TIME-DEPENDENT DENSITY FUNCTIONAL THEORY KERNELS FROM MANY-BODY PERTURBATION THEORY

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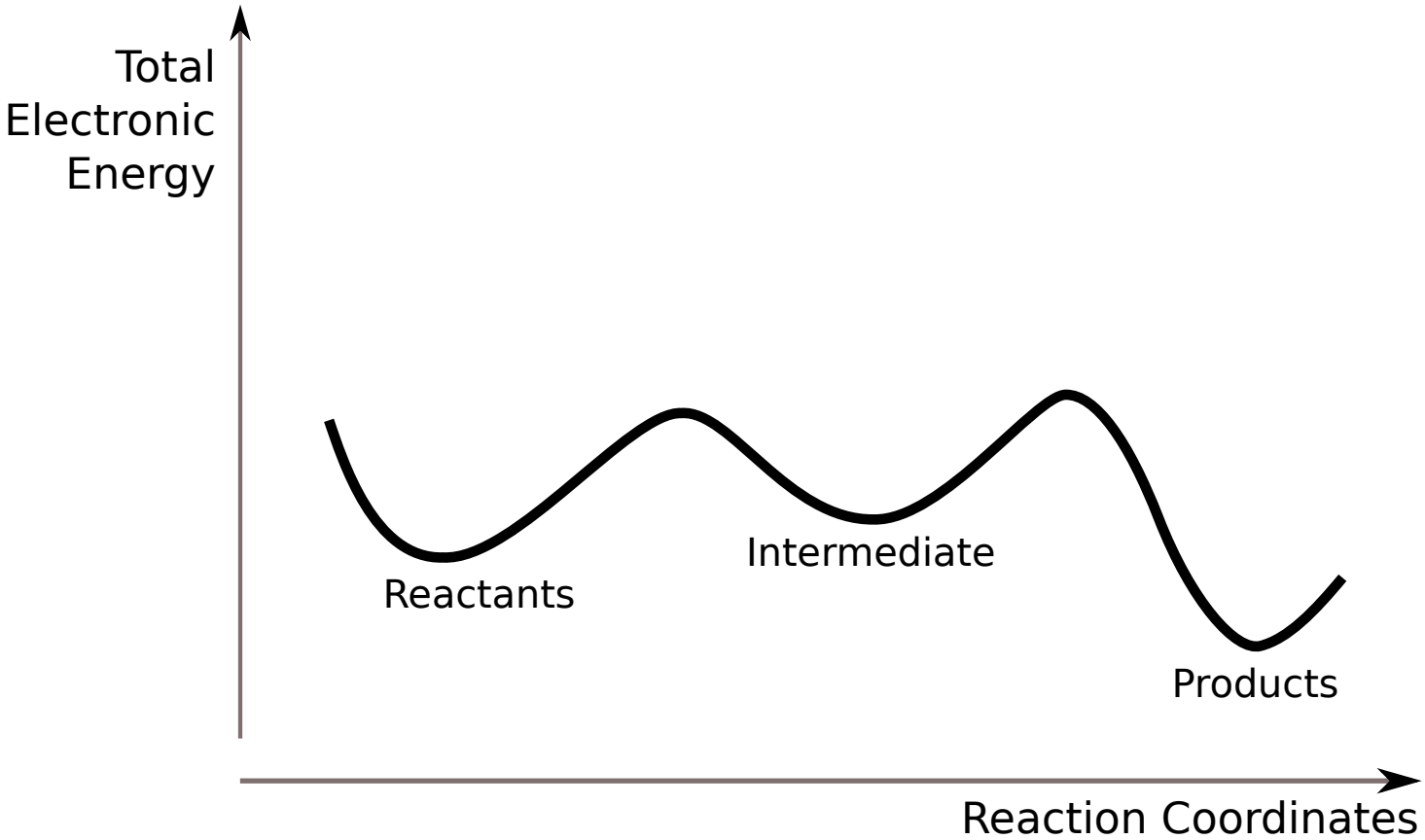
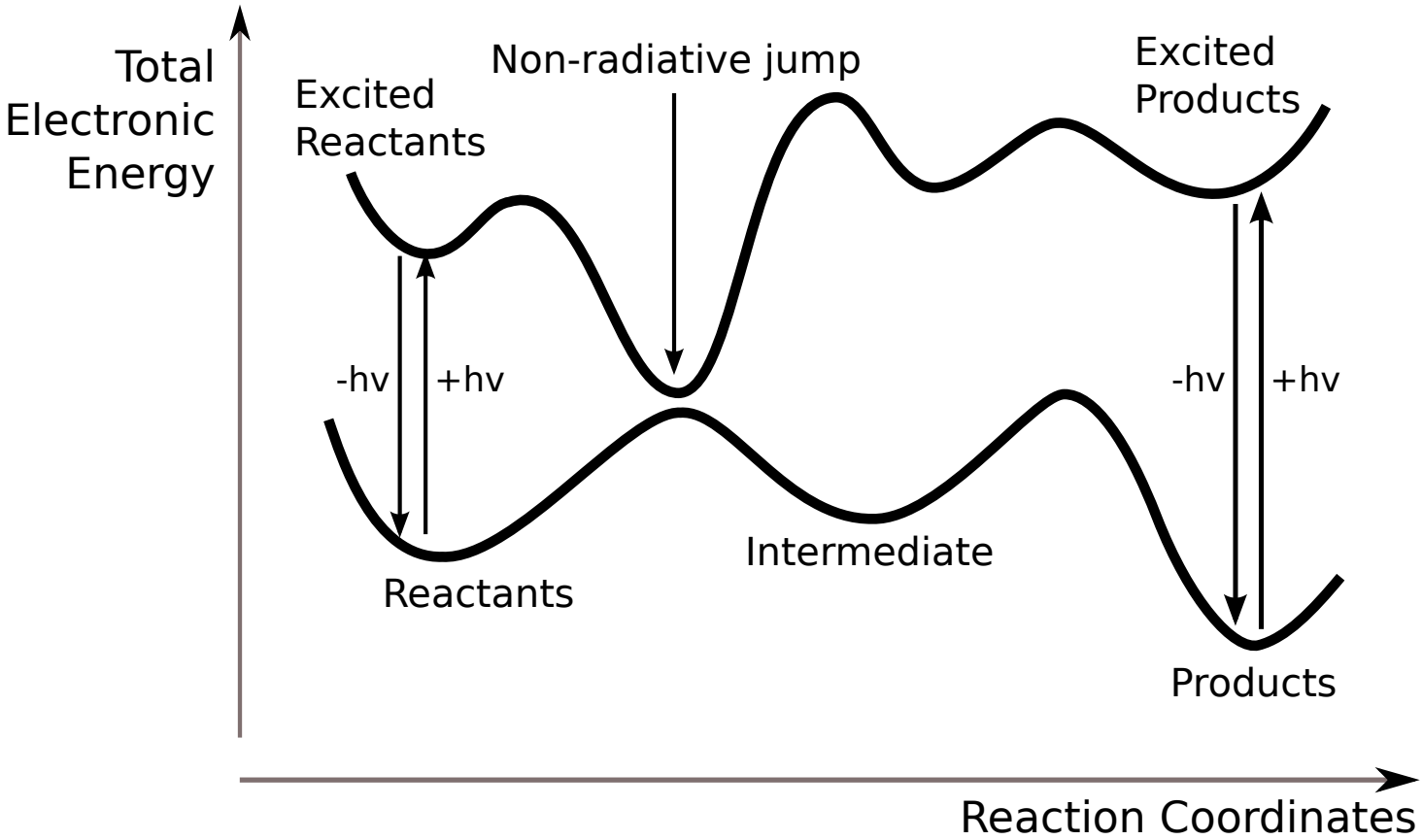
Ground-State Chemistry



Photochemistry



Photochemistry requirements

The ideal model must...

- include both **non-dynamical** and **dynamical** correlation.
- describe ground- and excited-state **potential energy surface interactions**.
- be **size consistent** and **size extensive**.
- be **efficient** enough to be able to perform dynamics.

Photochemists normally use...

CASPT2

- Systematic treatment of correlation
- Correct conical intersection
- Requires deep knowledge of the system
- Bad scaling

A-LR-TDDFT

- Only single excitations
- Not perfect conical intersection
- Require no prior knowledge
- Good scaling

LR-TDDFT in frequency space: Casida Equations

Casida constructed an RPA-like equation for TDDFT

(REF: M.E.C., Recent Developements and Applications of Modern Density Functional Theory, Theoretical and Computational Chemistry vol. 4, 1996, p.391.)

$$\begin{bmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}^*(\omega) & \mathbf{A}^*(\omega) \end{bmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

where

$$\begin{aligned} A^{\sigma\tau}_{ia,jb}(\omega) &= (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab}\delta_{\sigma\tau} + (ia|f^{\sigma\tau}_{Hxc}(\omega)|jb) \\ B^{\sigma\tau}_{ia,jb}(\omega) &= (ia|f^{\sigma\tau}_{Hxc}(\omega)|bj) \end{aligned}$$

and

$$(ia|f^{\sigma\tau}_{Hxc}(\omega)|jb) = \iint \psi^{\sigma,*}_i(\vec{\mathbf{r}}_1)\psi^{\sigma}_a(\vec{\mathbf{r}}_1) f^{\sigma\tau}_{Hxc}(\vec{\mathbf{r}}_1,\vec{\mathbf{r}}_2,\omega)\psi^{\tau,*}_j(\vec{\mathbf{r}}_2)\psi^{\tau}_b(\vec{\mathbf{r}}_2) d^3r_1 d^3r_2.$$

We can then write the linear response of the density as

$$\delta\rho^{\sigma}(\vec{\mathbf{r}},\omega) = \sum_{ia} X^{\sigma}_{ai}(\omega)\psi^*_a(\vec{\mathbf{r}})\psi_i(\vec{\mathbf{r}}) + Y^{\sigma}_{ia}(\omega)\psi^*_i(\vec{\mathbf{r}})\psi_a(\vec{\mathbf{r}})$$

Matrices $\mathbf{A}(\omega)$ and $\mathbf{B}(\omega)$ have the dimension of $N_{occ} \times N_{virt}$

Adiabatic Approximation

If the xc potential does not depend on the 'past' then

$$v_{xc}[\rho](\vec{\mathbf{x}},t) \approx v_{xc}[\rho_t](\vec{\mathbf{x}}) \rightarrow f_{xc}[\rho](\mathbf{1},\mathbf{2}) \approx \delta(t_1-t_2)\frac{\delta E_{xc}[\rho_t]}{\delta\rho_t(\vec{\mathbf{x}}_1)\delta\rho_t(\vec{\mathbf{x}}_2)}$$

where ρ_t is the density at time t and $E_{xc}[\rho]$ is the ground-state xc functional.
Such approximation turns Casida equations into

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

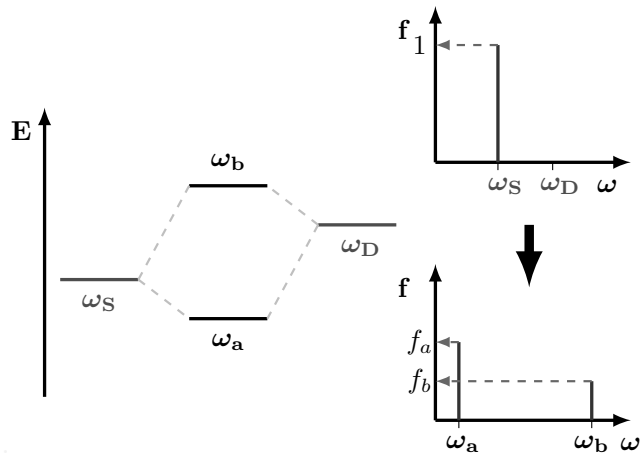
with

$$\begin{aligned} A^{\sigma\tau}_{ia,jb} &= (\epsilon_a-\epsilon_i)\delta_{ij}\delta_{ab}\delta_{\sigma\tau} + (ia|f^{\sigma\tau}_{Hxc}|jb) \\ B^{\sigma\tau}_{ia,jb} &= (ia|f^{\sigma\tau}_{Hxc}|bj) \end{aligned}$$

Matrices $\mathbf{A}$ and $\mathbf{B}$ $\rightarrow$ No explicit interaction with higher-excitations!

Dressed-TDDFT

Maitra *et al.*, JCP, **120**, 5932 (2004).⟶
Dressed-TDDFT: One single- and one double-excitation mixing.



$$\begin{bmatrix} \omega_S & \langle S|\hat{H}|D\rangle \\ \langle S|\hat{H}|D\rangle & \omega_D \end{bmatrix} \begin{pmatrix} C_S \\ C_D \end{pmatrix} = \omega \begin{pmatrix} C_S \\ C_D \end{pmatrix}$$

Applying the partitioning technique

$$\left(\omega_S + \frac{|\langle S|\hat{H}|D\rangle|^2}{\omega - \omega_D}\right) C_S = \omega C_S$$

Maitra et al. assigned the different parts as

$$[\chi_s^{-1}(\omega) - \chi^{-1}(\omega)]_{ia,ai} \approx \underbrace{(ia|f_{Hxc}|ai)}_{\text{Adiabatic Kernel}} + \frac{|H_{SD}|^2}{\omega - \omega_D}$$

Frequency dependence of the Kernel (I)

Starting from the definition of the kernel

$$f_{xc}(\mathbf{1},\mathbf{2}) = \frac{\delta v_{xc}[\rho](\mathbf{1})}{\delta\rho(\mathbf{1})} = \frac{\delta v_s[\rho](\mathbf{1})}{\delta\rho(\mathbf{2})} - \frac{\delta v_{ext}[\rho](\mathbf{1})}{\delta\rho(\mathbf{2})} - \frac{\delta v_H[\rho](\mathbf{1})}{\delta\rho(\mathbf{2})}$$

so that

$$f_{Hxc}(\mathbf{1},\mathbf{2}) = \chi_s^{-1}(\mathbf{1},\mathbf{2}) - \chi^{-1}(\mathbf{1},\mathbf{2})$$

The response functions of the non-interacting system requires the whole spectrum of excitations of the Kohn-Sham system

$$\begin{aligned}\chi_s(\vec{\mathbf{x}}_1,\vec{\mathbf{x}}_2,\omega) &= \lim_{\eta\to 0}\sum_M \frac{\langle\Psi_{s,0}|\hat{\rho}(\vec{\mathbf{x}}_1)|\Psi_{s,M}\rangle\langle\Psi_{s,M}|\hat{\rho}(\vec{\mathbf{x}}_2)|\Psi_{s,0}\rangle}{\omega + E_{s,M} - E_{s,0} + i\eta} \\ &+ \lim_{\eta\to 0}\sum_M \frac{\langle\Psi_{s,0}|\hat{\rho}(\vec{\mathbf{x}}_2)|\Psi_{s,M}\rangle\langle\Psi_{s,M}|\hat{\rho}(\vec{\mathbf{x}}_1)|\Psi_{s,0}\rangle}{\omega + E_{s,M} - E_{s,0} - i\eta}\end{aligned}$$

Frequency-Dependence of the Kernel (II)

The equation describing MB effects of four interacting particles is

$$L(\mathbf{1},\mathbf{2};\mathbf{3},4) = L_s(\mathbf{1},\mathbf{2};\mathbf{3},4)$$
$$+ \int L_s(\mathbf{1},\mathbf{2};\mathbf{3},4)\Xi_{Hxc}(\mathbf{3},4;\mathbf{5},\mathbf{6})L(\mathbf{5},\mathbf{6};\mathbf{7},8)\, d\mathbf{3}d4d\mathbf{5}d\mathbf{6}\,,$$

We need two-pair interaction, so we can fix two times to obtain

$$\mathbf{\Pi}(\omega) = \mathbf{\Pi}_s(\omega) + \mathbf{\Pi}_s(\omega)\mathbf{K}(\omega)\mathbf{\Pi}(\omega)$$

where $\mathbf{\Pi}(\omega) = \Pi(\vec{x}_1,\vec{x}_2;\vec{x}_3,\vec{x}_4;\omega)$ Now we can write the kernel as

$$\mathbf{K}(\omega) = \mathbf{\Pi}_s^{-1}(\omega) - \mathbf{\Pi}^{-1}(\omega)$$

Localization in space J.E. Harriman, PRA, **27**, 632, (1983); PRA, **34**,29 (1986)
In terms of the Harriman collapse and expansion operators

$$\hat{\Upsilon}\hat{\Sigma}_x(\vec{\mathbf{x}}_1,\vec{\mathbf{x}}_2) = \hat{\Sigma}_x(\vec{\mathbf{x}}_1,\vec{\mathbf{x}}_1) = \hat{v}_x(\vec{\mathbf{x}}_1) \qquad \hat{\Upsilon}^\dagger\hat{v}_x(\vec{\mathbf{x}}_1) = \delta(\vec{\mathbf{x}}_1-\vec{\mathbf{x}}_2)\hat{v}_x(\vec{\mathbf{x}}_1)$$

allows us to formally write our assumption

$$\chi(\vec{x}_1,\vec{x}_2;\omega) = \hat{\Upsilon}\Pi(\vec{x}_1,\vec{x}_2;\vec{x}_3,\vec{x}_4;\omega)\hat{\Upsilon}^\dagger = \Pi(\vec{x}_1,\vec{x}_1;\vec{x}_2,\vec{x}_2)$$

From MBPT to TDDFT (I)

Now, having the Dyson-like equation for the kernel

$$\boldsymbol{\chi}(\omega) - \boldsymbol{\chi}_s(\omega) = \boldsymbol{\chi}_s(\omega) f_{Hxc}(\omega) \boldsymbol{\chi}(\omega)$$

we can include our assumption $\boldsymbol{\chi}(\omega) = \hat{\boldsymbol{\Upsilon}} \boldsymbol{\Pi}(\omega) \hat{\boldsymbol{\Upsilon}}^\dagger$

$$\hat{\boldsymbol{\Upsilon}}(\boldsymbol{\Pi}(\omega) - \boldsymbol{\Pi}_s(\omega))\hat{\boldsymbol{\Upsilon}}^\dagger = (\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}_s(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger) f_{Hxc}(\omega) (\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger)$$

Applying the Born approximation we obtain

$$\hat{\boldsymbol{\Upsilon}}(\boldsymbol{\Pi}(\omega) - \boldsymbol{\Pi}_s(\omega))\hat{\boldsymbol{\Upsilon}}^\dagger = (\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}_s(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger) f_{Hxc}(\omega) (\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}_s(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger)$$

We can further simplify by writing

$$\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}_s(\omega)(\boldsymbol{\Pi}_s^{-1}(\omega) - \boldsymbol{\Pi}^{-1}(\omega))\boldsymbol{\Pi}(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger = (\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}_s(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger) f_{Hxc}(\omega) (\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}_s(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger)$$

and applying the simplification

$$\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}_s(\omega)(\boldsymbol{\Pi}_s^{-1}(\omega) - \boldsymbol{\Pi}^{-1}(\omega))\boldsymbol{\Pi}_s(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger = (\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}_s(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger) f_{Hxc}(\omega) (\hat{\boldsymbol{\Upsilon}}\boldsymbol{\Pi}_s(\omega)\hat{\boldsymbol{\Upsilon}}^\dagger)$$

From MBPT to TDDFT (II)

This is the Nanoquanta approximation

$$\mathbf{f}_{Hxc}(\omega) = \mathbf{\Lambda}_s(\omega)(\mathbf{\Pi}_s^{-1}(\omega) - \mathbf{\Pi}^{-1}(\omega))\mathbf{\Lambda}_s(\omega)$$

The construction then follows two parts:

1. Construction of the MBPT kernel

$$K'(\vec{\mathbf{x}}_3, \vec{\mathbf{x}}_4; \vec{\mathbf{x}}_5, \vec{\mathbf{x}}_6, \omega) = \Pi_s^{-1}(\vec{\mathbf{x}}_3, \vec{\mathbf{x}}_4; \vec{\mathbf{x}}_5, \vec{\mathbf{x}}_6, \omega) - \Pi^{-1}(\vec{\mathbf{x}}_3, \vec{\mathbf{x}}_4; \vec{\mathbf{x}}_5, \vec{\mathbf{x}}_6, \omega)$$

Ref.: J. Oddershede, P. Jørgensen, JCP, **66**,1541, (1977).

2. Treatment of the space localization

$$\Lambda_s(\vec{\mathbf{x}}_1; \vec{\mathbf{x}}_5, \vec{\mathbf{x}}_6, \omega) = (\hat{\Upsilon}\Pi_s(\vec{\mathbf{x}}_1, \vec{\mathbf{x}}_2; \vec{\mathbf{x}}_3, \vec{\mathbf{x}}_4, \omega)\hat{\Upsilon}^\dagger)^{-1}\hat{\Upsilon}\Pi_s(\vec{\mathbf{x}}_3, \vec{\mathbf{x}}_4; \vec{\mathbf{x}}_5, \vec{\mathbf{x}}_6, \omega)$$

Construction of the MBPT kernel

The polarization propagator can be written as

$$-\Pi(\omega) = (\hat{p}^\dagger \hat{q}|(\omega \breve{1} + \breve{H})^{-1}|\hat{r}^\dagger \hat{s})$$

By introducing a complete space of neutral excitations

$$\mathbf{T}^\dagger = \{\mathbf{T}_1^\dagger; \mathbf{T}_2^\dagger; ...\} = \{\hat{a}^\dagger \hat{i}, \hat{i}^\dagger \hat{a}; \hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}, \hat{j}^\dagger \hat{b} \hat{i}^\dagger \hat{a}; ...\}$$

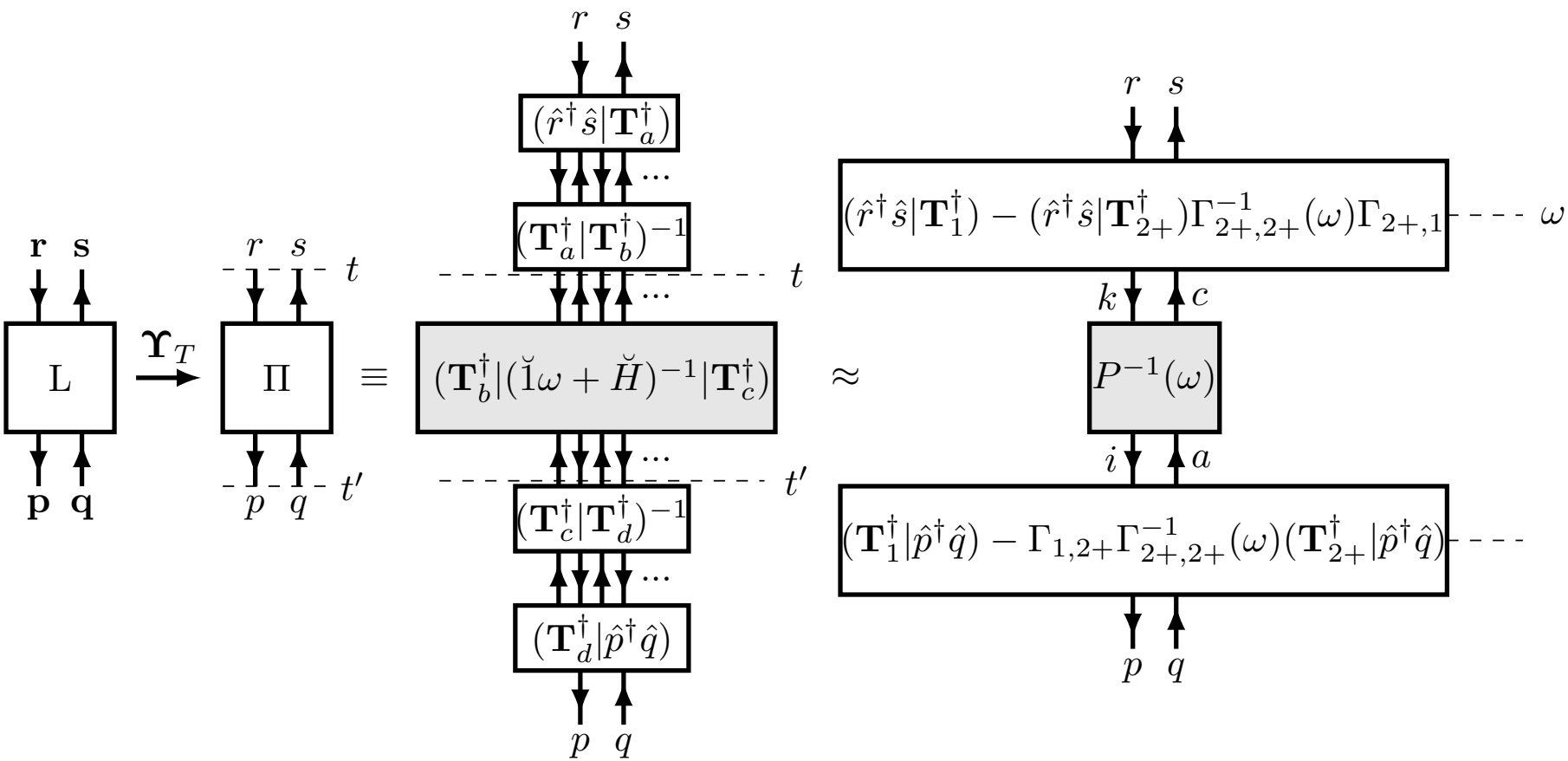
we can decouple the propagation of the pairs and the resolvent

$$-\Pi(\omega) = \left((\hat{p}^\dagger \hat{q}|\mathbf{T}_1)(\hat{p}^\dagger \hat{q}|\mathbf{T}_{2+})\right) \begin{bmatrix} \mathbf{\Gamma}_{1,1}(\omega) & \mathbf{\Gamma}_{1,2+} \\ \mathbf{\Gamma}_{2+,1} & \mathbf{\Gamma}_{2+,2+}(\omega) \end{bmatrix}^{-1} \begin{pmatrix} (\mathbf{T}_1^\dagger|\hat{r}^\dagger \hat{s}) \\ (\mathbf{T}_{2+}^\dagger|\hat{r}^\dagger \hat{s}) \end{pmatrix}$$

Applying the partitioning technique

$$\begin{aligned} -\Pi_{sr,qp}(\omega) &= [(\hat{p}^\dagger \hat{q}|\mathbf{T}_1^\dagger) - (\hat{p}^\dagger \hat{q}|\mathbf{T}_{2+}^\dagger)\mathbf{\Gamma}_{2+,2+}^{-1}(\omega)\mathbf{\Gamma}_{2+,1}]\mathbf{P}^{-1}(\omega) \times \\ &\times [(\mathbf{T}_1^\dagger|\hat{r}^\dagger \hat{s}) - \mathbf{\Gamma}_{1,2+}\mathbf{\Gamma}_{2+,2+}^{-1}(\omega)(\mathbf{T}_{2+}^\dagger|\hat{r}^\dagger \hat{s})] \\ &+ (\hat{p}^\dagger \hat{q}|\mathbf{T}_{2+}^\dagger)\mathbf{\Gamma}_{2+,2+}^{-1}(\omega)(\mathbf{T}_{2+}^\dagger|\hat{r}^\dagger \hat{s}) \end{aligned}$$

Dressed-TDDFT

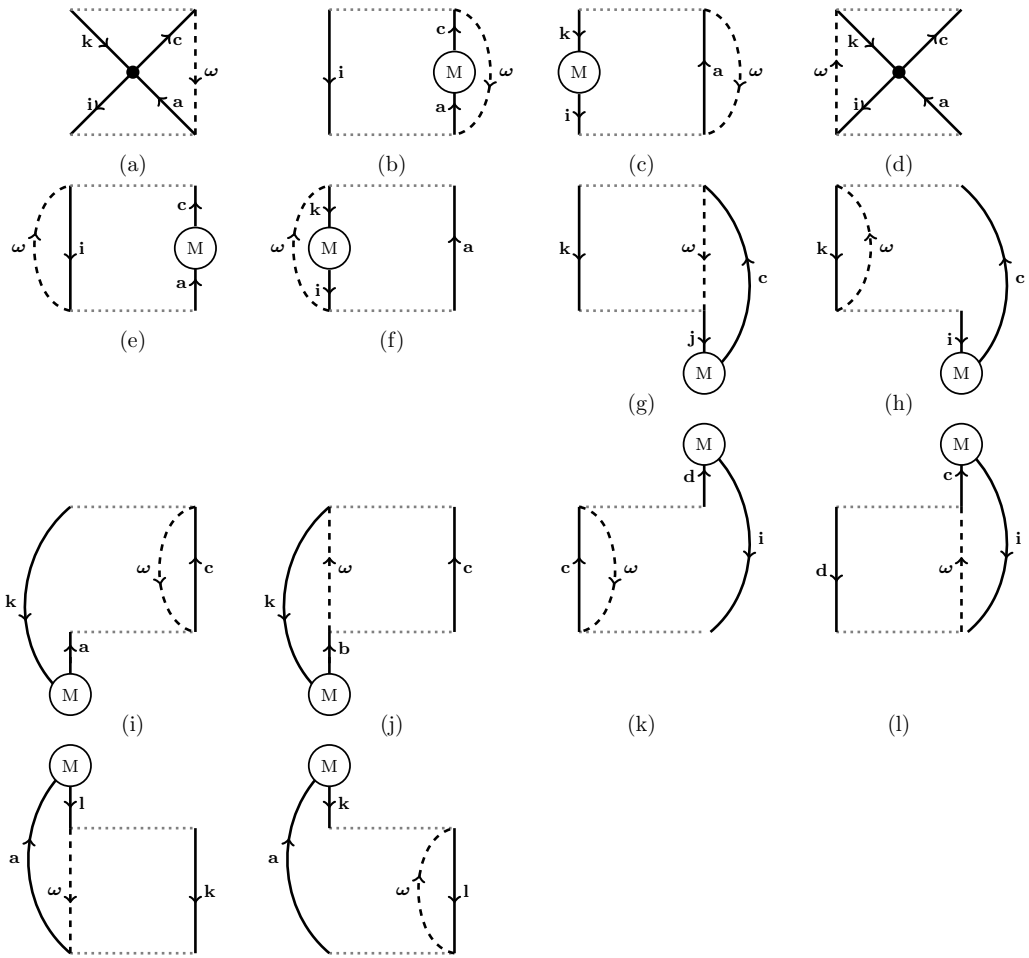


First-order: Exact Exchange

We can partition the Hamiltonian in

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \quad \rightarrow \quad \hat{H}^{(0)} = \hat{h}_s \quad ; \quad \hat{H}^{(1)} = \hat{W} - \hat{v}_{HF} + \hat{M}_{xc}$$

A.G., Phys. Rev. A. **57**, 3433 (1998)



First+Second-order: Double-Excitations

- Roughly 200 diagrams have to be considered
- Renormalization of the excit. operators to recover Hermiticity
- The resumed expressions are

$$[\Pi(\omega)-\Pi_s(\omega)]_{ai,ai} = (ai||ai) + M_{aa} - M_{ii} \quad \leftarrow \quad \text{1st order}$$

$$+\tfrac{1}{2}\sum_{lmb}\frac{|(ma||lb)|^2}{\epsilon_a+\epsilon_b-\epsilon_l-\epsilon_m}$$

$$-\tfrac{1}{2}\sum_{lab}\frac{|(ia||lb)|^2}{\epsilon_a+\epsilon_b-\epsilon_l-\epsilon_i} \quad \leftarrow \quad \text{2on order}$$

$$-\sum_{d}\frac{|M_{id}|^2}{\epsilon_d-\epsilon_i}$$

$$-\sum_{k}\frac{|M_{ka}|^2}{\epsilon_a-\epsilon_k}$$

$$+\sum_{jkbc}\frac{\left|\begin{array}{c}-\delta_{ji}(ba||ck)+\delta_{ki}(ba||cj)\\ -\delta_{ab}(ck||ij)+\delta_{ac}(bk||ij)\end{array}\right|^2}{\omega-\omega_{ikbc}}$$

Space-Localization

The space-localization makes the whole MB kernel ω-dependent

$$\mathbf{f}_{Hxc}(\omega) = \mathbf{\Lambda}(\omega)[\boldsymbol{K}'(0) + \boldsymbol{K}'(\omega)]\mathbf{\Lambda}_s{}^{\dagger}(\omega)$$

In a spirit somewhat related to the Nanoquanta kernel

$$\mathbf{f}_{Hxc}(\omega) = \mathbf{\Lambda}_s(\omega)[\boldsymbol{K}'(0) + \boldsymbol{K}'(\omega)]\mathbf{\Lambda}_s{}^{\dagger}(\omega)$$

Gonze-Scheffler Relations [X.G.,M.S.,PRL, 82, 4416 (1999)]: For the case of one pole well-separated from the others

$$\begin{aligned}(ia|\mathbf{f}_{Hxc}(\epsilon_{ai})|ai) &= (ia|\mathbf{\Lambda}_s(\epsilon_{ai})[\boldsymbol{K}'(0) + \boldsymbol{K}'(\epsilon_{ia})]\mathbf{\Lambda}_s(\epsilon_{ai})|ai) \\ &= (ii|[\boldsymbol{K}'(0) + \boldsymbol{K}'(\epsilon_{ia})]|aa)\end{aligned}$$

The complete ω-dependence of the localizer is unknown!!

General treatment of Localization

Expanding the kernel in terms of auxiliary basis functions

$$f_{Hxc}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2, \omega) = \sum_I c_I(\omega) f_I(\vec{\mathbf{r}}_1) g_I^*(\vec{\mathbf{r}}_2)$$

The localization condition is given by

$$(ia|f_{Hxc}(\omega)|jb) = (ia|K'(\omega)|jb)$$

Using the expansion, we can set up a linear system of equations

$$\sum_I c_I(\omega)(ia|f)(g|jb) = (ia|K'(\omega)|jb)$$

Conclusions

- Double Excitations are lost due to the adiabatic approximation.
- Starting from an exact formulation of the kernel, we derived a second-order correction to the kernel.
- The kernel has two functions: (i) shift the Kohn-Sham eigenvalues; (ii) introduce electron-hole correlation
- An extra frequency dependence arises from the localization of the kernel
- We propose a general method for treating the localization effects, which we believe introduce important physical content.

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