Kohn-Sham Theory and Approximate Functionals

1 Summary

The previous lecture sets the theoretical framework for density-functional theory (DFT), but does not provide proposals for practical calculations. The key paper in density-functional theory (W. Kohn and L. J. Sham, Phys. Rev., 1965) proposed a practical way to use the former concept. Their proposal can be seen in two steps:

- Firstly, it reduced the unknown bit to the quantitatively smallest size, by rewriting the functional as:

  $$E[n] = T_0[n] + \int d^3r n(r) \left(V_{ext}(r) + \frac{1}{2}\Phi(r) \right) + E_{xc}[n], \tag{1}$$

  where $T_0[n]$ stands for the kinetic energy of a system of non-interacting electrons of density $n(r)$, $\Phi(r)$ is the Hartree potential, and $E_{xc}[n]$ is the exchange-correlation energy.

- It transformed the original problem into a mean-field-like problem of non-interacting electrons moving in a suitably defined effective potential:

  $$V(r) = V_{ext}(r) + \Phi(r) + \frac{\delta E_{xc}[n]}{\delta n(r)}. \tag{2}$$

It should be noted that a line of active research is the search for good approximate forms of the universal functional F (or actually F-E_H), removing the Hartree component that can be computed easily). A main difficulty there comes from the kinetic energy functional itself, which is very much affected by, for instance, the shell structure of atoms. This is very easy to obtain for independent electrons using explicit antisymmetric wave-functions, but it is hard to recover as a functional of the density alone. This approach is called orbital-free density-functional theory (as opposed to the Kohn-Sham way, which involves orbitals).

2 Derivation of Kohn-Sham Single Particle Formalism

Following Jones and Gunnarsson, we take the functional as:

$$E[n] = T_0[n] + \int d^3 r n(r) \left(V_{ext}(r) + \frac{1}{2}\Phi(r) \right) + E_{xc}[n]. \tag{3}$$

The variational principle applied to this functional yields:

$$\frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_0[n]}{\delta n(r)} + V_{ext}(r) + \Phi(r) + \frac{\delta E_{xc}[n]}{\delta n(r)} = \mu. \tag{4}$$

where μ is the Langrange multiplier associated with the constraint that the particle number (integral of the density) is a given constant. Comparing this with the equation corresponding to a system under an effective potential $V(r)$:

$$\frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_0[n]}{\delta n(r)} + V(r) = \mu, \tag{5}$$

it is easy to see that the two mathematical problems are identical, as long as:

$$V(r) = V_{ext}(r) + \Phi(r) + V_{xc}[n](r), \tag{6}$$

where we have defined the exchange-correlation potential as:

$$V_{xc}[n](r) = \frac{\delta E_{xc}[n]}{\delta n(r)}. \tag{7}$$

3 Kohn-Sham Equations

The solution of the independent particle problem under the potential $V(r)$ is found by solving the Schrödinger equation:

$$\left(-\frac{1}{2}\nabla^2 + V(r) \right) \psi_i(r) = \epsilon_i \psi_i(r), \tag{8}$$

and obtaining the corresponding density:

$$n(r) = \sum_i f_i |\psi_i(r)|^2. \tag{9}$$

where f_i is the occupation of the state (can be the FD distribution).

The kinetic energy is computed as:

$$T_0[n((\mathbf{r})] = -\mathbf{\frac{1}{2}}\sum_{\mathbf{i}}^{\mathbf{N}}\langle\psi_{\mathbf{i}}|\nabla^{\mathbf{2}}|\psi_{\mathbf{i}}\rangle \tag{10}$$

It seems contradictory to write it as a functional of the density when we are calculating it from the single-particle ψ's, and (as said before) we do not have an explicit form that we can use to obtain it directly from the density. But it is indeed such a functional, and a universal one (system independent) as well. This can be seen when using the Levy construction for the independent-electron problem given by the Hamiltonian $H = T + V_{ext}$. Since there is no $V_e e$ term, Levy's universal functional in this case is precisely $T_0[n(r)]$. This means that the T_0 obtained above from the ψ's is the actual T_0 value associated to that density by Levy's functional. Given $n(r)$, plugging it into the functionals for the external-potential, Hartree and exchange-correlation energies, we get everything we need to obtain the ground state energy. And, actually, if we had the right Exc functional, both $n(r)$ and E_{GS} would correspond to the exact many-electron solution. On the other hand both the $\psi_i(r)$ wavefunctions and their eigenvalues, represent auxiliary magnitudes within the theory, with a priori no physical significance.

4 Exchange-Correlation Energy and Potential

Both $E_{xc}[n]$ and its functional derivative $V_{xc}[n](r)$ are unknown. DFT implies that there should be a functional form giving the exact exchange-correlation energy, but we do not know its shape. The Kohn-Sham (KS) formalism allows us to pack everything unknown into a quantitatively small term. Here we will introduce the first approximations to the exact functional. From here on we will be working with approximate theories based on (exact) DFT, but with approximate $E_{xc}[n]$ functionals. A general point of order first. For the exchange and correlation potential $V_{xc}[n](r)$ the theory assumes a single-particle local potential (remember that density-functional theory depends on the external potential being local). V_{xc} is at the same time a function of position and a functional of the density: the potential felt by a particle at a given point in space depends on the shape of the particle density everywhere, $V_{xc}[n](r)$. The first and most popular approximations are known as LDA and GGA, standing for local-density and generalized-gradient-density approximations, respectively. In a nutshell:

4.1 Local Density Approximation (LDA)

The first sensible approximation (in the Kohn-Sham paper itself) is considering that the potential at a given point in space depends on the density at that point only. In that case, the homogeneous electron liquid (HEL, fully interacting set of electrons in a flat external potential, otherwise called jellium) becomes a natural reference, since there, the density at a point is the same as anywhere else, a constant $n(\vec{r}) = n$

We can define the exchange-correlation energy density, $\epsilon_{xc}(n)$ as the exchange-correlation energy per electron in jellium, which is a function of electron density. We can then write a first approximation to $E_{xc}[n]$ as

$$E_{xc}^{LDA}[n] = \int d^3rn(r)\epsilon_{xc}^{HEG}(n(r)). \tag{11}$$

Actually, we do have an analytic expression for the exchange energy density, coming from solving the Hartree-Fock problem for the homogeneous electron liquid. An LDA approximation for exchange can be then directly written as:

$$E_x^{LDA}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/2} \int d^3rn(r)^{(4/3)}. \tag{12}$$

as used by Slater before DFT existed, based on the exchange energy expression of the HEL by Dirac. It is approximate, and therefore, the exact cancellation of self- interaction that we had in Hartree-Fock is no longer happening: LDA suffers from self-interaction error.

For the correlation energy, explicit many-electron wave function calculations were per- formed by D. M. Ceperley and B. J. Alder (Phys. Rev. Lett. 1980) for the homogeneous electron liquid using Quantum Monte Carlo for different densities. The correlation energy density $\varepsilon_c(n)$ was defined from the QMC total energy, removing the other (known) terms, including the exchange term $\varepsilon_x(n)$ implied above. The results were tabulated in that paper as shown in the Table below.

The correlation energy function for constant density can be read (interpolated) from that table. Various interpolation formulas have been proposed, taking into account expected limiting behaviors. Probably the most widely used in the one proposed by J. Perdew and A. Zunger (Phys. Rev. B, 1981) proposed the parametrized functional form in terms of $r_s = (4/3\pi n)^{-1/3}$

$$\varepsilon_c(r_s) = \begin{cases} A\mathrm{log}r_s + B + Cr_s\mathrm{log}r_s + Dr_s & r_s \leq 1 \\ a/(1 + b_1\sqrt{r_s} + b_2r_s) & r_s > 1 \end{cases} \tag{13}$$

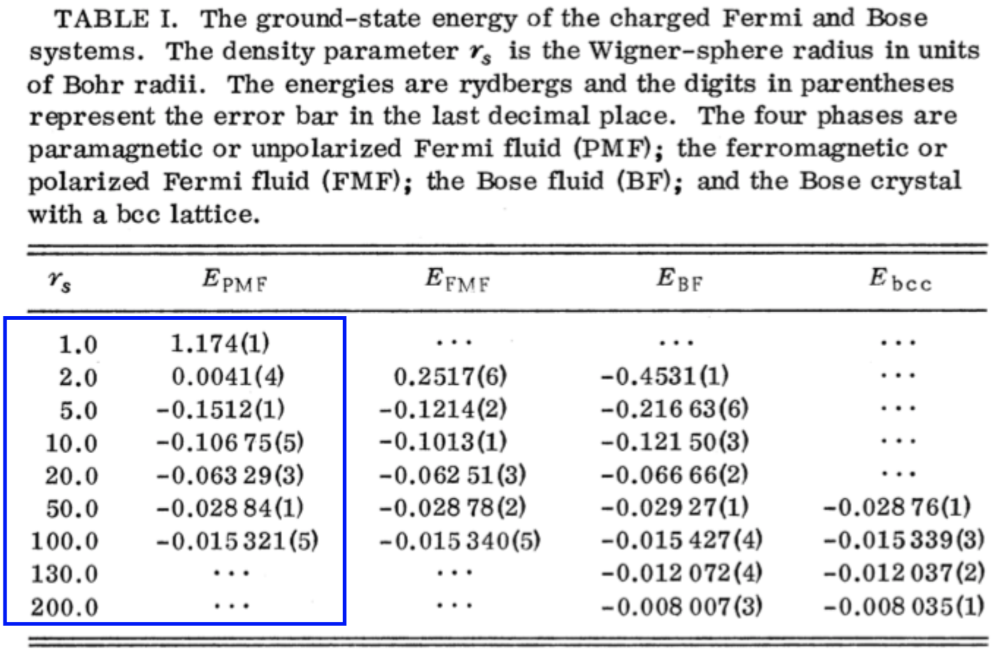


TABLE I. The ground-state energy of the charged Fermi and Bose systems. The density parameter r_s is the Wigner-sphere radius in units of Bohr radii. The energies are rydbergs and the digits in parentheses represent the error bar in the last decimal place. The four phases are paramagnetic or unpolarized Fermi fluid (PMF); the ferromagnetic or polarized Fermi fluid (FMF); the Bose fluid (BF); and the Bose crystal with a bcc lattice.

r_s	E_{PMF}	E_{FMF}	E_{BF}	E_{bcc}
1.0	1.174(1)	···	···	···
2.0	0.0041(4)	0.2517(6)	-0.4531(1)	···
5.0	-0.1512(1)	-0.1214(2)	-0.216 63(6)	···
10.0	-0.106 75(5)	-0.1013(1)	-0.121 50(3)	···
20.0	-0.063 29(3)	-0.062 51(3)	-0.066 66(2)	···
50.0	-0.028 84(1)	-0.028 78(2)	-0.029 27(1)	-0.028 76(1)
100.0	-0.015 321(5)	-0.015 340(5)	-0.015 427(4)	-0.015 339(3)
130.0	···	···	-0.012 072(4)	-0.012 037(2)
200.0	···	···	-0.008 007(3)	-0.008 035(1)

Figure 1: From: D. M. Ceperley and B. J. Alder (Phys. Rev. Lett. 1980)

using known results for the high-density regime, and otherwise fitting to the Ceperley- Alder QMC results (the low density part using a Padé approximant on $\sqrt{r_s}$).

With the defined $\varepsilon_x(n)$ and $\varepsilon_c(n)$ we have a fully fledged LDA approximation to DFT. They are surprisingly accurate. In the table below you see results for bond lengths in selected dimers. In many ways and systems, they are better than Hartree-Fock's, in spite of its also being a mean-field-like solution of the correlated problem.

The roundabout way to define the theory implies that the exchange term is approximate, only exact for jellium (while Hartree-Fock calculates it exactly for whatever system), while an approximation to electronic correlation is included, which is completely absent in Hartree-Fock. Importantly, however, the local character of the potential in LDA makes it extremely easier to calculate on a computer as compared to non-local Hartree-Fock, which tends to be a factor between 20 and 100 times more costly to calculate.

Bond length (Å)	Experiment	LDA	Error
H_2	0.74	0.77	0.03
B_2	1.59	1.60	0.02
N_2	1.10	1.10	0.00
F_2	1.42	1.38	0.04
Na_2	3.08	3.00	0.08
Al_2	2.47	2.46	0.01
P_2	1.89	1.89	0.01
S_2	1.89	1.89	0.00
Cl_2	1.99	1.98	0.01
Average			0.02

R G Parr & W Yang, *Density-Functional Theory of Atoms and Molecules*
Oxford University Press (1994)

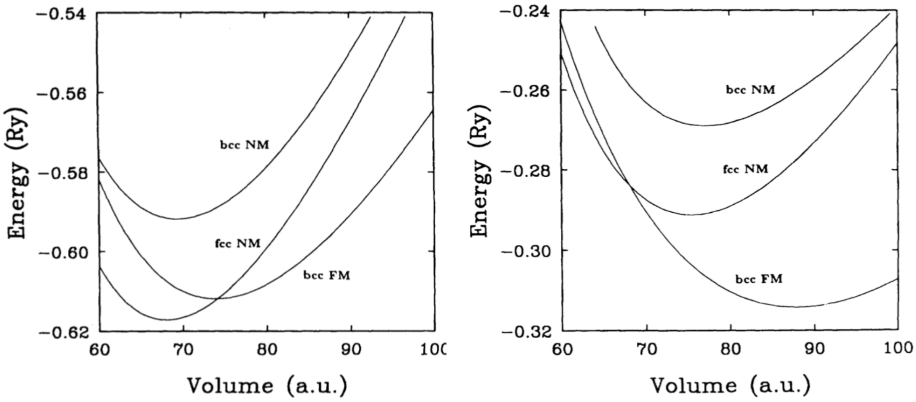
4.2 Generalized Gradient Approximation (GGA)

GGA improves upon LDA by including density gradients:

$$E_{xc}^{GGA}[n] = \int d^3 r n(r) \epsilon_{xc}(n, \nabla n). \tag{14}$$

Why "generalized"? Although originally proposed in the paper by Kohn and Sham, it was disappointingly inaccurate (in fact, LDA had been surprisingly successful!). Perdew noticed that the sum rule for n_{xc} integrating to -1 had to be enforced. The LDA approximation was shown to fulfill it by construction, but not any gradient expansion. Once noticed, the gradient approximations fulfilling it were called GGAs. After efforts in defining good GGAs, they have proved more accurate than LDA, and the extra computational cost is normally negligible. Problems with GGA, however:

- There is no natural reference for it, as there was for LDA. The homogeneous liquid does not help. This led to multiple proposals following different philosophies. Nowadays there are several hundred different GGAs around.



LDA GGA (PW91)

Figure 2: LDA Vs GGA for Fe

- They do not seem to represent a step in a systematic (expansion) way to improve on it.

A quite paradigmatic comparison of LDA versus GGA results is shown here:

5 Spin Polarisation in DFT

The previous result presents results for ferromagnetic iron, that is, with a net spontaneous magnetic moment per unit cell. Spontaneous refers to the fact that it is magnetised even in the absence of an external magnetic field.

The mentioned magnetisation results from unbalanced electron spins. Up to now we have considered electrons pairing up in single particle orbitals (in any of the previous approximations), but there are solutions that do not require that pairing, and that describe situations as the ferromagnetic iron in the figure. Such solutions are called spin polarised.

Within DFT, spin polarised solutions can also be obtained with a relatively straightforward generalisation of what has been studied so far. One can re-state the DFT theorems for the energy as a function of the density of spin-up electrons and that of spin-down electrons:

$$E[n^{\uparrow}, n^{\downarrow}] \tag{15}$$

defined as ever, but in each case the single-particle wave-functions for each spin are allowed to be different and their magnitude squared are summed up separately to obtain the separate densities.

That means that the usual particle density is

$$n(r) = n^{\uparrow}(r) + n^{\downarrow}(r), \tag{16}$$

with

$$n^{\sigma}(r) = \sum_i |\psi_i^{\sigma}(r)|^2. \tag{17}$$

The so-called spin density is defined as

$$n_s(r) = n^{\uparrow}(r) - n^{\downarrow}(r). \tag{18}$$

6 Total Energy and Double Counting

Finally, the total energy for the ground state obtained once the KS equations have been solved can be expressed as:

$$E = -\frac{1}{2}\sum_{\text{occ } i}\langle\psi_i|\nabla^2|\psi_i\rangle + \int d^3r n(r)\left[V_{\text{ext}}(r) + \frac{1}{2}v_H(r) + \epsilon_{xc}(n(r), \nabla n(r))\right], \tag{19}$$

or alternatively,

$$E = \sum_{\text{occ } i}\epsilon_i + \int d^3r n(r)\left[\epsilon_{xc}(n(r), \nabla n(r)) - V_{xc}(n(r), \nabla n(r)) - \frac{1}{2}v_H(r)\right]. \tag{20}$$

The second equation shows the double-counting correction also needed in DFT when computing the ground-state energy from the sum of the single-particle energies of the “occupied” states. The double counting for the Hartree term is also used in the HF solution (which also incorporates a term for the exchange). Notice the 1/2 factor in front of the Hartree energies. It relates to the fact that every pair should be counted only once. In basic electrostatics, given a distribution of charges, each charge feels the electrostatic potential energy originated by the presence of the rest. The electrostatic energy of the whole system is, however, not the sum over all charges times their corresponding potential energies, since that would count each interparticle interaction twice. For the same reason, the total energy for a system of electrons according to Hartree or Hartree-Fock approaches is not just the sum of eigenvalues corresponding to the occupied eigenvectors, but a term has to be subtracted to account for the double counting The one for the exchange-correlation term corrects for the fact that the energy contains the integral of the energy density, while the Kohn-Sham single-particle Hamiltonian contains the exchange-correlation potential.

$$\sum_i \epsilon_i \tag{21}$$

is sometimes called the band energy (in solid-state contexts) since that sum would represent the integration of the energy for the occupied bands.

7 The band gap Problem in DFT

The Kohn–Sham density functional theory is an in-principle-exact method for determining the ground-state density and total energy. However, good approximations to the density functional expression of other observables remain elusive. Despite this, KS orbitals and eigenvalues are often used as independent-particle expressions for band structures or response functions.

7.1 Interpretation of Kohn–Sham Eigenvalues

Kohn–Sham eigenvalues are sometimes interpreted as total energy differences, particularly electron addition or removal energies. However, this is only correct for the eigenvalue of the highest occupied state, which corresponds to the ionization energy when the exact KS potential is used. This result is sometimes called the "DFT Koopmans' theorem." Some important observations are:

- KS band structures should not be interpreted as physical electron addition or removal energies.
- Approximate functionals introduce additional errors, particularly self-interaction errors for localized states.
- The KS potential is a local and static potential, making it too inflexible to describe all states accurately.
- Functionals such as DFT+U, SIC, and hybrid functionals improve bandgap predictions because they incorporate non-local or state-dependent potentials.
- KS eigenvalues match exact excitation energies in the one-electron limit.

7.2 Janak's Theorem and Ionization Energy

Janak's theorem relates the KS eigenvalues to energy derivatives concerning fractional occupations:

$$\frac{\partial E}{\partial f_i} = \epsilon_i. \tag{22}$$

From this, one finds the meaning of the highest occupied eigenvalue, ϵ_N, by integrating:

$$E_N - E_{N-1} = \int_0^1 df_N \frac{\partial E}{\partial f_N} = \int_0^1 df_N \epsilon_N. \tag{23}$$

Thus, the ionization energy satisfies:

$$I = E_{N-1} - E_N = -\epsilon_N. \tag{24}$$

Similarly, for the electron affinity:

$$A = E_{N+1} - E_N = \epsilon_{N+1}. \tag{25}$$

However, this reasoning does not generalize to all eigenvalues since ϵ_{N+1} belongs to the $(N+1)$-electron system.

7.3 The Bandgap Problem and the Derivative Discontinuity

The fundamental bandgap of a material is defined in terms of total energy differences as:

$$E_g = E_{N+1} - E_N - (E_N - E_{N-1}). \tag{26}$$

If we express this in terms of KS eigenvalues, we obtain:

$$E_g = \epsilon_{N+1}(N+1) - \epsilon_N(N). \tag{27}$$

However, in KS-DFT, the commonly used bandgap is computed as the difference between the lowest unoccupied and highest occupied KS eigenvalues:

$$E_g^{KS} = \epsilon_{N+1}(N) - \epsilon_N(N). \tag{28}$$

Comparing this with the fundamental gap expression, we define the **derivative discontinuity** Δ:

$$E_g = E_g^{KS} + \Delta, \tag{29}$$

where the derivative discontinuity is given by:

$$\Delta = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N). \tag{30}$$

This discontinuity originates from the fact that the total energy $E(N)$ as a function of particle number N is not a smooth curve but consists of a series of straight-line segments with slope discontinuities at integer values of N. Mathematically, this means that:

$$\left.\frac{\partial E}{\partial N}\right|_{N^-} \neq \left.\frac{\partial E}{\partial N}\right|_{N^+}. \tag{31}$$

In a solid, where adding or removing an electron only changes the density by an infinitesimal amount, this discontinuity manifests as a rigid shift in the KS exchange–correlation potential across the system. This effect is crucial because:

- The exact functional should exhibit a nonzero Δ, which significantly affects the predicted bandgap.
- Standard functionals such as LDA and GGA do not include this discontinuity, leading to systematically underestimated bandgaps.
- Orbital-dependent functionals, such as exact exchange (EXX) and hybrid functionals, partially capture this effect, leading to improved bandgap predictions.

7.4 Implications of the Derivative Discontinuity

The presence of the derivative discontinuity has major implications for density functional approximations:

1. **Failure of Conventional Functionals:** Standard approximations like LDA and GGA are analytic functionals of the density and thus do not exhibit the required non-analyticity at integer N. As a result, these functionals predict bandgaps that are systematically too small.
2. **Orbital-Dependent Functionals:** Hybrid functionals and EXX functionals, which include non-local exchange effects, capture part of the derivative discontinuity and provide better bandgap predictions.

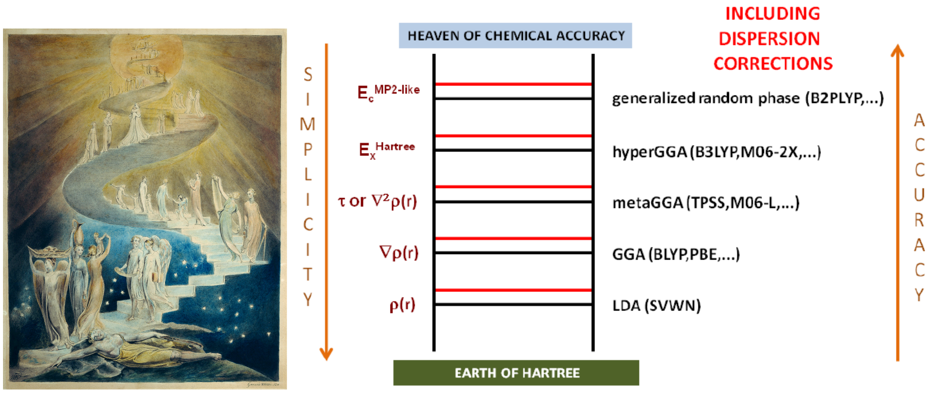


Figure 3: Jacobs Ladder analogy in the XC functional world

3. **Beyond KS-DFT:** Many-body approaches such as GW corrections explicitly account for Δ, leading to more accurate band structure predictions.

8 Beyond GGA: Jacob's Ladder

Unlike some quantum-chemistry approaches, the route towards exact solutions is not systematic. Approximate density functional theories are surprisingly accurate, and offer the best balance of accuracy(predictive power) versus efficiency. But if you need more accuracy, the path is not clear. The aspiration of systematic improvement of accuracy is called Jacob's Ladder in the community, taken the biblical concept of a staircase to Heaven, as in this painting by William Blake (British Museum)

However, the systematics is less systematic than one would wish. Here some of the acronyms mentioned in the ladder figure. Many of them relate to initials of the authors of the given papers.

1. LDA: The Perdew Zunger (PZ) parametrisation is probably the most popular LDA. There are others, but the differences are very minor since they all (or most) refer to the QMC results of Ceperley and Alder.

2. GGA: the lack of natural reference has resulted in many proposals (several hun- dred so far), which do vary considerably, since they reproduce different reference systems. It is worth distinguishing:

    - From chemistry: Perceived as semi-empirical, versus the truly ab initio quantum-chemical calculations, functionals were defined and

  fitted to reproduce properties of large sets of molecules obtained from wave-function methods. A popular one within this line is BLYP.
  - From physics. Perceived as truly from first principles, the functionals are defined using as many universal constraints from theory and theoretical references as possible. PBE is the most popular and probably successful one, together with its variants, revPBE, RPBE, PBEsol, and WC (unfortunate initials).

–

3. MetaGGA: Next level in the derivative expansion, second derivatives. But in- stead of the laplacian, using the kinetic-energy density (related). SCAN is being quite successful lately.
4. Hybrids(hyperGGA):Very successful and particularly popular in quantum chemistry, they consist of introducing a certain fraction α of the true Hartree-Fock exchange energy (and potential) for the system, keeping 1- α of the GGA exchange, with α varying between 20% and 30%, depending on the flavor. For some properties the improvement over GGAs performance is not surprising given that GGAs would overestimate while Hartree-Fock would underestimate, or vice- versa. The calculations, however, become much more demanding, since the full Hartree-Fock solution has to be found. The calculation of the exact exchange of Hartree Fock is not based on the density, but requires the single-particle wavefunctions. Hybrid functionals are, therefore, not strictly density functionals. Density functional theory can, however, be generalized to incorporate these type of functionals as shown in the next section.
5. RPA and Beyond (response function-based functionals)

8.1 Hybrid Functionals

Hybrid functionals mix a portion of the exact Hartree-Fock (HF) exchange energy with conventional exchange-correlation functionals from DFT:

$$E_{xc}^{\text{hybrid}} = \alpha E_x^{\text{HF}} + (1-\alpha) E_x^{\text{DFT}} + E_c^{\text{DFT}}, \tag{32}$$

where:

- E_x^{HF} is the non-local exchange integral from HF theory,

- E_x^{DFT} is the exchange energy from a conventional DFT functional (e.g., LDA or GGA),
- E_c^{DFT} is the correlation energy from a standard DFT approximation,
- α is a mixing parameter (typically 0.2–0.3).

8.1.1 Incorporation of Hybrid Functionals in DFT

In hybrid functionals, the exchange potential includes an explicit dependence on the KS orbitals:

$$V_x^{\mathrm{HF}}(r, r') = -\sum_i^{\mathrm{occ}} \psi_i^*(r')\psi_i(r)\frac{1}{|r - r'|}. \tag{33}$$

The KS equation becomes:

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(r) + V_H(r) + V_{xc}^{\mathrm{hybrid}}(r)\right)\psi_i(r) = \epsilon_i\psi_i(r), \tag{34}$$

where

$$V_{xc}^{\mathrm{hybrid}}(r) = \alpha V_x^{\mathrm{HF}}(r) + (1-\alpha)V_x^{\mathrm{DFT}}(r) + V_c^{\mathrm{DFT}}(r). \tag{35}$$

Generalized Kohn-Sham (GKS) Theory: To incorporate wavefunction-dependent functionals, the Generalized Kohn-Sham (GKS) framework allows functionals of the density matrix:

$$\gamma(r, r') = \sum_i^{\mathrm{occ}} \psi_i^*(r')\psi_i(r). \tag{36}$$

Another approach is the Optimized Effective Potential (OEP) method, which determines an effective local potential to approximate non-local exchange contributions.

8.1.2 Advantages and Limitations of Hybrid Functionals

- Advantages
  - **Improved Band Gaps**: Mitigates the ”bandgap problem” in standard DFT.
  - **Better Description of Localized Electrons**: Useful for transition metals and rare-earth elements.

  - **Enhanced Accuracy for Molecules**: Useful in quantum chemistry for reaction barriers and binding energies.

- Limitations

  - **Computational Cost**: More expensive due to non-local exchange integral evaluation.
  - **Empirical Nature**: The mixing parameter α is often determined empirically.
  - **Limited Applicability to Metals**: Hybrid functionals may fail for metallic systems.

8.2 Self-interaction

Remembering the discussion on self-interaction error in the context of the Hartree theory, it is worth noting that, although the exact Exc functional should give a self- interaction free theory, the mentioned approximate implementations do not. The approximate exchange term does not cancel the self interaction present in the Hartree term. There are ways to correct for self interaction within DFT (prominently in the same Perdew-Zunger paper proposing the LDA parametrization), but it is neither sim- ple nor clear the way to improve on this. Interestingly, since Hartree-Fock theory is self-interaction free, the hybrid functionals, inasmuch as they incorporate a fraction of exact exchange, they mitigate the problem. Indeed, some of the problems for which hybrid functionals improve over GGAs are ones in which self-interaction is an issue, namely, in systems with highly localized electrons, or, more clearly, in localized singly occupied states. In the latter, GGAs tend to delocalize the state as the electron would be repelled by its own density, which is clearly an artifact.

8.2.1 Van der Waals interactions

Dispersion interactions are quite hard to simulate from first principles. This is due to the following two facts:

- They result purely from electronic correlation. They result from the coupled (cor- related) quantum dipole fluctuations, and manifest themselves mostly in weak interactions between neutral molecules of weak polarity.

- The correlation is genuinely non-local, the potential at a given point depending on the particle density far away.

These interactions cannot be captured by local or semilocal correlation functionals such as LDA or GGAs, or even further up the ladder, since higher order derivatives do not help, and the non-locality in the hybrids is for exchange only, not for correlation. Dispersion interactions are extremely important in the configurations and dynamics of biomolecules and of many molecular crystals. For decades, this lack of dispersion in DFT limited its applicability considerably. The pressing need forced the appearance of empirical corrections of different kinds, the most popular one, due to Grimme, consisted in adding attractive interatomic forces with a r^{-6} decay, to the ab initio forces, making them depend on parameters that were fitted empirically.

In 2004, in a collaboration between Langreth in Rutgers and Lundqvist in Stockholm, a genuinely non-local correlation functional was proposed from theoretical considerations, as the first ab initio DFT with dispersion forces. There are now several variants of it, mostly tinkering with what is the best GGA exchange that should be added.

$$E = E_{\text{GGA-revPBE}} + E_{\text{LDA}} + E_{\text{xc}}^{\text{nl}} \tag{37}$$

$$E_{\text{xc}}^{\text{nl}} = \frac{1}{2} \iint d^3r_1 d^3r_2 \, n(r_1) n(r_2) \Phi(q_1, q_2, r_{12}) \tag{38}$$

$$q(n, \nabla n) = 1 + \frac{\epsilon_c^{\text{LDA}}(n)}{\epsilon_x^{\text{LDA}}(n)} + 0.8491 \left(\frac{\nabla n}{2nk_F} \right)^2 \tag{39}$$

$$k_F = (3\pi^2 n)^{1/3} \tag{40}$$

The non-local character of the functional made it extremely more costly computation- ally than a GGA. In 2010, however, Roman and Soler rewrote the functional in terms of a suitable expansion of products which made it much more efficient. Nowadays a VDW-DFT calculation on a typical system can represent 20-30% higher cost than a GGA.

8.3 Extensions of KS-DFT and Non-Local Effective Potentials

While standard KS-DFT assumes a local effective potential, many extensions introduce non-local effective potentials that depend on the wavefunctions rather than just the density. We have just seen two of them (Hybrids and vdW), but there are others as:

- Optimized Effective Potential (OEP) Method - A technique to approximate a local potential that mimics a non-local interaction. - The goal is to find a local potential $V_{\text{eff}}(r)$ that produces the same expectation values as a non-local exchange term.

- Quasiparticle Self-Consistent GW (QSGW) and Koopmans-Compliant Functionals - Incorporate energy-dependent and non-local potentials to improve upon KS-DFT deficiencies, especially for band gaps.

Reconciliation: Why HK Theorems Still Hold Despite the introduction of non-locality in the effective potential, the HK theorems remain valid because:

- The original HK theorem applies to the many-body system with a local $V_{\text{ext}}(r)$, ensuring that the ground-state density uniquely determines the total energy.
- KS-DFT is a reformulation, not a separate theory—the KS system is just an auxiliary system designed to reproduce the density of the true many-body system.
- In hybrid functionals and GKS, the introduction of non-locality occurs in the exchange-correlation potential, which is not constrained by HK theorems.

Thus, the **fundamental variational principle of DFT remains intact**, but the practical implementation moves beyond strict locality.