

A Primer in Density Functional Theory

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Outline

- 1 **Introduction: Pre-DFT**
 - The Problem, and the “traditional” solutions
 - The Thomas-Fermi model
- 2 **Theoretical Foundations**
 - Hohenberg-Kohn theorems
 - Levy constrained search formulation
 - Kohn-Sham formalism
 - The exchange and correlation functionals
- 3 **Extensions**
 - Time-dependent DFT
 - Other extensions



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The Electronic Many-Body Problem

- Non-relativistic time-independent many-electron problem:

$$\hat{\mathcal{H}}|\Phi\rangle = E|\Phi\rangle$$

$$\hat{\mathcal{H}} = \sum_{i=1}^N \hat{t}_i + \sum_{i=1}^N v_{\text{ext}}(\hat{\mathbf{r}}_i) + \sum_{i,j=1}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|},$$

$$v_{\text{ext}}(\vec{\mathbf{r}}) = \sum_{\alpha=1}^{N_{\text{nuclei}}} \frac{Z_{\alpha}}{|\vec{\mathbf{r}} - \vec{\mathbf{R}}_{\alpha}|}.$$

- In fact, what we really want are the values of the observables (at the ground state):

$$\mathcal{O}[\Phi] = \langle \Phi | \hat{\mathcal{O}} | \Phi \rangle.$$

For example, $\hat{\mathcal{O}} = \hat{\mathcal{H}}$, and we have the energy:

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The Variational Principle and the wave function approaches

- The variational equation is equivalent to Schrödinger's equation:

$$\frac{\delta}{\delta\Phi} \{ \langle \Phi | \hat{\mathcal{H}} | \Phi \rangle - E \langle \Phi | \Phi \rangle \} = 0,$$

where the variational search is done over all *antisymmetric* N -electron wave functions.

- Fully unconstrained search is not possible in general. The **wave function based** approaches assume a certain form for the wave function: The Rayleigh-Ritz method finds the extrema in a restricted space of wave functions.

i.e., Hartree-Fock: $|\Phi\rangle = \det[\varphi_1, \dots, \varphi_N] \Rightarrow$

$$E[\Phi] = \sum_{i=1}^N \langle \varphi_i | \hat{t} + \hat{v}_{\text{ext}} | \varphi_i \rangle + \sum_{i,j=1}^N \langle \varphi_i \varphi_j | \frac{1}{|\hat{r}_1 - \hat{r}_2|} | \varphi_i \varphi_j \rangle - \sum_{i,j=1}^N \langle \varphi_i \varphi_j | \frac{1}{|\hat{r}_1 - \hat{r}_2|} | \varphi_j \varphi_i \rangle.$$

$$\frac{\delta E}{\delta \varphi_i} - \sum_{j=1}^N (\lambda_{ij} \langle \varphi_i | \varphi_j \rangle - \delta_{ij}) = 0 \Rightarrow \boxed{\hat{F} \varphi_i = \epsilon_i \varphi_i} \quad (i = 1, \dots, N),$$

$$\hat{F} = \hat{t} + \hat{v}_{\text{ext}} + \hat{J} - \hat{K}.$$



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The Variational Principle and the wave function approaches

Denoting $x = (\vec{r}, \sigma)$:

$$\hat{J}\varphi_i(x) = \int dx' \frac{1}{|\vec{r} - \vec{r}'|} n(\vec{r}') \varphi_i(x).$$

$$\hat{K}\varphi_i(x) = \sum_{j=1}^N \int dx' \frac{1}{|\vec{r} - \vec{r}'|} \varphi_j^*(x') \varphi_i(x') \varphi_j(x).$$

$$[\text{In HF, } n(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2]$$

- The HF equations are a set of non-linear one-particle *Schrödinger-like* equations. The Coulomb and Fock operators depend on the solution orbitals, and thus they must be solved *self-consistently*.
- The Fock operator contains one non-local operator: the *exchange* \hat{K} .
- In Kohn-Sham DFT, on the contrary, the one-particle equations have only *local* operators.



Does state-of-the-art DFT do better than Hartree-Fock?

Atomization Energy of simple molecules (eV)

| | Li ₂ | C ₂ H ₂ | Set of 20 |
|--------------|-----------------|-------------------------------|-----------|
| Experimental | 1.04eV | 17.6eV | |
| Hartree-Fock | -0.94 | -4.9 | 3.1 |
| DFT/LDA | -0.05 | -2.4 | 1.4 |
| DFT/GGA | -0.2 | 0.4 | 0.35 |
| DFT/meta-GGA | -0.05 | -0.2 | 0.13 |

(Data from [Perdew 2000, Perdew 1999])



Density Matrices

- The wave-function contains too much information; the k -th order *reduced* density matrix suffice for k body operators, \hat{O}^k :

$$\langle \Phi | \hat{O}^k | \Phi \rangle = \int dx_1 \dots dx_k \hat{O}^k [\Gamma^{(k)}(x'_1, \dots, x'_k | x_1, \dots, x_k)].$$

$$\Gamma^{(k)}(x'_1, \dots, x'_k | x_1, \dots, x_k) = \binom{N}{k} \int dx_{k+1} \dots dx_N \Phi^*(x'_1, \dots, x'_k, x_{k+1}, \dots, x_N) \Phi(x_1, \dots, x_k, x_{k+1}, \dots, x_N).$$

- And most operators of interest are either one or two body operators:

$$\Gamma^{(1)}(x'_1 | x_1) = N \int dx_2 \dots dx_N \Phi^*(x'_1, x_2, \dots, x_N) \Phi(x_1, x_2, \dots, x_N).$$

$$\Gamma^{(2)}(x'_1, x'_2 | x_1, x_2) = \binom{N}{2} \int dx_3 \dots dx_N \Phi^*(x'_1, x'_2, x_3, \dots, x_N) \Phi(x_1, x_2, x_3, \dots, x_N)$$



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The Energy as a functional of $\Gamma^{(2)}$.

The energy is an exact functional solely of the first order density matrix, and of the diagonal of the second order density matrix:

$$E = \int dx \left[\frac{1}{2} \nabla^2 \Gamma^{(1)}(x|x') \right]_{x'=x} + \int dx v_{\text{ext}}(\vec{x}) \gamma^{(1)}(x) + \int dx \int dx' \frac{1}{|\vec{r} - \vec{r}'|} \gamma^{(2)}(x, x').$$

$$\gamma^{(1)}(x) = \Gamma^{(1)}(x|x).$$

$$\gamma^{(2)}(x, x') = \Gamma^{(2)}(x, x'|x, x').$$

Summing over spin in $\gamma^{(1)}$ one obtains the **electronic density**:

$$n(\vec{r}) = \sum_{\sigma} \gamma^{(1)}(\vec{r}\sigma).$$

Since $\Gamma^{(1)}$ can be obtained by explicit integration from $\Gamma^{(2)}$,

$$E = E[\Gamma^{(2)}].$$



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- Kinetic energy term:

$$T[\Gamma^{(1)}] = \int d^3r \left[\frac{1}{2} \nabla^2 \Gamma^{(1)}(x|x') \right]_{x'=x}.$$

It requires the full first order density matrix. Its numerical value does not coincide exactly with the Hartree-Fock kinetic energy.



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- External energy term:

$$E_{\text{ext}}[n] = \int d^3r v_{\text{ext}}(\vec{r}) n(\vec{r}).$$

It is an explicit functional of the density.



The Energy as a functional of $\Gamma^{(2)}$.

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- Interaction term.

$$U[\gamma^{(2)}] = \int d^3x \int d^3x' \frac{1}{|\vec{r} - \vec{r}'|} \gamma^{(2)}(x, x').$$

It is the most difficult term, arising from the two-body operator. It requires the second order density-matrix – although only the *diagonal* part. It can be split into a large, classical, **electrostatic Coulomb interaction**, U_0 , and the **exchange and correlation part of U**:

$$U = U_0 + E_{\text{xc}}; \quad U_0[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}.$$



The Variational Principle and the representability problem

- If $E = E[\Gamma^{(k)}]$ is exact (or is a suitable approximation), then:

$$\frac{\delta E}{\delta \Gamma^{(k)}} = 0.$$

solves the many-electron problem. Since we have an exact functional for $k = 2$, we have an exact variational approach for two-point functions, instead of for the N -point wave function!!

- But... we must perform a constrained search: $\Gamma^{(k)}$ must be N -representable:
 $\Gamma^{(k)}$ is N -representable if it stems from a N -particle wavefunction.
And the N -representability conditions for $k = 2$ are horribly difficult.
- The lower k , the easier the computational problem. Ideally, we would like to do a variational search over one-point functions, i.e. use a functional of the density:

$$E = E[n].$$

- Fortunately, any reasonable non-negative continuous n that integrates to N is N -representable.



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The Thomas-Fermi model

- From the previous *exact* energy functional, build a *density* energy functional by (a) using the classical electrostatic energy instead of the full interaction, and (b) substituting the exact kinetic term by the kinetic energy of a homogeneous electron gas:

$$E_{\text{TF}}[n] = 2.871 \int d^3r n^{5/3}(\vec{r}) - \int d^3r v_{\text{ext}}(\vec{r})n(\vec{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}.$$

The result is a **density functional**.

- The ground state energy can be obtained by applying the variational principle:

$$\frac{\delta}{\delta n} \left\{ E_{\text{TF}}[n] - \mu \left(\int d^3r n(\vec{r}) - N \right) \right\} = 0 \quad \Rightarrow$$

$$\mu = \frac{5}{3} 2.871 n^{2/3}(\vec{r}) - v_{\text{ext}}(\vec{r}) - \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}.$$

[Thomas 1927, Fermi 1927, March and Deb 1987]



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The Thomas-Fermi model

- The Thomas-Fermi-Dirac is an obvious extension: add the exchange energy of the homogeneous electron gas, which is also known exactly as a functional of the density.
- The TF approach was in principle ad-hoc: it was not known that an energy density functional even existed.
- Now we know that by improving the TF model one could obtain the *exact* result. This is nowadays called *orbital-free* DFT.
- Theorem: TF is exact in the limit of high atomic numbers and electron numbers.
- But... **Nonbinding Theorem: No molecular system is stable relative to dissociation into constituent fragments.**

[Lieb 1973, Simon 1977]



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The original Hohenberg-Kohn theorems

- If we know the external potential v_{ext} , and the number of electrons N we have, in principle all the information of the system (upon solution of Schrödinger equation). *Everything* is, in principle, a functional of v_{ext} .

$$\mathcal{O} = \langle \Phi | \hat{\mathcal{O}} | \Phi \rangle = \mathcal{O}[v_{\text{ext}}].$$

- We say that a density n is v -representable if it is the ground state density for a system of electrons characterized by some external potential v_{ext} .
- First HK theorem: **There exists a one-to-one mapping between v -representable electronic densities and external potentials.** [Hohenberg 1964]
- In other words: the density determines the external potential (to within trivial additive constants).
- Consequence: everything is, also, a functional of the density.

$$\mathcal{O} = \langle \Phi | \hat{\mathcal{O}} | \Phi \rangle = \mathcal{O}[n].$$

- The original theorem is only valid for non-degenerate ground states.



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The original Hohenberg-Kohn theorems

- We may then define the following functional, for all v -representable densities:

$$F_{\text{HK}}[n] = T[n] + U[n],$$

and, for a given v_{ext} :

$$E_{v_{\text{ext}}}[n] = F_{\text{HK}}[n] + \int d^3r n(\vec{r})v_{\text{ext}}(\vec{r}).$$

- Second HK theorem: If n_0 is the density that correspond to v_{ext} , for any other v -representable n :

$$E_{v_{\text{ext}}}[n] \geq E_{v_{\text{ext}}}[n_0] = E_0$$



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$$E_{v_{\text{ext}}}[n] = F_{\text{HK}}[n] + \int d^3r n(\vec{r})v_{\text{ext}}(\vec{r}).$$

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$$E_{v_{\text{ext}}}[n] \geq E_{v_{\text{ext}}}[n_0] = E_0$$



The original Hohenberg-Kohn theorems

Assuming differentiability of E_{vext} , the variational principle requires that the exact ground state density satisfy the stationary principle:

$$\delta \{ E_{\text{vext}}[n] - \mu \left[\int d^3r n(\vec{r}) - N \right] \} = 0,$$

which leads to an Euler-Lagrange equation in the form:

$$\mu = v_{\text{ext}}(\vec{r}) + \frac{\delta F_{\text{HK}}}{\delta n(\vec{r})}.$$

But we don't know the explicit form of $F_{\text{HK}}[n] = T[n] + U[n]!$



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 - Hohenberg-Kohn theorems
 - **Levy constrained search formulation**
 - Kohn-Sham formalism
 - The exchange and correlation functionals
- 3 Extensions
 - Time-dependent DFT
 - Other extensions



Levy constrained search formulation

- Variational principle, once again:

$$E_0 = \min_{\Phi} \{ \langle \Phi | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Phi \rangle \} .$$

$$E_0 = \min_n \{ \min_{\Phi \rightarrow n} \{ \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle \} + \int d^3 r n(\vec{r}) v_{ext}(\vec{r}) \} .$$

- If we define, over all N -representable densities,

$$F[n] = \min_{\Phi \rightarrow n} \{ \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle \} ,$$

we may define the following **density functional**:

$$E[n] = F[n] + \int d^3 r n(\vec{r}) v_{ext}(\vec{r}) ,$$

such that

$$E_0 = \min_n E[n] .$$

- We arrive to a variational approach, equivalent to the HK, but without the v -representability problem and valid for non-degenerate ground states.



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Kohn-Sham formalism

- The variational equation:

$$\mu = v_{\text{ext}}(\vec{r}) + \frac{\delta F}{\delta n(\vec{r})} .$$

is valid for any external potential, and also for any possible electronic interaction.

In particular, it is valid for a system of non-interacting electrons.

- The “Kohn-Sham system” S , is, for a given density n , that system of non-interacting electrons that has n as ground-state density. This is possible by tuning its external potential, that we will call “Kohn-Sham potential”, v_{KS} .
- For the Kohn-Sham system,

$$F_S[n] = T_S[n] .$$

We define the exchange and correlation functional, $E_{\text{xc}}[n]$, as:

$$F[n] = F_S[n] + U_0[n] + E_{\text{xc}}[n] .$$



Kohn-Sham formalism

- We now have two Euler-Lagrange equations that provide the same density:

$$\mu = v_{\text{ext}}(\vec{r}) + \frac{\delta F}{\delta n(\vec{r})}.$$

$$\mu = v_{\text{KS}}(\vec{r}) + \frac{\delta T_S}{\delta n(\vec{r})},$$

and this leads us to an expression for the Kohn-Sham potential:

$$v_{\text{KS}}(\vec{r}) = v_{\text{ext}}(\vec{r}) + \frac{\delta U_0}{\delta n(\vec{r})} + \frac{\delta E_{\text{xc}}}{\delta n(\vec{r})}.$$

- A system of non-interacting particles is described by a single Slater determinant, whose spin-orbitals may be obtained by solving a system of single particle equations, the “Kohn-Sham equations”:

$$-\frac{1}{2}\nabla^2\varphi_i(\vec{r}) + v_{\text{KS}}(\vec{r})\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r}).$$

$$n(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2.$$



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Kohn-Sham formalism

- The solution of the KS system provides us with the exact (in principle), electronic density n .
- There is, however, still one unknown part: the exchange and correlation energy functional $E_{xc}[n]$, and its functional derivative, the xc potential:

$$v_{xc}[n](\vec{r}) = \frac{\delta E_{xc}}{\delta n(\vec{r})}.$$

- The ground state energy E_0 may now be obtained as:

$$E_0 = T_S[n] + U_0[n] + E_{ext}[n] + E_{xc}[n],$$

or

$$E_0 = \sum_{i=1}^N \varepsilon_i - U_0[n] + E_{xc}[n] - \int d^3r n(\vec{r}) v_{xc}[n](\vec{r}).$$



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The exchange and correlation energy

- We may split E_{xc} into an *exchange* and a *correlation* part:

$$E_{xc}[n] = E_x[n] + E_c[n],$$

where

$$E_x[n] = \langle \Phi^{KS} | \hat{V}_{ee} | \Phi^{KS} \rangle.$$

- $E_x[n] \leq 0$.
- If $N = 1$, $E_x[n] = -U_0[n]$.
This means that the exchange energy cancels the *self interaction*.
- $E_c[n] \leq 0$.
- If $N = 1$, $E_c[n] = 0$.

- $$\lim_{r \rightarrow \infty} v_{xc}[n](\vec{r}) = -\frac{1}{r}.$$



Local Density Approximation (LDA)

- There is a system for which all the terms can be worked out exactly: the homogeneous electron gas (HEG). The correlation term cannot be obtained analytically, but can be computed to desired accuracy and parameterized.
- LDA:

$$E_{xc}[n] = \int d^3r n(\vec{r}) \varepsilon_{xc}^{\text{HEG}}(n(\vec{r})),$$

where $\varepsilon_{xc}^{\text{HEG}}(n(\vec{r}))$ is the exchange and correlation energy *density* of a HEG of (constant) density $n = n(\vec{r})$.

- It should be valid only for systems of *slowly varying* densities. But it turns out that it works in cases where it should not!
- It has proven very difficult to improve. Still today, it is extensively used in Solid State Physics – and also for molecules!
- The reason is that it fulfills many exact properties. The most notable failure is that it contains self-interaction.

[Ceperley 1980, Perdew 1981]



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[Ceperley 1980, Perdew 1981]



Generalized Gradient Approximation (GGA)

- GGA:

$$E_{xc}[n] = \int d^3r F[n(\vec{r}, \nabla n(\vec{r}))].$$

- This does not uniquely define the functional. Many attempts were made before something worked.
- Two *schools* of GGAs:
- Perdew. More *ab initio*, based on physical insight.
- Becke. More *empirical*, sometimes making use of adjustable parameters. Becke's functionals are the ones popularized DFT.
- GGA provides very good bond-lengths, vibrational frequencies, energy differences (atomization energies), ionization potentials. . .



Typical errors

| Property | L(S)DA | GGA |
|----------------|-----------------------------|---------------|
| E_x | 5% (not negative enough) | 0.5% |
| E_c | 100% (too negative) | 5% |
| bond length | 1% (too short) | 1% (too long) |
| structure | overly favors close packing | more correct |
| energy barrier | 100% (too low) | 30% (too low) |

$\frac{3}{4}$

One easy explanation to why LSDA and GGA work: cancellation of errors between E_x and E_c !



meta-GGA

- meta-GGA:

$$E_{xc}[n] = \int d^3r F[n(\vec{r}), \nabla n(\vec{r}), \nabla^2 n(\vec{r}), \tau(\vec{r})],$$

where we use, besides the Laplacian of the density, the kinetic energy density:

$$\tau(\vec{r}) = \sum_{i=1}^N |\varphi(\vec{r})|^2.$$

This is an expression in term of the orbitals. But it can be approximated, to first order, by:

$$\tau = \frac{|\nabla n|^2}{8n}.$$

[Perdew 1999, Tao 2003]



And beyond: Orbital Dependent Functionals.

$$E_{xc}[n] = E[\{\varphi_i[n]\}_{i=1}^N].$$

For example, this permits to obtain the exchange exactly:

$$E_x = \frac{1}{2} \sum_{k,l=1}^N \int d^3r \int d^3r' \frac{\varphi_k^*(\vec{r})\varphi_l(\vec{r})\varphi_l^*(\vec{r}')\varphi_k(\vec{r}')}{|\vec{r} - \vec{r}'|}.$$

This permits to define a functional without the self-interaction error.

- The potential has to be obtained by functional differentiation with respect to the densities.
- One has to resort to the Optimized Effective Potential (OEP) theory, which provides us with schemes to calculate the derivative.

See [Anisimov 2000], page 203, by T. Grabo et al.



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The time-dependent one-to-one mapping

- System \mathcal{S} : $\hat{H} = \hat{T} + \hat{W} + \hat{V}(t)$
 - $\hat{W} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$ is the electronic interaction.
 - $\hat{V}(t) = \sum_i v(\hat{r}_i, t)$ is the external field seen by the electrons.
 - $|\Phi(t=0)\rangle = |\Phi_0\rangle \Rightarrow n(\vec{r}, t) = \langle \Phi(t) | \hat{n}(\vec{r}) | \Phi(t) \rangle$.

- System \mathcal{S}' : $\hat{H}' = \hat{T} + \hat{W}' + \hat{V}'(t)$
 - Question: Given \hat{W}' , is there any $v'(\vec{r}, t)$ such that:

$$n'(\vec{r}, t) = \langle \Phi'(t) | \hat{n}(\vec{r}) | \Phi'(t) \rangle = n(\vec{r}, t) ?$$

- Answer: Yes, and it is unique.

[R. van Leeuwen, Phys. Rev. Lett. **82** 3863 (1999).]



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The Runge-Gross theorem, and the TDKS system

- Now assume that $W'=W$.
 $v'(\vec{r}, t) = v(\vec{r}, t)$ obviously, but the theorem also tells us that **it is unique**:
There exists a unique relationship between time-dependent densities and external potentials.
E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- And now assume that $W'=0$. I.e., we have a non-interacting system.

There exists a potential $v'(\vec{r}, t)$ for this non-interacting system such that it *reproduces* the density of the interacting system.

This is the so-called time-dependent Kohn-Sham potential, $v_{\text{KS}}(\vec{r}, t)$. The evolution of the non-interacting system may be easily obtained by propagating single-particle equations (i.e. Runge-Gross or td Kohn-Sham equations):

$$i \frac{\partial}{\partial t} \varphi_i(\vec{r}, t) = -\frac{1}{2} \nabla^2 \varphi_i(\vec{r}, t) + v_{\text{KS}}(\vec{r}, t) \varphi_i(\vec{r}, t).$$



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Retrieval of observables in TDDFT

- The density of the *real*, interacting system, may be retrieved from the single-particle orbitals that solve the *auxiliary*, non-interacting system:

$$n(\vec{r}, t) = \sum_{i=1}^N |\varphi_i(\vec{r}, t)|^2.$$

- The expectation value of any observable $\hat{Q}(t)$ is a unique functional of the time-dependent density by virtue of the Runge-Gross theorem:

$$Q(t) \equiv \langle Q(t) \rangle \equiv Q(t)[n].$$

- For example, the dipole-dipole 1st order dynamical polarizability would be:

$$\alpha_{\sigma\mu}[n](\omega) = -\frac{1}{E_{\mu}(\omega)} \int d^3r r r_{\sigma} \delta n(\vec{r}, \omega).$$



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But...

- RG is an *existence* theorem that is non-constructive: we do not know v_{KS} .
- As in gs DFT, a smaller unknown part may be isolated:

$$v_{\text{KS}}(\vec{r}, t) = v(\vec{r}, t) + u_{\text{Hartree}}[n](\vec{r}, t) + v_{\text{xc}}[n](\vec{r}, t),$$

where, by definition:

$$v_{\text{xc}}(\vec{r}, t) = \frac{\delta A_{\text{xc}}}{\delta n(\vec{r}, t)}.$$

In order to use the GS functionals, the adiabatic approximation has to be invoked:

$$A_{\text{xc}}[n] = \int_{t_0}^{t_f} d\tau E_{\text{xc}}[n_\tau]; \quad (n_\tau(\vec{r}) = n(\vec{r}, \tau)).$$

However, strong-field phenomena have proven to be especially demanding in terms of the xc approximations. Orbital-dependent functionals seem to be needed, which are non-adiabatic, and require the OEP formalism.

- Yet another problem: not all observables are explicit functionals of the td density. Most of them are unknown and have to be approximated. For example, the ionization probabilities.



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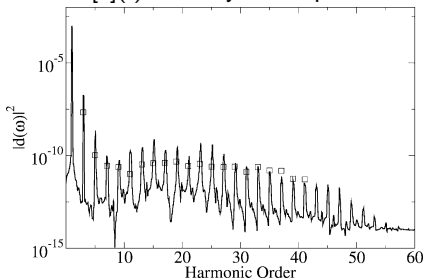


Non-linear regime

For large external perturbations (non-linear, or non-perturbative regime), one can directly propagate in time the TDKS equations. This permits, to obtain, e.g., harmonic spectra:

$$\sigma_{\text{emission}} \propto \left| \int dt e^{i\omega t} \frac{d}{dt} d[n](t) \right|^2,$$

where $d[n](t)$ is the system dipole moment: $d[n](t) = \int d^3r n(\vec{r})(t)x$.



Harmonic spectrum for He at $\lambda = 616$ nm and $I = 3.5 \cdot 10^{14}$ W/cm². Calculations at the exact-exchange (within the KLI approximation) level of theory. [C. A. Ullrich, S. Erhard and E. K. U. Gross, 1996)]



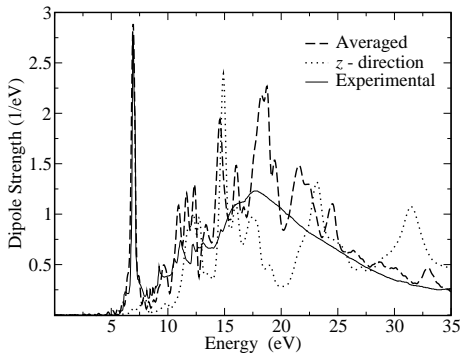
Linear Response TDDFT

- If we assume small perturbations, one can derive a linearized form of the TDKS equations: the response density is a linear functional of the perturbation.
- The translation of the linear response theory formalism to TDDFT leads to a tractable set of equations that permits to obtain:
 - Excitation energies, $\omega_I = E_I - E_0$.
 - Transition matrix elements, oscillatory strengths – corresponding to transitions between the ground state and the excited states.
- No excited **states**. No excited states densities. No matrix elements between excited states.
- It requires the *second functional derivative* of the exchange and correlation functional: the so-called kernel:

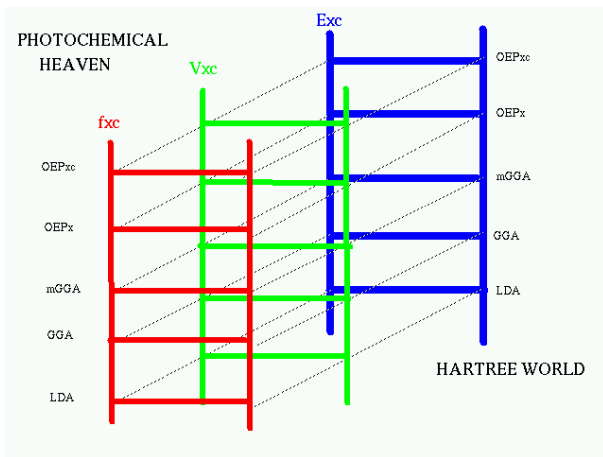
$$f_{xc}(\vec{r}t, \vec{r}'t) = \frac{\delta v_{xc}(\vec{r}, t)}{\delta n(\vec{r}', t')}.$$



Example: absorption spectrum of benzene



The Jacob's ladder of xc approximation



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 - **Other extensions**



Other extensions of DFT

- Spin-DFT.

Analogous to unrestricted Hartree-Fock. The basic variables are the spin densities $n_\sigma(\vec{r})$ ($\sigma = \uparrow, \downarrow$) ($n = n_\uparrow + n_\downarrow$). [vonBarth 1972]

- It permits to put some spin-dependent terms in the Hamiltonian.
- It provides better results for open-shell systems.

- Current-Spin DFT.

Useful for problems that involve magnetic fields. It is based on a generalized HK theorem, that establishes a mapping between (a) the density, and the **current density**, and (b) the external potential, which may be a vector potential. [Vignale 1987]






- Relativistic DFT. See Chapter 3 of [Fiolhais et al. 2003].

- Multi-component DFT.

If we have a system with different particles (e.g., the electrons and the different nuclei), we can treat all of them quantum-mechanically. We then have a different density for each specie. A generalization of the HK theorem can then be established in this case.







For Further Reading I

-  C. Fiolhais, F. Nogueira and M. A. L. Marques (Eds.),
A Primer in Density Functional Theory,
Lecture Notes in Physics **620**, (Springer, Berlin, 2003).
-  R. Parr and W. Yang,
Density Functional Theory of Atoms and Molecules,
(Oxford University Press, New York, 1989).
-  W. Koch and M. C. Holthausen,
A Chemist's guide to Density Functional Theory,
(Wiley-VCH Verlag, Weinheim, 2001).
-  J. M. Seminario (Ed.),
Recent Developments and Applications of Modern Density Functional Theory,
(Elsevier, Amsterdam, 1996).
-  N. H. March and B. M. Deb (Eds.),
Single-Particle Density in Physics and Chemistry,
(Academic Press, London, 1987).



For Further Reading II

-  V. I. Anisimov (Ed.),
Strong Correlations in Electronic Structure Calculations: Beyond the Local Density Approximation,
(Gordon&Breach, Amsterdam, 2000).
-  M. A. L. Marques, F. Nogueira, C. Ullrich, K. Burke, A. Rubio and E. K. U. Gross (Eds.),
TDDFT, Lecture notes
(Springer Verlag, Berlin, to be published in 2006).
-  R. F. Nalewajski (Ed.)
Topics in Current Chemistry,
(Springer, Heidelberg, 1996). See Chapter by E. K. U. Gross, J. F. Dobson and M. Petersilka, dedicated to TDDFT.
-  L. H. Thomas,
The calculation of atomic fields,
Proc. Camb. Phil. Soc. **23**, 542 (1927).



For Further Reading III



E. Fermi,

Un metodo statistico per la determinazione di alcune proprietà dell'atomo,

Rend. Accad., Lincei **54**, 2627 (1927).



P. Hohenberg and W. Kohn,

Inhomogeneous electron gas,

Phys. Rev. **136**, B864 (1964).



W. Kohn and L. J. Sham,

Self-consistent equations including exchange and correlation effects,

Phys. Rev. **140**, A1133 (1965).



W. Kohn,

Nobel Lecture,

Rev. Mod. Phys. **71**, 1253 (1999).








U. von Barth,

Basic Density-Functional Theory – An Overview,

Physica Scripta **T109**, 9 (2004).







For Further Reading IV

-  R. O. Jones and O. Gunnarsson,
The density functional formalism, its applications and prospects,
Rev. Mod. Phys. **61**, 689 (1989).
-  J. P. Perdew, K. Burke and M. Ernzerhof,
Generalized Gradient Approximation Made Simple,
Phys. Rev. Lett. **77**, 3865 (1996).
-  J. P. Perdew, S. Kurth, A. Zupan and P. Blaha,
Accurate Density Functional with Correct Formal Properties: A Step
Beyond the Generalized Gradient Approximation,
Phys. Rev. Lett. **82**, 2544 (1999).
-  E. H. Lieb and B. Simon,
Thomas-Fermi theory revisited,
Phys. Rev. Lett. **31**, 681 (1973).
-  E. H. Lieb and B. Simon,
The Thomas-Fermi theory of atoms, molecules and solids,
Adv. in Math. **23**, 22 (1977).



For Further Reading V

-  D. M. Ceperley and B. J. Alder,
Ground State of the Electron Gas by a Stochastic Method,
Phys. Rev. Lett. **45**, 566 (1980).
-  J. P. Perdew and A. Zunger,
Self-interaction correction to density-functional approximations for
many-electron systems,
Phys. Rev. B **23**, 5048 (1981).
-  U. von Barth and L. Hedin,
Spin-Density Functional Theory,
J. Phys. C **5**, 1629 (1972).
-  G. Vignale and M. Rasolt,
Density-functional theory in strong magnetic fields,
Phys. Rev. Lett. **59**, 2360 (1987).



For Further Reading VI



J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria,
Climbing the Density Functional Ladder: Nonempirical
Meta-Generalized Gradient Approximation Designed for Molecules
and Solids,
Phys. Rev. Lett. **91**, 146401 (2003).

