

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 checked 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 omitted in any of order II contributions, as it is usual in the litterature.

Note that:

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

with $\omega_i, \omega_j \dots$ the optical frequencies and $\omega_x, \omega_y \dots$ the vibrational frequencies.

1 Zero-point vibrationnal average (ZPVA)

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

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

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

2 Pure vibrational (pv) contribution to polarizability

$$\alpha^{pv} = [\mu^2]^0 + [\mu^2]^\Pi, \quad (3)$$

with:

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

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

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

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

3 Pure vibrational (pv) contribution to first hyperpolarizability

$$\beta^{pv} = [\mu\alpha]^0 + [\mu^3]^I + [\mu\alpha]^{II}, \quad (8)$$

with:

$$[\mu^3]^{1,0} = \frac{1}{2} \sum_{\mathcal{P}_{ijk}} \sum_{ab} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial^2 \mu_j}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_k}{\partial Q_b} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm2} \quad (9)$$

$$[\mu^3]^{0,1} = -\frac{1}{6} \sum_{\mathcal{P}_{ijk}} \sum_{abc} F_{abc} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \mu_j}{\partial Q_b} \right) \left(\frac{\partial \mu_k}{\partial Q_c} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm1} \lambda_c^{\pm2} \quad (10)$$

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

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

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

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

4 Pure vibrational (pv) contribution to second hyperpolarizability

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

with:

$$[\alpha^2]^{0,0} = \frac{1}{8} \sum_{\mathcal{P}_{ijkl}} \sum_a \left(\frac{\partial \alpha_{ij}}{\partial Q_a} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_a} \right) \lambda_a^{\pm23} \quad (16)$$

$$[\alpha^2]^{1,1} = -\frac{1}{16} \sum_{\mathcal{P}_{ijkl}} \sum_{abc} \left\{ F_{abc} \left(\frac{\partial^2 \alpha_{ij}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_c} \right) \lambda_{ab}^{\pm23} \lambda_c^{\pm23} (\omega_a^{-1} + \omega_b^{-1}) \right. \\ \left. + F_{bcc} \left(\frac{\partial^2 \alpha_{ij}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_a} \right) \lambda_a^{\pm23} \omega_b^{-2} \omega_c^{-1} \right\} \quad (17)$$

$$[\alpha^2]^{2,0} = \frac{1}{16} \sum_{\mathcal{P}_{ijkl}} \sum_{ab} \left(\frac{\partial^2 \alpha_{ij}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial^2 \alpha_{kl}}{\partial Q_a \partial Q_b} \right) \lambda_{ab}^{\pm23} \omega_a^{-1} \quad (18)$$

$$[\alpha^2]^{0,2} = \frac{1}{32} \sum_{\mathcal{P}_{ijkl}} \sum_{abcd} \left(\frac{\partial \alpha_{ij}}{\partial Q_c} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_d} \right) [F_{aab} F_{bcd} \lambda_c^{\pm23} \lambda_d^{\pm\sigma} \omega_b^{-2} + 2 F_{abc} F_{abd} \lambda_{ab}^{\pm23} \lambda_c^{\pm23} \lambda_d^{\pm\sigma}] \quad (19)$$

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

$$[\mu\beta]^{1,1} = -\frac{1}{24} \sum_{\mathcal{P}_{ijkl}} \sum_{abc} \left\{ F_{abc} \left[\left(\frac{\partial^2 \mu_i}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \beta_{jkl}}{\partial Q_c} \right) + \left(\frac{\partial^2 \beta_{jkl}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_i}{\partial Q_c} \right) \right] \lambda_{ab}^{\pm\sigma} \lambda_c^{\pm\sigma} (\omega_a^{-1} + \omega_b^{-1}) \right. \\ \left. + F_{bcc} \left[\left(\frac{\partial^2 \mu_i}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \beta_{jkl}}{\partial Q_a} \right) + \left(\frac{\partial^2 \beta_{jkl}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_i}{\partial Q_a} \right) \right] \lambda_a^{\pm\sigma} \omega_b^{-2} \omega_c^{-1} \right\} \quad (21)$$

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

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

$$[\mu^2\alpha]^{1,0} = \frac{1}{4} \sum_{\mathcal{P}_{ijkl}} \sum_{ab} \left\{ \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial^2 \alpha_{jk}}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \mu_l}{\partial Q_b} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm3} \right. \\ \left. + 2 \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial^2 \mu_j}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial \alpha_{kl}}{\partial Q_b} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm23} \right\} \quad (24)$$

$$[\mu^2\alpha]^{0,1} = -\frac{1}{4} \sum_{\mathcal{P}_{ijkl}} \sum_{abc} F_{abc} \left(\frac{\partial \mu_j}{\partial Q_b} \right) \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \alpha_{jk}}{\partial Q_c} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm1} \lambda_c^{\pm23} \quad (25)$$

$$[\mu^4]^{1,1} = -\frac{1}{2} \sum_{\mathcal{P}_{ijkl}} \sum_{abcd} F_{abc} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \mu_j}{\partial Q_b} \right) \left(\frac{\partial^2 \mu_k}{\partial Q_c \partial Q_d} \right) \left(\frac{\partial \mu_l}{\partial Q_d} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm1} \lambda_c^{\pm23} \lambda_d^{\pm3} \quad (26)$$

$$[\mu^4]^{2,0} = \frac{1}{2} \sum_{\mathcal{P}_{ijkl}} \sum_{abc} F_{abc} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial^2 \mu_j}{\partial Q_a \partial Q_b} \right) \left(\frac{\partial^2 \mu_k}{\partial Q_b \partial Q_c} \right) \left(\frac{\partial \mu_l}{\partial Q_c} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm23} \lambda_c^{\pm\sigma} \quad (27)$$

$$[\mu^4]^{0,2} = \frac{1}{8} \sum_{\mathcal{P}_{ijkl}} \sum_{abcde} F_{abc} F_{cde} \left(\frac{\partial \mu_i}{\partial Q_a} \right) \left(\frac{\partial \mu_j}{\partial Q_b} \right) \left(\frac{\partial \mu_k}{\partial Q_d} \right) \left(\frac{\partial \mu_l}{\partial Q_e} \right) \lambda_a^{\pm\sigma} \lambda_b^{\pm1} \lambda_c^{\pm23} \lambda_d^{\pm2} \lambda_e^{\pm3} \quad (28)$$

References

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