Hunting double excitations

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Abstract

The spectra of isolated systems is known to be described quite well by Casida's approach to Time-Dependent Density-Functional-Theory (TDDFT) for many closed shell systems, within the adiabatic approximation. On the other hand the same framework is known to perform quite poorly for open shell systems. The reason of this deficiency can be found in the failure of the adiabatic approximation in describing double excitations, that leads, therefore, to the break of the spin symmetries of the system [1]. One would encounter analogues deficiencies using the Bethe Salpeter (BSE) approach with a static kernel $W^{RPA}(\omega)$. A solution to the problem is the use of dynamical kernels. This work aims to scrutinize the dynamical structure that the BSE kernel and/or the exchange correlation kernel of TDDFT should have in order to describe double excitations. Following the same line of previous works on the study of removal/addition of electrons [2] and of excited states of nuclei [3,4], we find out that second order Feynman diagrams do the right job. We show some preliminary tests on model systems.

TDDFT (and BSE)

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X_I \\ Y_I \end{pmatrix} = \omega_I \begin{pmatrix} X_I \\ Y_I \end{pmatrix} \qquad (1)$$

$$A_{ij\sigma,hk\tau} = \delta_{i,h}\delta_{j,k}\delta_{\sigma,\tau}(\epsilon_{i\sigma} - \epsilon_{j\sigma}) + f^{Hxc}_{ij\sigma,hk\tau}(\omega)$$

$$B_{ij\sigma,hk\tau} = f^{Hxc}_{ij\sigma,kh\tau}(\omega)$$

$$f^{Hxc}_{ij\sigma,hk\tau} = \int d^3\mathbf{r}d^3\mathbf{r}'\psi_{i\sigma}(\mathbf{r})\psi^*_{j\sigma}(\mathbf{r})\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f^{xc}_{\sigma\tau}(\mathbf{r},\mathbf{r}';\omega)\right]\psi^*_{h\tau}(\mathbf{r}')\psi_{k\tau}(\mathbf{r}')$$

Simple consideration if $f_{xc}(\omega) \sim f_{xc}(0)$

- matrix dimension = single excitation number
  --> double excitations missing

Are double excitations important?

- energy consideration (spin symmetry!)

Ref. [1,5] ...Pina's presentations for more details.

Mathematical point of view

$$\begin{pmatrix} S & C \\ C^\dagger & D \end{pmatrix} \begin{pmatrix} \mathbf{e}_1 \\ \mathbf{e}_2 \end{pmatrix} = \omega_I \begin{pmatrix} \mathbf{e}_1 \\ \mathbf{e}_2 \end{pmatrix}$$

Problem = [n x n]
S = [m x m]

$$\left(S + C(\omega_I - D)^{-1}C^\dagger\right)\mathbf{e}_1 = \omega_I \mathbf{e}_1 \qquad K(\omega)$$

We can learn: which structure the kernel should satisfy
Cfr: Casida[1] and Maitra[2]

Why is it important to have the right structure:

e.g. for n=3 and m=2:

the right structure should be

$$K(\omega) = \frac{1}{\omega - d}\begin{pmatrix} a^2 & ab \\ ba & b^2 \end{pmatrix}$$

det(S+K(ω)-ω)=0 is a 3rd degree equation as det(K(ω))=0
→ 3 solutions

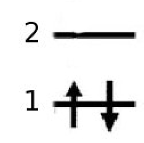
other forms such as

$$K(\omega) = \frac{1}{\omega - d}\begin{pmatrix} a^2 & 0 \\ 0 & b^2 \end{pmatrix}$$

as det(K(ω))≠0, give that det(S+K(ω)-ω)=0 is a 4th degree eq.
→ one spurious solution

Model System

(Tamm Dancoff approx)



If $d = (\epsilon_{2\uparrow} - \epsilon_{1\uparrow}) + (\epsilon_{2\uparrow} - \epsilon_{1\uparrow})$ or

$d = (\epsilon_{2\downarrow} - \epsilon_{2\downarrow}) + (\epsilon_{2\uparrow} - \epsilon_{1\uparrow})$

$$f^{K3}_{xc} = \begin{pmatrix} 0 & 2U_aU_b \\ 2U_aU_b & 0 \end{pmatrix} \qquad f^{K1}_{xc} = -f^{K3}_{xc}$$

$$f^{K4}_{xc} = \begin{pmatrix} 2U_aU_b & 0 \\ 0 & 2U_aU_b \end{pmatrix} \qquad f^{K2}_{xc} = -f^{K4}_{xc}$$

$$f^{K5}_{xc} = \begin{pmatrix} 0 & U_a^2 + U_b^2 \\ U_a^2 + U_b^2 & 0 \end{pmatrix} \qquad f^{K6}_{xc} = -f^{K5}_{xc}$$

$$f^{\Sigma 2}_{xc} = \begin{pmatrix} U_a^2 + U_b^2 & 0 \\ 0 & U_a^2 + u_b^2 \end{pmatrix} \qquad f^{\Sigma 1}_{xc} = -f^{\Sigma 2}_{xc}$$

no over-counting!!

Terms counting twice the same excitation cancel out. The over-counting originates from a mechanism similar to the self-screening effects in GW calculation. Ref [7]

If $d = (\epsilon_{2\uparrow} - \epsilon_{1\uparrow}) + (\epsilon_{2\downarrow} - \epsilon_{2\downarrow})$

$$f^{K3}_{xc} = \begin{pmatrix} 0 & 2U_aU_b \\ 2U_aU_b & 0 \end{pmatrix} \qquad f^{K1}_{xc} = 0$$

$$f^{K4}_{xc} = \begin{pmatrix} 2U_aU_b & 0 \\ 0 & 2U_aU_b \end{pmatrix} \qquad f^{K2}_{xc} = 0$$

$$f^{K5}_{xc} = \begin{pmatrix} 0 & U_a^2 + U_b^2 \\ U_a^2 + U_b^2 & 0 \end{pmatrix} \qquad f^{K6}_{xc} = 0$$

$$f^{\Sigma 2}_{xc} = \begin{pmatrix} U_a^2 + U_b^2 & 0 \\ 0 & U_a^2 + u_b^2 \end{pmatrix} \qquad f^{\Sigma 1}_{xc} = 0$$

Here $U_a = U_{11,12}$ and $U_b = U_{22,21}$

The whole kernel is:

$$f_{xc} = \frac{1}{\omega - (\epsilon_{2\uparrow} - \epsilon_{1\uparrow}) + (\epsilon_{2\downarrow} - \epsilon_{2\downarrow})}\begin{pmatrix} (U_a + U_b)^2 & (U_a + U_b)^2 \\ (U_a + U_b)^2 & (U_a + U_b)^2 \end{pmatrix}$$

$\det(f_{xc}(\omega)) = 0$ .... ok!

We finally solve the equation det(A(ω)-ω)=0 where A is defined in eq. (1) and we obtain:

- Triplet equation:

$$\omega_I = \Delta\epsilon - W_1$$

- Second order singlet equation:

$$\omega_I = \Delta\epsilon + 2U_1 - W_1 + \frac{2(U_a + U_b)^2}{\omega - 2\Delta\epsilon}$$

Here $U_1 = U_{12,12}$, $W_1 = U_{11,22}$

For weak coupling $(U_a + U_b) \simeq 0$:

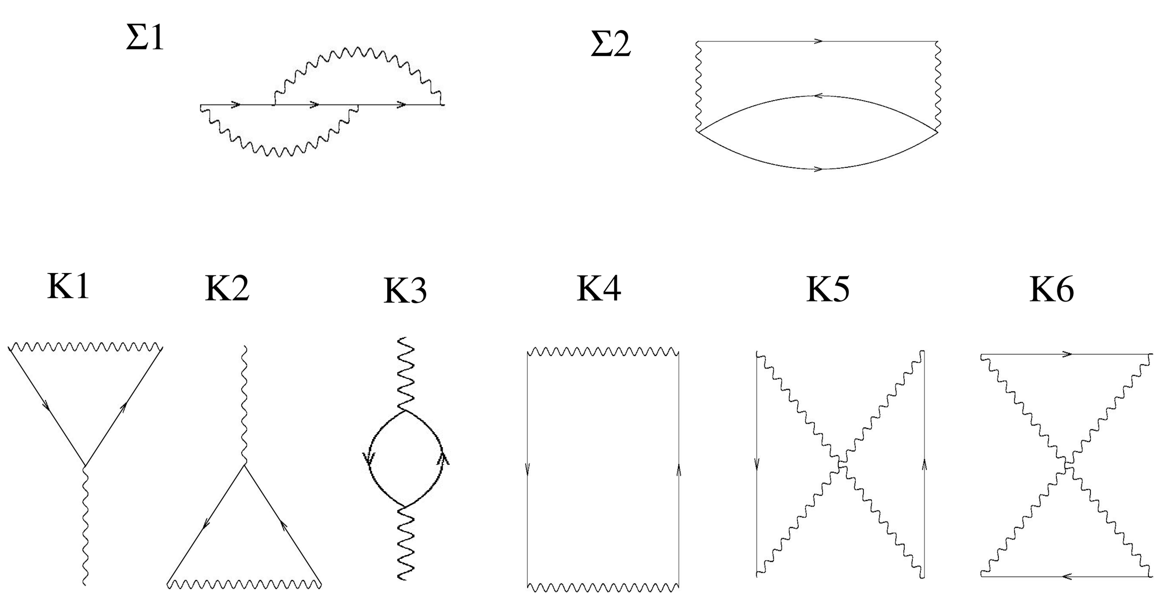
$$\omega_T = \Delta\epsilon - W_1$$

$$\omega_{S,1} = \Delta\epsilon + 2U_1 - W_1 \qquad \omega_{S,2} = 2\Delta\epsilon$$

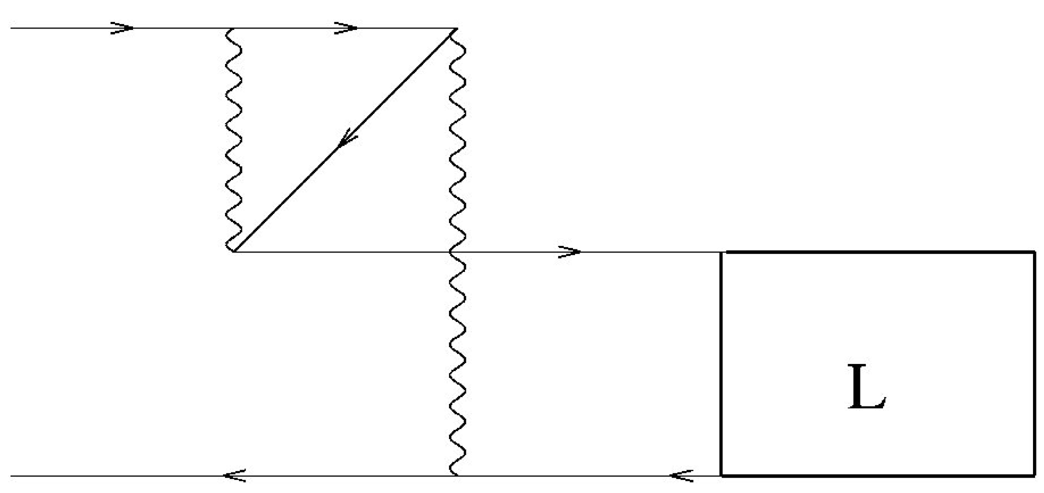
Physical point of view

Feynman diagrams

Second order diagrams for K and Σ (Ref.[2,3,4])



and why they contains double excitations (diagram K1)



From BSE kernel to TDDFT

- From literature (Ref. [6])

$$f^{(1)}_{xc}(1,2) = \chi^{-1}_{KS}(1,2) - \chi_0^{-1}(1,2)$$

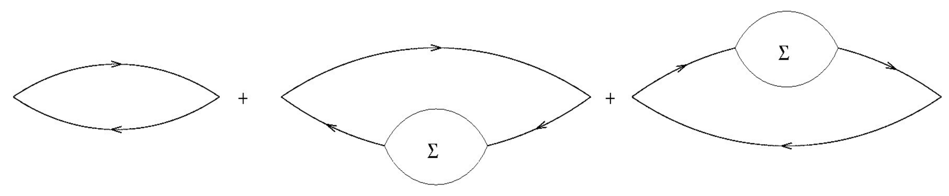
$$f^{(2)}_{xc}(1,2) \simeq -i\chi_0^{-1}(1,3)G(3,4)G(5,3)K(45,67)G(6,8)G(8,7)\chi_0^{-1}(8,2)$$

- For Σ and K dynamical and at the same level of approximation, we have to elaborate $f^{(1)}_{xc}$ using:

$$\chi_0(1,2) = -iG(1,2)G(2,1)$$

$$G(1,2) = G_s(1,2) + G_s(1,3)(\Sigma_d(\omega)(3,4) - \Sigma_s(3,4))G(4,2)$$

(here 's' is for static and 'd' for dynamical)



- After some manipulation the result is:

$$f^{(1)}_{xc}(1,2) = \chi^{-1}_{KS}(1,2) - \chi_s^{-1}(1,2)$$

$$f^{(\Sigma)}_{xc}(1,2) \simeq -i\chi_s^{-1}(1,3)\big[(G_s(4,3)\Sigma_d(5,4)G_s(6,5))G_s(3,6) + G_s(3,6)(G_s(3,4)\Sigma_d(4,5)G_s(5,6))\big]\chi_s^{-1}(6,2) \qquad (2)$$

$$f^{(K)}_{xc}(1,2) \simeq -i\chi_s^{-1}(1,3)G_s(3,4)G_s(5,3)K(45,67)G_s(6,8)G_s(8,7)\chi_s^{-1}(8,2)$$

...now we have to choose K(ω) and Σ(ω)

The result (TDA); only diagram K1 here:

$$f^{K1}_{xc}(\omega) = \sum_{nm\gamma_1\gamma_2} \frac{-i\delta_{\sigma,\tau}\delta_{\sigma,\gamma_1}\delta_{\gamma_1,\gamma_2}\, U^0_{n_1j\sigma;n_4k\sigma}U^0_{ih\sigma;n_1n_4\sigma}\,\Theta\big((\epsilon_{i\sigma} - \epsilon_{k\tau}) + (\epsilon_{m\gamma_2} - \epsilon_{n\gamma_1})\big)}{\omega - [(\epsilon_{i\sigma} - \epsilon_{k\tau}) + (\epsilon_{m\gamma_1} - \epsilon_{n\gamma_2})] + 2i\eta} + \frac{-i\delta_{\sigma,\tau}\delta_{\sigma,\gamma_1}\delta_{\gamma_1,\gamma_2}\, U^0_{n_1j\sigma;n_4k\sigma}U^0_{ih\sigma;n_1n_4\sigma}\,\Theta\big((\epsilon_{h\tau} - \epsilon_{j\sigma}) + (\epsilon_{n\gamma_2} - \epsilon_{m\gamma_1})\big)}{\omega - [(\epsilon_{h\tau} - \epsilon_{j\sigma}) + (\epsilon_{n\gamma_2} - \epsilon_{m\gamma_1})] + 2i\eta}$$

Conclusions:

We pointed out:

- which is the right mathematical structure of a kernel containing double excitations;
- through Feynman diagrams, which physics should be included;
- applying the method to a model system, how over counting disappears;

...this preliminary results could be the starting point for the research of dynamical kernel which includes more physics than 2nd order one (maybe the RPA kernel...--> Pina's talk)

"Work in progress":

How to evaluate all 8 second order Feynman diagrams knowing only one of them...
....ask the author!

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