DFT for excited states: Progress in LR-TDDFT

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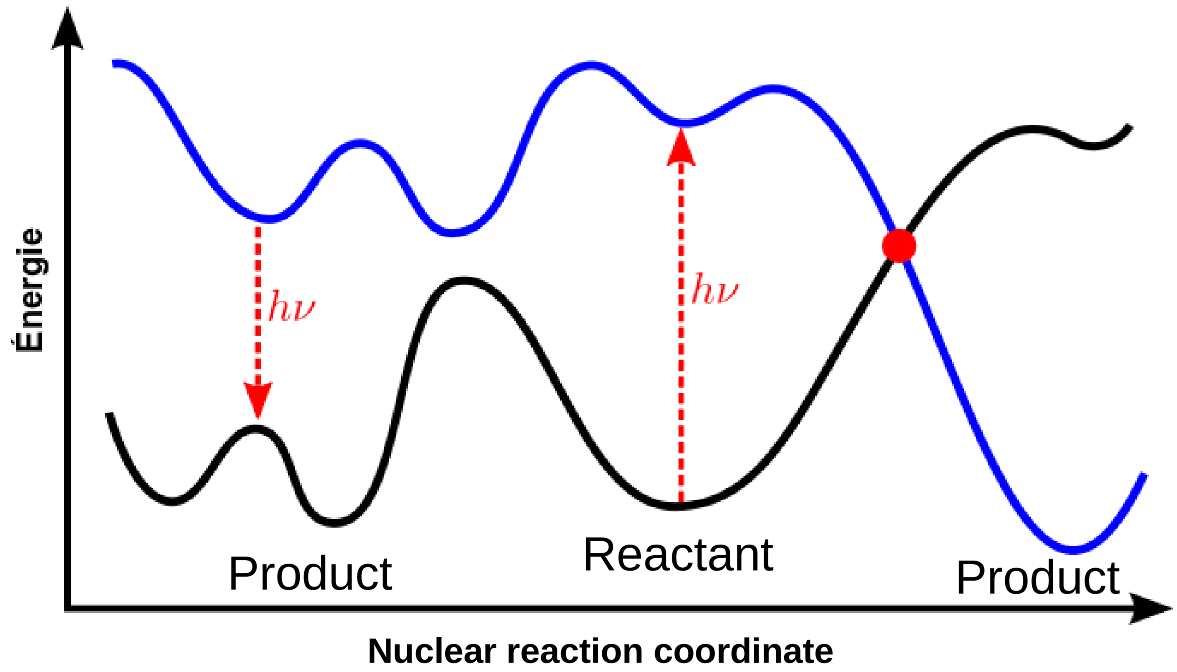
Photochemistry

Potential energy surfaces



$$\hat{H} = \hat{T}_n + \hat{T}_e + V(\mathbf{r}, \mathbf{R})$$

$$\hat{H}\Psi_i(\mathbf{r}, \mathbf{R}) = E_i \Psi_i(\mathbf{r}, \mathbf{R})$$

Electronic Born-Oppenheimer SE

$$\hat{H}_e = \hat{T}_e + V(\mathbf{r}, \mathbf{R}) \qquad \hat{H}_e \psi_i(\mathbf{r}; \mathbf{R}) = U_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

Nuclear:

$$\left(\hat{T}_n + U_i(\mathbf{R})\right) \chi_j(\mathbf{R}) - \sum_i \Lambda_{ji} \chi_i(\mathbf{R}) = E \chi_j(\mathbf{R})$$

Non-adiabatic coupling: $\Lambda_{ji} = \delta_{ij} \hat{T}_n - \int d\mathbf{r} \psi_j^*(\mathbf{r}; \mathbf{R}) \hat{T}_n \psi_i^*(\mathbf{r}; \mathbf{R})$

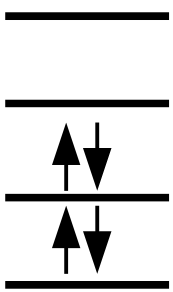
Electronic SE: Full CI

Full CI: $U_i(\mathbf{R}) = \langle \psi_i(\mathbf{R}) | \hat{H}_e | \psi_i(\mathbf{R}) \rangle \quad |\psi_i\rangle = (c_{0,i}\hat{1} + \hat{\mathbf{S}}_i + \hat{\mathbf{D}}_i + \hat{\mathbf{T}}_i + \hat{\mathbf{Q}}_i + ...)\,|0\rangle$

$$\hat{\mathbf{S}} = \sum_{ai} c_{ai}\hat{a}_a^\dagger \hat{a}_i \qquad \hat{\mathbf{D}} = \sum_{aibj} c_{aibj}\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \quad \hat{\mathbf{T}} = \sum_{aibjck} c_{aibjck}\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_k \hat{a}_j \hat{a}_i$$

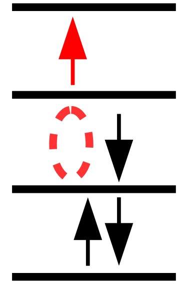
<u>Reference:</u>

$|0\rangle =$



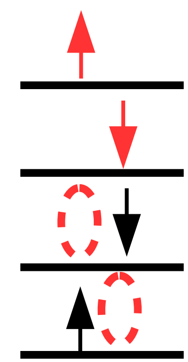
<u>Single excitation:</u>

$\hat{a}_a^\dagger \hat{a}_i |0\rangle =$



<u>Double excitation:</u>

$\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i |0\rangle =$



$$\begin{bmatrix}
\langle 0|\hat{H}_e|0\rangle & 0 & \langle 0|\hat{H}_e|D\rangle & 0 & 0 & ... \\
0 & \langle S|\hat{H}_e|S\rangle & \langle S|\hat{H}_e|D\rangle & \langle S|\hat{H}_e|T\rangle & 0 & ... \\
\langle D|\hat{H}_e|0\rangle & \langle D|\hat{H}_e|S\rangle & \langle D|\hat{H}_e|D\rangle & \langle D|\hat{H}_e|T\rangle & \langle D|\hat{H}_e|Q\rangle & ... \\
0 & \langle T|\hat{H}_e|S\rangle & \langle T|\hat{H}_e|D\rangle & \langle T|\hat{H}_e|T\rangle & \langle T|\hat{H}_e|Q\rangle & ... \\
0 & 0 & \langle Q|\hat{H}_e|D\rangle & \langle Q|\hat{H}_e|T\rangle & \langle Q|\hat{H}_e|Q\rangle & ... \\
... & ... & ... & ... & ... & ...
\end{bmatrix}$$

Excited states from DFT

$$\hat{H}_e = \hat{T}_e + V(\mathbf{r}, \mathbf{R})$$
$$\hat{H}_e \psi_i(\mathbf{r}; \mathbf{R}) = U_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

Ensemble DFT

$$\rho^w = \sum_i w_i \rho_i \qquad E^w = \sum_i w_i E[\rho_i]$$
$$\sum_i w_i = 1 \qquad w_i \geq 0$$

Ex, two states:

$$E^w = (1-w)E_0 + wE_1$$
$$\frac{dE^w}{dw} = E_1 - E_0 = \epsilon_L^w - \epsilon_H^w + \left. \frac{dE_{xc}^w[\rho^w]}{d\eta} \right|_{\eta \to w}$$

Fromager, et al. Phys. Rev. B, 95, 035120 (2017)
Gross, Oliveira, Kohn, Phys. Rev. A, 37, 2809 (1988)

$$\hat{H}(t) = \hat{T}_e + V(\mathbf{r}, \mathbf{R}) + v_{ext}(\mathbf{r}, t)$$
$$i\hbar \frac{\partial \psi_i(\mathbf{r}, t; \mathbf{R})}{\partial t} = \hat{H}(t) \psi_i(\mathbf{r}, t; \mathbf{R})$$
$$\hat{H}_e \psi_0(\mathbf{r}; \mathbf{R}) = U_0(\mathbf{R}) \psi_0(\mathbf{r}; \mathbf{R})$$

Time-dependent DFT

Response theory:

$$\delta\rho(\omega) = \chi(\omega)\delta v_{ext}(\omega)$$

Resonance condition:

$$\chi(\omega_I) = \pm\infty$$

Non-interacting system:

$$\chi(\omega) \approx \chi_s(\omega) + \chi_s(\omega) f_{Hxc}(\omega) \chi_s(\omega)$$

Ex, two states:

$$E_1 - E_0 = \epsilon_L^0 - \epsilon_H^0 + (LH|f_{Hxc}(E_1 - E_0)|HL)$$

TDDFT fundamentals

Runge-Gross theorem: $\rho(\mathbf{r},t) \rightarrow \mathbf{j}(\mathbf{r},t) \rightarrow v_{appl}(\mathbf{r},t) + c(t)$

Constrains:

(i) $v_{appl}(\mathbf{r},t)$ must be *t*-analytic

(ii) $\lim_{\mathbf{r}\rightarrow\infty} \rho(\mathbf{r},t) = 0$

Runge-Gross-Vignale action principle:

$$A[\rho] = \int_{-\infty}^{+\infty} dt \langle \Psi[\rho](t) | \hat{H} - i\frac{\partial}{\partial t} | \Psi[\rho](t) \rangle - i \langle \Psi[\rho](t) | \Psi[\rho](t) \rangle$$

Runge, E; Gross, E. K. U. Rev. Lett. 52 (12): 997–1000, (1984) ; G. Vignale, Phys. Rev. A 77, 062511 (2008)

Exact TDDFT

Exchange-correlation potential:

$$v_{xc}[\rho;\Phi_0;\Psi_0](\mathbf{r},t) = \frac{\delta A_{xc}[\rho;\Phi_0;\Psi_0]}{\delta\rho(\mathbf{r},t)}$$

Interacting initial state

Non-interacting initial state

All densities from *t0* to time *t*

Memory

$$\chi(\omega) \approx \chi_s(\omega) + \chi_s(\omega) f_{Hxc}(\omega)\chi_s(\omega)$$

$$f_{Hxc}(\mathbf{r},\mathbf{r}',\omega) = \frac{\delta v_{xc}(\mathbf{r},\omega)}{\partial\rho(\mathbf{r}',\omega)}$$

Exact Casida equations:

$$\begin{pmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ -\mathbf{B}^*(\omega) & -\mathbf{A}^*(\omega) \end{pmatrix} \begin{pmatrix} \mathbf{X}(\omega) \\ \mathbf{Y}(\omega) \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X}(\omega) \\ \mathbf{Y}(\omega) \end{pmatrix}$$

Full CI

$$A_{ia,jb}(\omega) = \left(\epsilon_a^0 - \epsilon_i^0\right)\delta_{ij}\delta_{ab} + (ia|\, f_{Hxc}(\omega)\,|bj)$$

$$B_{ia,jb}(\omega) = (ai|\, f_{Hxc}(\omega)\,|bj)$$

Adiabatic TDDFT

Exchange-correlation potential:

$$v_{xc}[\rho;\Phi_0;\Psi_0](\mathbf{r},t) \approx v_{xc}^{AA}[\rho_t](\mathbf{r}) = \frac{\delta E_{xc}[\rho_t]}{\delta \rho_t(\mathbf{r})}\delta(t)$$

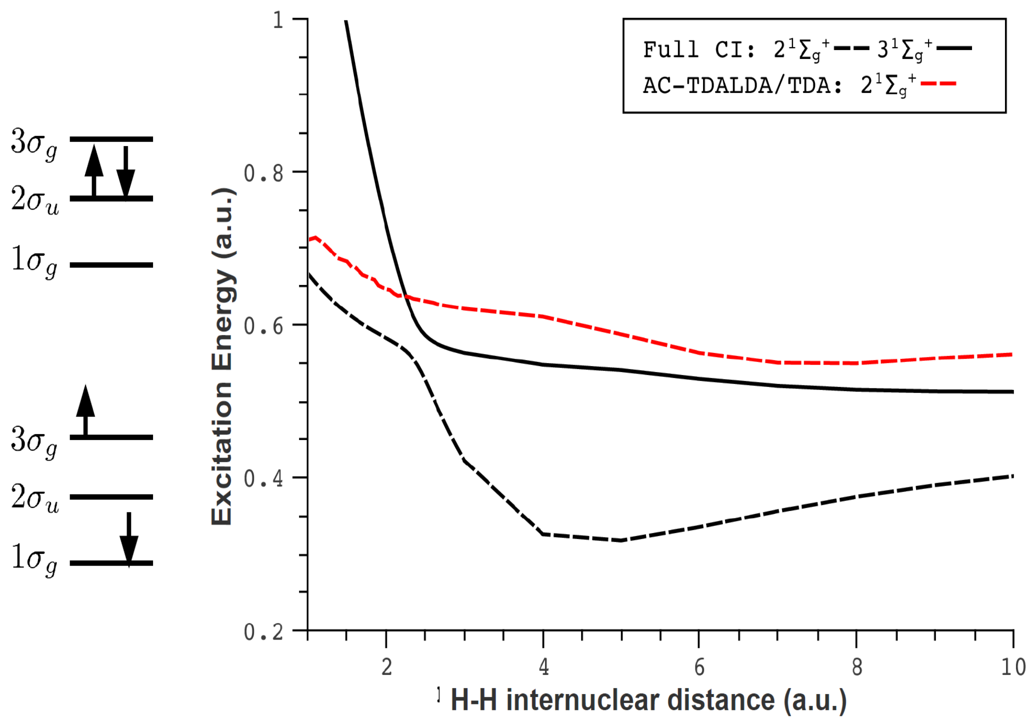
$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$A_{ia,jb} \approx \left(\epsilon_a^0 - \epsilon_i^0\right)\delta_{ij}\delta_{ab} + (ia|\, f_{Hxc}\,|bj)$$

$$B_{ia,jb} \approx (ai|\, f_{Hxc}\,|bj)$$

<u>CIS</u>

$$\omega = \left(\epsilon_a^0 - \epsilon_i^0\right)\delta_{ij}\delta_{ab} + (ia|\, f_{Hx}\,|bj)$$



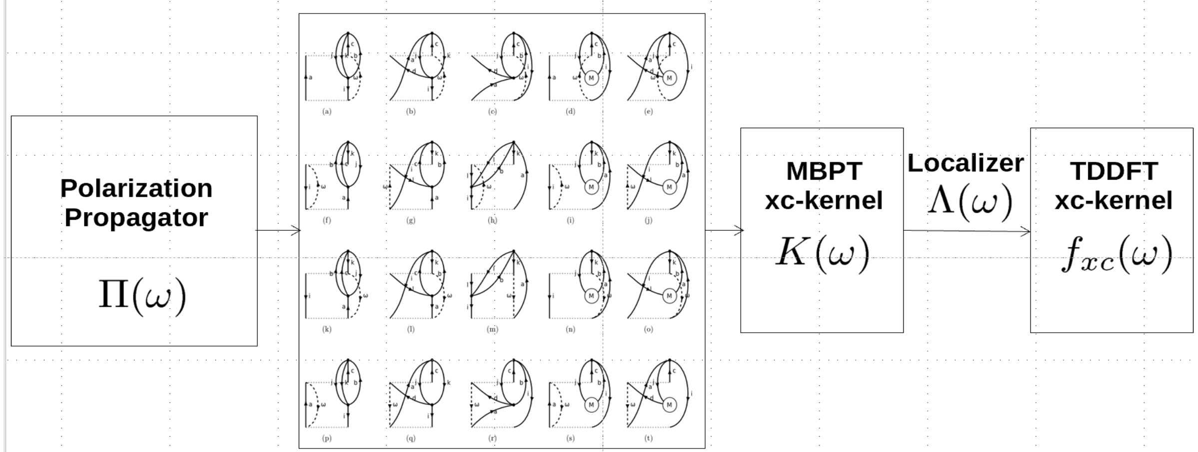
MBPT corrections to TDDFT

$$f_{Hxc}(\omega) = \chi_s^{-1}(\omega) - \chi^{-1}(\omega)$$

$$\downarrow \quad \chi(\omega) = \Upsilon \Pi(\omega) \Upsilon^\dagger$$

$$f_{Hxc}(\omega) = \left(\Upsilon \Pi_s(\omega) \Upsilon^\dagger\right)^{-1} \left[\Pi(\omega) - \Pi_s(\omega)\right] \left(\Upsilon \Pi_s(\omega) \Upsilon^\dagger\right)^{-1}$$

$$\downarrow$$



$$\downarrow$$

$$f_{Hxc}(\omega) \approx \Pi(\omega) - \Pi_s(\omega)$$

Density-Functional Methods for Excited States,
Topics Current Chemistry, 368, 1-60.

MBPT corrections to TDDFT

$$f_{Hxc}(\omega) = \chi_s^{-1}(\omega) - \chi^{-1}(\omega)$$

Density-Functional Methods for Excited States, Topics Current Chemistry, 368, 1-60.

$$\begin{pmatrix} \langle S|\hat{H}_e - E_0|S\rangle & \langle S|\hat{H}_e|D\rangle \\ \langle D|\hat{H}_e|S\rangle & \langle D|\hat{H}_e - E_0|D\rangle \end{pmatrix} \begin{pmatrix} c_S \\ c_D \end{pmatrix} = \omega \begin{pmatrix} c_S \\ c_D \end{pmatrix}$$

Löwdin partitioning technique:

$$\left[\langle S|\hat{H}_e - E_0|S\rangle + \langle S|\hat{H}_e|D\rangle \left(\omega 1_D - \langle D|\hat{H}_e - E_0|D\rangle\right)^{-1} \langle D|\hat{H}_e|S\rangle\right] c_S = \omega c_S$$

$$\left[\langle S|\hat{H}_e - E_0|S\rangle + A_D(\omega)\right] c_S = \omega c_S$$

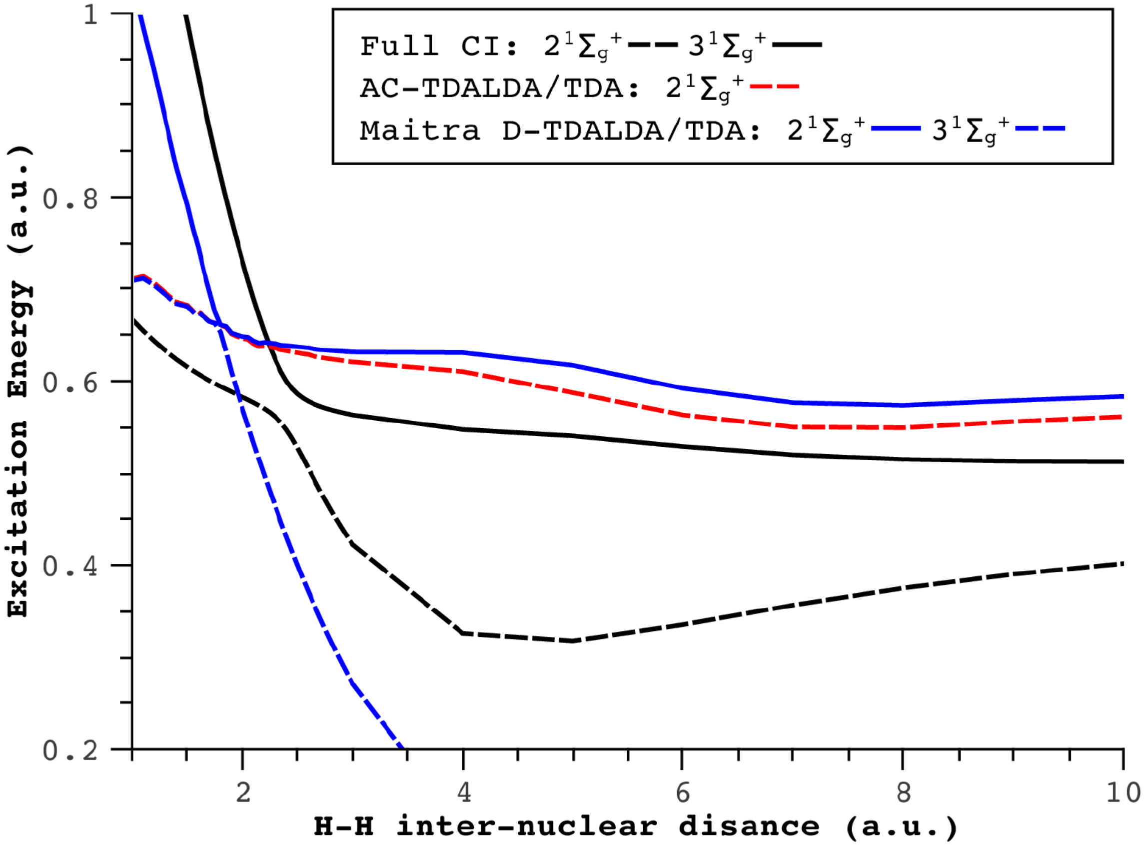
Adiabatic approximation:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

Dressed adiabatic approximation:

$$\longrightarrow \begin{pmatrix} \mathbf{A} + \mathbf{A}_D(\omega) & \mathbf{B} + \mathbf{B}_D(\omega) \\ -\mathbf{B}^* - \mathbf{B}_D^*(\omega) & -\mathbf{A}^* - \mathbf{A}_D^*(\omega) \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

Dressed TDDFT



Dressed TDDFT

$$\begin{pmatrix} E_0 & 0 & \langle 0|\hat{H}_e|D\rangle \\ 0 & \langle S|\hat{H}_e|S\rangle & \langle S|\hat{H}_e|D\rangle \\ \langle D|\hat{H}_e|0\rangle & \langle D|\hat{H}_e|S\rangle & \langle D|\hat{H}_e|D\rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_S \\ c_D \end{pmatrix} = \omega \begin{pmatrix} c_0 \\ c_S \\ c_D \end{pmatrix}$$

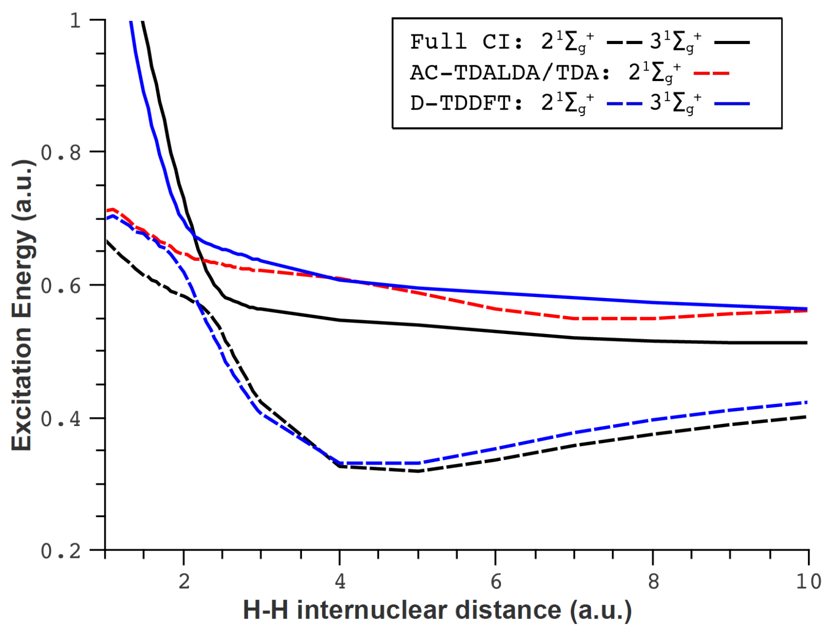
Löwdin partitioning technique

Adiabatic approximation:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

Full dressed adiabatic approximation:

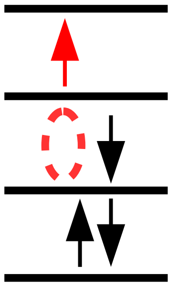
$$\begin{pmatrix} \mathbf{A} + \mathbf{A}_{0D}(\omega) & \mathbf{B} + \mathbf{B}_{0D}(\omega) \\ -\mathbf{B}^* - \mathbf{B}^*_{0D}(\omega) & -\mathbf{A}^* - \mathbf{A}^*_{0D}(\omega) \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$



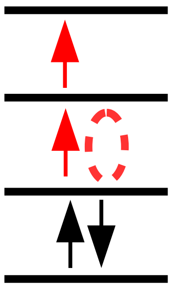
Spin-Flip TDDFT

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}^{SP}_{\alpha\alpha,\alpha\alpha} & \mathbf{A}^{SP}_{\alpha\alpha,\beta\beta} & 0 & 0 \\ \mathbf{A}^{SP}_{\beta\beta,\alpha\alpha} & \mathbf{A}^{SP}_{\beta\beta,\beta\beta} & 0 & 0 \\ 0 & 0 & \mathbf{A}^{SF}_{\alpha\beta,\alpha\beta} & 0 \\ 0 & 0 & 0 & \mathbf{A}^{SF}_{\beta\alpha,\beta\alpha} \end{pmatrix}$$

Spin-preserving excitation:

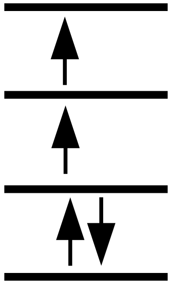


Spin-flip excitation:



Spin-flip TDDFT: $\mathbf{A}^{SF}\mathbf{X}^{SF} = \omega^{SF}\mathbf{X}^{SF}$

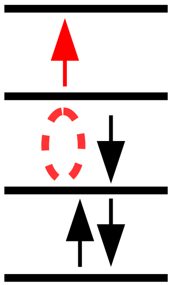
$$|0'\rangle =$$



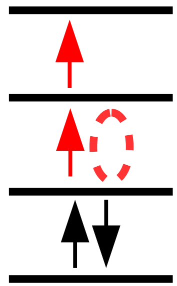
Spin-Flip TDDFT

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}^{SP}_{\alpha\alpha,\alpha\alpha} & \mathbf{A}^{SP}_{\alpha\alpha,\beta\beta} & 0 & 0 \\ \mathbf{A}^{SP}_{\beta\beta,\alpha\alpha} & \mathbf{A}^{SP}_{\beta\beta,\beta\beta} & 0 & 0 \\ 0 & 0 & \mathbf{A}^{SF}_{\alpha\beta,\alpha\beta} & 0 \\ 0 & 0 & 0 & \mathbf{A}^{SF}_{\beta\alpha,\beta\alpha} \end{pmatrix}$$

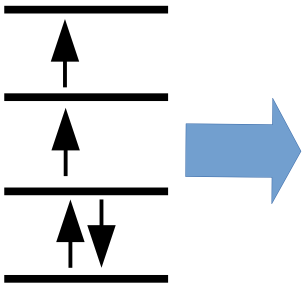
Spin-preserving excitation:



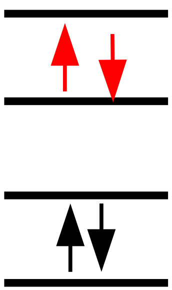
Spin-flip excitation:



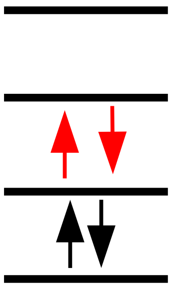
Spin-flip TDDFT: $\mathbf{A}^{SF}\mathbf{X}^{SF} = \omega^{SF}\mathbf{X}^{SF}$



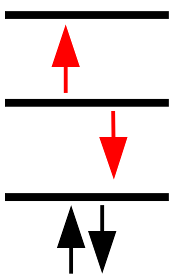
Double excitation + S=0 reference:

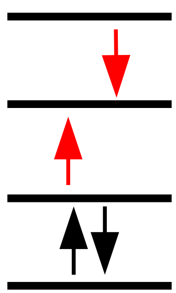


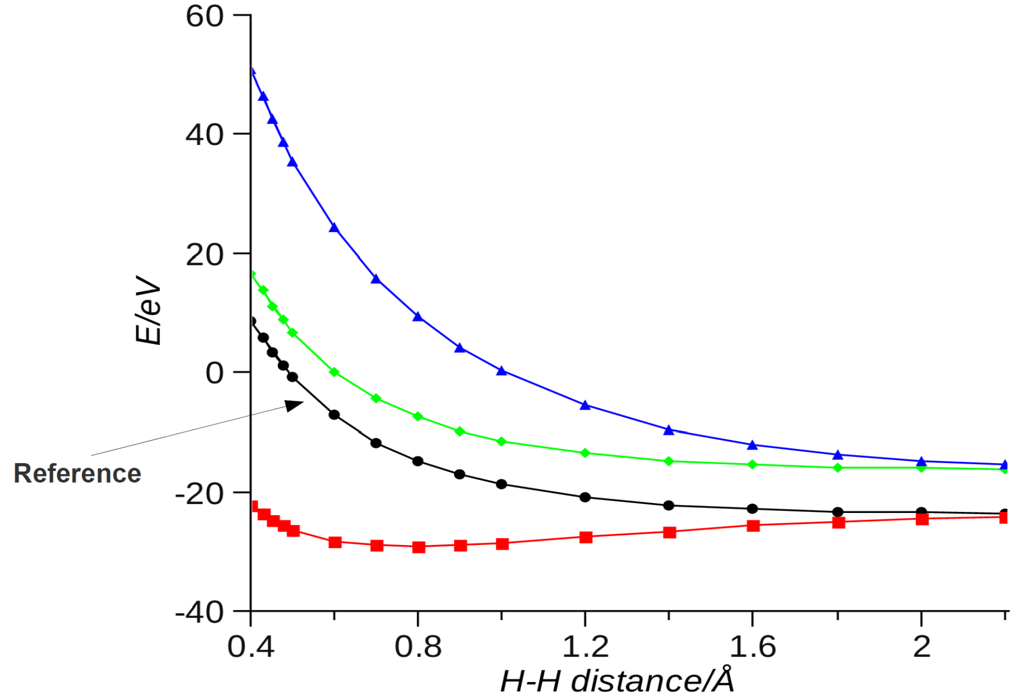
$|0\rangle =$



Singlet+Triplet:



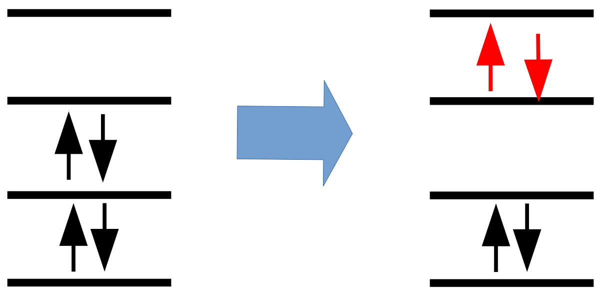




From Dressed to Spin-Flip TDDFT

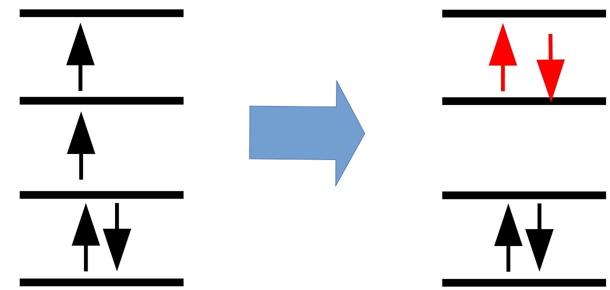
Dressed spin-preserving TDDFT:

$$|0\rangle =$$



Spin-flip TDDFT:

$$|0'\rangle =$$



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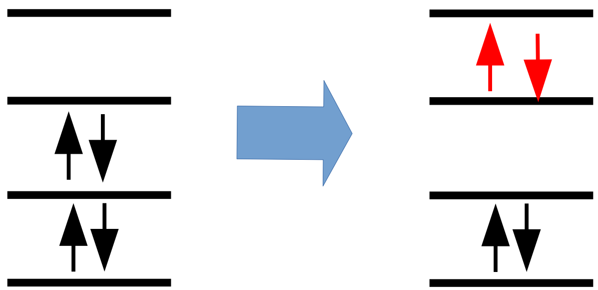

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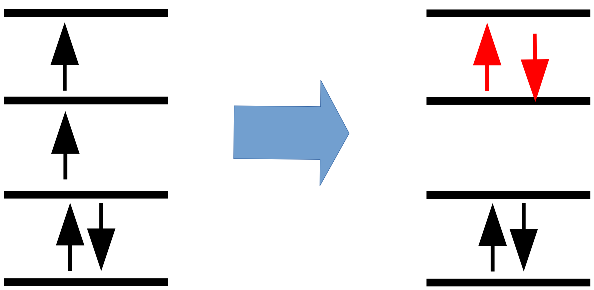
$$|0'\rangle =$$

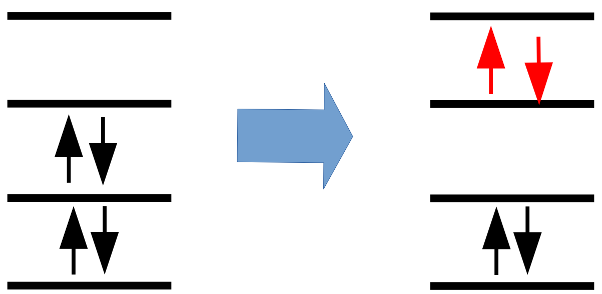


$$a^\dagger_{i,\alpha} a^\dagger_{j,\beta} a_{b,\beta} a_{a,\alpha} |0\rangle = a^\dagger_{j,\beta} a_{a,\alpha} \left[a^\dagger_{i,\alpha} a_{b,\beta} \right] |0\rangle = \left[a^\dagger_{j,\beta} a_{a,\alpha} \right] |0'\rangle$$

From Dressed to Spin-Flip TDDFT

Dressed spin-preserving TDDFT:

$|0\rangle =$



Spin-flip TDDFT:

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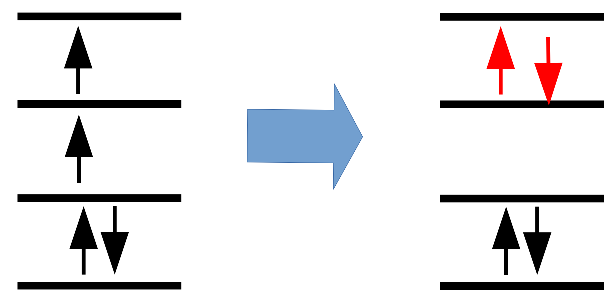
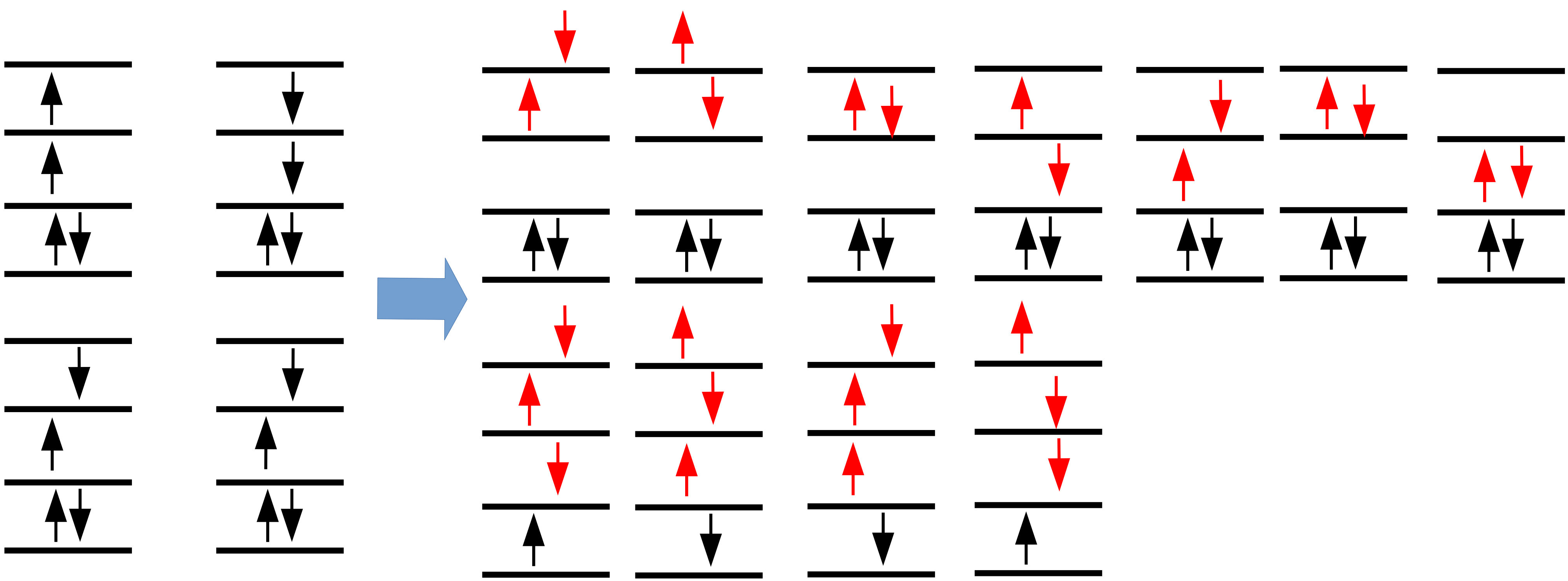


$$a^{\dagger}_{i,\alpha}a^{\dagger}_{j,\beta}a_{b,\beta}a_{a,\alpha}\,|0\rangle = \left[a^{\dagger}_{j,\beta}a_{a,\alpha}\right]\boxed{a^{\dagger}_{i,\alpha}a_{b,\beta}\,|0\rangle} = \left[a^{\dagger}_{j,\beta}a_{a,\alpha}\right]|0'\rangle$$



From Dressed to Spin-Flip TDDFT

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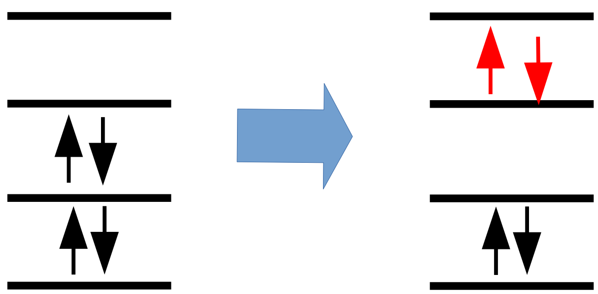
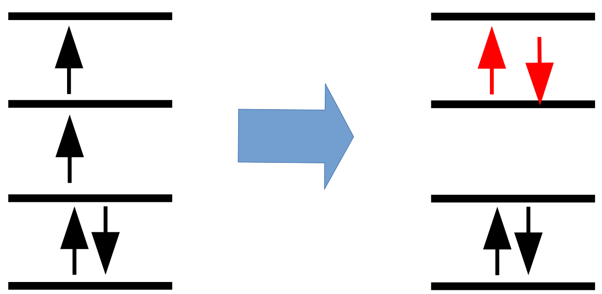
$|0\rangle =$



Spin-flip TDDFT:

$|0'\rangle =$



$$a^{\dagger}_{i,\alpha} a^{\dagger}_{j,\beta} a_{b,\beta} a_{a,\alpha} \left|0\right\rangle = \left[a^{\dagger}_{j,\beta} a_{a,\alpha}\right] \boxed{a^{\dagger}_{i,\alpha} a_{b,\beta} \left|0\right\rangle} = \left[a^{\dagger}_{j,\beta} a_{a,\alpha}\right] \left|0'\right\rangle$$

$$\mathbf{A}(\omega)\mathbf{X}(\omega) = \omega\mathbf{X}(\omega) \quad \Rightarrow \quad \mathbf{A}\mathbf{X} = \omega\mathbf{X}$$