MBPT versus TDDFT

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Outline

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Overall comparison

MBPT

MBPT: based on Green's functions.

One-particle G: electron addition and removal.

Two-particle G_2: for example, electron-hole excitation (optics etc)

TDDFT

TDDFT: only neutral excitations (optics etc)

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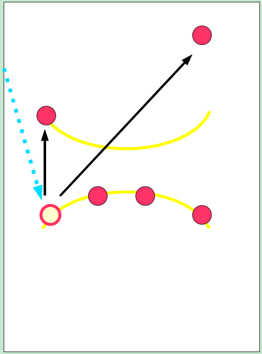
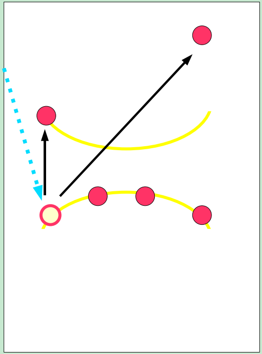


MBPT: based on the idea of moving (quasi-)particles around.

Overall comparison

MBPT

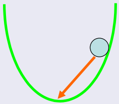


MBPT: based on the idea of moving (quasi-)particles around.

Overall comparison

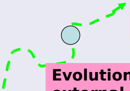
TDDFT moves density around

Equilibrium position: minimization of E



Ground state: DFT min[E]

Density propagation



Trajectory: extrema of the action A

Evolution of the system (its density) due to external field: TD-DFT [A]

Runge and Gross 1984

Outline

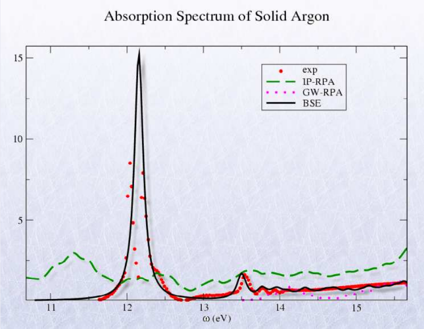
Strong points

MBPT

MBPT is intuitive - and leads to intuitive (reliable!) approximations

One-particle G: electron addition and removal - GW

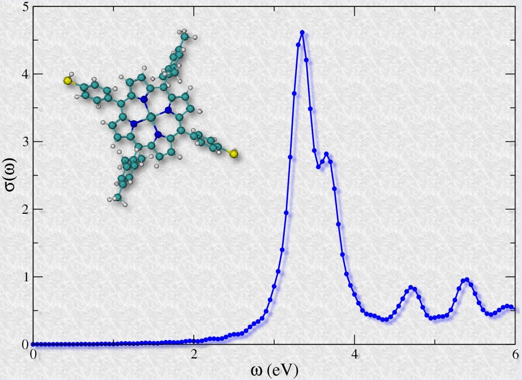
Two-particle G_2: for example, electron-hole excitation (optics etc) - BSE



Strong points

TDDFT

MBPT deals with variations of the (local!) density - it is efficient!



Outline

Two Particles

Bethe-Salpeter Equation

We work in transition space...

$$L(1234,\omega) \Rightarrow L^{(n_3 n_4)}_{(n_1 n_2)}(\omega) =$$

$$= \int d(1234) L(1234,\omega)\phi_{n_1}(1)\phi^*_{n_2}(2)\phi_{n_3}(3)\phi^*_{n_4}(4)$$

... and go back in real space.

$$L^{(n_3 n_4)}_{(n_1 n_2)}(\omega) \Rightarrow L(1234,\omega) \Rightarrow L(1133,\omega)$$

$$\phi_{KS}(\mathbf{r})$$

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$$\phi_{\mathrm{KS}}(\mathbf{r})$$

Bethe-Salpeter Equation

Polarizability in BSE (only resonant approximation)

$$L(\mathbf{r},\mathbf{r}',\omega) = \sum_{\lambda} \frac{\sum_{vc} A_{\lambda}^{(vc)} \phi_v(\mathbf{r})\phi_c^*(\mathbf{r})\phi_v^*(\mathbf{r}')\phi_c(\mathbf{r}') A_{\lambda}^{*(vc)}}{\omega - E_{\lambda}^{exc} + i\eta}$$

Onida, Reining, Rubio, RMP **74**, 601 (2002)

http://theory.polytechnique.fr/people/sottile/Tesi_dot.pdf

Bethe-Salpeter Equation

$E_\lambda, \; A_\lambda$ solution of the BSE in transition space

$$H^{2p,exc}_{(vc)(v'c')} A^{(v'c')}_\lambda = E^{exc}_\lambda A^{(vc)}_\lambda$$

Only resonant approximation

Bethe-Salpeter Equation

$E_\lambda,\ A_\lambda$ solution of the BSE in transition space

$$H^{2p,exc}_{(vc)(v'c')} A_\lambda^{(v'c')} = E_\lambda^{exc} A_\lambda^{(vc)}$$

Only resonant approximation

Bethe-Salpeter Equation

Excitonic (2p) Hamiltonian

$$H^{exc}_{(vc)(v'c')} = \int \phi_v(1)\phi^*_c(2) \left[\left(L^0\right)^{-1} + v - W \right] \phi_{v'}(3)\phi^*_{c'}(4)$$

$$H^{exc}_{(vc)(v'c')} = (E_c - E_v)\, \delta_{vv'}\delta_{cc'} + v^{v'c'}_{vc} - W^{v'c'}_{vc}$$

Bethe-Salpeter Equation versus TDDFT

BSE Screening equation

$$L = L^0 + L^0(v - W)L$$

TDDFT screening equation

$$\chi = \chi^0 + \chi^0(v + f_{xc})\chi$$

TDDFT

Work in transition space ?

$$L^{TDDFT}(1234,\omega) \Rightarrow L_{(n_1 n_2)}^{(n_3 n_4)}(\omega) =$$

$$= \int d(1234) L^{TDDFT}(1234,\omega)\phi_{n_1}(1)\phi^*_{n_2}(2)\phi_{n_3}(3)\phi^*_{n_4}(4)$$

... and go back in real space.

$$L_{(n_1 n_2)}^{TDDFT,(n_3 n_4)}(\omega) \Rightarrow L(1234,\omega) \Rightarrow L^{TDDFT}(1133,\omega)$$

$$\phi_{KS}(\mathbf{r})$$

TDDFT

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$$L^{TDDFT}(1234,\omega) \Rightarrow L^{(n_3 n_4)}_{(n_1 n_2)}(\omega) =$$

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TDDFT

Polarizability in TDDFT (only resonant approximation)

$$L^{TDDFT}(\mathbf{r},\mathbf{r}',\omega) = \sum_{\lambda} \frac{\sum_{vc} \bar{A}_{\lambda}^{(vc)} \phi_v(\mathbf{r})\phi_c^*(\mathbf{r})\phi_v^*(\mathbf{r}')\phi_c(\mathbf{r}')\bar{A}_{\lambda}^{*(vc)}}{\omega - \bar{E}_{\lambda} + i\eta}$$

TDDFT

$E_\lambda,\ A_\lambda$ solution of TDDFT in transition space

$$H^{2p,TDDFT}_{(vc)(v'c')}\bar{A}^{(v'c')}_\lambda = \bar{E}_\lambda \bar{A}^{(vc)}_\lambda$$

Only resonant approximation, similar for full

TDDFT

$E_\lambda, \ A_\lambda$ solution of TDDFT in transition space

$$H^{2p,TDDFT}_{(vc)(v'c')}\bar{A}^{(v'c')}_\lambda = \bar{E}_\lambda \bar{A}^{(vc)}_\lambda$$

Only resonant approximation, similar for full

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TDDFT (2p) Hamiltonian

$$H^{TDDFT}_{(vc)(v'c')} = \int \phi_v(1)\phi^*_c(2) \left[(\chi^0)^{-1} + v + f_{xc}\right] \phi_{v'}(3)\phi^*_{c'}(4)$$

$$H^{TDDFT}_{(vc)(v'c')} = \left(E^{KS}_c - E^{KS}_v\right) \delta_{vv'}\delta_{cc'} + v^{v'c'}_{vc} + fxc^{v'c'}_{vc}$$

TDDFT

4 point formulation

$$\chi^0(\mathbf{r},\mathbf{r}',\omega) = \sum_{vc} \frac{\phi_v(\mathbf{r})\phi_c^*(\mathbf{r})\phi_v^*(\mathbf{r}')\phi_c(\mathbf{r}')}{\omega - (\epsilon_c - \epsilon_v) + i\eta}$$

$$\chi^0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,\omega) = \sum_{vc} \frac{\phi_v(\mathbf{r}_1)\phi_c^*(\mathbf{r}_2)\phi_v^*(\mathbf{r}_3)\phi_c(\mathbf{r}_4)}{\omega - (\epsilon_c - \epsilon_v) + i\eta}$$

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TDDFT

4 point formulation

$$v(\mathbf{r}-\mathbf{r}') \Longrightarrow v(\mathbf{r}_1-\mathbf{r}_3)\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(\mathbf{r}_3-\mathbf{r}_4)$$

$$f_{xc}(\mathbf{r}-\mathbf{r}') \Longrightarrow f_{xc}(\mathbf{r}_1-\mathbf{r}_3)\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(\mathbf{r}_3-\mathbf{r}_4)$$

cf. Casida, TD-HF !

BSE

$$v(\mathbf{r}-\mathbf{r}') \Longrightarrow v(\mathbf{r}_1-\mathbf{r}_3)\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(\mathbf{r}_3-\mathbf{r}_4)$$

$$W(\mathbf{r}-\mathbf{r}') \Longrightarrow W(\mathbf{r}_1-\mathbf{r}_2)\delta(\mathbf{r}_1-\mathbf{r}_3)\delta(\mathbf{r}_2-\mathbf{r}_4)$$

BSE: unavoidable 4-point formulation, TDDFT *sometimes* convenient!

TDDFT

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Bethe-Salpeter Equation versus TDFFT

What is the meaning of the A_λ?

Interactions

We work in transition space...

$$I^{(n_3 n_4)}_{(n_1 n_2)}(\omega) =$$
$$= \int d(1234) I(1234,\omega)\phi_{n_1}(1)\phi^*_{n_2}(2)\phi_{n_3}(3)\phi^*_{n_4}(4)$$

... precisely:

$$v^{(n_3 n_4)}_{(n_1 n_2)}(\omega) =$$
$$= \int d(13) v(13)\phi_{n_1}(1)\phi^*_{n_2}(1)\phi_{n_3}(3)\phi^*_{n_4}(3)$$

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$$= \int d(13) v(13) \phi_{n_1}(1) \phi^*_{n_2}(1) \phi_{n_3}(3) \phi^*_{n_4}(3)$$

Interactions

... precisely:

$$fxc^{(n_3 n_4)}_{(n_1 n_2)}(\omega) =$$

$$= \int d(13) fxc(13,\omega)\phi_{n_1}(1)\phi^*_{n_2}(1)\phi_{n_3}(3)\phi^*_{n_4}(3)$$

... precisely:

$$W^{(n_3 n_4)}_{(n_1 n_2)}(\omega) =$$

$$= \int d(12) W(12,\omega)\phi_{n_1}(1)\phi^*_{n_2}(2)\phi_{n_3}(2)\phi^*_{n_4}(1)$$

Interactions

... precisely:

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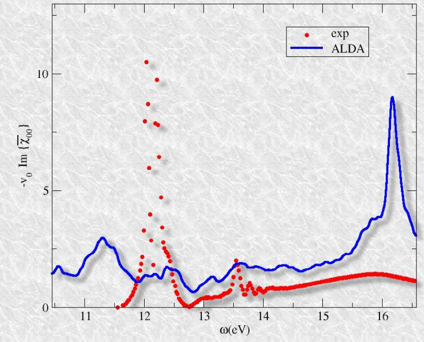
Strong points

Long range - short range



Outline

Gap problem

The gap problem

Kohn Sham versus QP gap

$$\Sigma = v_{xc} - \Delta \sum_v f_v(\mathbf{x}) f_v^*(\mathbf{x}')$$

$$\begin{aligned} G(\mathbf{x}, t; \mathbf{x}', t') &= -i \sum_j f_j(\mathbf{x}) f_j^*(\mathbf{x}') e^{-i\varepsilon_j(t-t')} \times \\ &\times \quad [\Theta(t-t')\Theta(\varepsilon_j - \mu) - \Theta(t'-t)\Theta(\mu - \varepsilon_j)]; \end{aligned}$$

$$\Sigma = v_{xc} + i\Delta G(\mathbf{x}, \mathbf{x}', t, t^+)$$

$$i\delta\Sigma/\delta G = f_{xc} - \Delta$$

Cancellation between QP gap correction and exciton binding

Outline

Time propagation

Time Evolution of KS equations

$$[H_{KS}(t)]\,\phi_i(\mathbf{r},t) = i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_i^{occ} |\phi_i(\mathbf{r},t)|^2$$

$$\phi(t) = \hat{U}(t,t_0)\phi(t_0)$$

$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau H(\tau)\hat{U}(\tau,t_0)$$

A. Castro *et al.* J.Chem.Phys. **121**, 3425 (2004)

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Time Evolution of KS equations

Photo-absorption cross section σ

$$\sigma(\omega) = \frac{4\pi\omega}{c} Im(\alpha(\omega))$$

$$\alpha(t) = -\int d\mathbf{r} V_{ext}(\mathbf{r}, t) n(\mathbf{r}, t)$$

Time Evolution ....

Time evolution of the MBPT equations?

$(\partial/\partial t)G$..... Kwong and Bonitz, Phys. Rev. Lett. **84**, 1768 (2000)