Adiabatic approx → λ^2 dominance correction, small λ
- truncate Taylor series as $\lambda \to 0$ align ⇒ KS transition freq.
- weakly correlated & in that limit ⇒ 90% accuracy, 1st order to λ
- KS freq good start & Adiabatic corrections 1st order is right

Week 5/6/7 Questions

- oscillator strength should go λ ⇒ problem breaks down in double excitation → λ^2
- artificiality of model
- λ vs λ^2; oscill vs. freq ↳ means freq more accurate than oscill.

May 16, 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:

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

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.
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.
7. The oscillator strength of a transition is proportional to the numerator of χ, i.e.

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

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 $\lambda \to 0$?

   $f^{HXC}(\omega \to 0)$, $\omega \to$ important double excitation

   (a) Given Kieron's explanation as to why the adiabatic approximation performs well for single excitations in molecules, which do you expect to be more accurate, the transition frequency or the oscillator strength? → Rabi oscillation is poor

9. Use Equation 7.25 from Ullrich to extract $\Im\chi_s$ for our problem, and check you can get $\Re\chi_s$ using the Kramers-Kronig relation. Repeat for χ (full) and for f_{HXC} (might be a trick for f_{HXC})

   next week, poles complication; Kramer Konig conditions

10. Replace the denominator in f_{HXC} with $\omega^2 - 2 - \lambda - \lambda^2$. Now recalculate your answers for $\lambda = \frac{1}{4}, \frac{1}{2}, 1$ and plot all transition frequencies and oscillator strengths as a function of λ, both exactly and in the adiabatic approximation. How do errors in the adiabatic approximation behave as $\lambda \to 0$? Compare corrections to the Kohn-Sham transitions and oscillator strengths, and their percent error. Can you derive exact formulas in this limit, and check them against your numerical results? look at how much it change

    → use prob. 10)

11. Try to expand the kernel $f_{\text{HXC}}^{\lambda}(\omega)$ as a Taylor series in powers of λ. Can you make it work? If not, say what goes wrong. If it does work, prove it by getting the correct expansion for transition frequencies and oscillator strengths.

Double of Adiabatic approx. ⇒ - Mukammel results - higher order will have higher excitation from KS value
- KS Double excita - corrections to the errors of KS freq.
(make λ infinitesimal) ⇒ 2 times single excitation

a) Use eqn 7.25 from Ullrich to extract $Im\, \chi_s$ for our problem, & check you can get $\mathbb{R}\chi_s$ using Kramers-Konig. Repeat for χ & for f_{Hxc}

$$\cancel{P\frac{1}{\omega^2-1} - i\pi\delta(\omega)} \to$$

$$Im\,\chi_s(\omega) = -P\int_0^\infty \frac{d\omega'}{\pi}\frac{2\omega}{\omega'^2-\omega^2} R\,\chi_s(\omega')$$

$$\oint \frac{dz}{2\pi i}\frac{\chi_s(z)}{z-\omega+i\eta} = 0$$

$$P\frac{1}{\omega^2-1} - i\pi\delta(\omega-1) = P\frac{1}{(\omega+1)(\omega-1)} - i\pi \cancel{\delta(\omega-1)}\,\chi_s(\omega) = 0$$

$$\chi_s(\omega) = \frac{1}{i\pi} P\frac{1}{(\omega+1)(\omega-1)}$$

Lehmann Rep.

$$\chi_s(\omega) = \frac{A}{\omega+1} + \frac{B}{\omega-1} = \frac{-\frac{1}{2}}{\omega+1} + \frac{\frac{1}{2}}{\omega-1}$$

$$= \frac{-1}{2(\omega+1)} + \frac{1}{2(\omega-1)}$$ ✓

$$\lim_{\eta\to 0^+}\left(\oint \frac{dz}{2\pi i}\left(\frac{-1}{2(z+1)} + \frac{1}{2(z-1)}\right)\frac{1}{z-1+i\eta} = 0\right)$$

$$\left(P\frac{1}{\omega-1} - i\pi\delta(\omega-1)\right)$$

$$\int_0^\infty \frac{d\omega}{2\pi i}\left(\frac{-1}{2(\omega+1)} + \frac{1}{2(\omega-1)}\right)\left(P\frac{1}{\omega-1}\right) - i\pi\delta(\omega-1)\underbrace{\left(\frac{-1}{2(\omega+1)} + \frac{1}{2(\omega-1)}\right)}_{=0}\Bigg]$$

$$\int_0^\infty \frac{d\omega}{2\pi i}\Bigg[\underbrace{P\left(\frac{1}{\omega-1}\right)\left(\frac{-1}{2(\omega+1)} + \frac{1}{2(\omega-1)}\right)} \quad \underbrace{}$$

use mathematica

$$\chi_s(\omega) = \underbrace{P\int_0^\infty \frac{d\omega}{4\pi i}\frac{1}{(\omega-1)^2}}_{Im\,\chi_s(\omega)} + \underbrace{P\int_0^\infty d\omega \frac{\delta(\omega-1)}{4(\omega-1)}}_{Re\,\chi_s(\omega)}$$

2nd order pole for full χ

10) $f^{(\lambda)}_{HXC}(\omega) = \lambda + \frac{\lambda^2\omega^2}{\omega^2-2-\lambda-\lambda^2} = \chi_s^{-1} - \chi^{-1}$

$$\lambda + \frac{\lambda^2\omega^2}{\omega^2-2-\lambda-\lambda^2} = \omega^2 - 1 - \chi^{-1}$$

$$\chi^{-1} = \omega^2 - 1 - \lambda - \underbrace{\frac{\lambda^2\omega^2}{\omega^2-2-\lambda-\lambda^2}}$$

adiabatic approx: $\chi^{-1} = \omega^2 - 1 - \lambda$

$$\chi = \frac{1}{\omega^2-1-\lambda}$$

$\lambda = \frac{1}{4}$ $\quad \chi = \frac{1}{\omega^2 - 5/4} = \frac{1}{(\omega+\frac{\sqrt{5}}{2})(\omega-\frac{\sqrt{5}}{2})}$

$\boxed{\omega = \pm\frac{\sqrt{5}}{2}} = \pm 1.1180$ $\quad f_1 \propto \lim_{\omega\to\frac{\sqrt{5}}{2}} \frac{1}{(\omega+\frac{\sqrt{5}}{2})(\omega-\frac{\sqrt{5}}{2})}(\omega-\frac{\sqrt{5}}{2})$

$$= \boxed{0.4472}$$

$\lambda = \frac{1}{2}$ $\quad \chi = \frac{1}{\omega^2 - \frac{3}{2}}$ $\quad f_1 \propto \lim_{\omega\to\sqrt{\frac{3}{2}}} \frac{1}{(\omega+\sqrt{\frac{3}{2}})(\omega-\sqrt{\frac{3}{2}})}(\omega-\sqrt{\frac{3}{2}})$

$\boxed{\omega \pm \sqrt{\frac{3}{2}}} = \pm 0.866025$ $\quad = \frac{1}{2}\sqrt{\frac{2}{3}} = \boxed{0.4082}$

$\lambda = 1$ $\quad \chi = \frac{1}{\omega^2-2} = \frac{1}{(\omega+\sqrt{2})(\omega-\sqrt{2})}$

$\boxed{\omega = \pm\sqrt{2}}$ $\quad f_1 \propto \lim_{\omega\to\sqrt{2}} \frac{(\omega-\sqrt{2})}{(\omega+\sqrt{2})(\omega-\sqrt{2})}$

$$= \frac{1}{2\sqrt{2}} = \boxed{0.3535}$$

10) $\chi^{-1} = \omega^2 - 1 - \lambda - \dfrac{\lambda^2\omega^2}{\omega^2 - 2 - \lambda - \lambda^2}$

$$= \frac{\left(\omega^4 - 2\omega^2 - \lambda\omega^2 - \lambda^2\omega^2 - \omega^2 + 2 + \lambda + \lambda^2 - \lambda\omega^2 + 2\lambda + \lambda^2 + \lambda^3 - \lambda^2\omega^2\right)}{\omega^2 - 2 - \lambda - \lambda^2}$$

$$= \frac{\omega^4 - (2 + \lambda + \lambda^2 + \lambda + \lambda^2)\omega^2 + 2 + 3\lambda + 2\lambda^2 + \lambda^3}{\omega^2 - \lambda^2 - \lambda - 2}$$

$$\chi = \frac{\omega^2 - \lambda^2 - \lambda - 2}{\omega^4 - (3 + 2\lambda + 2\lambda^2)\omega^2 + \lambda^3 + 2\lambda^2 + 3\lambda + 2}$$

Mathematica

$\boxed{\omega = \{\pm 1.1322, \pm 1.7940\}}$

$\lambda = \frac{1}{2}$ $\quad \chi = \dfrac{\omega^2 - 2.75}{\omega^4 - 4.5\omega^2 + 4.125}$

$$f_1 \propto \lim_{\omega \to 1.1322} \frac{\omega^2 - 2.75}{(\omega + 1.1322)(\omega + 1.7940)(\omega - 1.7940)}$$

$$= \boxed{0.334795}$$

$$f_2 \propto \lim_{\omega \to 1.7940} \frac{\omega^2 - 2.75}{(\omega + 1.1322)(\omega - 1.1322)(\omega + 1.7940)}$$

$$= \boxed{0.06742}$$ ← normalize

Mathematica

$\boxed{\omega = \{\pm 1.08829, \pm 1.5623\}}$

$\lambda = \frac{1}{4}$ $\quad \chi = \dfrac{\omega^2 - 2.3125}{\omega^4 - 3.625\omega^2 + 2.89063}$

$$f_1 \propto \lim_{\omega \to 1.08824} \frac{\omega^2 - 2.3125}{(\omega + 1.08829)(\omega + 1.5623)(\omega - 1.5623)}$$

$$= \boxed{0.4125}$$

$$f_2 \propto \lim_{\omega \to 1.5623} \frac{\omega^2 - 2.3125}{(\omega + 1.08829)(\omega - 1.08829)(\omega + 1.5623)}$$

$$= \boxed{0.03268}$$

↑ normalize

10) $\lambda = 1$ $\lambda = \dfrac{\omega^2 - 4}{\omega^4 - 7\omega^2 + 8}$

Mathematica

$$\boxed{\omega = \{\pm 1.19935, \pm 2.3583\}}$$

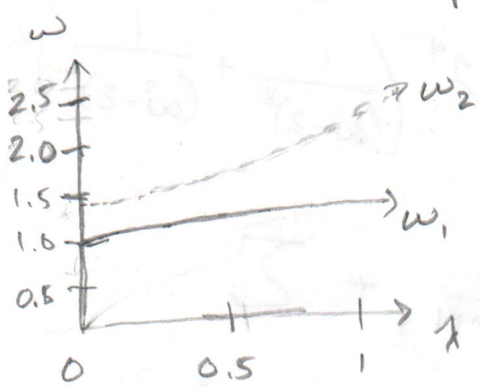
$$f_1 \propto \lim_{\omega \to 1.1994} \frac{\omega^2 - 4}{(\omega + 1.19935)(\omega + 2.3583)(\omega - 2.3583)} = \boxed{0.2590}$$

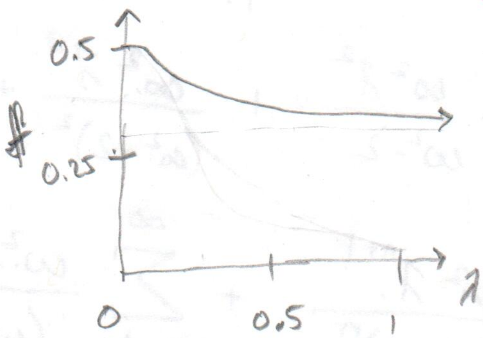
$$f_2 \propto \lim_{\omega \to 2.3583} \frac{\omega^2 - 4}{(\omega + 1.19935)(\omega - 1.19935)(\omega + 2.3583)} = \boxed{0.0803}$$

normalize

In terms of λ,

$$\omega(\lambda) = \left\{ \pm\sqrt{\frac{3}{2} + \lambda + \lambda^2 - \frac{1}{2}\sqrt{1 + 4\lambda^2(2 + \lambda + \lambda^2)}},\ \pm\sqrt{\lambda + \lambda^2 + \frac{1}{2}\left(3 + \sqrt{1 + 4\lambda^2(2 + \lambda + \lambda^2)}\right)} \right\}$$





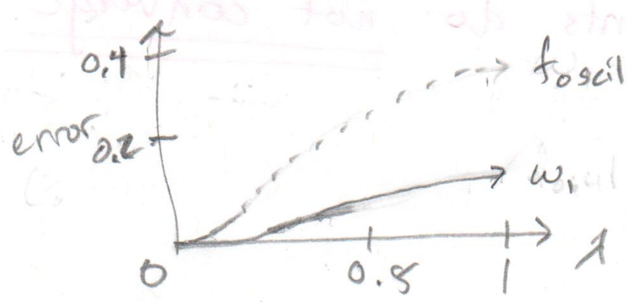
- Real space $\hat{H}$, then oscillator strength garanteed to be normalized
- adiabatic approx has oscillator strength of 1

$$\omega\_error(\lambda) = -1 + \frac{\sqrt{2}\sqrt{1+\lambda}}{\sqrt{3 + 2\lambda(1+\lambda) - \sqrt{1 + 4\lambda^2(2 + \lambda + \lambda^2)}}}$$

$$\lim_{\lambda \to 0} \omega\_error(\lambda) = -1 + \frac{\sqrt{2}}{\sqrt{3 - 1}} = 1 - 1 = \boxed{0}$$

$$oscil\_error(\lambda) = \frac{\left(-\sqrt{1+\lambda} - \sqrt{1+\lambda}\sqrt{1 + 4\lambda^2(2 + \lambda + \lambda^2)} + \dfrac{\sqrt{2 + 8\lambda^2(2 + \lambda + \lambda^2)}}{\sqrt{3 + 2\lambda(1+\lambda) - \sqrt{1 + 4\lambda^2(2 + \lambda + \lambda^2)}}}\right)}{\sqrt{1+\lambda}\left(1 + \sqrt{1 + 4\lambda^2(2 + \lambda + \lambda^2)}\right)}$$

$$\lim_{\lambda \to 0} oscil\_error(\lambda) = 0$$



fosc1l error is

ω_1 error is linear w/ λ

11) Expand kernel $f^{\lambda}_{Hxc}(\omega)$ as taylor series in powers of λ

$$f^{\lambda}_{Hxc}(\omega) = \lambda + \frac{\lambda^2 \omega^2}{\omega^2 - 2 - \lambda - \lambda^2}$$

$$f(x) = f(0) + \frac{f'(0)\lambda}{1!} + \frac{f''(0)\lambda^2}{2!} + \cdots \quad \text{where } 0 \le \lambda \le 1$$

$$\Rightarrow f^{\lambda}_{Hxc}(\omega) = \frac{\lambda}{1!} + \frac{2\omega^2\lambda^2}{2!(\omega^2-2)} + \frac{6\omega^2\lambda^3}{3!(\omega^2-2)^2} + \frac{24\omega^2\lambda^4}{4!}\left(\frac{1}{(\omega^2-2)^3} + \frac{1}{(\omega^2-2)^2}\right) + \cdots$$

$$= \lambda + \frac{\omega^2\lambda^2}{\omega^2-2} + \frac{\omega^2\lambda^3}{(\omega^2-2)^2} + \omega^2\lambda^4\left(\frac{1}{(\omega^2-2)^3} + \frac{1}{(\omega^2-2)^2}\right) + \cdots$$

→ iffy, after this

$$= \lambda + \sum_{n=1}^{\infty} \frac{\omega^2\lambda^{n+1}}{(\omega^2-2)^n} + \sum_{n=1}^{\infty} \frac{\omega^2\lambda^{n+1}\, n}{(\omega^2-2)^{n+1}} + \sum \cdots$$

Ratio test: $\lim_{n\to\infty}\left|\frac{\omega^2\lambda^{n+2}}{(\omega^2-2)^{n+1}} \cdot \frac{(\omega^2-2)^n}{\omega^2\lambda^n}\right| = \lim_{n\to\infty}\left|\frac{\lambda^2}{(\omega^2-2)}\right|$

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

$$\frac{\lambda^2}{\omega^2-2} < 1 \qquad \omega^2 - 2 > \lambda^2$$

$$\omega^2 > \lambda^2 + 2 \Rightarrow \omega > \pm\sqrt{\lambda^2+2} \qquad \text{series converges if}$$

$\Rightarrow$ No, $f^{\lambda}_{Hxc}(\omega)$ Taylor series ~~around λ does not~~ converge

coeffucents do not converge

Prob (1) $f^{\lambda}_{Hxc}(\omega) = \underbrace{\frac{\lambda^2 \omega^2}{\omega^2 - 2 - \lambda - \lambda^2}}_{\text{infinite error, divergence DNE}} + \lambda$

$$\simeq \frac{\lambda^2\omega^2}{\omega^2-2}\left(\frac{1}{1-\frac{\lambda+\lambda^2}{\omega^2-2}}\right) + \lambda$$

$$\simeq \underbrace{\frac{\lambda^2\omega^2}{\omega^2-2} + \frac{\omega^2\lambda^2(\lambda+\lambda^2)}{(\omega^2-2)^2} + \ldots}$$

well defined in Taylor series of numerator & denominator individually

$\Rightarrow$ coefficients of Taylor Series are diverging due to the poles

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$\Rightarrow$ Dirac 1933, TDHF to obtain exchange of uniform e^- gas. (Bloch did it first)

2001 Furche

- Exact functional $\rightarrow$ calculated w/ circular dichrosim in chiral systems (via density $\downarrow$ TD DFT or TD current density)
  - $\rightarrow$ exact?
- $\vec{J}(t,x)$ is KS current density
- no gauranteed there TD XC current fields
- Andy Teal & Helgaker $\Rightarrow$ Adiabatic connection on static magnetic field

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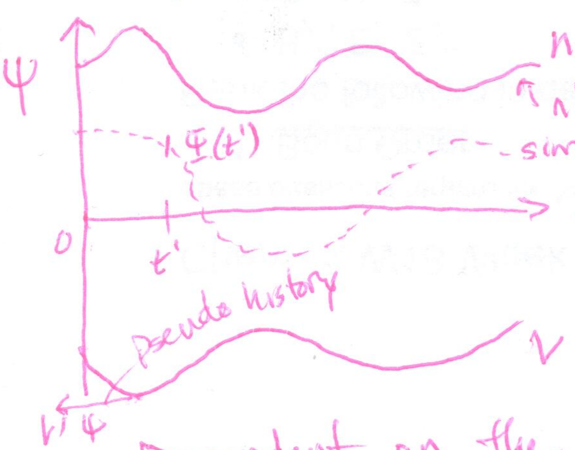
Memory in TDDFT



$n[v, \Phi]$
$n[v_t, \Phi(t')]$
simulation

- TD Schrödinger 1st order
  - $\hookrightarrow$ exact condition
  - nondegenerate, no dep. Φ_0
- Backward in time
- Apply pseudo-prehistory to get the density
- could always attach pot. to actual pot. to apply density alone in rescale.

- Dependent on the past