Week 8/9 Questions

May 28, 2020

In a non-spin decomposed DFT treatment, Casida's equations are 7.138 with

$$C_{qq'} = \omega_q^2 \, \delta_{qq'} + 4\sqrt{\omega_q \omega_{q'}} M_{qq'} \qquad\qquad q = (i, \, a).$$

Suppose you have 2 transitions only, with $\omega_1 = 9$ eV and $\omega_2 = 12$ eV, and the matrix elements of M are $M_{11} = 3$ eV, $M_{22} = 2$ eV, and $M_{12} = 0.2$ eV.

1. Find the exact transition frequencies.
2. Repeat (1) in the Tamm-Dancoff Approximation. What percent error does it make in each ω? What percent error does it make in the shift from the Kohn-Sham transition frequencies?
3. Repeat (1) in the Small Matrix Approximation, answering the same questions as in (2).
4. Repeat (3) for the single-pole approximation. Which is the bigger source of error, SMA or TDA?

In fact, the Kohn-Sham oscillator strengths are $f_1 = \frac{9}{10}$ and $f_2 = \frac{1}{10}$.

5. Calculate the exact oscillator strengths. Check the Thomas–Reiche–Kuhn sum rule.
6. Repeat (5) in TDA and report percent errors. Is the sum rule satisfied?
7. Repeat (3) and (4) for oscillator strengths.
8. Using Lorentzians of width 0.2, plot the absorption spectra for (a) KS, (b) exact, (c) in TDA, (d) in SMA. Comment.