* ⇒ Do xc pieces better than TD KS pieces?
⇒ Adiab gives good transit. freq. correl. states are similar
⇒ what dim. param. determines what come close in ω space

pg189: Ch. 9 ⇒ Double excitation - unambiguously define

ok.

*Calc & Read Ch. 8 & 9

Week 5/6 Questions

May 9, 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:

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

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 $f^{(\lambda)}_{\text{HXC}}(\omega)$ 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.

   ⇒ simplification Hubbard model
5. Redo Question 4 with $\lambda = \frac{1}{2}$ and $\lambda = \frac{1}{4}$. Look at the transition frequencies and explain what is happening. Then, look at the analytic form of the exact solution and expand in powers of λ to understand better. Comment again on the validity of the adiabatic approximation.
6. Redo Question 4 with 4 replaced by 25 in the denominator of Equation 2, and again comment on the validity of the adiabatic approximation.

   $f^{(\lambda)}_{Hxc}(\omega) = \lambda + \lambda^2\omega^2/(\omega^2 - 25)$
7. The oscillator strength of a transition is proportional to the numerator of χ, i.e.

   - hardwired to real space Hamiltonian
   - prove the sum rule

   $$f_i \propto \lim_{\omega \to \omega_i} \chi(\omega)\,(\omega - \omega_i) \tag{3}$$

   - Gauge freedom, form oscil. str. change a lot ⇒ ① Dipole ② momentum-current ⇓ give same answer - none true for discrete model on grid / basis

   - relative osc. str.

   For Question 4, calculate f_i for both transitions, normalize them to add to 1, and say how much is in the double excitation.
8. Repeat Question 5, but studying oscillator strengths. What happens in the adiabatic approximation? How do oscillator strengths behave as $\lambda \to 0$?

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

$\chi^{-1}(\vec{r},\vec{r}',\omega) = \omega^2 - \frac{3}{2} - \frac{1}{4}\frac{\omega^2}{\omega^2-4}$

$= \dfrac{4(\omega^4 - 4\omega^2) - 6(\omega^2-4) - \omega^2}{4(\omega^2-4)}$

$\omega = \{\pm 1.170, \pm 2.093\}$

$f^{(1/4)}_{HXC}(\omega) = \frac{1}{4} + \frac{1}{16}\frac{\omega^2}{\omega^2-4} = \omega^2 - 1 - \chi^{-1}(\vec{r},\vec{r}',\omega)$

$\chi^{-1}(\vec{r},\vec{r}',\omega) = \omega^2 - \frac{5}{4} - \frac{1}{16}\frac{\omega^2}{\omega^2-4}$

$16(\omega^4 - 4\omega^2) - 20(\omega^2-4) - \omega^2$

$\omega = \pm 1.106, \pm 2.022$

5) Transition freq. getting smaller.

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

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

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

$$= \frac{\omega^4 - 5\omega^2 - \lambda\omega^2 - \lambda^2\omega^2 + 4 + 4\lambda}{\omega^2-4}$$

$$\omega = \pm\frac{\sqrt{5+\lambda+\lambda^2 \pm \sqrt{9-6\lambda+11\lambda^2-2\lambda^3+\lambda^4}}}{\sqrt{2}}$$

expand around $\lambda = 0$ & obtain Taylor Series

$$\omega_- = \frac{\sqrt{5+\lambda+\lambda^2 - \sqrt{9-6\lambda+11\lambda^2-2\lambda^3+\lambda^4}}}{\sqrt{2}} = 1 + \frac{\lambda}{2} - \frac{7\lambda^2}{24} - \frac{11\lambda^3}{144} - \frac{5\lambda^4}{1152} + \frac{2143\lambda^5}{20736} + O(\lambda^6)$$

$$\omega_+ = \frac{\sqrt{5+\lambda+\lambda^2 + \sqrt{9-6\lambda+11\lambda^2+2\lambda^3+\lambda^4}}}{\sqrt{2}} = 2 + \frac{\lambda^2}{3} + \frac{\lambda^3}{9} - \frac{\lambda^4}{36} - \frac{13\lambda^5}{162} + O(\lambda^6)$$

$\lambda=1$, adiabatic $\sim \pm\sqrt{2} = \pm 1.41421$ } 14.89% error

$\lambda=1$, exact ± 1.23095

$\lambda=\frac{1}{2}$, adiabatic $\pm\sqrt{3/2} = 1.22474$ } 4.63% error

$\lambda=\frac{1}{2}$, exact 1.17049

$\lambda=\frac{1}{4}$, adiabatic $\pm\sqrt{\frac{5}{4}} = 1.11803$ } 1.12% error

$\lambda=\frac{1}{4}$, exact 1.10566

zeroth order is KS & 2nd term is adiabatic; 1st order λ, nonzero $n(r)$ & $n(r')$; correction to adiab. is $\lambda^2 \to$ small; turn off λ mimic optical transitions; turn on λ, adiabatic give exact ans; & ω is indep.

Error improves w/ $\lambda \to 0$

why get good results adiab. correct. ① λ ② weakly correlated

$\to$ (locality of functional)

6) $f^{(\lambda)}_{Hxc}(\omega) = \lambda + \dfrac{\lambda^2\omega^2}{\omega^2 - 25} = \omega^2 - 1 - \chi^{-1}(\vec{r},\vec{r}',\omega)$

$$\chi^{-1}(\vec{r},\vec{r}',\omega) = \omega^2 - 1 - \lambda - \frac{\lambda^2\omega^2}{\omega^2-25}$$

$$= \frac{\omega^4 - 25\omega^2 - \omega^2 + 25 - \lambda\omega^2 + 25\lambda - \lambda^2\omega^2}{\omega^2 - 25}$$

$$= \frac{\omega^4 - 26\omega^2 - \lambda\omega^2 - \lambda^2\omega^2 + 25 + 25\lambda}{\omega^2 - 25}$$

$$\omega = \pm\frac{\sqrt{26 + \lambda + \lambda^2 \pm \sqrt{576 - 48\lambda + 53\lambda^2 + 2\lambda^3 + \lambda^4}}}{\sqrt{2}}$$

$\lambda = \frac{1}{2}$, exact ± 1.2183, ± 5.0265 } 16.08 % error

$\lambda = \frac{1}{2}$, adiabatic ± 1.4142

$\lambda = \frac{1}{4}$, exact ± 1.11657, ± 5.00657 } 0.13 % error

$\lambda = \frac{1}{4}$, adiabatic ± 1.11803

smaller λ, greater accuracy while larger λ results in greater error

$\lambda = 1$, exact, ± 1.38, ± 5.11

become smaller

- deviations from KS values

- exact 9.0eV, KS 8.9eV, & TDKS 9.2eV ⇒ look at relative KS gs 8.9eV

transition freq & around $\lambda = 1$

f_{Hxc} ⇒ ± 5 & KS ± 1 → shifting away since not close to the poles ± 5 ⇒ improved error

orig f_{Hxc} ± 2

→ λ small better, shift pole better

⇒ neither λ nor shift alone explain adiab. perform well, combination of both

→ Pretend Xc slowly varying, most taken care by KS & Hartree

7) from prob 4)

$$\chi(\omega) = \left(\omega^2 - 2 - \frac{\omega^2}{\omega^2 - 4}\right)^{-1} = \left(\frac{\omega^4 - 4\omega^2 - \omega^2 + 8 - \omega^2}{\omega^2 - 4}\right)^{-1}$$

$$= \left(\frac{\omega^4 - 6\omega^2 + 8}{\omega^2 - 4}\right)^{-1}$$

$$f_1^{(\lambda=1)} \propto \lim_{\omega \to 1.199} \frac{\omega^2 - 4}{(\omega + 1.199)(\omega + 2.358)(\omega - 2.358)} = 6.259197$$

$$f_2 \propto \lim_{\omega \to 2.358} \frac{\omega^2 - 4}{(\omega + 1.199)(\omega - 1.199)(\omega + 2.358)} = 0.0802471$$

$$\boxed{\begin{array}{ll} f_1 = 0.7636 & \omega_1 = 1.199 \\ f_2 = 0.2364 & \omega_2 = 2.358 \end{array}}$$

$\Rightarrow$ two e^- excitation leave normal occupied

- Hubbard models, careful look at λ dep.
- Real sys. conj. polyenes low lying double excitation
- $\lambda \to 0$, slater det. & how much overlap
- Character diff. than reg. ψ theory

8) $$\chi(\omega) = \frac{\omega^2 - 4}{\omega^4 - 5\omega^2 - \lambda\omega^2 - \lambda^2\omega^2 + 4 + 4\lambda}$$ full kernal

Adiabatic approx: $f^{\lambda}_{Hxc}(\omega=0) = \lambda = \chi_s^{-1}(\omega) - \chi^{-1}(\omega)$

$$\chi(\omega) = \frac{1}{\omega^2 - 1 - \lambda} \qquad @\ \lambda = 0,\ \chi(\omega) = \frac{1}{\omega^2 - 1}$$

$$f_1 \propto \lim_{\omega \to 1} \frac{1}{\omega + 1} = \frac{1}{2} = 0.5$$

$$\boxed{f_1 = 0.5,\ \omega = 1\ \text{au}}$$

Double excitation

$f_1 = 1,\ \omega = 1$ au ; $f_2 = 0$, au => Johnny

=> Follow-up Q's, given explanation adiab. works well for single excitation, which is more accurate?

→ transition freq or oscillator str?

8) $f_i \propto \lim_{\omega \to \omega_i} \chi(\omega)(\omega - \omega_i)$

$\lambda = \frac{1}{2}$, $\chi(\vec{r}, \vec{r}, \omega) = \dfrac{4(\omega^2 - 4)}{4(\omega^4 - 4\omega^2) - 6(\omega^2 - 4) - \omega^2}$

$= \dfrac{4(\omega^2 - 4)}{(\omega - 1.170)(\omega + 1.170)(\omega + 2.093)(\omega - 2.093)}$

$f_1 \propto \lim_{\omega \to \omega_1 = 1.170} \chi(\omega)(\omega - 1.170) = \lim_{\omega \to \omega_1} \dfrac{4(\omega^2 - 4)}{(\omega + 1.170)(\omega + 2.093)(\omega - 2.093)}$

$= 1.4935$

$f_2 \propto \lim_{\omega \to \omega_2 = 2.093} \chi(\omega)(\omega - 2.093) = \lim_{\omega \to \omega_2} \dfrac{4(\omega^2 - 4)}{(\omega - 1.170)(\omega + 1.170)(\omega + 2.093)}$

$= 0.12077$

$N^2 \begin{pmatrix} 1.4935 & 0.12077 \end{pmatrix} \begin{pmatrix} 1.4935 \\ 0.12077 \end{pmatrix} = 1$

$N = 0.67455$

$$\boxed{\begin{array}{ll} f_1 = 0.9252 & \omega_1 = 1.170 \\ f_2 = 0.0806 & \omega_2 = 2.093 \end{array}}$$

$\lambda = \frac{1}{4}$

$f_1 = 0.928$

$f_2 =$