- SMA better since coupling is smaller
- Double pole approx - 2006 paper Kieron
- output coupling

X & Y
↳ occupied & unoccupied

2nd deriv. Hessian (orb. rot.)
↳ f_{HXC} (A+B) & (A-B)

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.

KS shift

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? — overall bigger error; induces bigger error to

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? — TDA not follow sum-rule
7. Repeat (3) and (4) for oscillator strengths. SMA - follows same value - same as KS value; SPA - over estimate, not follow sum rule
8. Using Lorentzians of width 0.2, plot the absorption spectra for (a) KS, (b) exact, (c) in TDA, (d) in SMA. Comment. - SMA & SPA overlap

1) $C Z = \Omega^2 Z$

$\omega_1 = 9\,eV$, $\omega_2 = 12\,eV$

$$C = \begin{pmatrix} 9^2 + 4\cdot 9\cdot 3 & 4\sqrt{9\cdot 12}\cdot 0.2 \\ 4\sqrt{9\cdot 12}\cdot 0.2 & 12^2 + 4\cdot 12\cdot 2 \end{pmatrix} = \begin{pmatrix} 189 & 8.31384 \\ 8.31384 & 240 \end{pmatrix}$$

$\boxed{\Omega_{exact} = \pm 15.5345\,eV, \pm 13.6996\,eV}$

KS-shifts errors

3) $C^{SMA} = \begin{pmatrix} 189 & 0 \\ 0 & 240 \end{pmatrix}$ $\boxed{\Omega = \pm 15.4919\,eV, \pm 13.7477\,eV}$

$\boxed{\%\text{ Errors } 0.274\%,\ 0.3513\%}$

K=2M

4) $C^{SPA} = \begin{pmatrix} 9 + 2\cdot 3 & 0 \\ 0 & 12 + 2\cdot 2 \end{pmatrix} = \begin{pmatrix} 15 & 0 \\ 0 & 16 \end{pmatrix}$; consider A off-diags as well

$\boxed{\Omega = 15\,eV, 16\,eV}$

KS-shift → higher errors

$\boxed{\%\text{ errors } 9.492\%\ \ 2.996\%}$

4) SPA → TDA + SMA from prob. 2; mixed up approx.

5) $f_1 = \frac{9}{10}$ & $f_2 = \frac{1}{10}$ ⇒ KS oscillator strengths

$$f_n = \frac{2\Omega_n}{3} \sum_{\mu=1}^{3} \left|\langle \Psi_n | \hat{r}_\mu | \Psi_0 \rangle\right|^2$$

$$= \frac{2}{3} \sum_{i=1}^{3} \left| x_i^T (\underline{A} - \underline{B})^{1/2} Z_n \right|^2$$

Gabe: Diag. C mat & inverse

eqn 7.145

Bhupalee

$$X_i^{KS} = \frac{3 f_i}{2\omega_i}$$

$$(A-B)^{1/2} \rightarrow \omega^{1/2}$$

06/07/20: Week 8/9 Questions

2) TDA approximation

$$\underline{A} X = \underline{\underline{\Omega}} X$$

$$\det(\underline{A} - \Omega \mathbb{1}) X = 0$$

$$\boxed{\Omega^{TDA} = \{14.86, 16.14\}}$$

$$\boxed{\%\text{ error: } 8.47\% \quad 3.90\%}$$

since $\underline{C} = (\underline{A} - \underline{B})^{1/2} (\underline{A} + \underline{B}) (\underline{A} - \underline{B})^{1/2}$,

$$A_{ij} = \delta_{ij} \omega_i + 2 M_{ij}$$

$$A_{11} = 9 + 2 \cdot 3 = 15$$

$$A_{12} = 2(0.2) = 0.4 = A_{21}$$

$$A_{22} = 12 + 2(2) = 16$$

$$\underline{A} = \begin{pmatrix} 15 & 0.4 \\ 0.4 & 16 \end{pmatrix}$$

KS transition freqs:

$$\Delta\omega_{exact} = \omega_{exact} - \omega_s = \{4.6996, 3.53451\}$$

$$\Delta\omega_{TDA} = \omega_{TDA} - \omega_s = \{8.85969, 4.14031\}$$

$$\boxed{\%\text{ error KS shift} \quad 24.68\% \quad 17.14\%}$$

3) Small matrix approx.

$$C_{ij} = 0 \qquad \underline{C} = \begin{pmatrix} 189 & 0 \\ 0 & 240 \end{pmatrix} \qquad \underline{C} Z = \Omega^2 Z$$

$$\boxed{\Omega^{SMA} = \{\pm 13.747, \pm 15.4919\} \quad \%\text{ error} \quad 0.3513\% \quad 0.2741\%}$$

$$\boxed{\Delta\omega_{SMA} = \{4.7477, 3.4919\} \quad \%\text{ error KS shift} \quad 1.02\%, \ 1.20\%}$$

4) Single Pole Approx. - combines TDA & SMA

$$\boxed{\Omega^{SPA} = \{15, 16\} \quad \%\text{ error} \quad 9.492\% \quad 2.496\%}$$

$$\boxed{\Delta\omega_{SPA} = \{6, 4\} \quad \%\text{ error KS-shift} \quad 27.67\% \quad 13.1698\%}$$

⇒ TDA greater source for error.

5) eqn 7.146) $f_n = \frac{2}{3}\sum_{i=1}^{3} \left| X_i^T (\underline{A} - \underline{B})^{1/2} Z_n \right|^2$

$\begin{pmatrix} \omega_p & 0 \\ 0 & \omega_{p'} \end{pmatrix}$ eigenvectors

eqn 7.52) $f_n = \frac{2\Omega_n}{3}\sum_{\mu=1}^{3} |\langle \Psi_n | \hat{r}_\mu | \Psi_0 \rangle|^2$

$\cancel{\sum_{\mu=1}^{3}} |\langle \Psi_n | \hat{r}_\mu | \Psi_0 \rangle|^2 = \frac{3 f_n}{2\Omega_n}$

$\hat{r}_\mu = \sum_i^N r_{\mu,i}$ μ^{th} component of N-elec positi operator

components

$\hat{r}_\mu |\Psi_0\rangle = \sum_n \left(\frac{3 f_n}{2\Omega_n}\right)^{1/2} |\Psi_n\rangle$

$\vec{X} \Rightarrow$ eigenvectors where Z_n

$f_1 = \frac{2}{3}\sum_{i=1}^{3} \left| X_i^T (\underline{A} - \underline{B})^{1/2} Z_n \right|^2$

$= 2 \left| Z_n^T (A - B)^{1/2} Z_n \right|^2$

$\vec{X}_i = \left(\frac{3 f_1^{ks}}{2\Omega_1}, \frac{3 f_2^{ks}}{2\Omega_2}\right)^{1/2} = 2 \left| (0.1569, 0.9876) \begin{pmatrix} \sqrt{9} & 0 \\ 0 & \sqrt{12} \end{pmatrix} \begin{pmatrix} 0.1569 \\ 0.9876 \end{pmatrix} \right|^2$

$$\boxed{f_1 = \frac{2}{3} \left| \left(\frac{3 \cdot f_1^{ks}}{2\Omega_1^{ks}}, \frac{3 f_2^{ks}}{2\Omega_2^{ks}} \right)^{1/2} \begin{pmatrix} \sqrt{9} & 0 \\ 0 & \sqrt{12} \end{pmatrix} \begin{pmatrix} -0.9876 \\ 0.1569 \end{pmatrix} \right|^2 = 0.7873}$$

$$\boxed{f_2 = 0.2127}$$

$$\boxed{f_1 + f_2 = 1 \text{, yes confirmed}}$$

6) TDA oscillator strengths

$$f_2 = \frac{2}{3}\left| \left(\frac{3 f_1^{ks}}{2 \Omega_1^{ks}}, \frac{3 f_2^{ks}}{2 \Omega_2^{ks}} \right)^{1/2} \begin{pmatrix} \sqrt{5} & 0.4 \\ 0.4 & \sqrt{5} \end{pmatrix}^{1/2} \begin{pmatrix} 0.331 \\ 0.9436 \end{pmatrix} \right|^2$$

$= \cancel{0.49738}\ 0.566384$

$f_1 = 1.17148$

$f_1 + f_2 = 1.73786 \neq 1$ not satisfied

7) Repeat for SMA

$$f_1^{SMA} = \frac{2}{3}\left| \left(\frac{3}{2}\frac{f_1^{ks}}{\Omega_1^{ks}}, \frac{3}{2}\frac{f_2^{ks}}{\Omega_2} \right) \begin{pmatrix} \sqrt{15.491} & 0 \\ 0 & \sqrt{13.747} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right.$$

$= 1.5492$

$f_2^{SMA} = 0.1146$

$f_1^{SMA} + f_2^{SMA} = 1.6638 \neq 1$

not satisfied

$f_1^{SPA} = 1.5$ $f_2^{SPA} = 0.1333$ $f_1^{SPA} + f_2^{SPA} = 1.633$

not satisfied