Week 5 Questions

May 4, 2020

In a very simple world, there is only one single excitation, and the Kohn-Sham response function has the form:

$$\chi_s(\omega) = \frac{1}{\omega^2 - 1} \tag{1}$$

and the HXC kernel has the form:

$$f_{\text{HXC}}^{(\lambda)}(\omega) = \lambda + \frac{\lambda^2\omega^2}{\omega^2 - 4} = \lambda + \frac{\lambda^2\omega^2}{(\omega-2)(\omega+2)} \tag{2}$$

everything is in atomic units, and λ measures the strength of the electron-electron interaction.

1. Find the Kohn-Sham transition frequencies (forward and back).
2. What is $f_{\text{HXC}}^{(\lambda)}(\omega)$ in the adiabatic approximation?
3. For $\lambda = 1$, calculate the approximate transition frequency in the adiabatic approximation. Does it differ noticeably from your answer to (1.)?
4. Again, for $\lambda = 1$, find the transition frequency with the full kernel. How has the spectrum changed qualitatively? How do your answers compare with the previous ones? Comment on the accuracy of the adiabatic approximation and its major failing here.

2) $\lim_{\omega\to 0} f_{HXC}^{(\lambda)}(\omega) = \lim_{\omega\to 0}\left(\lambda + \frac{\lambda^2\omega^2}{\omega^2-4}\right) = \lambda$

1) Find poles $\chi_s(\omega) = \frac{1}{\omega^2-1}$ $\quad \omega^2 - 1 = 0 \quad \omega = \pm 1$ a.u are forward & reverse transition freq.

3) $f_{HXC}^{(1)}(\omega=0) = 1 = \chi_s^{-1}(r,r',\omega) - \chi^{-1}(r,r',\omega)$ adiabatic approx.

$\chi^{-1}(r,r',\omega) = \omega^2 - 1 - \lambda - \frac{\lambda^2\omega^2}{\omega^2-4} \xrightarrow{\lambda=1} \omega^2 - 2 - \frac{\omega^2}{\omega^2-4} \Rightarrow \pm\sqrt{2}$

4) $f_{HXC}^{(1)}(\omega) = \lambda + \frac{\lambda^2\omega^2}{\omega^2-4} = 1 + \frac{\omega^2}{\omega^2-4}$ $\rightarrow$ ~~poles $\omega = \pm 2$ a.u. are transition freq w/ full kernel~~

$= \frac{2\omega^2-4}{\omega^2-4} = 2\,\frac{\omega^2-2}{\omega^2-4}$

Repeat from Q's 3

KS

adiabatic approx. ~ ~~14~~ 17%

non-adiabatic approx ~16%

- freq dependence give double excitation from nonadiabatic
- adiabatic approx. removes extra freq.; shifts too much
- full kernel gives single & double excitation

- Highly accurate GS KS density → χ_s calculate & only one trans. freq.
- exact χ, invert χ_s & χ to give f_{xc} & no functional derivative required ⇒ eqn 7.77)

⇒ next weeks hw, a little harder on same system

<u>Redo Probs. 3 & 4</u>

3) $\lambda = 1$ $\quad \cancel{f^{(1)}_{Hxc}(\omega) = 1 = \chi_s^{-1}(\vec{r},\vec{r}',\omega) - \chi^{-1}(\vec{r},\vec{r}',\omega)}$ $\quad -\frac{\omega^2}{\omega^2-4}$

$$\cancel{-\frac{\omega^2}{\omega^2-4} + 1 = \frac{1}{\omega^2-1} - \chi^{-1}(\vec{r},\vec{r}',\omega)}$$

$$\cancel{\chi^{-1}(\vec{r},\vec{r}',\omega) = \frac{1}{\omega^2-1} - 1 = \frac{-\omega^2+2}{\omega^2-1} + \frac{\omega^2}{\omega^2-4}}$$

$$f^{(1)}_{Hxc}(\omega) = 1 + \frac{\omega^2}{\omega^2-4} = \chi_s^{-1}(\vec{r},\vec{r}',\omega) - \chi^{-1}(\vec{r},\vec{r}',\omega)$$

$$1 + \frac{\omega^2}{\omega^2-4} = \omega^2 - 1 - \chi^{-1}(\vec{r},\vec{r}',\omega)$$

$$\chi^{-1}(\vec{r},\vec{r}',\omega) = \omega^2 - 1 - 1 - \underbrace{\frac{\omega^2}{\omega^2-4}}_{\lim_{\omega\to 0}}$$

$$= \omega^2 - 2$$

$\boxed{\omega = \pm\sqrt{2}}$, yes it is different

4) $$f^{(1)}_{Hxc}(\omega) = 1 + \frac{\omega^2}{\omega^2-4} = \omega^2 - 1 - \chi^{-1}(\vec{r},\vec{r}',\omega)$$

$$\chi^{-1}(\vec{r},\vec{r}',\omega) = \omega^2 - 2 - \frac{\omega^2}{\omega^2-4}$$

$$= \frac{\omega^4 - 4\omega^2 - \omega^2 - 2\omega^2 + 8}{\omega^2-4}$$

$$= \frac{\omega^4 - 7\omega^2 + 8}{\omega^2-4}$$

$$\boxed{\omega = \{\pm 1.199, \pm 2.358\}}$$