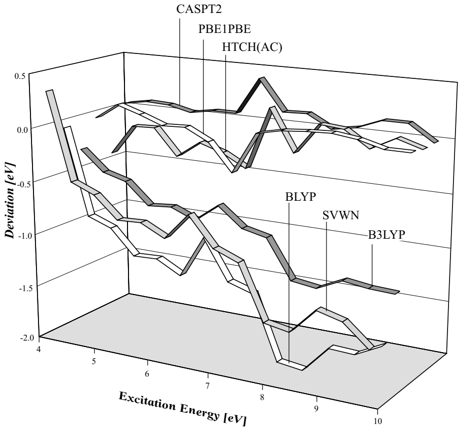
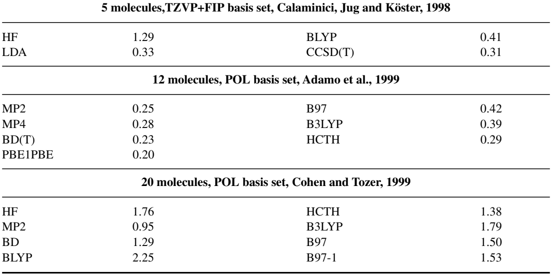


Figure 9-2. Performance of various functionals in the framework of time-dependent DFT for excitation energies of ethylene.

Asymptotic-correction V

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

Asymptotic-correction VI

- The asymptotic correction does fix what is called the one-electron self-interaction error.
- But there is no clear way to apply an asymptotic correction in the bulk phase. And the self-interaction error manifests itself there too.
- We know that Hartree–Fock is free of self-interaction, so one solution to the problem is to include more and more Hartree–Fock-type exchange in KS-DFT. But this leads to an overall loss in accuracy.

Asymptotic-correction VII

- A better solution is to use *range-separation*: Split the e-e interaction operator into a short- and long-range part:

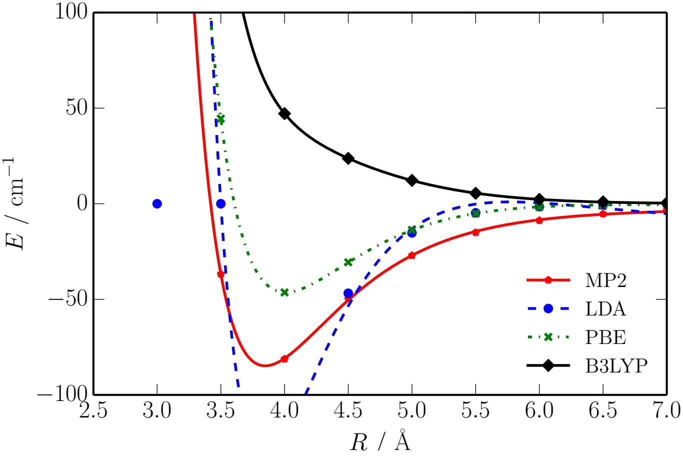
  $$\frac{1}{r_{12}} = \frac{\operatorname{erfc}(\beta r_{12})}{r_{12}} + \frac{(1 - \operatorname{erfc}(\beta r_{12}))}{r_{12}}$$

  The complementary error function is chosen as it allows easy integral evaluation. Now use DFT on the short-range part and Hartree–Fock-exachange on the long-range part. In this way you get the best of both worlds.
- Functionals such as `CamB3LYP` use this principle.
- It is also possible to use post-Hartree–Fock methods on the long-range part. For example, you could use MP2. This would allow the dispersion interaction to be described by DFT. More on this next.

Dispersion I

The other problem with DFT is that almost all conventional functionals fail to describe the dispersion (sometimes called the van der Waals) interaction. This is a long-range and non-local interaction that arises from the correlation of quantum menchanical fluctuations on the interaction species.
Consider the argon dimer: this is a dispersion-bound system, that is, the attraction between two argon atoms arises purely from the dispersion interaction. This is typical of the rare-gas atoms. On the next slide we see interaction energies calculated for this system with MP2, LDA, PBE and B3LYP using the `aug-cc-pVTZ` basis set using the counterpoise correction.

Dispersion II



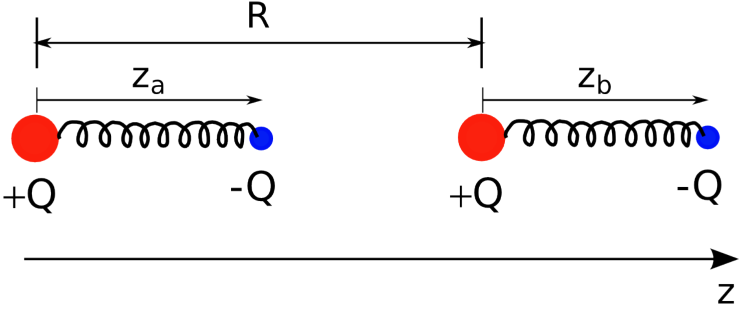
Dispersion III

- The reference MP2 energies exhibit the classic interaction energy curve as expected. Recall that MP2 is not perfect for this system, but it will serve as a reference here.
- The density functionals are all over the place. LDA and PBE show some binding but is it from the dispersion?
- The clue is in the long-range behaviour: all density functionals decay to zero much too quickly with R.
- On the other hand, the dispersion energy (in the MP2 tail) is more slowly decaying as R^{-6}.
- B3LYP is completely repulsive!

Why is this the case?

Drude Model I

The dispersion energy cannot be described in terms of classical interactions as the electrostatic and induction terms can. A semi-classical picture is required.



Drude Model II

Model each molecule with a fixed charge $+Q$ at the centre and an oscillating charge $-Q$. In the usual scaled units (i.e. energy in units of $h\nu = \hbar\omega$, length in units of $(\hbar^2/km)^{1/4}$) the Hamiltonian is (assuming infinite separation):

$$\mathcal{H} = -\frac{1}{2}\frac{\partial^2}{\partial {z_A}^2} + \frac{1}{2}{z_A}^2 - \frac{1}{2}\frac{\partial^2}{\partial {z_B}^2} + \frac{1}{2}{z_B}^2. \tag{5}$$

The energy is the sum of the individual energies, i.e., $E_{v_A v_B} = v_A + v_B + 1$. The ground state energy $(v_A = v_B = 0)$ is 1 unit, i.e. $h\nu$.

Drude Model III

If the instantaneous displacements are $z_A(t)$ and $z_B(t)$, the dipole moments on A and B are $\mu_A = -Qz_A(t)$ and $\mu_B = -Qz_B(t)$, respectively.
At a finite separation R, these dipoles interact. The general form of the dipole–dipole interaction energy is (derived later)

$$E_{\mu\mu} = -\frac{\mu_A\mu_B}{R^3}\left(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi\right),$$

Here, $\theta_A = \theta_B = \pi$ and $\phi = 0$ so the Hamiltonian at finite separations has the additional term cz_Az_B where $c = -\frac{2Q^2}{R^3}$.

Drude Model IV

Using the new variables $Z_1 = \sqrt{\frac{1}{2}}(z_A + z_B)$ and $Z_2 = \sqrt{\frac{1}{2}}(z_A - z_B)$, the potential term in the Hamiltonian becomes

$$V = \frac{1}{2}{z_A}^2 + c z_A z_B + \frac{1}{2}{z_B}^2 = \frac{1}{2}(1+c){Z_1}^2 + \frac{1}{2}(1-c){Z_2}^2,$$

while the kinetic energy is unchanged in form:

$$T = -\frac{1}{2}\frac{\partial^2}{\partial {z_A}^2} - \frac{1}{2}\frac{\partial^2}{\partial {z_B}^2} = -\frac{1}{2}\frac{\partial^2}{\partial {Z_1}^2} - \frac{1}{2}\frac{\partial^2}{\partial {Z_2}^2}.$$

Drude Model V

So we now have an oscillator Z_1 with frequency $\sqrt{1+c}$, and another, Z_2, with frequency $\sqrt{1-c}$. The allowed energies (in the original scaled units) are now $(v_1+\frac{1}{2})\sqrt{1+c}+(v_2+\frac{1}{2})\sqrt{1-c}$. In a classical system the coupling doesn't change the minimum energy, which occurs when both oscillators are at rest. That is, $z_A = z_B = 0$, so $Z_1 = Z_2 = 0$ also, and the total energy is zero. A quantum system, however, has zero-point energy: 1 unit in the original uncoupled system.

Drude Model VI

When $v_1 = v_2 = 0$ the energy of the interacting system is

$$\begin{aligned} E = \frac{1}{2}(\sqrt{1+c} + \sqrt{1-c}) &= \frac{1}{2}[(1 + \frac{1}{2}c - \tfrac{1}{8}c^2 + \cdots) \\ &\qquad + (1 - \frac{1}{2}c - \tfrac{1}{8}c^2 - \cdots)] \\ &= 1 - \tfrac{1}{8}c^2 - \cdots . \end{aligned}$$

That is, the zero-point energy is smaller for the correlated oscillators than for the uncoupled ones, whether c is positive or negative. The stabilization energy is the Drude approximation to the disperion.

Drude Model VII

The Drude expression for the dispersion energy is $-\frac{1}{8}c^2 = -\frac{Q^4}{2R^6}$ which varies as $\frac{1}{R^6}$. The coefficient of this term is usually labeled C_6 and, inserting the energy factors scaled out, is defined as

$$C_6 = \frac{\hbar\omega Q^4}{2(4\pi\epsilon_0)^2 k^2}.$$

We now need to relate Q and k to measurable quantities. This is done using classical ideas.

Drude Model VIII

If the charge $-Q$ extends by z in an electric field E then balancing forces we must have $kz = -QE$, or $z = -\frac{QE}{k}$. Now, by definition, $\mu = -zQ = \frac{Q^2}{k}E$. But, by definition of the polarizability, $\mu = \alpha E$, therefore

$$\alpha = \frac{Q^2}{k}.$$

This allows us to re-write the C_6 as

$$\boxed{C_6 = \frac{\hbar\omega\alpha^2}{2(4\pi\epsilon_0)^2}.}$$

Drude Model IX

In 3-dimensions this expression becomes

$$C_6 = \frac{3\hbar\omega\alpha^2}{4(4\pi\epsilon_0)^2},$$

Q: Show this!

and taking, as London did, $\hbar\omega = E_I$, the ionization energy, we get

$$\boxed{C_6 = \frac{3E_I\alpha^2}{4(4\pi\epsilon_0)^2}.}$$

This is an approximation, but it contains all the correct physics. The dispersion energy is always attractive (at second-order) and can be interpreted as arising from a correlation in the electronic fluctuations on the molecules.

Drude Model X

- In this phenomenological model, the dispersion energy arises from the correlations of quantum fluctuations. It is a purely quantum phenomenon and has no classical analogue.
- Further, it as it is a non-local phenomenon, we can now understand why local and semi-local density functional are unable to describe this energy. Functionals need to be explicitly non-local to be able to describe the dispersion energy.
- However many density functionals can be corrected to account for the missing dispersion by adding to the DFT energy a term like:

$$E_{\mathrm{disp}} = -\sum_{b>a} f_{\mathrm{switch}}(\beta r_{ab}) \frac{C_6^{ab}}{r_{ab}^6},$$

Drude Model XI

where a and b are atomic sites separated by r_{ab} and with a dispersion coefficient C_6^{ab}. The switching function $f_{\mathrm{switch}}(\beta r_{ab})$ which typically depends on one or more parameters (here only one is indicated) has to be very carefully chosen to avoid double-counting the dispersion at short range. Also, this switching function needs to be tuned to each density functional.

- The most popular of such corrections is by Stefan Grimme.
- In many of these models, it is assumed that the dispersion coefficient between atoms is fixed and does not vary with changes in chemical environment. This is often a poor approximation.
- Furthermore, the C_6 term is only one term in the dispersion expansion and it is generally angular-dependent.

Drude Model XII

- Additionally, for semiconductors and metals additional terms (as low as C_2) arise from plasmon modes. These are long wavelength fluctuations arising from the conduction electrons. For such systems the above model breaks down.
- There are explicitely non-local functionals which do not need this correction, but in practice, this correction, if well tuned, can be more accurate than many other more sophisticated non-local functionals.

Lab & AMH report I

Density functional calculations:

```
dft
  xc b3lyp
end
set geometry "Ar+Ar"
task dft
unset geometry "Ar+Ar"

scf; vectors atomic; end

set geometry "Ar+ghost"
task dft
unset geometry "Ar+ghost"
```

Lab & AMH report II

This would be a standard DFT calculation in NWChem with the B3LYP functional. To define the PBE functional use:

```
dft
  xc xpbe96 cpbe96
end
```

And to define the PBE0 functional use:

```
dft
  xc pbe0
end
```

Lab & AMH report III

To define the Grimme dispersion correction with, say, PBE0, use:

```
dft
  xc  pbe0
  disp
end
```