An Introduction to the Density Functional Theory

Autumn School on Correlated Electrons: Many-Body Methods for Real Materials

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Xavier Blase

Institut Néel, CNRS, Grenoble, France.

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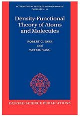

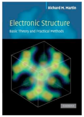

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Quantum mechanics reminder

Quantum states of an N-electron system are described by a wavefunction:

$$\psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, ..., \mathbf{r}_N\sigma_N) \quad \text{with } \mathbf{r}_i \text{ and } \sigma_i \text{ space and spin variables.}$$

The probability to find N electrons with spins $(\sigma_1, ..., \sigma_N)$ in the elementary volume $d\mathbf{r}_1 d\mathbf{r}_2 ... d\mathbf{r}_N$ centred in $\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N$ is given by

$$d^{3N}\mathcal{P} = |\psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, ..., \mathbf{r}_N\sigma_N)|^2 d\mathbf{r}_1 d\mathbf{r}_2 ... d\mathbf{r}_N.$$

By definition, the charge density can be found by integrating over (N-1) space-variables and over spins:

$$n(\mathbf{r}) = N \int d\sigma dx_2 ... dx_N \, |\psi(\mathbf{r}\sigma, x_2, ..., x_N)|^2 \qquad \text{where } \; x_i = (\mathbf{r}_i, \sigma_i)$$

with $n(\mathbf{r})d\mathbf{r}$ the number of electrons in the elementary volume $d\mathbf{r}$ centred in $\mathbf{r}$. By normalization of ψ one obtains: $\int d\mathbf{r} \; n(\mathbf{r}) = N$.

Hamiltonian and expectations values

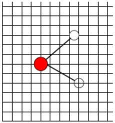
The electronic Hamiltonian is actually known (atomic units):

$$\hat{H} = \sum_{i=1}^{N} \frac{-\nabla_i^2}{2} + \sum_{i=1}^{N} v^{ions}(\mathbf{r}_i) + \sum_{i<j} \frac{1}{r_{ij}} \quad \text{with} \quad v^{ions}(\mathbf{r}) = -\sum_{I} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}|}$$

We did not include the ions (positions $\{\mathbf{R}_I\}$) kinetic energy. v^{ions} is the ionic potential acting on electrons. The energy of the system is given by the "expectation value" of the Hamiltonian (let's forget spin):

$$\langle\psi|\hat{H}|\psi\rangle = \int \cdots \int d\mathbf{r}_1 d\mathbf{r}_2 ... d\mathbf{r}_N \; \psi^*(\{\mathbf{r}_i\})\hat{H}(\{\mathbf{r}_i\}, \{\nabla_{\mathbf{r}_i}\})\psi(\{\mathbf{r}_i\})$$

Take a water molecule (10 electrons) and perform this integral by discretizing the space in a small $10\times10\times10$ grid → $10^{3N} = 10^{30}$ electronic configurations to sample, to be compared to petaflofic (10^{15}) modern computers !!



Let's change paradigm : the mean-field Density Functional Theory ....

Prolegomena: 1-body operators and the density

The electron-ion energy reads: $V^{ions-e} = \sum_i \langle\psi\big|v^{ions}(\mathbf{r}_i)\big|\psi\rangle$ with:

$$\begin{aligned}\langle\psi\big|v^{ions}(\mathbf{r}_i)\big|\psi\rangle &= \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \; v^{ions}(\mathbf{r}_i)|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)|^2 \\ &= \int d\mathbf{r} d\mathbf{r}_2 \dots d\mathbf{r}_N \; v^{ions}(\mathbf{r})|\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2\end{aligned}$$

where we have renamed all variables and in particular ($\mathbf{r}_i \Rightarrow \mathbf{r}$) and reshuffled all space positions thanks to the symmetry properties of $|\psi|^2$.
As a result, all N terms are identical yielding:

$$V^{ions-e} = N \int d\mathbf{r} \; v^{ions}(\mathbf{r}) \int d\mathbf{r}_2 \dots d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 = \int d\mathbf{r} \; v^{ions}(\mathbf{r}) n(\mathbf{r})$$

$\Rightarrow v^{ions}$ acts only on the charge density : no need for the full many-body wavefunction and 3N-integrals to get the V^{ions-e} energy !!

2-body operators and the density of pairs

The electron-electron interaction energy: $V^{ee} = \sum_{i<j} \langle\psi| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} |\psi\rangle$ can also be simplified by renaming and reshuffling the integration variables:

$$\langle\psi| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} |\psi\rangle = \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}_3 \dots d\mathbf{r}_N \, \frac{|\psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2}{|\mathbf{r} - \mathbf{r}'|}$$

yielding $N(N-1)/2$ identical terms so that $V^{ee} = \int d\mathbf{r} d\mathbf{r}' \frac{\rho_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$ with:

$$\rho_2(\mathbf{r}, \mathbf{r}') = \frac{N(N-1)}{2} \int d\mathbf{r}_3 \dots d\mathbf{r}_N \, |\psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2$$

the density of pairs with $\int d\mathbf{r} d\mathbf{r}' \rho_2(\mathbf{r}, \mathbf{r}') = \frac{N(N-1)}{2}$.

There is no need for all the details of the many-body wavefunctions and 3N-integrals: we only need averaged (mean-field) quantities !!

BUT we do not know how to build $\rho_2(\mathbf{r}, \mathbf{r}')$ without the knowledge of ψ.

The density functional theory (DFT) for ground-states

Preliminaries : room temperature is of the order of 26 meV, namely much smaller than typical electronic energy gaps or band dispersions → most unperturbed (no strong light, etc.) solids or molecules are close to their lowest energy (ground) state with wavefunction ψ_{GS} and energy E_{GS}.

The variational principles provides a way to find ψ_{GS} and energy E_{GS}:

$$E_{GS} = \min_{\psi} E[\psi] \quad \text{with} \quad E[\psi] = \langle \psi | \hat{H} | \psi \rangle \quad \text{and} \quad \langle \psi | \psi \rangle = 1$$

This is the standard approach where the energy is <u>a functional</u> of the many-body wavefunction ψ. The dramatic result from Hohenberg and Kohn (1965) is that one can show that the ground-state energy can be written as a functional of the charge density !

$$E_{GS} = \min_{\psi} E[\psi] \quad \Longrightarrow E_{GS} \overset{DFT}{=} \min_{n} E[n] \quad \text{with} \quad \int d\mathbf{r}\, n(\mathbf{r}) = N.$$

This is an EXACT result, namely there is an exact mean-field theory for the problem of the ground-state energy in N-electron systems !!

Demonstration for non-degenerate ground-states

The ionic potential acts on the charge density and the electronic Hamiltonian (no ion-ion interaction) reads:

$$\hat{H} = \hat{T} + \hat{V}^{ee} + \int d\mathbf{r}\ v^{ext}(\mathbf{r})n(\mathbf{r}), \quad \text{with} \ \ \hat{T} \ \text{kinetic energy operator}$$

where $v^{ext} = v^{ions}$ (the ions are "external" to the N-electron system).

Theorem : given $n(\mathbf{r})$ a ground-state charge density, then there exist only one external potential $v^{ext}(\mathbf{r})$ that realizes $n(\mathbf{r})$.

(Reductio ad adsurdum) Assume there exist 2 external potential $v_1^{ext}(\mathbf{r})$ and $v_2^{ext}(\mathbf{r})$ that lead to the same ground-state charge density:

$$\begin{array}{lcl} v_1^{ext}(\mathbf{r}) & \Longrightarrow & \hat{H}_1 \Longrightarrow \psi_1^{GS} \Longrightarrow n(\mathbf{r}) \\ v_2^{ext}(\mathbf{r}) & \Longrightarrow & \hat{H}_2 \Longrightarrow \psi_2^{GS} \Longrightarrow n(\mathbf{r}) \end{array}$$

Demonstration for non-degenerate ground-states (2)

Using the variational principle:

$$\begin{aligned}\langle\psi_1|\hat{H}_1|\psi_1\rangle &< \langle\psi_2|\hat{H}_1|\psi_2\rangle = \langle\psi_2|\hat{H}_2|\psi_2\rangle + \langle\psi_2|\hat{H}_1 - \hat{H}_2|\psi_2\rangle \\ E_1^{GS} &< E_2^{GS} + \int d\mathbf{r}\left(v_1^{ext} - v_2^{ext}\right)(\mathbf{r})n(\mathbf{r})\end{aligned}$$

Starting now from $\langle\psi_2|\hat{H}_2|\psi_2\rangle$ (switching 1 and 2 indices) one obtains:

$$E_2^{GS} < E_1^{GS} + \int d\mathbf{r}\left(v_2^{ext} - v_1^{ext}\right)(\mathbf{r})n(\mathbf{r})$$

and by adding the two inequalities:

$$E_1^{GS} + E_2^{GS} < E_2^{GS} + E_1^{GS} \qquad \text{IMPOSSIBLE!}$$

The demonstration hinges on strict inequalities, namely assuming non-degenerate ground-state. This is the celebrated 1964 theorem by Hohenberg and Kohn.

Ground-state energy as a functional of the charge density

It follows that the charge density completely determines the external potential and thus the Hamiltonian (just add the universal kinetic and V^{ee} operators) and thus the ground-state wavefunction ψ_{GS}.

$$\begin{tikzcd}
v^{ext} \arrow[r] & \hat{H} \arrow[r] & \psi_{GS} \arrow[r] & n(\mathbf{r}) \arrow[lll, bend left]
\end{tikzcd}$$

Since $n(\mathbf{r})$ determines ψ_{GS}, then it determines univocally the ground state total energy $E_{GS} = \langle \psi_{GS} | \hat{H} | \psi_{GS} \rangle$. It can be shown further as a corollary (Exercise) that the variational principle can be now used for E_{GS} as a functional of the charge density.

$$E_{GS} = \min_{\psi} E[\psi] \quad \Longrightarrow E_{GS} \overset{DFT}{=} \min_{n} E[n] \quad \text{with} \quad \int d\mathbf{r}\, n(\mathbf{r}) = N.$$

Problem : the unknown Hohenberg and Kohn functional

The ground-state energy as a functional of the charge density is usually written with the Hohenberg and Kohn "universal" functional F_{HK}:

$$E[n] = F_{HK}[n] + \int d\mathbf{r} \; v^{ion}(\mathbf{r}) n(\mathbf{r}) \quad \text{with} \quad F_{HK}[n] = T[n] + V^{ee}[n]$$

with the kinetic $T[n]$ and electron-electron interaction $V^{ee}[n]$ energies.

But we do not know how to write $T[n]$ and $V^{ee}[n]$ as a function of the charge density n ! This is where exact DFT stops and where approximations begin ...

Exercise. Kinetic energy per unit volume of the non-interacting homogeneous electron gas : $T[n]/V = C_{TF} \times n^{5/3}$ (Thomas-Fermi).

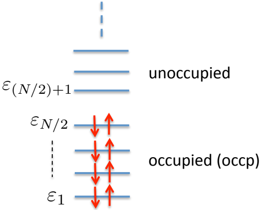
Exercise. Kinetic energy for the hydrogen atom (von Weizsäcker) reads : $2T[n] = \int d\mathbf{r} \; (\vec{\nabla} \sqrt{n(\mathbf{r})})^2$.

Kohn and Sham (1965) : back to wavefunctions !

The idea of Kohn and Sham is to introduce a fictitious non-interacting electron gas under the effect of an external effective potential $v^{eff}(\mathbf{r})$ such that the ground-state charge density and energy are the same than the true system.

With non-interacting electrons, the amplitude of probability to find an electron somewhere is independent of the position of other electrons : we are back to one-body wavefunctions $\{\phi_n(\mathbf{r})\}$ such that:

$$\begin{aligned}
\left(-\frac{\nabla^2}{2}\right. &+ \left. v^{eff}(\mathbf{r})\right)\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r}) \\
T_0 &= \sum_n^{occp} \langle\phi_n|\frac{-\nabla^2}{2}|\phi_n\rangle \\
n(\mathbf{r}) &= \sum_n^{occp} |\phi_n(\mathbf{r})|^2
\end{aligned}$$



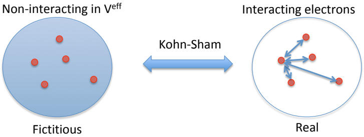
The fictitious Kohn-Sham non-interacting system

What is this v^{eff} potential ? We use the variational principle for $E[n] = F_{HK}[n] + \int d\mathbf{r} v^{ion}(\mathbf{r}) n(\mathbf{r})$ under the constraint (Lagrange parameter μ) that the charge density integrates to N electrons:

$$\frac{\partial}{\partial n(\mathbf{r})}\left[E[n] - \mu\left(\int n(\mathbf{r}) d\mathbf{r} - N\right)\right] = 0$$

$$\Longrightarrow \frac{\partial F_{HK}}{\partial n(\mathbf{r})} + v^{ext}(\mathbf{r}) = \mu$$

(Euler-Lagrange equation)



For the 2 systems to be equivalent (same energy and charge density), with $E^{KS} = T^0 + \int d\mathbf{r} v^{eff}(\mathbf{r}) n(\mathbf{r})$:

$$\frac{\partial F_{HK}}{\partial n(\mathbf{r})} + v^{ion}(\mathbf{r}) = \mu = \frac{\partial T^0}{\partial n(\mathbf{r})} + v^{eff}(\mathbf{r})$$

$$\Longrightarrow v^{eff}(\mathbf{r}) = v^{ion}(\mathbf{r}) + \frac{\partial \Big[F_{HK} - T^0 \Big]}{\partial n(\mathbf{r})}$$

Now : $F_{HK}[n] = T[n] + V^{ee}[n] = T^0 + J[n] + \Big(T - T^0 + V^{ee} - J \Big)$

$J[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ is the (classical) Hartree energy.

Define $E^{XC}[n] = T - T^0 + V^{ee} - J$ the exchange-correlation (XC) energy to obtain:

$$\begin{aligned} v^{eff}(\mathbf{r}) &= v^{ion}(\mathbf{r}) + \frac{\partial J[n]}{\partial n(\mathbf{r})} + \frac{\partial E^{XC}[n]}{\partial n(\mathbf{r})} \\ &= v^{ion}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V^{XC}(\mathbf{r}) \end{aligned}$$

NOTE: within "Kohn-Sham DFT", the exchange-correlation energy contains a kinetic component ($T - T^0$) !!

The local density approximation (LDA)

So far everything is exact ! The nice things is that we now how to calculate T^0 and J and what is unknown (E^{XC}) has been reformulated as an energy difference ($T - T^0 + V^{ee} - J$) supposedly smaller than the original $F_{HK}[n]$. But still, how to we get now $E^{XC}[n]$ and $v^{XC}(\mathbf{r})$?

Inspired by historical ideas (Thomas-Fermi), HK and KS proposed very early the Local Density Approximation, defining an exchange-correlation energy per particle that only depends on the local charge density:

$$E^{XC}[n] \simeq \int d\mathbf{r}\; n(\mathbf{r}) \epsilon^{XC,LDA}\Big(n(\mathbf{r})\Big)$$

Once this approximation is done, $\epsilon^{XC,LDA}\Big(n(\mathbf{r})\Big)$ can be taken to be the exchange-correlation energy of an homogeneous interacting electron gas of uniform density: $\bar{n} = n(\mathbf{r})$.

David Ceperley and Berni Alder (PRL 1980)

They performed Quantum Monte Carlo calculations of the total energy $E(\bar{n})$ of an homogeneous interacting electron gas (HEG) of density $\bar{n}$.

For the HEG, the kinetic energy T^0 of the non-interacting system with density $\bar{n}$ and the Hartree potential $J(\bar{n})$ can be calculated analytically. By subtraction the XC energy $E^{XC}(\bar{n}) = E(\bar{n}) - T^0(\bar{n}) - J(\bar{n})$ is obtained.

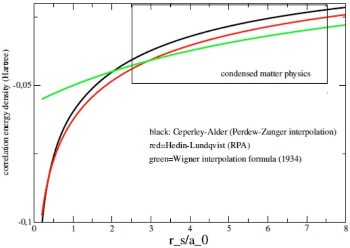
The numerical (QMC) data can be fitted by clever functional forms (VWN80, PZ81, PW92, etc.) yielding the LDA functionals !

NOTE: The exchange energy can be calculated analytically for the HEG (Dirac and Slater) → obtain the "correlation-only" $\epsilon^C(\bar{n})$ energy per electron.

$$K[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d\mathbf{r}\; n^{4/3}(\mathbf{r}) \Longrightarrow \text{local exchange from Slater HEG formula}$$

Real systems are not in the low or high density limit

Standard extended condensed-matter or solid-state-physics systems are difficult since they are not in a limit where standard perturbation theory starting from the high or low-density limits can work "accurately".



Correlation energy density for the interacting electron gas as a function of the Wigner-Seitz radius (r_S) which is the radius of the gedanken sphere whose volume is the total volume divided by the number of electrons ($\Omega_{WS} = 4\pi r_S^3/2 = \Omega/N$).

Analytic low-density (Wigner limit where potential energy dominates) and high-density (RPA limit where kinetic energy dominates) provide analytic "asymptotic" forms for developing functionals.

Real systems are usually inhomogeneous

(Hohenberg and Kohn, PRB 1964)

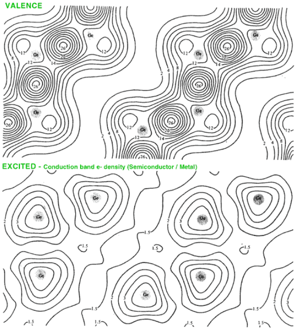
IV. CONCLUDING REMARKS

In the preceding sections we have developed a theory of the electronic ground state which is exact in two limiting cases: The case of a nearly constant density ($n=n_0+\tilde{n}(r), \tilde{n}(r)/n_0 \ll 1$) and the case of a slowly varying density. Actual electronic systems do not belong to either of these two categories. The most promising formulation of the theory at present appears to be that obtained by partial summation of the gradient expansion (Sec. III.4). It has, however, not yet been tested in actual physical problems.

(Kohn and Sham, PRB 1965)

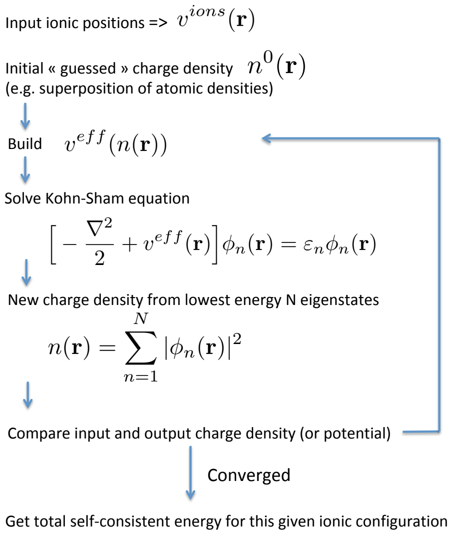
In atoms and molecules one can distinguish three regions: (1) A region near the atomic nucleus, where the electronic density is high and therefore, in view of case (*b*) above, we expect our procedure to be satisfactory. (2) The main "body" of the charge distribution where the electronic density $n(\mathbf{r})$ is relatively slowly varying, so that our approximation (2.3) for ϵ_{xc} is expected to be satisfactory as discussed in case (a) above. (3) The "surface" of atoms and the overlap regions in molecules. Here our approximation (2.3) has no validity and therefore we expect this region to be the main source of error. We do not expect an accurate description of chemical binding.

High density limit: kinetic energy dominates
Approximation (2.3) = local density approximation



Plot of the charge density $|\psi_{n\mathbf{k}}|^2$ associated with the top of the valence bands and bottom of the conduction bands in Germanium, a "nearly" metal (courtesy Prof. Majewsky, Virginia U.)

Self-consistent DFT Kohn-Sham calculations



Input ionic positions => $v^{ions}(\mathbf{r})$

Initial « guessed » charge density $n^0(\mathbf{r})$
(e.g. superposition of atomic densities)

Build $v^{eff}(n(\mathbf{r}))$

Solve Kohn-Sham equation

$$\left[-\frac{\nabla^2}{2}+v^{eff}(\mathbf{r})\right]\phi_n(\mathbf{r})=\varepsilon_n\phi_n(\mathbf{r})$$

New charge density from lowest energy N eigenstates

$$n(\mathbf{r})=\sum_{n=1}^{N}|\phi_n(\mathbf{r})|^2$$

Compare input and output charge density (or potential)

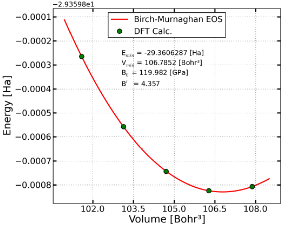
Converged

Get total self-consistent energy for this given ionic configuration

Lattice parameter of solids

Assume one studies an FCC crystal (Si) => the only structural parameter is the lattice constant

One calculate the total energy as a function of the lattice constant or unit cell volume.



The minimum energy gives the equilibrium lattice constant (0°K).

Lattice parameters in metals and non-metals

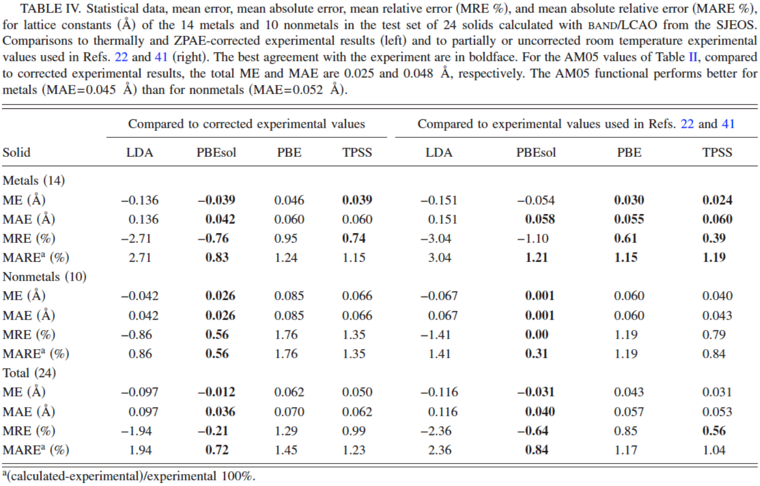


TABLE IV. Statistical data, mean error, mean absolute error, mean relative error (MRE %), and mean absolute relative error (MARE %), for lattice constants (Å) of the 14 metals and 10 nonmetals in the test set of 24 solids calculated with BAND/LCAO from the SJEOS. Comparisons to thermally and ZPAE-corrected experimental results (left) and to partially or uncorrected room temperature experimental values used in Refs. 22 and 41 (right). The best agreement with the experiment are in boldface. For the AM05 values of Table II, compared to corrected experimental results, the total ME and MAE are 0.025 and 0.048 Å, respectively. The AM05 functional performs better for metals (MAE=0.045 Å) than for nonmetals (MAE=0.052 Å).

	Compared to corrected experimental values				Compared to experimental values used in Refs. 22 and 41			
Solid	LDA	PBEsol	PBE	TPSS	LDA	PBEsol	PBE	TPSS
Metals (14)								
ME (Å)	−0.136	**−0.039**	0.046	**0.039**	−0.151	−0.054	**0.030**	**0.024**
MAE (Å)	0.136	**0.042**	0.060	0.060	0.151	**0.058**	**0.055**	**0.060**
MRE (%)	−2.71	**−0.76**	0.95	**0.74**	−3.04	−1.10	**0.61**	**0.39**
MARE[a] (%)	2.71	**0.83**	1.24	1.15	3.04	**1.21**	**1.15**	**1.19**
Nonmetals (10)								
ME (Å)	−0.042	**0.026**	0.085	0.066	−0.067	**0.001**	0.060	0.040
MAE (Å)	0.042	**0.026**	0.085	0.066	0.067	**0.001**	0.060	0.043
MRE (%)	−0.86	**0.56**	1.76	1.35	−1.41	**0.00**	1.19	0.79
MARE[a] (%)	0.86	**0.56**	1.76	1.35	1.41	**0.31**	1.19	0.84
Total (24)								
ME (Å)	−0.097	**−0.012**	0.062	0.050	−0.116	**−0.031**	0.043	0.031
MAE (Å)	0.097	**0.036**	0.070	0.062	0.116	**0.040**	0.057	0.053
MRE (%)	−1.94	**−0.21**	1.29	0.99	−2.36	**−0.64**	0.85	**0.56**
MARE[a] (%)	1.94	**0.72**	1.45	1.23	2.36	**0.84**	1.17	1.04

[a] (calculated-experimental)/experimental 100%.

Figure: Assessing the performance of recent density functionals for bulk solids, Csonka et al., Phys. Rev. B 79, 155107 (2009). (courtesy Prof. János G. Ángyán)

DFT/LDA charge density in inhomogeneous systems

As shown here for solid argon, with very inhomogeneous charge densities, the DFT/LDA charge density is in excellent agreement with higher level approaches [PRB 74, 045102 (2006)].

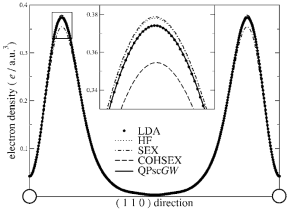


FIG. 7. Argon: density along the direction (1 1 0) within different approximations. The inset is a close-up of the region around the maximum.

[PRB 57, 15293 (1998)]

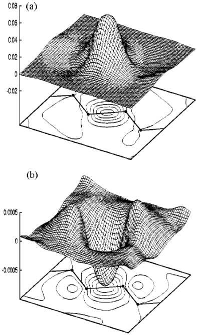


FIG. 2. (a) The VMC one-body density matrix, $\rho_{\rm VMC}(\mathbf{r},\mathbf{r}')$ and (b) $\rho_{\rm VMC}(\mathbf{r},\mathbf{r}')-\rho_{\rm LDA}(\mathbf{r},\mathbf{r}')$, in the (110) plane passing through the atoms with $\mathbf{r}$ fixed at the bond center. ρ is normalized such that $\rho(\mathbf{r},\mathbf{r})=n(\mathbf{r})$, the charge density at the bond center. The silicon atoms and bonds are shown schematically.

$$\rho_{VMC}(\mathbf{r},\mathbf{r}') = N \int \psi^*(\mathbf{r},\mathbf{r}_2,...,\mathbf{r}_N)\psi(\mathbf{r}',\mathbf{r}_2,...,\mathbf{r}_N)\; d\mathbf{r}_2...d\mathbf{r}_N$$

$$\rho_{LDA}(\mathbf{r},\mathbf{r}') = \sum_n \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')\theta(E_F - \varepsilon_n)$$

The exchange correlation XC hole and its sum rule

Rewriting the pair density as: $2\rho_2(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}')\Big[1 + h(\mathbf{r},\mathbf{r}')\Big]$, with h called the pair-correlation function, one can express the V^{ee} energy in function of the Hartree energy J and the XC hole density $\rho_{XC}(\mathbf{r},\mathbf{r}')$:

$$V^{ee} = J + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\ \frac{\rho(\mathbf{r})\rho_{XC}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \text{with} \quad \rho_{XC}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}')h(\mathbf{r},\mathbf{r}')$$

It is easy to demonstrate (Exercise):

$$\int d\mathbf{r}'\rho_2(\mathbf{r},\mathbf{r}') = \frac{(N-1)}{2}\rho(\mathbf{r}) \quad \text{and} \quad \int d\mathbf{r}'\ \rho_{XC}(\mathbf{r},\mathbf{r}') = -1.$$

yielding the XC-hole sum rule !! The XC energy is the Coulomb energy between electrons and their XC-hole, namely the depletion of one electron (through exchange and Coulomb repulsion) dynamically created around each electron. The $(1/2)$ term in the XC energy is an adiabatic factor : the XC hole grows with the electron and would not exist without it.

The spherically averaged XC hole and LDA "success"

The success of DFT/LDA even for highly inhomogeneous systems can be related to the quality of the "spherically averaged" exchange-correlation hole and the fact that the LDA XC-hole satisfies the correct sum-rule.

$$E^{XC} = \frac{1}{2}\int d\mathbf{r}_1 \rho(\mathbf{r}_1)\Big[\int d\mathbf{r}_2 \frac{\rho_{xc}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_2-\mathbf{r}_1|}\Big] \quad \text{and} \quad \int d\mathbf{r}_2\ \rho_{xc}(\mathbf{r}_1,\mathbf{r}_2) = -1.$$

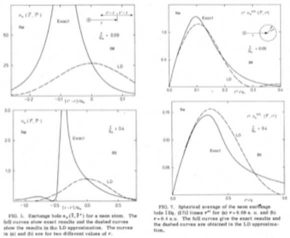
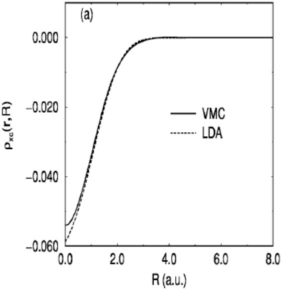


FIG. 5. Exchange hole $n_x(\vec{r},\vec{r}')$ for a neon atom. The full curves show exact results and the dashed curves show the results in the LD approximation. The curves in (a) and (b) are for two different values of r.

FIG. 7. Spherical average of the neon exchange hole [Eq. (17)] times r'^2 for (a) $r=0.09$ a. u. and (b) $r=0.4$ a.u. The full curves give the exact results and the dashed curves are obtained in the LD approximation.

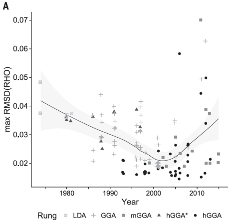
Exact versus LDA exchange hole for Neon atom along specific directions (left) and spherically averaged (right). (Gunnarsson et al. PRB 1979)



Exact (VMC) versus LDA spherically averaged XC-hole for silicon. [PRB 57, 15293 (1998)]

The jungle of XC functionals

Can we improve on the LDA ? Yes, but this is a tough job to progress along all fronts (total energy, structural properties, atomization energy, charge density, bulk modulus, etc.) and with universality (molecules are not extended solids, insulators are not metals !)



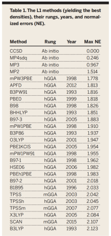


Table 1. The L1 methods (yielding the best densities), their rungs, years, and normalized errors (NE).

Method	Rung	Year	Max NE
CCSD	Ab initio		0.000
MP4sdq	Ab initio		0.246
MP3	Ab initio		0.967
MP2	Ab initio		1.514
mPW3PBE	hGGA	1998	1.778
APFD	hGGA	2012	1.813
B3PW91	hGGA	1993	1.816
PBE0	hGGA	1999	1.818
B98	hGGA	1998	1.826
BHHLYP	hGGA	1993	1.851
B97-3	hGGA	2005	1.883
mPW1PBE	hGGA	1998	1.910
B3P86	hGGA	1993	1.937
O3LYP	hGGA	2001	1.947
PBE1KCIS	hGGA	2005	1.954
mPW1PW91	hGGA	1998	1.955
B97-1	hGGA	1998	1.962
HSE06	hGGA	2006	1.982
PBEh1PBE	hGGA	1998	1.983
B97-2	hGGA	2001	2.018
B1B95	hGGA	1996	2.033
TPSS	mGGA	2003	2.042
TPSSh	hGGA	2003	2.045
TPSSm	mGGA	2007	2.077
X3LYP	hGGA	2005	2.084
SCAN	mGGA	2015	2.107
B3LYP	hGGA	1993	2.123

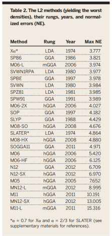


Table 2. The L2 methods (yielding the worst densities), their rungs, years, and normalized errors (NE).

Method	Rung	Year	Max NE
$X\alpha$*	LDA	1974	3.777
SP86	GGA	1986	3.821
M06-L	mGGA	2006	3.974
SVWN1RPA	LDA	1980	3.977
SPBE	GGA	1997	3.978
SVWN	LDA	1980	3.984
SPZ81	LDA	1981	3.985
SPW91	GGA	1991	3.989
M06-2X	hGGA	2006	4.027
SOP	GGA	1997	4.182
SLYP	GGA	1988	4.429
M08-SO	hGGA	2008	4.676
SLATER*	LDA	1974	4.864
M08-HX	hGGA	2008	4.880
SOGGA11	GGA	2011	4.971
M06	hGGA	2006	5.420
M06-HF	hGGA	2006	6.125
N12	GGA	2012	6.709
N12-SX	hGGA	2012	6.970
M05	hGGA	2005	7.652
MN12-L	mGGA	2012	8.995
M11	hGGA	2011	10.191
MN12-SX	hGGA	2012	13.005
M11-L	mGGA	2011	15.316

*α = 0.7 for $X\alpha$ and α = 2/3 for SLATER (see supplementary materials for references).

Quality of the DFT charge density for atoms and ions, from: Density functional theory is straying ("going away") from the path toward the exact functional , Perdew et al. *Science* **355**, 49 (2017)

Tested functionals : LDA, generalized gradient approximation (GGA), meta-GGA (mGGA), and hybrid (hGGA) rungs. The hGGA* contain 100% of exact exchange.

Second ”rung” : generalized gradient approximation

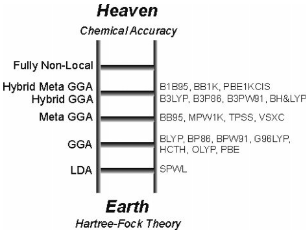
These GGA functionals do not include (non-local) exact exchange and offer (as LDA) a cubic scaling with system size.

The fact that the charge density is varying can be described to lowest order by a functional of the density and its gradient (Taylor expansion):

$$E_{XC}^{GGA}[n] = \int d\mathbf{r}\; n(\mathbf{r})\; \epsilon_{XC}^{GGA}(n(\mathbf{r}), \vec{\nabla} n(\mathbf{r}))$$

There are GGA functionals for the exchange energy and other for the correlation energy.

XC functionals ”Jacob's ladder” from Perdew et al. in J. Chem. Phys. 123, 062201 (2005).



Well-known functionals: PW91 = Perdew and Wang (book 1991 + PRB, 46 (1992) 6671); PBE = Perdew, Becke and Ernzherof (PRL 96) ; BLYP = Becke (GGA for exchange; PRA 1988) and Lee,Yang, Parr (GGA for correlation; PRB 1988); etc.

Lattice parameters in metals and non-metals

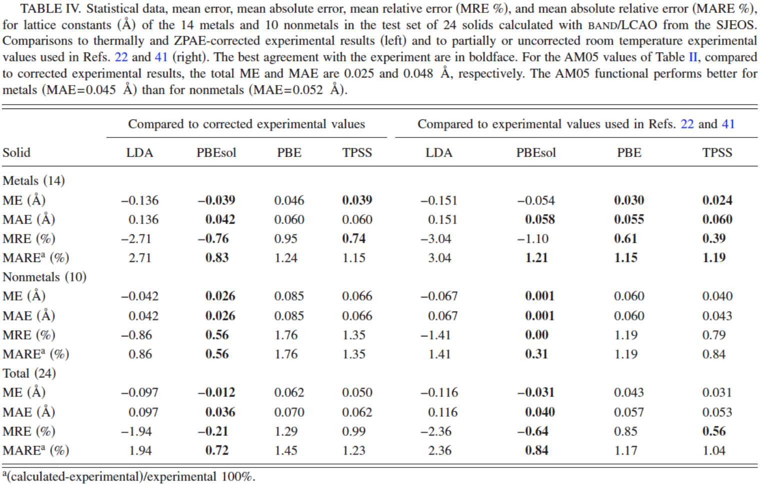


TABLE IV. Statistical data, mean error, mean absolute error, mean relative error (MRE %), and mean absolute relative error (MARE %), for lattice constants (Å) of the 14 metals and 10 nonmetals in the test set of 24 solids calculated with BAND/LCAO from the SJEOS. Comparisons to thermally and ZPAE-corrected experimental results (left) and to partially or uncorrected room temperature experimental values used in Refs. 22 and 41 (right). The best agreement with the experiment are in boldface. For the AM05 values of Table II, compared to corrected experimental results, the total ME and MAE are 0.025 and 0.048 Å, respectively. The AM05 functional performs better for metals (MAE=0.045 Å) than for nonmetals (MAE=0.052 Å).

	Compared to corrected experimental values				Compared to experimental values used in Refs. 22 and 41			
Solid	LDA	PBEsol	PBE	TPSS	LDA	PBEsol	PBE	TPSS
Metals (14)								
ME (Å)	−0.136	**−0.039**	0.046	**0.039**	−0.151	−0.054	**0.030**	**0.024**
MAE (Å)	0.136	**0.042**	0.060	0.060	0.151	**0.058**	**0.055**	**0.060**
MRE (%)	−2.71	**−0.76**	0.95	**0.74**	−3.04	−1.10	**0.61**	**0.39**
MARE[a] (%)	2.71	**0.83**	1.24	1.15	3.04	**1.21**	**1.15**	**1.19**
Nonmetals (10)								
ME (Å)	−0.042	**0.026**	0.085	0.066	−0.067	**0.001**	0.060	0.040
MAE (Å)	0.042	**0.026**	0.085	0.066	0.067	**0.001**	0.060	0.043
MRE (%)	−0.86	**0.56**	1.76	1.35	−1.41	**0.00**	1.19	0.79
MARE[a] (%)	0.86	**0.56**	1.76	1.35	1.41	**0.31**	1.19	0.84
Total (24)								
ME (Å)	−0.097	**−0.012**	0.062	0.050	−0.116	**−0.031**	0.043	0.031
MAE (Å)	0.097	**0.036**	0.070	0.062	0.116	**0.040**	0.057	0.053
MRE (%)	−1.94	**−0.21**	1.29	0.99	−2.36	**−0.64**	0.85	**0.56**
MARE[a] (%)	1.94	**0.72**	1.45	1.23	2.36	**0.84**	1.17	1.04

[a] (calculated-experimental)/experimental 100%.

Figure: Assessing the performance of recent density functionals for bulk solids, Csonka et al., Phys. Rev. B 79, 155107 (2009). (courtesy Prof. János G. Ángyán)

Part II: Kohn-Sham Electronic energy levels

It is traditional, in particular in solid state-physics when studying periodic systems, to use "Kohn-Sham eigenvalues" as electronic energy levels to understand molecular orbital energies or band-structures in solids. In fact, the Kohn-Sham eigenvalues are just Lagrange multipliers imposing Kohn-Sham orbital orthonormalization when minimizing the energy:

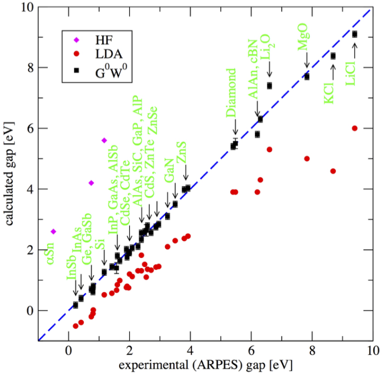
$$\frac{\partial}{\partial \phi^*(\mathbf{r})}\Big[E[\{\phi_n(\mathbf{r})\}] - \sum_n \lambda_n\big(\langle \phi_n|\phi_n\rangle - 1\big)\Big] = 0$$

leads to (Exercise)

$$\Big[-\frac{\nabla^2}{2} + v^{ion}(\mathbf{r}) + \int d\mathbf{r}'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V^{XC}(\mathbf{r})\Big]\phi_n(\mathbf{r}) = \lambda_n\phi_n(\mathbf{r})$$

Writing $\lambda_n = \varepsilon_n$, is it correct to identify the Kohn-Sham eigenvalues "ε_n" to electronic energy levels ??

Band gap of solids using Kohn-Sham eigenvalues

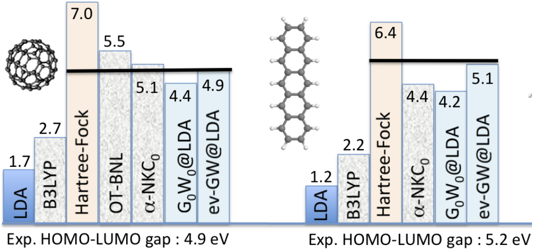


Compilation of band gaps for extended solids (courtesy Valerio Olevano) as obtained from DFT-LDA Kohn-Sham eigenvalues (red dots), from Hartree-Fock eigenvalues (pink diamonds) and within a more accurate many-body perturbation theory (G^0W^0) as compared to ARPES experiments (blue dashed diagonal).

Clearly, the LDA Kohn-Sham gaps are definitely too small while the HF gaps are dramatically too large. Using hybrid functionals can lead to an excellent gap by tuning the balance between local functionals and exact exchange, but how can we be predictive if one has a tuning parameter ?

Band gap of gas phase organic molecules

Using Kohn-Sham eigenvalues for frontier orbitals ($\varepsilon_{HOMO/LUMO}$), one can also attempt to calculate the ionization potential, the electronic affinity and the gap. Again, the results are very poor in general.

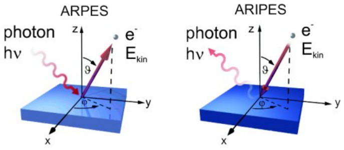


Gap of pentacene and C_{60} as compared to experiment. LDA Kohn-Sham gaps are too small, and Hartree-Fock too large.

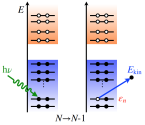
The NKC calculations ("Koopman's compliant" functionals, Borghi et al. PRB 90, 075135) and OT-BNL (Optimally-tuned range-separated hybrid functionals, Refaely-Abramson et al. PRB 84, 075144) aim at providing a rational mixing of local and exact exchange functionals.

Experimental photoemission data

Electronic energy levels are determined experimentally using direct photoemission (occupied levels) and inverse photoemission (unoccupied levels).

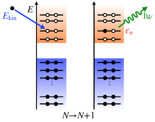


From http://www.ieap.uni-kiel.de/surface/ag-kipp/arpes/arpes.htm



Energy conservation:
$h\nu + E_0^N = E_{kin} + E_n^{N-1}$

Identify: $\varepsilon_n = E_0^N - E_n^{N-1}$ $(< \mu)$.



Energy conservation:
$E_{kin} + E_0^N = h\nu + E_n^{N-1}$

Identify: $\varepsilon_n = E_n^{N+1} - E_0^N$ $(> \mu)$.

What we call electronic energy levels, related to the energy of an electron in the solid, are given as differences of energy between the total energy of the (N+1)- or (N-1)electron systems in one of their eigenstates and the N-electron system ground-state energy (unoccupied states).

Kohn-Sham : Total energy and sum of eigenvalues

The total GS energy can be written :

$$E = \sum_{i=1}^{N} \langle \phi_i | \frac{-\nabla^2}{2} | \phi_i \rangle + \int d\mathbf{r}\; v^{ion}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}'\; \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{XC}[n]$$

The sum of eigenvalues for occupied levels read:

$$\sum_{i=1}^{N} \varepsilon_i = \sum_{i=1}^{N} \langle \phi_i \Big| \frac{-\nabla^2}{2} + v^{ion}(\mathbf{r}) + \int d\mathbf{r}'\; \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v^{XC}(\mathbf{r}) \Big| \phi_i \rangle$$

with $v^{XC}(\mathbf{r}) = \partial E^{XC}[n] / \partial n(\mathbf{r})$, so that:

$$E = \sum_{i=1}^{N} \varepsilon_i - J[n] + E^{XC}[n] - \int d\mathbf{r}\; v^{XC}(\mathbf{r}) n(\mathbf{r})$$

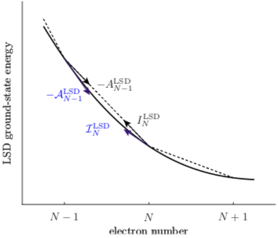
No obvious relation between total energy and sum of eigenvalues. Cannot interpret Kohn-Sham eigenvalues as removal/addition energies !

The Janak theorem [PRB 18, 7165 (1978)]

By working out a generalization of the Kohn-Sham scheme to ”fractional occupation” of energy levels, Janak (PRB 18, 7165) was able to demonstrate the following property, where n_i is the occupation of the electronic energy level ”i” (n_i=0 or 1 within Kohn-Sham DFT) :

$$\varepsilon_i = \left.\frac{\partial E}{\partial n_i}\right|_{n_i=0,1}$$

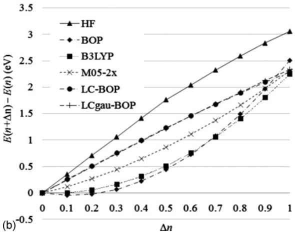
the variation of the total energy for an infinitesimal variation of the occupation around the n_i=0 or 1 values.



This is different from the variation of the total energy upon integer change of the number of electrons unless the total energy is linear between integer number of electrons (Figure from Dabo et al. PRB 82, 115121).

Piece-wise linearity of the total energy E(N)

It was shown that the exact total ground-state energy E(N) is piece-wise linear with respect to the number of electrons N (Perdew, Parr, Levy, Balduz 1982). Unfortunately, the ”pure DFT” (no exact exchange) total energy E(N) is continuous and convex with N.

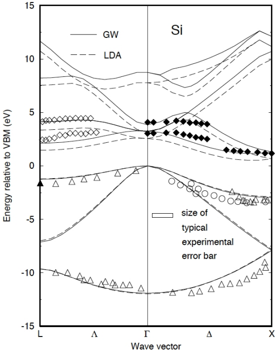


On the contrary, HF total energies are concave. This provides a rational for mixing local functional with exact exchange in such amount that the piece-wise linearity is recovered (Figure from Tsuneda et al. JCP 33, 174101; E(N) for C_2H_4).

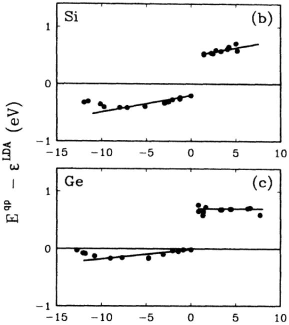
Optimally tuned functionals: tuning the amount of exact exchange so that e.g. $\varepsilon^{KS}_{HOMO} = E(N) - E(N-1)$ leads to a (close to) correct piece-wise linearity of $E[N + \delta n]$ and a much better gap in general.

Beyond the band gap problem

We have shown that the Kohn-Sham gap strongly depends on the functional used. What about the overall band structure ?



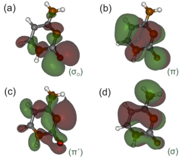
(Left) Silicon band structure within LDA, an accurate many-body (GW) approach and experimental data (triangles/diamonds). Band structures aligned at the top of the valence bands. (Right) Difference between the GW (QP=quasiparticle) and LDA energies for Si and Ge (Hybertsen, Louie, 1986).



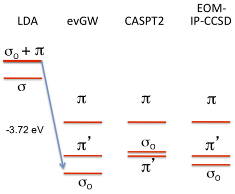
For extended solids with delocalized states, the DFT Kohn-Sham error consists mainly in a "scissor" that reduces the gap within LDA (increases it within HF). The Kohn-Sham band structures remain extremely useful !!

The self-interaction problem

This interpretation in terms of a "gap problem only" fails when the system combines localized and extended states because of self-interaction problem : within local DFT, an electron interacts with itself through the density-dependent XC potential (think of a DFT calculation on the Hydrogen atom!) This "destabilizing" effect pushes occupied localized states higher in energy than delocalized ones.



HOMO to (HOMO-3) in cytosine
(DNA nucleobases)

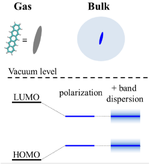


HOMO, (HOMO-1) and (HOMO-2) energy levels for cytosine within several formalisms. The localized σ_O state (localized on oxygen) is erroneously located as the HOMO within LDA (Faber et al. 2011).

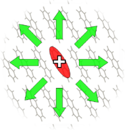
This self-interaction problem is reduced when introducing some amount of exact exchange (HF is self-interaction free; remember : $J_{ii} = K_{ii}$).

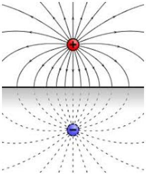
Dynamical polarization effects ("image charges")

In a photoemission process, the target system is charged. In the case of localized charges (molecular systems), this charge polarizes the surrounding medium that "reacts" (reaction field) to stabilize the added hole or electron. This is similar to the standard "image charge" physics.



Induced dipole interaction closes the gap by ~2eV





This effect CANNOT be reproduce by DFT/HF (or hybrid) Kohn-Sham calculations on neutral systems. In molecular systems (e.g. bulk pentacene) it can be "mimicked" by imposing a long-range $1/\varepsilon_M r$ tail to the exchange potential in a range-separated formalism, with ε_M the macroscopic dielectric constant of the medium.

Summary and beyond

DFT is a ground-state formalism not formally designed to access electronic excitations. However, besides the "band gap" problem and for extended states (itinerant electrons), the Kohn-Sham (KS) band structure gives valuable informations.

Further, KS eigenstates can be used as "zeroth order" eigenstates to build higher order correlated techniques, within e.g. perturbation theory ! For example the independent-electron KS electronic susceptibility:

$$\chi^0(\mathbf{r},\mathbf{r}';i\omega) = 2\sum_{ja} \frac{\phi_j^*(\mathbf{r})\phi_a(\mathbf{r})\phi_a^*(\mathbf{r}')\phi_j(\mathbf{r}')}{i\omega - (\varepsilon_a - \varepsilon_j)} + cc$$

can be used to build the RPA correlation energy (lecture Prof. X. Ren):

$$E_C^{RPA} = \frac{1}{2\pi}\int_0^{+\infty} d\omega \;\; Tr[ln(1-\chi^0(i\omega)v) + \chi^0(i\omega)v]$$

Summary and beyond (II)

The independent electron susceptibility χ_0 can also be used to calculate the screened Coulomb potential $W = v + v\chi_0 W$ leading to the $\Sigma = iGW$ exchange-correlation self-energy, with G the Kohn-Sham one-body Green's function:

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_i^{occp} \frac{\phi_i(\mathbf{r})\phi_i(\mathbf{r}')}{\omega - \varepsilon_i - i\eta} + \sum_a^{unoccup} \frac{\phi_a(\mathbf{r})\phi_a(\mathbf{r}')}{\omega - \varepsilon_a + i\eta}$$

Further, one can imagine techniques combining DFT/Kohn-Sham for itinerant electrons and more sophisticated explicitly correlated techniques for localized or strongly correlated electrons.

DFT is a cheap and fast mean-field ground-state techniques. Use it for what it is supposed to do (structural, vibrational, etc. properties) and keep a critical but interested eye on what it is not supposed to achieve.

END

Exercise: Assessing v^{eff} through the Kohn-Sham equation

Since we look for the total energy as a functional of one-body (normalized) wavefunctions $\{\phi_n(\mathbf{r})\}$, we can also use the variational principal with respect to these one-body wavefunctions:

$$\frac{\partial}{\partial\phi^*(\mathbf{r})}\Big[E[\{\phi_n(\mathbf{r})\}] - \sum_n \lambda_n\big(\langle\phi_n|\phi_n\rangle - 1\big)\Big] = 0 \quad \text{with:}$$

$$\frac{\partial T^0}{\partial\phi_n^*(\mathbf{r})} = -\frac{\nabla^2}{2}\phi_n(\mathbf{r}), \qquad \frac{\partial}{\partial\phi_n^*(\mathbf{r})} = \frac{\partial n(\mathbf{r})}{\partial\phi_n^*(\mathbf{r})}\frac{\partial}{\partial n(\mathbf{r})} = \phi_n(\mathbf{r})\frac{\partial}{\partial n(\mathbf{r})} \Longrightarrow$$

$$\frac{\partial\Big[\int d\mathbf{r}\, v^{ion}(\mathbf{r})n(\mathbf{r}) + J[n] + E^{XC}[n]\Big]}{\partial\phi^*(\mathbf{r})} = \Big[v^{ion}(\mathbf{r}) + \frac{\partial J[n]}{\partial n(\mathbf{r})} + \frac{\partial E^{XC}[n]}{\partial n(\mathbf{r})}\Big]\phi_n(\mathbf{r})$$

$$\Big[-\frac{\nabla^2}{2} + v^{ion}(\mathbf{r}) + \int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V^{XC}(\mathbf{r})\Big]\phi_n(\mathbf{r}) = \lambda_n\phi_n(\mathbf{r})$$

Exercise : exchange-correlation hole and sum

Rewrite the pair density as: $2\rho_2(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}')\Big[1 + h(\mathbf{r},\mathbf{r}')\Big]$ with h called the pair-correlation function to express the XC energy in function of the Hartree energy J and the XC hole density $\rho_{XC}(\mathbf{r},\mathbf{r}')$:

$$V^{ee} = J + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \; \frac{\rho(\mathbf{r})\rho_{XC}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \text{with} \quad \rho_{XC}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}')h(\mathbf{r},\mathbf{r}')$$

Demonstrate that:

$$\int d\mathbf{r}'\rho_2(\mathbf{r},\mathbf{r}') = \frac{(N-1)}{2}\rho(\mathbf{r})$$

to obtain the XC hole sum rule: $\int d\mathbf{r}' \; \rho_{XC}(\mathbf{r},\mathbf{r}') = -1$. The XC energy can be seen as the Coulomb energy between electrons and their XC-hole, namely the depletion of one electron (through exchange and Coulomb repulsion) dynamically created around each electron. The (1/2) term in the XC energy is an adiabatic factor : the XC hole grows with the electron and would not exist without it.

Exercise : long-range behaviour of exchange energy density $\epsilon_X(\mathbf{r})$ in finite size systems

Using for simplicity one-body orbitals such as KS or HF orbitals:

$$E_X = \int d\mathbf{r}\ \epsilon_X(\mathbf{r}) \quad \text{with} \quad \epsilon_X(\mathbf{r}) = -\frac{1}{2}\sum_{ij}^{occp} \int d\mathbf{r}'\ \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Taking the position $\mathbf{r}$ to go far away in the vacuum, and since the eigenstates $\{\phi_{i/j}\}$ decay exponentially in the vacuum:

$$\begin{aligned}\epsilon_X(\mathbf{r}) &= -\frac{1}{2}\sum_{ij}^{occp} \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})}{r} \int d\mathbf{r}'\ \phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}') \\ &= -\frac{1}{2}\sum_{ij}^{occp} \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})}{r}\delta_{ij} = -\frac{n(\mathbf{r})}{2r}\end{aligned}$$

Note that for spin compensated systems, $n(\mathbf{r}) = 2n_\uparrow(\mathbf{r}) = 2n_\downarrow(\mathbf{r})$ and we recover a (-1/r) potential for an electron interacting through exchange with electrons of same spin only.

Appendix A: Occupation and density matrix

We introduce here the density matrix, showing that the kinetic energy does not need as well the knowledge of the full many-body wavefunction. We further introduce natural orbitals, namely one-body orbitals generating the exact charge-density, and the idea of fractional occupations that we will briefly discussed when invoking Janak's theorem. This stands as a generalization to the Kohn-Sham approach.

We introduce the first-order reduced density matrix:

$$\gamma(\mathbf{r},\mathbf{r}') = N \int d\mathbf{r}_2 ... d\mathbf{r}_N \; \psi^*(\mathbf{r},\mathbf{r}_2,\dots,\mathbf{r}_N)\psi(\mathbf{r}',\mathbf{r}_2,\dots,\mathbf{r}_N)$$

with $\gamma(\mathbf{r},\mathbf{r}) = n(\mathbf{r}) \geqslant 0$ and $\gamma(\mathbf{r},\mathbf{r}') = \gamma^*(\mathbf{r}',\mathbf{r})$ and (Exercise):

$$T = \sum_{i=1}^{N} \langle \psi_i | \frac{-\nabla^2_{\mathbf{r}_i}}{2} | \psi_i \rangle = \int d\mathbf{r} \left[\frac{-\nabla^2_{\mathbf{r}}}{2} \gamma(\mathbf{r}',\mathbf{r}) \right]_{\mathbf{r}=\mathbf{r}'}$$

Appendix A : Occupation and density matrix (II)

Since γ is definite positive and Hermitian its eigenvalues $\{f_i\}$ are real and positive. Calling $\{\xi_i\}$ the corresponding eigenvectors:

$$\mathrm{Tr}\hat{\gamma} = \int d\mathbf{r}\ \gamma(\mathbf{r},\mathbf{r}) = \int d\mathbf{r}\ n(\mathbf{r}) = N = \sum_i \langle \xi_i | \hat{\gamma} | \xi_i \rangle = \sum_i f_i$$

$$\begin{aligned} n(\mathbf{r}) &= \sum_i f_i \langle \mathbf{r} | \xi_i \rangle \langle \xi_i | \mathbf{r} \rangle = \sum_i f_i |\xi_i(\mathbf{r})|^2 \\ T &= \sum_i f_i \langle \xi_i | \frac{-\nabla^2_{\mathbf{r}_i}}{2} | \xi_i \rangle \end{aligned}$$

This is an exact formulation in terms of ("natural") one-body orbitals with fractional occupancy as a generalization of Kohn-Sham approach !

The Hartree-Fock (HF) approach

One keep the EXACT Hamiltonian but make an approximation on the many-body wavefunction ψ under the form of a single Slater determinant built from one-body eigenstates $\{\phi_n(x) = \phi_n(\mathbf{r}) \otimes \sigma_n\}$ (Roothan 1951). This is just adding the anti-symmetrization principle on top of the classical Hartree approximation where the probability of finding an electron somewhere is independent of the other electron positions.

$$\psi_{HF}(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \dots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \dots & \phi_N(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1(x_N) & \phi_2(x_N) & \dots & \phi_N(x_N) \end{vmatrix}$$

A cumbersome calculation leads to the energy with respect to the $\{\phi_n\}$:

$$E[\phi_n] = \langle\psi|\hat{H}|\psi\rangle = \sum_{i=1}^{N} \langle\phi_n(\mathbf{r})| -\nabla_{\mathbf{r}}^2/2 + v^{ions}(\mathbf{r}) |\phi_n(\mathbf{r})\rangle + \frac{1}{2}\sum_{ij}(J_{ij} - K_{ij})$$

The Hartree-Fock (HF) approach (continued)

The J_{ij} and K_{ij} terms are the Coulomb Hartree and exchange integrals.

$$\begin{aligned} J_{ij} &= \int d\mathbf{r}_1 d\mathbf{r}_2\ \phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_1)\frac{1}{r_{12}}\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2) \\ K_{ij} &= \int d\mathbf{r}_1 d\mathbf{r}_2\ \phi_j(\mathbf{r}_1)\phi_i^*(\mathbf{r}_1)\frac{1}{r_{12}}\phi_i(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2) \times \langle\sigma_i|\sigma_j\rangle \end{aligned}$$

The $\{\phi_n\}$ eigenstates are obtained using the <u>variational principle</u>, i.e. minimizing $\langle\psi|\hat{H}|\psi\rangle$ under the constraint of normalization of the one-body orbitals → minimize $\Omega[\{\lambda_n,\phi_n\}] = E[\phi_n] - \sum_n \lambda_n[\langle\phi_n|\phi_n\rangle - 1]$

$$\frac{\partial\Omega}{\partial\phi_n^*(\mathbf{r})} = 0 \ \ \Rightarrow \ \ \left(\frac{-\nabla_{\mathbf{r}}^2}{2} + v^{ions} + v^H\right)\phi_n(\mathbf{r}) - [\hat{k}\phi_n](\mathbf{r}) = \lambda_n\phi_n(\mathbf{r})$$

with V^H the classical Hartree potential :

$$v^H(\mathbf{r}) = \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \quad \text{and} \quad [\hat{k}\phi_n](\mathbf{r}) = \sum_{k=1}^{N}\int d\mathbf{r}'\ \frac{\phi_k(\mathbf{r})\phi_k^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_n(\mathbf{r}')\langle\sigma_k|\sigma_n\rangle$$

Hartree-Fock limitations and correlation energy

Since within HF the variational principal is restricted to a very limited set of many-body wavefunctions, the ground-state HF total energy is an upper-bound for the true ground-state energy. The correlation energy is by definition the difference between the exact energy and the Hartree-Fock energy: $E^{C} = E^{exact} - E^{HF}$.

In the Hartree approximation, the probability of finding two electrons $\mathbf{r}$, and $\mathbf{r}'$ are uncorrelated (despite the classical Hartree potential) $\Rightarrow$ electrons can come very close to each other and the energy increases due to Coulomb repulsion.

Within HF, only electrons with same spin are correlated thanks to the exchange energy $\Rightarrow$ electron with opposite spins are not correlated and can come close to each other with large Coulomb repulsion penality !

Note: J_{ii} and K_{ii} cancel out (related below to lack of self-interaction)

Note: the "λ_n" are just Lagrange parameters !

Example : GGA for exchange energy density

For small systems (atoms, etc.) the exchange energy represents most of the XC energy. Using dimensionality arguments the lowest gradient correction (LGC) for the exchange energy density reads:

$$E_X^{LGC} = E_X^{LDA} - \beta \sum_\sigma \int d\mathbf{r}\, \rho_\sigma^{4/3} x_\sigma^2 \quad \text{with} \quad x_\sigma = \frac{|\nabla \rho_\sigma|}{\rho_\sigma^{4/3}} \quad \text{adimensional}$$

This was a failure: E_X^{LGC} does not satisfy the exchange-hole sum rule, leads to divergency in the vacuum where $\rho(\mathbf{r})$ decays exponentially, etc. Further, the potential felt by an electron far away from an atom, molecule, surface, etc. should scale as (-1/r). This term comes from the exchange potential, yielding for exchange density of energy: (Exercise).

$$\lim_{r\to\infty} \epsilon_X(\mathbf{r}) \simeq -\frac{\rho(\mathbf{r})}{2r} \quad \text{with} \quad \rho(\mathbf{r}) = 2\rho_\uparrow(\mathbf{r}) = 2\rho_\downarrow(\mathbf{r}) \quad \text{(unpolarized system)}$$

Ref: Density-functional exchange-energy approximation with correct asymptotic behavior, A. D. Becke, PRA 1988.

Example : GGA for exchange energy density (2)

Becke proposed in 1988 an exchange functional (B88) that scales smoothly between the small and large $x_\sigma = |\nabla \rho_\sigma| / \rho_\sigma^{4/3}$:

$$E_X^{B88} = E_X^{LDA} - \beta \sum_\sigma \int d\mathbf{r}\, \rho_\sigma^{4/3} \frac{x_\sigma^2}{1 + 6\beta \sinh^{-1}(x_\sigma)} \qquad (\beta \ \text{parameter})$$

The GGA correction vanishes for small gradients ($x_\sigma \to 0$). With $\rho(\mathbf{r}) \simeq e^{-\alpha r}$ for large r, $x_\sigma \to e^{\alpha r/3}$ and $\sinh^{-1}(x_\sigma) \to \alpha r/3$, the correct (vacuum) asymptotic behaviour is recovered. This is the exchange functional used in the BLYP functional (B=Becke88). Here exact relations (asymptotic behaviour, low or high density limit, sum rules, etc.) lead to a functional form. Complementary to fitting strategies. The B88 exploits both approaches.

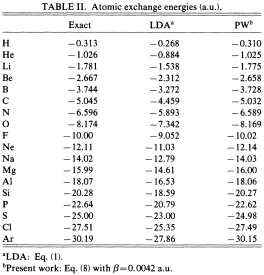


TABLE II. Atomic exchange energies (a.u.).

	Exact	LDA[a]	PW[b]
H	−0.313	−0.268	−0.310
He	−1.026	−0.884	−1.025
Li	−1.781	−1.538	−1.775
Be	−2.667	−2.312	−2.658
B	−3.744	−3.272	−3.728
C	−5.045	−4.459	−5.032
N	−6.596	−5.893	−6.589
O	−8.174	−7.342	−8.169
F	−10.00	−9.052	−10.02
Ne	−12.11	−11.03	−12.14
Na	−14.02	−12.79	−14.03
Mg	−15.99	−14.61	−16.00
Al	−18.07	−16.53	−18.06
Si	−20.28	−18.59	−20.27
P	−22.64	−20.79	−22.62
S	−25.00	−23.00	−24.98
Cl	−27.51	−25.35	−27.49
Ar	−30.19	−27.86	−30.15

[a] LDA: Eq. (1).

[b] Present work: Eq. (8) with $\beta = 0.0042$ a.u.

Hybrid functionals

For the Kohn-Sham system, we know how to calculate the "exact" exchange energy "associated with" the Kohn-Sham eigenstates $\{\phi_n\}$.

$$E_X = -\frac{1}{2}\sum_{ij}^{occp}\int\int d\mathbf{r}d\mathbf{r}'\;\frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

This is more expansive than pure density functionals (Hartree-Fock (HF) scales as N^4 with system size) but helps in several directions:

- it offers clearly the correct asymptotic behavior for the electronic potential in the vacuum and satisfies the exchange-hole sum rule
- it helps curing the self-interaction (SI) problem : within DFT, since the charge density depends on the occupied orbitals, the action of $v^{eff}[n]$ on an occupied orbital amounts to have an electron interacting with itself (consider the H atom system!). This is a dramatic problem for localized orbitals. This does not exist within HF since the SI in the Hartree and exchange energies cancel out !

Hybrid functionals (2)

However, mixing 100% of exact exchange with a density dependent correlation functional leads (in general) to a failure ! Density-dependent XC functionals are usually built "together" for reproducing the total XC potential properties ! Namely, they benefit from large error cancellations.

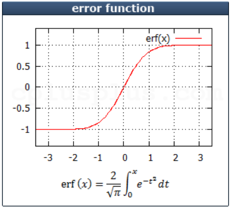
Considerations built on the "adiabatic connection" between the non-interacting and interacting electronic systems generated the historical Becke "half and half" functional :
$E^{XC} = 0.5E^{X}(HF) + 0.5E^{X}(Slater) + E^{C}(\text{LYP=Lee-Yang-Parr})$.

With fitting strategy on "56 (small molecules) atomization energies, 8 proton affinities, and 10 first-row total atomic energies", the "Becke 3 parameters" (B3 of B3LYP) exchange functional (Becke JCP 1993) mixes Slater LDA and B88 GGA exchange with 20% of exact exchange .

Using perturbation theory, Perdew, Burke and Ernzerhof advocated 25% of exact exchange, leading to the 1996 PBE0 functional.

Range-separated hybrids (CAM-B3LYP, LC-ωPBE, etc.)

Defining a short-range (SR) and long-range (LR) Coulomb interaction thanks e.g. to the error function erf allows to define a short-range and long-range exchange potential:



$$v_X^{LR}(\omega) = -\sum_i^{occp} \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}')\frac{erf(\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

Once can now replace a fraction of the short-range exchange by a local (Slater) or semilocal (GGA) exchange functional and keep a fraction of long-range exchange ! Provides more flexibility to fulfill long-range asymptotic potential shape (keeping up to 100% of LR exchange) with local exchange tuning as developed within the GGA world.

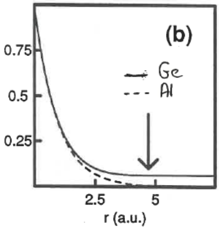
The CAM-B3LYP includes 65% of LR exact exchange with $\omega = 0.33$ and the LC-ωPBE includes 100% of LR exact exchange with $\omega = 0.4$.

Refs: T. Leininger, H. Stoll, H.-J. Werner, A. Savin, Chem. Phys. Lett. 275 (1997) 151; H. Iikura, T. Tsuneda, T. Yanai, K. Hirao, J. Chem. Phys. 115 (2001) 3540.

Range-separated hybrids (RSH) in solids !!

Due to screening, the effective electron-electron interaction is exponentially decaying in metals and reduce by the macroscopic dielectric constant in semiconductors : the long-range (-1/r) behaviour of electronic potential in the vacuum does NOT apply in solids ! The HSE03 and HSE06 (Heyd-Scuseria-Ernzerhof) functionals are range-separated hybrids with the exact exchange kept in the short-range, NOT the long-range !

Ratio W(r)/v(r) of screened versus bare Coulomb potentials in Germanium and Aluminum (Raffaele Resta, SISSA Lecture notes) .



NOTE: several RSH for solids with long-range potential controled by the dielectric constant are being developed for obtaining good electronic properties, not total energies and structure (see e.g. Density-based mixing parameter for hybrid functionals, Marques et al. PRB 2011).

Refs: "Hybrid functionals based on a screened Coulomb potential", Heyd-Scuseria-Ernzerhof JCP 2003;

Correlation energy within the RPA formalism

The fifth rung of functionals stairway is to calculate the correlation energy within many-body perturbation theory, namely an explicit formulation in terms of molecular orbitals. The RPA energy is a promising approach that offers $\mathcal{O}(N^4)$ scaling with system size, and efficient $\mathcal{O}(N^3)$ formalisms are appearing.

$$E_C^{RPA} = \frac{1}{2\pi} \int_0^{+\infty} d\omega \; Tr[ln(1 - \chi^0(i\omega)v) + \chi^0(i\omega)v]$$

where v is the bare Coulomb operator and $\chi_0(i\omega)$ the independent electron susceptibility:

$$\chi^0(\mathbf{r}, \mathbf{r}'; i\omega) = 2 \sum_{ja} \frac{\phi_j^*(\mathbf{r})\phi_a(\mathbf{r})\phi_a^*(\mathbf{r}')\phi_j(\mathbf{r}')}{i\omega - (\varepsilon_a - \varepsilon_j)} + cc$$

where the $\{\varepsilon_n, \phi_n\}$ eigenstates are typically Hartree-Fock or Kohn-Sham eigenstates.

Correlation energy within the RPA formalism (II)

The RPA correlation energy includes long-range dispersion effects (such as van der Waals) that are missing in local or GGA functionals !

References:

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- Kaltak, Klimeš, Kresse, Low Scaling Algorithms for the RPA: Imaginary Time and Laplace Transformations. JCTC 2014, 10, 2498-2507.