Vibrational contributions to electronic properties
Formulas implemented in NACHOS

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Abstract

The following formulas are due to the incredible work of Bishop and Kirtman [1]. The results were cheked against a paper by Bishop [2]. For completeness, one can also check their original contributions [3, 4, 5]. Note that the form of their 1992 paper [5] was used for $[\mu^2]^{2,0}$ (and derivated). Quartic force constants and third order derivatives of electronic properties were omited in any of order II contributions, as it is usual in the litterature.

Note that:

$$\lambda^{\pm ij\ldots}_{xy\ldots} = [(\omega_x+\omega_y+\ldots)+(\omega_i+\omega_j+\ldots)]^{-1}[(\omega_x+\omega_y+\ldots)-(\omega_i+\omega_j+\ldots)]^{-1},$$

with ω_i, ω_j ... the optical frequencies and ω_x, ω_y ... the vibrational frequencies.

1 Zero-point vibrationnal average (ZPVA)

For any electronic property P, $\Delta P^{ZPVA} = [P]^{1,0} + [P]^{0,1}$, with

$$[P]^{1,0} = \frac{1}{4}\sum_a \left(\frac{\partial^2 P}{\partial Q_a^2}\right)\omega_a^{-1} \tag{1}$$

$$[P]^{0,1} = -\frac{1}{4}\sum_{ab} F_{abb}\left(\frac{\partial P}{\partial Q_a}\right)\omega_a^{-2}\,\omega_b^{-1} \tag{2}$$

2 Pure vibrational (pv) contribution to polarizability

$$\alpha^{pv} = [\mu^2]^0 + [\mu^2]^{\mathrm{II}}, \tag{3}$$

with:

$$[\mu^2]^{0,0} = \frac{1}{2}\sum_{\mathcal{P}_{ij}}\sum_a \left(\frac{\partial \mu_i}{\partial Q_a}\right)\left(\frac{\partial \mu_j}{\partial Q_a}\right)\lambda_a^{\pm\sigma} \tag{4}$$

$$[\mu^2]^{1,1} = -\frac{1}{4}\sum_{\mathcal{P}_{ij}}\sum_{abc}\left(\frac{\partial^2 \mu_i}{\partial Q_a\partial Q_b}\right)\left\{F_{abc}\left(\frac{\partial \mu_j}{\partial Q_c}\right)\lambda_{ab}^{\pm\sigma}\,\lambda_c^{\pm\sigma}\,(\omega_a^{-1}+\omega_b^{-1}) + F_{bcc}\left(\frac{\partial \mu_j}{\partial Q_a}\right)\lambda_a^{\pm\sigma}\,\omega_b^{-2}\,\omega_c^{-1}\right\} \tag{5}$$

$$[\mu^2]^{2,0} = \frac{1}{4}\sum_{\mathcal{P}_{ij}}\sum_{ab}\left(\frac{\partial^2 \mu_i}{\partial Q_a\partial Q_b}\right)\left(\frac{\partial^2 \mu_j}{\partial Q_a\partial Q_b}\right)\lambda_{ab}^{\pm\sigma}\,\omega_a^{-1} \tag{6}$$

$$[\mu^2]^{0,2} = \frac{1}{8}\sum_{\mathcal{P}_{ij}}\sum_{abcd}\left(\frac{\partial \mu_i}{\partial Q_c}\right)\left(\frac{\partial \mu_j}{\partial Q_d}\right)\left[F_{aab}\,F_{bcd}\,\lambda_c^{\pm\sigma}\lambda_d^{\pm\sigma}\,\omega_b^{-2} + 2\,F_{abc}\,F_{abd}\,\lambda_{ab}^{\pm\sigma}\,\lambda_c^{\pm\sigma}\,\lambda_d^{\pm\sigma}\right] \tag{7}$$

3 Pure vibrational (pv) contribution to first hyperpolarizability

$$\beta^{pv} = [\mu\alpha]^0 + [\mu^3]^{\mathrm{I}} + [\mu\alpha]^{\mathrm{II}}, \tag{8}$$

with:

$$[\mu^3]^{1,0} = \frac{1}{2} \sum_{\mathcal{P}_{ijk}} \sum_{ab} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial^2 \mu_j}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_k}{\partial Q_b} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm 2} \tag{9}$$

$$[\mu^3]^{0,1} = -\frac{1}{6} \sum_{\mathcal{P}_{ijk}} \sum_{abc} F_{abc} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \mu_j}{\partial Q_b} \right) \left(\frac{\partial \mu_k}{\partial Q_c} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm 1} \lambda_c^{\pm 2} \tag{10}$$

$$[\mu\alpha]^{0,0} = \frac{1}{2} \sum_{\mathcal{P}_{ijk}} \sum_{a} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \alpha_{jk}}{\partial Q_a} \right) \lambda_a^{\pm\sigma} \tag{11}$$

$$\begin{aligned}[\mu\alpha]^{1,1} = -\frac{1}{8} \sum_{\mathcal{P}_{ijk}} \sum_{abc} \Bigg\{ F_{abc} \left[\left(\frac{\partial^2 \mu_i}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \alpha_{jk}}{\partial Q_c} \right) + \left(\frac{\partial^2 \alpha_{jk}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_i}{\partial Q_c} \right) \right] \lambda_{ab}^{\pm\sigma} \lambda_c^{\pm\sigma} (\omega_a^{-1} + \omega_b^{-1}) \\ + F_{bcc} \left[\left(\frac{\partial^2 \mu_i}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \alpha_{jk}}{\partial Q_a} \right) + \left(\frac{\partial^2 \alpha_{jk}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_i}{\partial Q_a} \right) \right] \lambda_a^{\pm\sigma} \omega_b^{-2} \omega_c^{-1} \Bigg\}\end{aligned} \tag{12}$$

$$[\mu\alpha]^{2,0} = \frac{1}{4} \sum_{\mathcal{P}_{ijk}} \sum_{ab} \left(\frac{\partial^2 \mu_i}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial^2 \alpha_{jk}}{\partial Q_a \partial Q_b} \right) \lambda_{ab}^{\pm\sigma} \omega_a^{-1} \tag{13}$$

$$[\mu\alpha]^{0,2} = \frac{1}{8} \sum_{\mathcal{P}_{ijk}} \sum_{abcd} \left(\frac{\partial \mu_i}{\partial Q_c} \right) \left(\frac{\partial \alpha_{jk}}{\partial Q_d} \right) \left[F_{aab} F_{bcd} \lambda_c^{\pm\sigma} \lambda_d^{\pm\sigma} \omega_b^{-2} + 2 F_{abc} F_{abd} \lambda_{ab}^{\pm\sigma} \lambda_c^{\pm\sigma} \lambda_d^{\pm\sigma} \right] \tag{14}$$

4 Pure vibrational (pv) contribution to second hyperpolarizability

$$\gamma^{pv} = \underbrace{[\alpha^2]^0 + [\mu\beta]^0}_{\text{Order 0}} + [\mu^2\alpha]^{\mathrm{I}} + \underbrace{[\alpha^2]^{\mathrm{II}} + [\mu\beta]^{\mathrm{II}} + [\mu^4]^{\mathrm{II}}}_{\text{Order II}}, \tag{15}$$

with:

$$[\alpha^2]^{0,0} = \frac{1}{8} \sum_{\mathcal{P}_{ijkl}} \sum_{a} \left(\frac{\partial \alpha_{ij}}{\partial Q_a} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_a} \right) \lambda_a^{\pm 23} \tag{16}$$

$$\begin{aligned}[\alpha^2]^{1,1} = -\frac{1}{16} \sum_{\mathcal{P}_{ijkl}} \sum_{abc} \Bigg\{ F_{abc} \left(\frac{\partial^2 \alpha_{ij}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_c} \right) \lambda_{ab}^{\pm 23} \lambda_c^{\pm 23} (\omega_a^{-1} + \omega_b^{-1}) \\ + F_{bcc} \left(\frac{\partial^2 \alpha_{ij}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_a} \right) \lambda_a^{\pm 23} \omega_b^{-2} \omega_c^{-1} \Bigg\}\end{aligned} \tag{17}$$

$$[\alpha^2]^{2,0} = \frac{1}{16} \sum_{\mathcal{P}_{ijkl}} \sum_{ab} \left(\frac{\partial^2 \alpha_{ij}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial^2 \alpha_{kl}}{\partial Q_a \partial Q_b} \right) \lambda_{ab}^{\pm 23} \omega_a^{-1} \tag{18}$$

$$[\alpha^2]^{0,2} = \frac{1}{32} \sum_{\mathcal{P}_{ijkl}} \sum_{abcd} \left(\frac{\partial \alpha_{ij}}{\partial Q_c} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_d} \right) \left[F_{aab} F_{bcd} \lambda_c^{\pm 23} \lambda_d^{\pm\sigma} \omega_b^{-2} + 2 F_{abc} F_{abd} \lambda_{ab}^{\pm 23} \lambda_c^{\pm 23} \lambda_d^{\pm\sigma} \right] \tag{19}$$

$$[\mu\beta]^{0,0} = \frac{1}{6} \sum_{\mathcal{P}_{ijkl}} \sum_{a} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \beta_{jkl}}{\partial Q_a} \right) \lambda_a^{\pm\sigma} \tag{20}$$

$$[\mu\beta]^{1,1} = -\frac{1}{24} \sum_{\mathcal{P}_{ijkl}} \sum_{abc} \left\{ F_{abc} \left[\left(\frac{\partial^2 \mu_i}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \beta_{jkl}}{\partial Q_c} \right) + \left(\frac{\partial^2 \beta_{jkl}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_i}{\partial Q_c} \right) \right] \lambda_{ab}^{\pm\sigma} \lambda_c^{\pm\sigma} (\omega_a^{-1} + \omega_b^{-1}) \right.$$

$$\left. + F_{bcc} \left[\left(\frac{\partial^2 \mu_i}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \beta_{jkl}}{\partial Q_a} \right) + \left(\frac{\partial^2 \beta_{jkl}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_i}{\partial Q_a} \right) \right] \lambda_a^{\pm\sigma} \omega_b^{-2} \omega_c^{-1} \right\} \tag{21}$$

$$[\mu\beta]^{2,0} = \frac{1}{12} \sum_{\mathcal{P}_{ijkl}} \sum_{ab} \left(\frac{\partial^2 \mu_i}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial^2 \beta_{jkl}}{\partial Q_a \partial Q_b} \right) \lambda_{ab}^{\pm\sigma} \omega_a^{-1} \tag{22}$$

$$[\mu\beta]^{0,2} = \frac{1}{24} \sum_{\mathcal{P}_{ijkl}} \sum_{abcd} \left(\frac{\partial \mu_i}{\partial Q_c} \right) \left(\frac{\partial \beta_{jkl}}{\partial Q_d} \right) \left[F_{aab} F_{bcd} \lambda_c^{\pm\sigma} \lambda_d^{\pm\sigma} \omega_b^{-2} + 2 F_{abc} F_{abd} \lambda_{ab}^{\pm\sigma} \lambda_c^{\pm\sigma} \lambda_d^{\pm\sigma} \right] \tag{23}$$

$$[\mu^2\alpha]^{1,0} = \frac{1}{4} \sum_{\mathcal{P}_{ijkl}} \sum_{ab} \left\{ \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial^2 \alpha_{jk}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_l}{\partial Q_b} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm 3} \right.$$

$$\left. + 2 \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial^2 \mu_j}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_b} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm 23} \right\} \tag{24}$$

$$[\mu^2\alpha]^{0,1} = -\frac{1}{4} \sum_{\mathcal{P}_{ijkl}} \sum_{abc} F_{abc} \left(\frac{\partial \mu_j}{\partial Q_b} \right) \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \alpha_{jk}}{\partial Q_c} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm 1} \lambda_c^{\pm 23} \tag{25}$$

$$[\mu^4]^{1,1} = -\frac{1}{2} \sum_{\mathcal{P}_{ijkl}} \sum_{abcd} F_{abc} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \mu_j}{\partial Q_b} \right) \left(\frac{\partial^2 \mu_k}{\partial Q_c \partial Q_d} \right) \left(\frac{\partial \mu_l}{\partial Q_d} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm 1} \lambda_c^{\pm 23} \lambda_d^{\pm 3} \tag{26}$$

$$[\mu^4]^{2,0} = \frac{1}{2} \sum_{\mathcal{P}_{ijkl}} \sum_{abc} F_{abc} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial^2 \mu_j}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial^2 \mu_k}{\partial Q_b \partial Q_c} \right) \left(\frac{\partial \mu_l}{\partial Q_c} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm 23} \lambda_3^{\pm\sigma} \tag{27}$$

$$[\mu^4]^{0,2} = \frac{1}{8} \sum_{\mathcal{P}_{ijkl}} \sum_{abcde} F_{abc} F_{cde} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \mu_j}{\partial Q_b} \right) \left(\frac{\partial \mu_k}{\partial Q_d} \right) \left(\frac{\partial \mu_l}{\partial Q_e} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm 1} \lambda_c^{\pm 23} \lambda_d^{\pm 2} \lambda_e^{\pm 3} \tag{28}$$

References

[1] David M. Bishop, Josep M. Luis, and Bernard Kirtman. Additional compact formulas for vibrational dynamic dipole polarizabilities and hyperpolarizabilities. *The Journal of Chemical Physics*, 108(24):10013–10017, June 1998.

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[4] David M. Bishop and Bernard Kirtman. A perturbation method for calculating vibrational dynamic dipole polarizabilities and hyperpolarizabilities. *The Journal of Chemical Physics*, 95(4):2646–2658, August 1991.

[5] David M. Bishop and Bernard Kirtman. Compact formulas for vibrational dynamic dipole polarizabilities and hyperpolarizabilities. *The Journal of Chemical Physics*, 97(7):5255–5256, October 1992.