Introduction to Time-Dependent Density-Functional Theories

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Abbreviated Outline

DFT = Density-Functional Theory

not to be confused with Discrete Fourier Transform

TDDFT = Time-Dependent Density-Functional Theory

sometimes just TDFT

TDCDFT = Time-Dependent Current-Density-Functional Theory

Density-Functional Theory

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

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

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:

$$n_0(\mathbf{r}) = N \int \prod_{i=2}^{N} d^3 r_i \, |\Phi_0(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2$$

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 $|\Phi'\rangle = |\Phi\rangle \exp(-\mathrm{i}\Delta t)$).

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

$$V(\mathbf{r}) \longrightarrow n_0(\mathbf{r})$$

The Hohenberg-Kohn Theorems

P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, 864 (1964).

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

$$V(\mathbf{r}) \longleftrightarrow n_0(\mathbf{r})$$

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 $V_{\rm ext}(\mathbf{r})$,

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

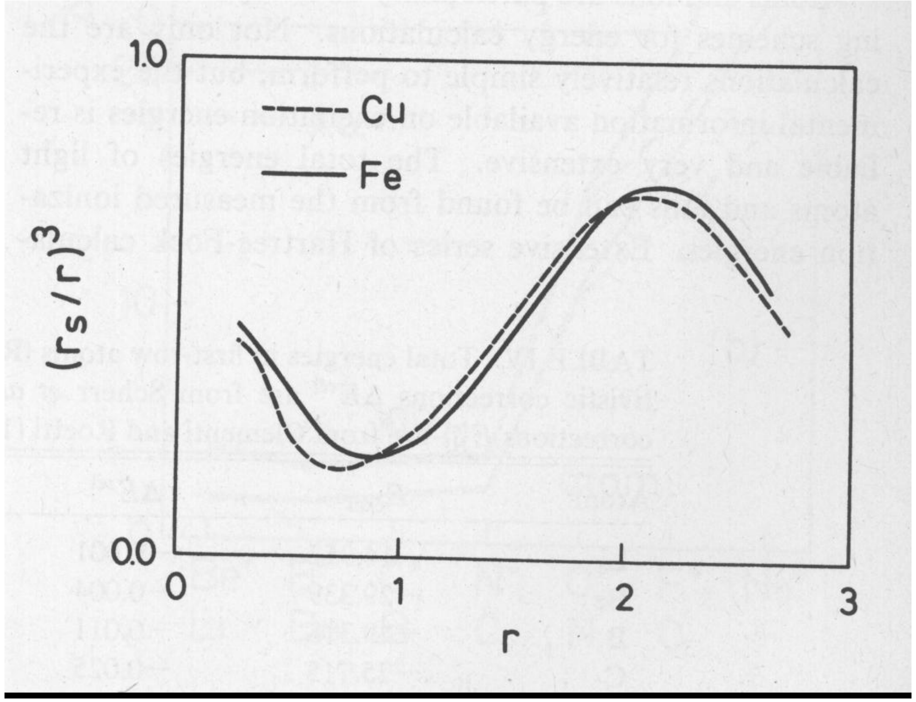
Solve:

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

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.



From R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).

Kohn-Sham Mapping

W. Kohn and L. J. Sham, *Phys. Rev.* **140**, 1133 (1965).

"Shuffle the pack" – $F[n] = T_\mathrm{s}[n] + \frac{1}{2}\int d^3r\, d^3r'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_\mathrm{xc}[n]$

$$\Rightarrow \frac{\delta T_\mathrm{s}[n]}{\delta n(\mathbf{r})} + \underbrace{\int d^3r'\, \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V_\mathrm{xc}(\mathbf{r}) + V_\mathrm{ext}(\mathbf{r})}_{V_\mathrm{eff}(\mathbf{r})} = \mu$$

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

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:

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

where

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

and

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

- Since $V_{\rm eff}(\mathbf{r})$ 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 $E_{\rm xc}[n]$!

Local Density Approximation

$$E_{\mathrm{xc}}[n] = \int d^3r\, \epsilon_{\mathrm{xc}}^{\mathrm{hom}}\,(n(\mathbf{r}))\, n(\mathbf{r})$$

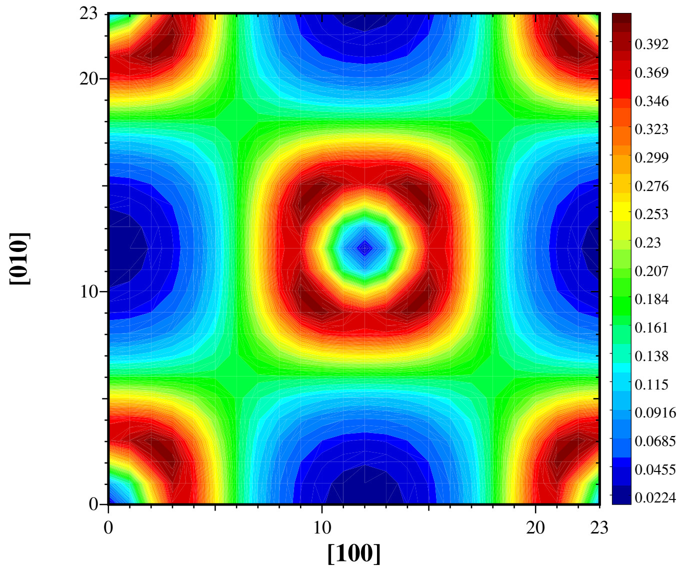
- $E_{\mathrm{xc}}[n]$ for the homogeneous electron gas is known from Quantum Monte Carlo
  D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980),

- and their results have been parametrised
  J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

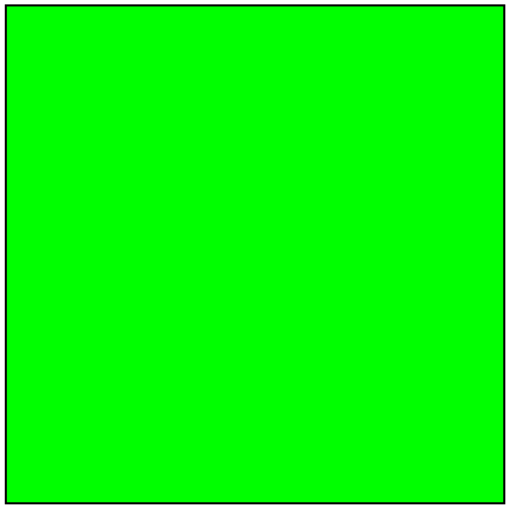
Successes

The LDA has no right to succeed:

Charge density in (001) plane



Homogeneous electron gas



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

Exact Conditions

- Exchange-correlation hole sum rule:

$$\int d^3r'\, n_{\rm xc}(\mathbf{r},\mathbf{r}') = -1$$

- $E_{\rm xc}[n]$ depends only weakly on the *shape* of the exchange-correlation hole

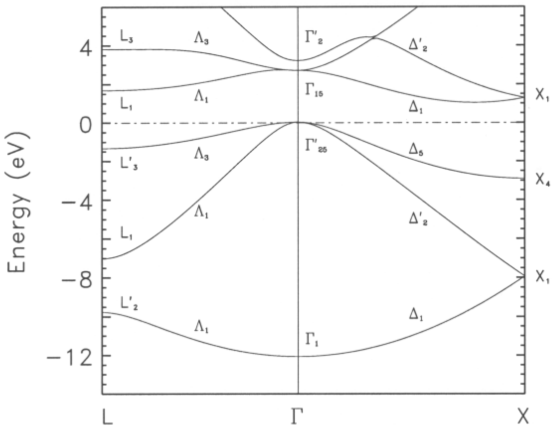
- Newton's Third Law:

$$\begin{aligned}\int d^3r\, n(\mathbf{r})\nabla V_{\rm xc}(\mathbf{r}) &= 0\\ \int d^3r\, n(\mathbf{r})\, \mathbf{r}\times\nabla V_{\rm xc}(\mathbf{r}) &= 0\end{aligned}$$

Failures

- Self-interaction (c.f. Hartree-Fock) – for the hydrogen atom:
  - $V_{\mathrm{eff}}(\mathbf{r}) = -\dfrac{1}{r}$
  - therefore $V_{\mathrm{xc}}(\mathbf{r}) = -V_{\mathrm{H}}(\mathbf{r})$
  - $E_0^{\mathrm{LDA}} =$ -0.89 Ry

- The "band-gap" problem:
  - 'Kohn-Sham eigenvalues have no physical significance.'
  - Sham-Schlüter equation relates $V_{\mathrm{xc}}(\mathbf{r})$ to thr self-energy of many-body theory



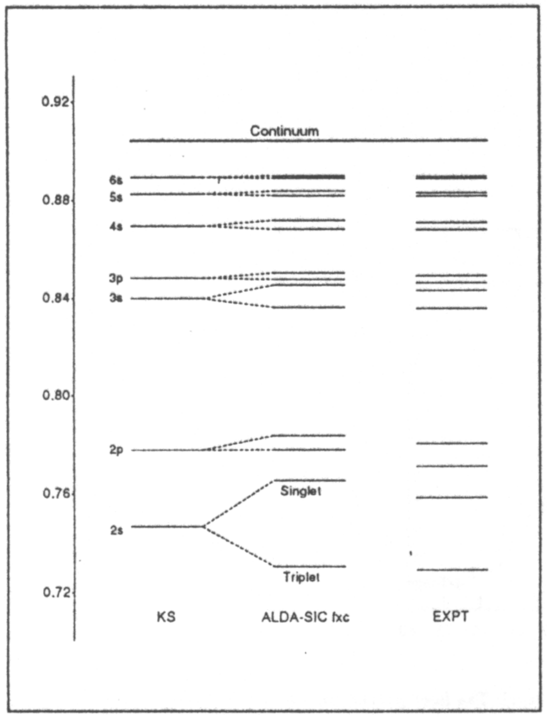
G. L. Zhao, D. Bagayoko and T. D. Williams (unpublished)

Time-Dependent Density-Functional Theory

Why the excitement?

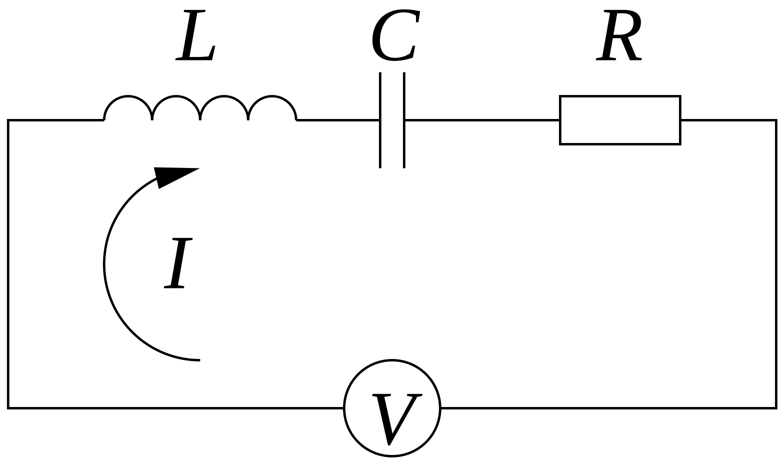
- Study time-dependent phenomena e.g. response of atoms to intense laser pulses (electromagnetic field strengths comparable to electron-nuclear field).

- Study excited states of a system e.g. He atom:



M. Petersilka (unpublished)

Response Functions



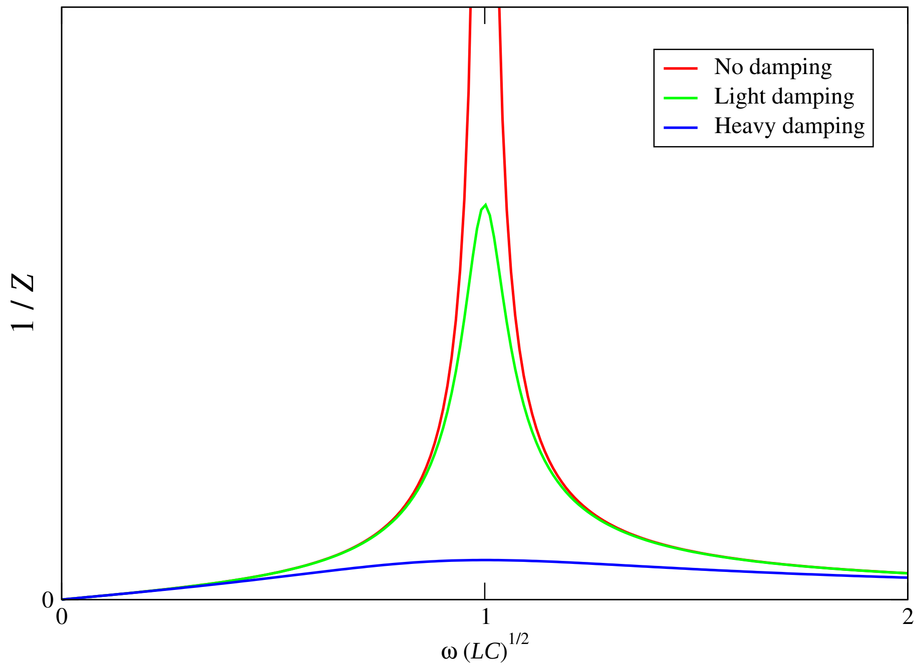
When subject to an applied time-dependent voltage $V(t) = V_0 \exp(\mathrm{i}\omega t)$, the above circuit responds with a current $I(t) = I_0 \exp(\mathrm{i}\omega t)$ where the response is characterised by an impedance Z given by:

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

Resonance and Excitation

The undamped system $(R = 0)$ can respond without applied voltage at the frequency ω 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 ω. The response function has poles at *all* the excitation energies of the system.

Time-Dependent Density-Functional Theory

The Runge-Gross theorem E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984) establishes the one-to-one mapping between time-dependent densities and potentials (analogous to the Hohenberg-Kohn theorem).

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

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

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

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

Exchange-Correlation Kernel

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

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

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

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 $\chi_0(\mathbf{r}, \mathbf{r}', \omega)$ we can put everything together:

$$\begin{aligned}\chi_0^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta V_{\text{eff}}(\mathbf{r}, \omega)}{\delta n(\mathbf{r}', \omega)} &= \frac{\delta V_{\text{ext}}(\mathbf{r}, \omega)}{\delta n(\mathbf{r}', \omega)} + \frac{\delta V_{\text{H}}(\mathbf{r}, \omega)}{\delta n(\mathbf{r}', \omega)} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \\ &= \chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) + \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega)\end{aligned}$$

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

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

A *static* calculation gives us the information we need.

Exact Conditions

- $f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',t-t')=0$ for $t<t'$
- As $\omega\to\infty$, $f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\omega)$ approaches a real function
- $f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\omega)-f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\infty)$ satisfies Kramers-Kronig relations
- $f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\omega)=f^{*}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',-\omega)$
- $f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\omega)=f_{\mathrm{xc}}(\mathbf{r}',\mathbf{r},\omega)$

Newton's Third Law again

- Recall

$$\int d^3r\, n(\mathbf{r})\nabla V_{\rm xc}(\mathbf{r}) = 0$$

- Take functional derivative with respect to n($\mathbf{r}$'):

$$\nabla' V_{\rm xc}(\mathbf{r}') + \int d^3r\, n(\mathbf{r})\nabla f_{\rm xc}(\mathbf{r},\mathbf{r}',\omega) = 0$$

- Multiply by $n(\mathbf{r}')$ and integrate over $\mathbf{r}'$:

$$\int d^3r \int d^3r'\, n(\mathbf{r})n(\mathbf{r}')\nabla f_{\rm xc}(\mathbf{r},\mathbf{r}',\omega) = 0$$

- Similarly

$$\int d^3r \int d^3r'\, n(\mathbf{r})n(\mathbf{r}')\, \mathbf{r}\times\nabla f_{\rm xc}(\mathbf{r},\mathbf{r}',\omega) = 0$$

Translational invariance

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

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

- The exchange-correlation potential must satisfy:

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

- 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:

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

- 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 $f_{\mathrm{xc}}^{\mathrm{hom}}(n, |\mathbf{r}-\mathbf{r}'|, \omega)$ is:

- Non-local in space
- Frequency dependent

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

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

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

Compare

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

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:

$$\mathbf{u}(\mathbf{r},t) = \frac{\mathbf{j}(\mathbf{r},t)}{n(\mathbf{r},t)}$$

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

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

  - 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:

$$\int d^3r\, n(\mathbf{r})\nabla f_{\rm xc}(\mathbf{r},\mathbf{r}',\omega) = -\nabla' V_{\rm xc}(\mathbf{r}')$$

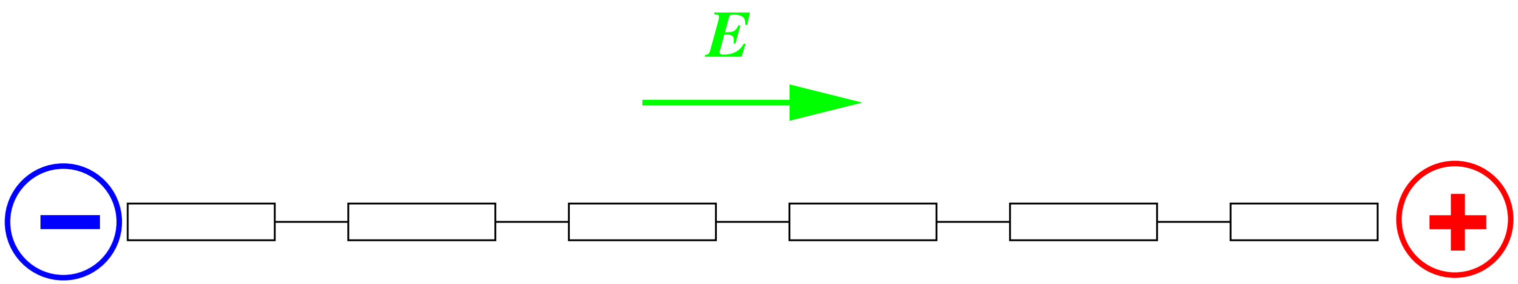
- For a sufficiently slowly varying density, $f_{\rm xc}(\mathbf{r},\mathbf{r}',\omega)$ can be replaced by the (short-ranged) homogeneous electron gas limit:

$$f_{\rm xc}^{\rm hom}(n(\mathbf{r}), q=0, \omega)\nabla n(\mathbf{r}) = \nabla V_{\rm xc}(\mathbf{r})$$

- 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

G. Vignale and W. Kohn, *Phys. Rev. Lett.* **77**, 2037 (1996).

- 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
- Satisifes exact conditions
- Caveat: only valid for high frequencies
- But when did that ever stop us?

Results

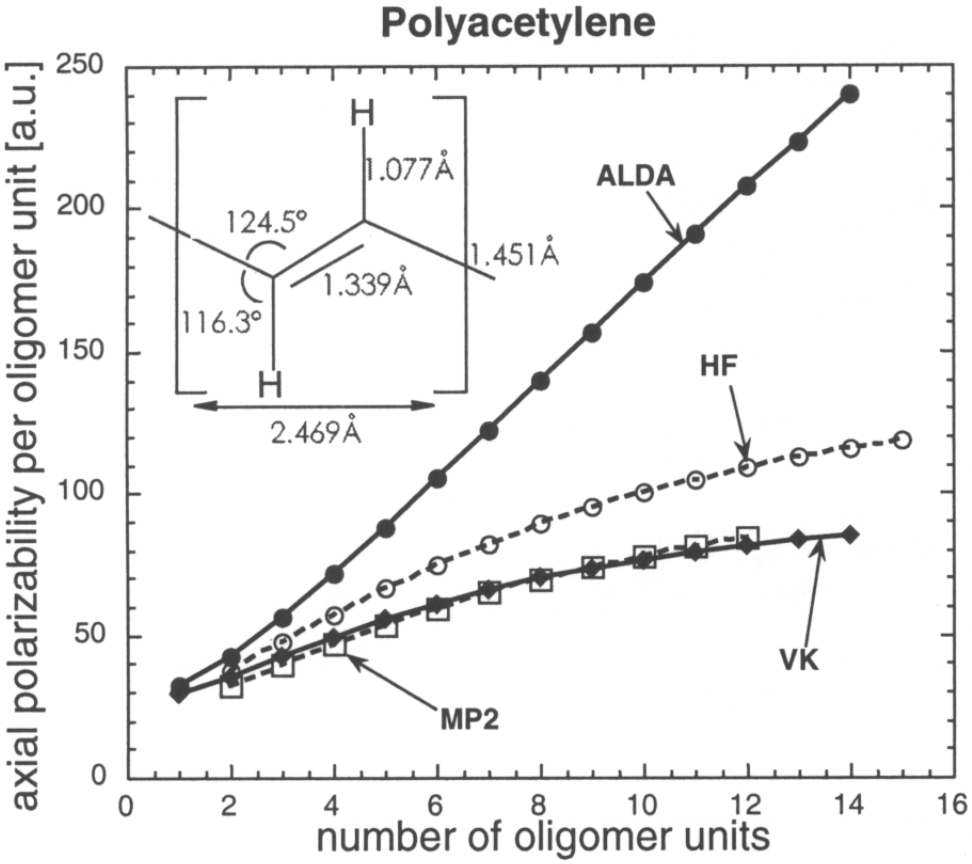


FIG. 1. ALDA and VK static axial polarizability of polyacetylene compared with restricted Hartree-Fock [18] and MP2 [22] results.

M. van Faassen *et al.*, *Phys. Rev. Lett.* **88**, 186401 (2002).