Week 5/6/7 Questions

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 $\lambda \to 0$?

   (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?

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 and for f_{HXC} (might be a trick for f_{HXC})

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?

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.