

Time-dependent density functional theory

Hande Üstünel

November 1, 2007

Outline

- 1 Introduction
- 2 DFT vs TDDFT
- 3 Excitation energies

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The TDDFT idea

General DFT idea

Map a system of N interacting particles onto one with N noninteracting particles

$$\Psi(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_N) \implies \{\phi_i(\vec{r})\} \quad (i = 1, \dots, N)$$

- **Time-independent** formalism \Rightarrow **ground state** theory (static potential)
- **Time-dependent** formalism \Rightarrow **excited states** (time-dependent potential)
- Time-independent formalism fails to describe single-particle excitations well.
- Interaction with electromagnetic field — spectroscopy

DFT vs TDDFT — looking ahead

DFT	TDDFT
Ground state	Excited states
Hohenberg-Kohn theorem	Runge-Gross theorem
Minimum of total energy	Stationary point of the action
Stationary orbitals	Time-dependent orbitals
Stationary density	Time-dependent density

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Hohenberg-Kohn theorem I

There is a one-to-one correspondence between any external potential on the system and the resulting electron density (up to a constant).

Two external potentials differing by **more than** an additive constant

$$v_{\text{ext}}^1(\vec{r}) - v_{\text{ext}}^2(\vec{r}) \neq \text{constant}$$

result in two different densities

$$n^1(\vec{r}) \neq n^2(\vec{r}).$$

Runge-Gross theorem I

There is a one-to-one correspondence between any time-dependent external potential on the system and the resulting time-dependent density (up to a **time-dependent constant**).

Two external potentials differing by **more than** a time-dependent constant

$$v_{\text{ext}}^1(\vec{r}, t) - v_{\text{ext}}^2(\vec{r}, t) \neq C(t)$$

result in two different densities

$$n^1(\vec{r}, t) \neq n^2(\vec{r}, t).$$

Hohenberg-Kohn theorem II

The energy can be written as a **functional** of the density, $n(\vec{r})$.

$$E[n] = \underbrace{T[n] + E_H[n] + E_{xc}[n]}_{\text{universal}} + E_{\text{ext}}[n]$$

$$T[n] = -\frac{1}{2} \sum_i \int \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r})$$

$$E_H[n] = \frac{1}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}d\vec{r}'$$

$$E_{xc}[n] = \int n(\vec{r})\epsilon_{xc}(n(\vec{r}))d\vec{r}$$

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

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$

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Runge-Gross Theorem III

The action integral can be written as a **functional** of the time-dependent density, $n(\vec{r}, t)$.

- Ψ is uniquely determined by the density.

$$A = \int_{t_0}^{t_1} dt \left\langle \Psi[n] \left| i \frac{\partial}{\partial t} - \hat{H} \right| \Psi[n] \right\rangle$$

where

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$$

- The universal part this time :

$$B[n] = A[n] + \int_{t_0}^{t_1} dt \int d\vec{r} n(\vec{r}, t) V_{ext}(\vec{r}, t)$$

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Exchange and correlation in DFT

Exchange and correlation defined as the difference between the total energies of the interacting and noninteracting systems

- The real and uncorrelated **kinetic** energies

$$T^{\text{real}} = \left\langle \Psi^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t) \left| \hat{T} \right| \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t) \right\rangle$$

$$T^u = -\frac{1}{2} \sum_i \int d\vec{r} \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r})$$

- The real and uncorrelated **interaction** energies

$$E_{ee}^{\text{real}} = \int d\vec{r} d\vec{r}' \frac{n(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \quad E_{ee}^u = \int d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$E_{xc} = T^{\text{real}} - T^u + E_{ee}^{\text{real}} - E_{ee}^u$$

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Exchange and correlation in TDDFT

- Kinetic energy analog

$$S_w[n] = \int_{t_0}^{t_1} dt \left\langle \Psi_w[n](t) \left| i \frac{\partial}{\partial t} - \hat{T} \right| \Psi_w[n](t) \right\rangle$$

- Interaction energy analog

$$E_{ee}^{\text{real}} = \int_{t_0}^{t_1} \int d\vec{r} d\vec{r}' V_{ee} n(\vec{r}, \vec{r}', t)$$

$$E_{ee}^u = \frac{1}{2} \int_{t_0}^{t_1} \int d\vec{r} d\vec{r}' n(\vec{r}, t) V_{ee}(\vec{r}, \vec{r}') n(\vec{r}', t)$$

$$A_{xc}[n] = E_{ee}^{\text{real}} - E_{ee}^u + S_0[n] - S_w[n]$$

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Exchange-correlation approximation

LDA (Local Density Approximation) in DFT

For slow **spatial** variation

$$E_{xc}[n] = \int d\vec{r} n(\vec{r}) \varepsilon_{xc}^{hom}[n(\vec{r})]$$

ALDA (Adiabatic Local Density Approximation) in DFT

For slow **spatial** and **temporal** variation

$$E_{xc}[n] = \int d\vec{r} n(\vec{r}, t) \varepsilon_{xc}^{hom}[n(\vec{r}, t)]$$

No memory is retained in the density.

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Kohn-Sham equations in DFT

Kohn-Sham equations \Rightarrow minimize energy : $\frac{\delta E[n]}{\delta n(\vec{r})}$

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{\text{xc}} \right] \phi_i(\vec{r}) = \varepsilon \phi_i(\vec{r})$$

- One-particle equations with an effective potential.
- Solve through a self-consistent loop.

Kohn-Sham equations in TDDFT

Kohn-Sham equations \Rightarrow stationary point of action : $\frac{\delta A[n(\vec{r}, t)]}{\delta n(\vec{r}, t)}$

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}, t) + \int d\vec{r}' \frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|} + V_{\text{xc}} \right] \phi_i(\vec{r}, t) = i \frac{\partial \phi_i(\vec{r}, t)}{\partial t}$$

- Euler-Lagrange equations
- Solve through a self-consistent loop.

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How to calculate excitation energies

- Begin with the Kohn-Sham wavefunctions for the occupied ground-state orbitals : $\{\phi_i^{(0)}(\vec{r})\} \Rightarrow n_0(\vec{r})$
- Consider perturbing potential $v_1(\vec{r}, t)$ and response $n_1(\vec{r}, t)$
- Linear response theory — Fourier components

$$n_1(\vec{r}, \omega) = \int d\vec{r}' \chi(\vec{r}, \vec{r}'; \omega) v_1(\vec{r}', \omega)$$

$\chi(\vec{r}, \vec{r}'; \omega)$: response function

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How to calculate excitation energies

- Replace $v_1(\vec{r}, t)$ with $v_1^{KS}(\vec{r}, t)$

$$n_1(\vec{r}, \omega) = \int d\vec{r}' \chi_{KS}(\vec{r}, \vec{r}'; \omega) v_1^{KS}(\vec{r}', \omega)$$

- From perturbation theory

$$\chi_{KS}(\vec{r}, \vec{r}', \omega) = \sum_{i,j} (f_i - f_j) \frac{\phi_i(\vec{r})^* \phi_j(\vec{r}) \phi_j(\vec{r}') \phi_i(\vec{r}')}{\omega - (\epsilon_i - \epsilon_j) + i\delta} \quad (1)$$

- Solve self-consistently to obtain excited energies.
- Better than static theory because it includes dynamic screening

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Shortcomings

- Captures only single electron-hole excitations (absorption)

$$\Psi(t) = \begin{vmatrix} \phi_1(\vec{r}_1, t) & \phi_1(\vec{r}_2, t) & \cdots & \phi_1(\vec{r}_N, t) \\ \phi_2(\vec{r}_1, t) & \phi_2(\vec{r}_2, t) & \cdots & \phi_2(\vec{r}_N, t) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_N(\vec{r}_1, t) & \phi_N(\vec{r}_2, t) & \cdots & \phi_N(\vec{r}_N, t) \end{vmatrix}$$

- Doesn't allow for mixing of the single electron-hole excitation, e.g. plasmon excitations (EELS)