Analytic calculations of hyper-Raman spectra

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Vibrational hyper-Raman (hR) spectroscopy is related to its well-known Raman counterpart, and these phenomena are in several ways analogous, but the selection rules for each are different. In the commonly used double-harmonic approximation, the Raman selection rule for a vibrational mode is $\partial\alpha/\partial Q_a \neq 0$, where α is the molecular electronic polarizability and Q_a is the normal coordinate of mode a. The corresponding hR selection rule is $\partial\beta/\partial Q_a \neq 0$, where β is the molecular electronic first hyperpolarizability. This means that modes that are "dark" in one spectroscopy can show a nonzero signal in the other, and hR spectroscopy can therefore be a useful addition to regular Raman (and IR) spectroscopy [1].

We present analytic hR spectra in the double-harmonic approximation for benzonitrile and RDX, calculated within the open-ended response formalism of A. J. Thorvaldsen *et al.* [2] The levels of theory currently supported in this scheme correspond to those in calculations made in 2006 [1], but the present code is formulated in the atomic orbital (AO) basis, thereby enabling the possibility of using linearly scaling procedures in future work.

We also present suggestions for improved accuracy and spectral detail by the use of upcoming developments in the open-ended response code. These improvements include:

- The inclusion of electrical and mechanical anharmonicity by double perturbation treatment [3], using high-order energy and polarization property derivatives such as cubic force constants and second geometrical derivatives of β.

- Correction of fundamental normal mode frequencies using high-order energy derivatives.

- Treatment of both frequency [4] and intensity effects associated with Fermi resonances between overtones/combination frequencies and fundamental frequencies.

- DFT response properties using upcoming developments for high-order XC derivatives in the XCFun library [5-6].

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