Introduction to Time-Dependent Density-Functional Theories

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Abbreviated Outline

\[ \text{DFT} = \text{Density-Functional Theory} \]
\[ \text{not to be confused with Discrete Fourier Transform} \]

\[ \text{TDDFT} = \text{Time-Dependent Density-Functional Theory} \]
\[ \text{sometimes just TDF} \]

\[ \text{TDCDFT} = \text{Time-Dependent Current-Density-Functional Theory} \]
Density-Functional Theory

Consider a system of many interacting particles (e.g. electrons):

\[
\hat{H} = \underbrace{\hat{T}}_{-\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2} + \underbrace{\hat{W}}_{\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}} + \underbrace{\hat{V}}_{\sum_{i=1}^{N} V(\mathbf{r}_i)}
\]

Given \( N \) and \( V(\mathbf{r}) \) we have therefore specified:

- the Hamiltonian \( \hat{H} \)
- all the stationary states, including the ground-state \( \Phi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \)
- expectation values for all observables \( \langle O \rangle = \langle \Phi | \hat{O} | \Phi \rangle \)
- i.e. everything there is to know!

But what’s new?
The Density

One observable is the density – for the ground-state it is:

\[ n_0(r) = N \int \prod_{i=2}^{N} d^3r_i |\Phi_0(r, r_2, \ldots, r_N)|^2 \]

Like all observables, it is unchanged by a shift in the zero of energy because this only affects the phase of the wavefunctions (if \( \hat{H}' = \hat{H} + \Delta \) then \( |\Phi'\rangle = |\Phi\rangle \exp(-i\Delta t) \)).

Ignoring rigid shifts in the potential \( V(r) \) there is a one-to-one mapping

\[ V(r) \longrightarrow n_0(r) \]
The Hohenberg-Kohn Theorems


First: proves that this one-to-one-mapping can be reversed:

\[ V(\mathbf{r}) \leftrightarrow n_0(\mathbf{r}) \]

i.e. give me a (reasonable) density and I can tell you which potential (to within an additive constant) gives rise to it in the ground-state.

So given \( n_0(\mathbf{r}) \) I can also tell you:

- the number of electrons \( N = \int d^3r \, n_0(\mathbf{r}) \)
- the Hamiltonian \( \hat{H} \)
- the stationary states...
- everything!
Density-Functionals

An interesting subset of “everything” includes the expectation values of energy operators e.g.

$$F[n_0] = \langle \Phi_0 | \hat{T} | \Phi_0 \rangle + \langle \Phi_0 | \hat{W} | \Phi_0 \rangle$$

which can be therefore be expressed as a functional of the density.

Second: a variational principle: for a specified external potential $V_{\text{ext}}(r)$,

$$E_0 = \min_{n(r)} \left\{ F[n] + \int d^3 r V_{\text{ext}}(r)n(r) \right\}$$

Solve:

$$\delta \left\{ F[n] + \int d^3 r V_{\text{ext}}(r)n(r) - \mu \left( \int d^3 r n(r) - N \right) \right\} = 0$$
But...

We have only established the existence of $F[n]$ – we don’t (yet?) know what it is!

- Explicit density-functionals have not been very successful (except in some simple cases).
- The kinetic energy is the trickiest part.

Kohn-Sham Mapping


“Shuffle the pack” – \( F[n] = T_s[n] + \frac{1}{2} \int d^3r \, d^3r' \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n] \)

\[
\Rightarrow \frac{\delta T_s[n]}{\delta n(r)} + \int d^3r' \frac{n(r')}{|r-r'|} + V_{xc}(r) + V_{ext}(r) = \mu
\]

This is the equation we would get for a system of non-interacting particles moving in potential \( V_{\text{eff}}(r) \).

We have mapped the system of interacting particles onto a system of non-interacting particles with

- the same ground-state density
- but a different (though related) external potential
Kohn-Sham Equations

The non-interacting problem is easy to solve:

\[ \left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \]

where

\[ n_0(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \]

and

\[ T_s[n] = -\frac{1}{2} \sum_{i=1}^{N} \int d^3r \, \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) \]

- Since \( V_{\text{eff}}(\mathbf{r}) \) is density-dependent, we need to solve these equations self-consistently.
- The problem of evaluating the kinetic energy from the density is overcome...
- ...but the buck has just been passed to \( E_{\text{xc}}[n] \)!
Local Density Approximation

\[ E_{xc}[n] = \int d^3r \epsilon_{xc}^{\text{hom}}(n(r)) n(r) \]

- \( E_{xc}[n] \) for the homogeneous electron gas is known from Quantum Monte Carlo

- and their results have been parametrised
Successes

The LDA has no right to succeed:

\[
E_{xc}[n] = \frac{1}{2} \int d^3r \, d^3r' \frac{n(r)n_{xc}(r', r')}{|r - r'|}
\]
Exact Conditions

- Exchange-correlation hole sum rule:
  \[ \int d^3r' n_{xc}(\mathbf{r}, \mathbf{r}') = -1 \]

- \( E_{xc}[n] \) depends only weakly on the shape of the exchange-correlation hole

- Newton’s Third Law:
  \[ \int d^3r \ n(\mathbf{r}) \nabla V_{xc}(\mathbf{r}) = 0 \]
  \[ \int d^3r \ n(\mathbf{r}) \mathbf{r} \times \nabla V_{xc}(\mathbf{r}) = 0 \]
Failures

- Self-interaction (c.f. Hartree-Fock) – for the hydrogen atom:
  - \( V_{\text{eff}}(r) = -\frac{1}{r} \)
  - therefore \( V_{\text{xc}}(r) = -V_H(r) \)
  - \( E_{0}^{\text{LDA}} = -0.89 \text{ Ry} \)

- The “band-gap” problem:
  - ‘Kohn-Sham eigenvalues have no physical significance.’
  - Sham-Schlüter equation relates \( V_{\text{xc}}(r) \) to the self-energy of many-body theory

G. L. Zhao, D. Bagayoko and T. D. Williams (unpublished)
Time-Dependent Density-Functional Theory

Why the excitement?

- Study time-dependent phenomena e.g. response of atoms to intense laser pulses (electromagnetic field strengths comparable to electron-nuclear field).
- Study excited states of a system e.g. He atom:

M. Petersilka (unpublished)
When subject to an applied time-dependent voltage $V(t) = V_0 \exp(i\omega t)$, the above circuit responds with a current $I(t) = I_0 \exp(i\omega t)$ where the response is characterised by an impedance $Z$ given by:

$$Z(\omega) = \frac{V_0}{I_0} = R + i \left( \omega L - \frac{1}{\omega C} \right)$$
Resonance and Excitation

The undamped system \((R = 0)\) can respond without applied voltage at the frequency \(\omega\) where:

\[
|Z(\omega)| = \sqrt{R^2 + \left(\omega L - \frac{1}{\omega C}\right)^2} = 0
\]

For a system of electrons, TDDFT allows us to calculate the response of the density to a time-dependent perturbing potential at frequency \(\omega\). The response function has poles at all the excitation energies of the system.
Time-Dependent Density-Functional Theory


The density-density response function $\chi(r, r', \omega)$ gives the density response of the system to a time-dependent perturbation $\delta V_{\text{ext}}(r, \omega) \exp(-i\omega t)$:

$$\delta n(r, \omega) = \int d^3r' \chi(r, r', \omega) \delta V_{\text{ext}}(r', \omega)$$

The Runge-Gross theorem means we can make the mapping across to an equivalent non-interacting system which will be perturbed by:

$$\delta V_{\text{eff}}(r, \omega) = \delta V_{\text{ext}}(r, \omega) + \int d^3r' \frac{\delta n(r', \omega)}{|r - r'|} + \int d^3r' f_{\text{xc}}(r, r', \omega) \delta n(r', \omega)$$
Exchange-Correlation Kernel

The exchange-correlation kernel $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ is defined in the linear response regime by:

$$f_{xc}(\mathbf{r}, \mathbf{r}', t - t') = \left. \frac{\delta V_{xc}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \right|_{n_0(\mathbf{r})}$$

which can be Fourier transformed to get $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$.

Note that the exchange-correlation potential can respond to all past density-fluctuations over all space: the kernel is nonlocal in both space *and* time.

The analogy to a local density approximation in the time domain is an adiabatic approximation which makes the exchange-correlation kernel frequency-independent.
Calculating the Response Function

Denote the density-density response function for the non-interacting system by $\chi_0(r, r', \omega)$ we can put everything together:

$$\chi_0^{-1}(r, r', \omega) = \frac{\delta V_{\text{eff}}(r, \omega)}{\delta n(r', \omega)} = \frac{\delta V_{\text{ext}}(r, \omega)}{\delta n(r', \omega)} + \frac{\delta V_{H}(r, \omega)}{\delta n(r', \omega)} + f_{xc}(r, r', \omega)$$

$$= \chi^{-1}(r, r', \omega) + \frac{1}{|r - r'|} + f_{xc}(r, r', \omega)$$

The same quantity can also be calculated from the Kohn-Sham orbitals $\{\psi_i(r)\}$:

$$\chi_0^{-1}(r, r', \omega) = \sum_{jk} (f_k - f_j) \frac{\psi_j(r)\psi^*_k(r)\psi^*_j(r')\psi_k(r')}{\omega - (\varepsilon_j - \varepsilon_k) + i\eta}$$

A static calculation gives us the information we need.
Exact Conditions

- \( f_{xc}(\mathbf{r}, \mathbf{r}', t - t') = 0 \) for \( t < t' \)

- As \( \omega \to \infty \), \( f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \) approaches a real function

- \( f_{xc}(\mathbf{r}, \mathbf{r}', \omega) - f_{xc}(\mathbf{r}, \mathbf{r}', \infty) \) satisfies Kramers-Kronig relations

- \( f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f^*_{xc}(\mathbf{r}, \mathbf{r}', -\omega) \)

- \( f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc}(\mathbf{r}', \mathbf{r}, \omega) \)
Newton’s Third Law again

• Recall
\[ \int d^3r \ n(r) \nabla V_{xc}(r) = 0 \]

• Take functional derivative with respect to \( n(r') \):
\[ \nabla' V_{xc}(r') + \int d^3r \ n(r) \nabla f_{xc}(r, r', \omega) = 0 \]

• Multiply by \( n(r') \) and integrate over \( r' \):
\[ \int d^3r \int d^3r' \ n(r)n(r') \nabla f_{xc}(r, r', \omega) = 0 \]

• Similarly
\[ \int d^3r \int d^3r' \ n(r)n(r') \mathbf{r} \times \nabla f_{xc}(r, r', \omega) = 0 \]
Translational invariance

- Consider a rigid boost $\mathbf{R}(t)$ of a static density $n(\mathbf{r})$:

$$n'(\mathbf{r}, t) = n(\mathbf{r} - \mathbf{R}(t)), \quad \mathbf{R}(0) = 0$$

- The exchange-correlation potential must satisfy:

$$V_{xc}[n'](\mathbf{r}, t) = V_{xc}[n](\mathbf{r} - \mathbf{R}(t))$$

- Universally valid, though first discovered for the special case of a harmonic external potential driven by force $\mathbf{F}(t)$ where $\mathbf{R}(t)$ is the classical motion: harmonic potential theorem.
Adiabatic LDA

The simplest approximation for the exchange-correlation kernel:

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') \frac{d}{dn^2} \left[ n \epsilon_{xc}^{\text{hom}}(n) \right] \bigg|_{n=n_0(\mathbf{r})}$$

- Local in space
- Frequency independent
- i.e. local in time

Again, what right has such a simple approximation to succeed?
Successes and Failures

Good results for isolated systems (atoms and small molecules) e.g. excitation energies of atoms.

- Satisfies all exact conditions (crudely)...

- ... except the frequency-dependent response of the homogeneous electron gas

Bad for extended systems e.g. long molecular chains – overestimates polarisabilities along the chain.
Frequency-dependent LDA

Response of the homogeneous electron gas $f_{xc}^{\text{hom}}(n, |r - r'|, \omega)$ is:

- Non-local in space
- Frequency dependent

Ambiguity in making a local approximation: do we evaluate the density $n$ at $r$ or $r'$?

In the limit that the wavelength of the density perturbation exceeds the range of $f_{xc}(n, |r - r'|, \omega)$ it doesn't matter!

$$f_{xc}^{\text{GK}}[n](r, r', \omega) = \delta(r - r')f_{xc}^{\text{hom}}(n(r), q = 0, \omega)$$

Compare

$$f_{xc}^{\text{ALDA}}[n](r, r', \omega) = \delta(r - r')f_{xc}^{\text{hom}}(n(r), q = 0, \omega = 0)$$
Fluid Dynamics

- Frequency-dependent response of the homogeneous electron gas is recovered...
- ...but several other exact conditions (e.g. translational invariance) are violated!
- Make an analogy with fluid dynamics:

\[ u(r, t) = \frac{j(r, t)}{n(r, t)} \]

- Substitute in the (linearised) continuity equation \( \frac{\partial n(r, t)}{\partial t} = -\nabla \cdot j(r, t) \) to get:

\[ \frac{\partial \delta n(r, t)}{\partial t} = -n_0(r) \nabla \cdot u(r, t) - u(r, t) \cdot \nabla n_0(r) \]

- First term is *compressive* – frequency-dependent
- Second term is *rigid* – frequency-independent
Time-Dependent Current-Density-Functional Theory

One of the most promising recent developments.
(See also the local-with-memory density approximation, 1D only so far).

- Recall:
  \[
  \int d^3r \, n(r) \nabla f_{xc}(r, r', \omega) = -\nabla' V_{xc}(r')
  \]

- For a sufficiently slowly varying density, \( f_{xc}(r, r', \omega) \) can be replaced by the (short-ranged) homogeneous electron gas limit:
  \[
  f_{xc}^{\text{hom}}(n(r), q = 0, \omega) \nabla n(r) = \nabla V_{xc}(r)
  \]

- Impossible since the right-hand side is frequency-independent!

- The exchange-correlation kernel for an inhomogeneous system must be long-ranged and non-local
Example: Molecular Chains

- External field induces charges at the end points of the chain

- Influence of these charges should result in a counteracting exchange-correlation potential along the chain

- But local approximations can’t see these charges!

- Hence the polarisability is overestimated by the ALDA

- Need an ultra-non-local exchange-correlation functional
Enter the Current Density


- Current must flow to establish the induced charges
- The *local* current tells us about non-local changes in the density
- Can replace the ultra-non-local density approximation by a local current density approximation
- Satisfies exact conditions
- Caveat: only valid for high frequencies
- But when did that ever stop us?
Results

FIG. 1. ALDA and VK static axial polarizability of polyacetylene compared with restricted Hartree-Fock [18] and MP2 [22] results.