Excited-to-excited transition dipoles

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March 2, 2024

By neglecting the response of the XC kernel and the Hartree XC kernel, the element of the first hyperpolarizability tensor in the sTD-DFT framework are: [1]

$$\beta_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2) = -\left\langle\left\langle\hat{\mu}_\zeta;\hat{\mu}_\sigma,\hat{\mu}_\tau\right\rangle\right\rangle_{\omega_1,\omega_2} = \mathcal{A}_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2) - \mathcal{B}_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2), \tag{1}$$

with $\omega_\varsigma = -\omega_1-\omega_2$, and:

$$\mathcal{A}_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2) = \sum_{\mathcal{P}}\sum_{ia,ja} x_{ia,\zeta}(\omega_\varsigma)\,[-\mu_{ij,\sigma}]\,y_{ja,\tau}(\omega_2), \tag{2}$$

$$\mathcal{B}_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2) = \sum_{\mathcal{P}}\sum_{ia,ib} x_{ia,\zeta}(\omega_\varsigma)\,[-\mu_{ab,\sigma}]\,y_{ib,\tau}(\omega_2), \tag{3}$$

where $\sum_{\mathcal{P}}$ is the sum over the sequence of permutations of the pairs of components and energies, $\{(\zeta,\omega_\varsigma),(\sigma,\omega_1),(\tau,\omega_2)\}$. For example,

$$\mathcal{A}_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2) = \sum_{ia,ja}\left\{\begin{array}{l} x_{ia,\zeta}(\omega_\varsigma)\,[-\mu_{ij,\sigma}]\,y_{ja,\tau}(\omega_2) + x_{ia,\zeta}(\omega_\varsigma)\,[-\mu_{ij,\tau}]\,y_{ja,\sigma}(\omega_1) \\ +x_{ia,\sigma}(\omega_1)\,[-\mu_{ij,\zeta}]\,y_{ja,\tau}(\omega_2) + x_{ia,\sigma}(\omega_1)\,[-\mu_{ij,\tau}]\,y_{ja,\zeta}(\omega_\varsigma) \\ +x_{ia,\tau}(\omega_2)\,[-\mu_{ij,\zeta}]\,y_{ja,\sigma}(\omega_1) + x_{ia,\tau}(\omega_2)\,[-\mu_{ij,\sigma}]\,y_{ja,\zeta}(\omega_\varsigma) \end{array}\right\},$$

and the same goes for $\mathcal{B}$.

The spectra representation of linear response vectors $\mathbf{x}_\zeta(\omega)$ and $\mathbf{y}_\zeta(\omega)$ is given by: [2]

$$x_{ia,\zeta}(\omega) = \sum_{|m\rangle}\mu_{ia,\zeta}\,(x^m_{ia}+y^m_{ia})\,\left[\frac{x^m_{ia}}{\omega-\omega_m} - \frac{y^m_{ia}}{\omega+\omega_m}\right],$$

$$y_{ia,\zeta}(\omega) = \sum_{|m\rangle}\mu_{ia,\zeta}\,(x^m_{ia}+y^m_{ia})\,\left[\frac{y^m_{ia}}{\omega-\omega_m} - \frac{x^m_{ia}}{\omega+\omega_m}\right],$$

where $\mathbf{x}^m$ and $\mathbf{y}^m$ are the amplitude vectors associated to excited state $|m\rangle$. Thus, the "residue" of the linear response vectors are:

$$\begin{aligned}
\lim_{\omega_1\to-\omega_m}(\omega_1+\omega_m)\,x_{ia,\zeta}(\omega_1) &= \mu_{ia,\zeta}\,(x^m_{ia}+y^m_{ia})\,(-y^m_{ia}),\\
\lim_{\omega_1\to-\omega_m}(\omega_1+\omega_m)\,y_{ia,\zeta}(\omega_1) &= \mu_{ia,\zeta}\,(x^m_{ia}+y^m_{ia})\,(-x^m_{ia}),\\
\lim_{\omega_2\to\omega_n}(\omega_2-\omega_n)\,x_{ia,\zeta}(\omega_2) &= \mu_{ia,\zeta}\,(x^n_{ia}+y^n_{ia})\,(x^n_{ia}),\\
\lim_{\omega_2\to\omega_n}(\omega_2-\omega_n)\,y_{ia,\zeta}(\omega_2) &= \mu_{ia,\zeta}\,(x^n_{ia}+y^n_{ia})\,(y^n_{ia}).
\end{aligned}$$

Following Ref. [2], the double residue of the quadratic response function is:

$$\lim_{\omega_1\to-\omega_m}\lim_{\omega_2\to\omega_n}(\omega_1+\omega_m)\,(\omega_2-\omega_n)\,\left\langle\left\langle\hat{\mu}_\zeta;\hat{\mu}_\sigma,\hat{\mu}_\tau\right\rangle\right\rangle_{\omega_1,\omega_2}$$

$$= \langle 0|\hat{\mu}_\zeta|m\rangle\,\langle m|\hat{\mu}_\sigma - \delta_{mn}\,\langle 0|\hat{\mu}_\sigma|0\rangle\,|n\rangle\,\langle n|\hat{\mu}_\tau|0\rangle \tag{4}$$

$$= \lim_{\omega_1\to-\omega_m}\lim_{\omega_2\to\omega_n}(\omega_1+\omega_m)\,(\omega_2-\omega_n)\,[\mathcal{B}_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2) - \mathcal{A}_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2)]. \tag{5}$$

In particular, from Eq. (2):

$$\lim_{\omega_1\to-\omega_m}\lim_{\omega_2\to\omega_n}(\omega_1+\omega_m)(\omega_2-\omega_n)\,\mathcal{A}_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2)$$
$$=\sum_{ia,ja}\left\{\begin{array}{l}\mu_{ia,\zeta}\,(x_{ia}^m+y_{ia}^m)\,(-y_{ia}^m)\,[-\mu_{ij,\zeta}]\,\mu_{ja,\tau}\,(x_{ja}^n+y_{ja}^n)\,(y_{ja}^n)\\+\mu_{ia,\tau}\,(x_{ia}^n+y_{ia}^n)\,(x_{ia}^n)\,[-\mu_{ij,\zeta}]\,\mu_{ja,\zeta}\,(x_{ja}^m+y_{ja}^m)\,(-x_{ja}^m)\end{array}\right\},$$

and, from Eq. (3),

$$\lim_{\omega_1\to-\omega_m}\lim_{\omega_2\to\omega_n}(\omega_1+\omega_m)(\omega_2-\omega_n)\,\mathcal{B}_{\zeta\sigma\tau}(\omega_\varsigma;\omega_1,\omega_2)$$
$$=\sum_{ia,ib}\left\{\begin{array}{l}\mu_{ia,\zeta}\,(x_{ia}^m+y_{ia}^m)\,(-y_{ia}^m)\,[-\mu_{ab,\zeta}]\,\mu_{ib,\tau}\,(x_{ib}^n+y_{ib}^n)\,(y_{ib}^n)\\+\mu_{ia,\tau}\,(x_{ia}^n+y_{ia}^n)\,(x_{ia}^n)\,[-\mu_{ab,\zeta}]\,\mu_{ib,\zeta}\,(x_{ib}^m+y_{ib}^m)\,(-x_{ib}^m)\end{array}\right\}.$$

Since,

$$\langle 0|\hat{\mu}_\zeta|m\rangle=\sqrt{2}\sum_{ia}\vec{\mu}_{ia,\zeta}\,(x_{ia}^m+y_{ia}^m),$$

equating Eqs. (4) and (5) results in: [2, 3]

$$\langle m|\hat{\mu}_\zeta-\delta_{mn}\,\langle 0|\hat{\mu}_\zeta|0\rangle\,|n\rangle=\frac{1}{2}\left\{\sum_{ia,ib}\mu_{ab,\zeta}\,[x_{ia}^n\,x_{ib}^m+y_{ia}^m\,y_{ib}^n]-\sum_{ia,ja}\mu_{ij,\zeta}\,[x_{ia}^n\,x_{ja}^m+y_{ia}^m\,y_{ja}^n]\right\}. \tag{6}$$

References

[1] Marc de Wergifosse and Stefan Grimme. Nonlinear-response properties in a simplified time-dependent density functional theory (std-dft) framework: Evaluation of the first hyperpolarizability. *J. Chem. Phys.*, 149:024108, 2018.

[2] Marc de Wergifosse and Stefan Grimme. Nonlinear-response properties in a simplified time-dependent density functional theory (sTD-DFT) framework: Evaluation of excited-state absorption spectra. *J. Chem. Phys.*, 150:094112, 2019.

[3] Marc de Wergifosse and Stefan Grimme. Perspective on Simplified Quantum Chemistry Methods for Excited States and Response Properties. *J. Phys. Chem. A*, 125:3841–3851, 2021.