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Anharmonic vibrational properties by a fully automated second-order perturbative approach

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This paper describes the implementation of a fully automated code for the building of anharmonic force constants and their use in a second-order perturbative evaluation of vibrorotational parameters. Next, a number of test applications are discussed, which show the strengths and limits of various computational levels. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1824881]

I. INTRODUCTION

Infrared (IR) and Raman spectroscopies are among the most powerful techniques for characterizing medium size molecules, but proper assignment of spectra is often not straightforward especially for unstable species or nonstandard bonding situations. In the last years computation of harmonic force fields by quantum mechanical methods has provided an unvaluable aid in this connection thanks to the development of more reliable models with good scaling properties and of the corresponding user friendly computer codes. However, introduction of suitable scaling factors is unavoidable at this level due to both limitations of the quantum chemical models and neglect of anharmonicity. Thus it becomes interesting to investigate if effective approaches going beyond the harmonic level can offer further significant improvements. For small molecules converged rovibrational levels can be obtained by fully variational methods.[1–3] However for large molecules some approximation becomes unavoidable concerning both the form of the potential and the rovibrational treatment. The most successful approaches are at present based on truncated two- or three-mode potentials and on self-consistent[4–10] (VSCF) and/or second-order perturbative[11–18] vibrational treatments. In particular, second-order perturbation theory (PT2), which provides closed expressions for most of the spectroscopic parameters required for the analysis of the experimental frequencies appears still very effective for the study of polyatomic molecules of medium dimensions.[19–24] Of course, the PT2 approach cannot give the same results of a converged variational computation. For instance, the PT2 expressions are (at least in one dimension) exact for a Morse oscillator, and therefore certainly not correct for the incomplete quartic development, which is the most practical representation of the potential for large molecules. However, as noticed by Handy and co-workers[20,25] the "Morsification" of the quartic potential leads often to an effective inclusion of nearly exact higher order terms. Thus, the PT2 predictions can be closer to experiment than their variational counterparts. Starting from analytical second derivatives, the third and semidiagonal fourth derivatives needed for second-order perturbation can be effectively computed by a finite difference approach which scales linearly with the number of normal modes and can take full advantage of parallel architectures with relatively small memory. Although the theory underlying the PT2 model is well established, its use in systematic work also by nonspecialists requires the development of a general, user friendly, and open ended package. To this end, I thought it interesting to implement PT2 vibrational computations in the Gaussian package,[26] thus allowing the selection of different methods ranging from molecular mechanics to the most refined post-Hartree-Fock procedures and including mixed methods. In the course of the implementation a number of methodological and numerical improvements have been introduced, which will be analyzed in some detail in the first part of the present paper, together with alternative choices for dealing with the problems of symmetry handling and of resonances. In the second part of this study, the vibrational spectra of a number of small molecules will be studied by different quantum mechanical (QM) methods in order to better illustrate the potentialities of the approach. One of the most significant outcomes of this analysis is that reliable spectroscopic properties of semirigid molecules can be computed with last generation density functionals and the results can be further improved coupling structures and harmonic force fields computed at higher levels with discrete Fourier transform (DFT) anharmonic corrections computed by methods rooted in the density functional theory (DFT).

II. THE METHOD

Anharmonic force fields are computed more efficiently exploiting the linear relationship between normal $\mathbf{Q}$ and cartesian displacement $\mathbf{x}$ coordinates.

$$\mathbf{Q}=\mathbf{L}^{+}\mathbf{M}^{1/2}\mathbf{x}, \tag{1}$$

where, by convention, all the components of $\mathbf{Q}$ and $\mathbf{x}$ vanish at the reference geometry, $\mathbf{M}$ is the diagonal matrix of atomic masses, and $\mathbf{L}$ is the matrix of (columnwise) eigenvectors of the mass weighted cartesian force constant matrix $\mathbf{M}^{-1/2}\mathbf{F}\mathbf{M}^{-1/2}$. The second-derivative matrix over normal modes, $\mathbf{\Phi}$ is

$$\mathbf{\Phi}=\mathbf{L}^{+}\mathbf{M}^{-1/2}\mathbf{F}\mathbf{M}^{-1/2}\mathbf{L} \tag{2}$$

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and is diagonal when evaluated at the equilibrium geometry with eigenvalues λ proportional to the squares of harmonic vibrational frequencies ω. It is then possible to evaluate third energy derivatives with respect to normal coordinates by numerical differentiations of analytical Hessian matrices at geometries displaced by small increments $\boldsymbol{\delta}\mathbf{Q}$ from the reference geometry:[12]

$$\mathbf{\Phi}_{ijk}=\frac{1}{3}\left(\frac{\mathbf{\Phi}_{jk}(\delta Q_i)-\mathbf{\Phi}_{jk}(-\delta Q_i)}{2\delta Q_i}+\frac{\mathbf{\Phi}_{ki}(\delta Q_j)-\mathbf{\Phi}_{ki}(-\delta Q_j)}{2\delta Q_j}+\frac{\mathbf{\Phi}_{ij}(\delta Q_k)-\mathbf{\Phi}_{ij}(-\delta Q_k)}{2\delta Q_k}\right). \tag{3}$$

The numerical calculation of fourth derivatives requires, in principle, simultaneous displacements along two normal coordinates, which would be quite expensive.

Displacements along a single normal coordinate at a time are sufficient, however, to evaluate terms with at most three distinct indices, which include all the even derivatives required to compute rovibrational energies by second-order perturbation theory:

$$\mathbf{\Phi}_{ijkk}=\frac{\mathbf{\Phi}_{ij}(\delta Q_k)+\mathbf{\Phi}_{ij}(-\delta Q_k)-2\mathbf{\Phi}_{ij}(0)}{\delta Q_k^2} \tag{4}$$

$$\mathbf{\Phi}_{iikk}=\frac{1}{2}\left(\frac{\mathbf{\Phi}_{ii}(\delta Q_k)+\mathbf{\Phi}_{ii}(-\delta Q_k)-2\mathbf{\Phi}_{ii}(0)}{\delta Q_k^2}+\frac{\mathbf{\Phi}_{kk}(\delta Q_i)+\mathbf{\Phi}_{kk}(-\delta Q_i)-2\mathbf{\Phi}_{kk}(0)}{\delta Q_i^2}\right). \tag{5}$$

Note that for nonlinear molecules these computations require at most the Hessian matrices at $6N$-11 different points, N being the number of atoms in the molecule. The magnitude of the displacements δQ has to be chosen as a compromise value to minimize two types of round-off errors.[12,14] For a small displacement the numerator in the above equations is very small; it may be only one or two orders of magnitude larger than the error due to convergence of self-consistent field (SCF) and coupled perturbed (CP) calculations $(10^{-8}\,E_h)$. For a large displacement the contamination with higher order force constants and coupling between the modes becomes an issue. As a result of both types of error, the equivalent force constants obtained by differentiation along normal modes will differ, sometimes significantly. These problems can be partially alleviated by averaging the equivalent force constants (see equations above). Furthermore, when using Kohn-Sham (KS) methods, the grid used in numerical quadrature introduce a further error.[14] A possible criterium for choosing the displacements can be based on the increase of the quadratic approximation $\Delta E^{(2)}$ to the potential energy over the equilibrium geometry:[19,20]

$$\Delta Q_i=\left(\frac{\Delta E^{(2)}}{\lambda}\right)^{1/2}. \tag{6}$$

This energy selection has been included in the program as an option, but extensive numerical experimentation has shown that a single ΔQ value between 0.003 and 0.01 Å performs a very good job for all QM methods except DFT. In this latter case values between 0.01 and 0.03 Å for all the displacements and fine grids (at least 99 radial and 590 angular points) in both SCF and coupled perturbed Kohn-Sham (CPKS) computations provide good compromises between numerical accuracy and computational burden. In summary, a displacement around 0.01 Å could be quite satisfactory in most circumstances: this is the default option in the latest version of the code. Please note that a tight geometry optimization (i.e., residual gradients less than 10^{-7} hartree/bohrs [or radian]) is a mandatory prerequisite for reliable anharmonic analysis irrespective of the specific QM method.

The vibrational Hamiltonian $\mathbf{H}_{\text{vib}}$ can be convenientely expressed in wave number units using reduced normal coordinates $\mathbf{q}$,

$$q_i=\gamma^{1/2}Q_i, \tag{7}$$

where

$$\gamma_i=\frac{\lambda_i^{1/2}}{\hbar}=\frac{2\pi c\omega_i}{\hbar}. \tag{8}$$

It consists of the sum of the zeroth order harmonic term and successive terms $\mathbf{H}_{\text{vib}}^i$ containing the contribution of cubic, quartic, etc., components of the potential. The second-order term includes also a kinetic contribution arising from the vibrational angular momentum $\mathbf{j}_\alpha$,

$$\mathbf{H}_{\text{vib}}=\mathbf{H}_{\text{vib}}^0+\mathbf{H}_{\text{vib}}^1+\mathbf{H}_{\text{vib}}^2=1/2\sum_r \omega_r(p_r^2+q_r^2)+1/6\sum_{rst}\phi_{rst}q_rq_sq_t+1/24\sum_{rstu}\phi_{rstu}q_rq_sq_tq_u+\sum_\alpha B_\alpha^e j_\alpha^2, \tag{9}$$

$$j_\alpha=\sum_{i<j}\zeta_{ij}^\alpha(q_ip_j-q_jp_i). \tag{10}$$

In the above equations α identifies a rotational axis, B_α^e the corresponding equilibrium rotational constant, and ζ_{ij}^α is a Coriolis coupling constant

$$\zeta_{ij}^\alpha=\sum_k (L_{ik}^\beta L_{jk}^\gamma-L_{ik}^\gamma L_{jl}^\beta). \tag{11}$$

Finally $\phi_{rst}=(\omega_r\omega_s\omega_t)^{-1/2}\mathbf{\Phi}_{rst}$ and similarly for the quartic constants. Starting from the solutions $|\mathbf{v}_i^0\rangle$ of the harmonic problem (corresponding to the H_{vib}^0 Hamiltonian) the vibrational wave functions $|\mathbf{v}_i\rangle$ are obtained by second-order perturbation theory,

$$|\mathbf{v}_i\rangle=|\mathbf{v}_i^0\rangle+|\mathbf{v}_i^1\rangle+|\mathbf{v}_i^2\rangle, \tag{12}$$

using all nonresonant energy terms of H_{vib} followed by a variational treatment of the relevant resonant interactions.

This leads to an effective vibrational Hamiltonian matrix for the nearly degenerate set of $|\mathbf{v}_i\rangle$, $|\mathbf{v}_j\rangle$ states, which can be written in the form

$$\langle \mathbf{v}_i|\mathbf{H}_{\rm vib}^{\rm eff}|\mathbf{v}_j\rangle = \langle \mathbf{v}_i^0|\mathbf{H}_{\rm vib}^2|\mathbf{v}_j^0\rangle + \langle \mathbf{v}_i^1|\mathbf{H}_{\rm vib}^1|\mathbf{v}_j^0\rangle + \langle \mathbf{v}_i^0|\mathbf{H}_{\rm vib}^1|\mathbf{v}_j^1\rangle. \tag{13}$$

The diagonal terms can be represented by the standard bilinear form in the quantum numbers of the different normal modes:

$$\langle v_i|H_{\rm vib}^{\rm eff}|v_i\rangle = \xi_0 + \sum \omega_i\left(n_i + \frac{1}{2}\right) + \sum_{i\leq j} \xi_{ij}\left(n_i + \frac{1}{2}\right)\left(n_j + \frac{1}{2}\right), \tag{14}$$

where the ξ constants are simple functions of the cubic and quartic force constants (vide infra).

The vibrotational Hamiltonian $\mathbf{H}_{\rm vibrot}$ is obtained by adding the rotational energy terms,

$$\mathbf{H}_{\rm vibrot} = \mathbf{H}_{\rm vib} + \sum_\alpha B_\alpha^e J_\alpha^2 + \sum_{\alpha,\beta}\sum_r B_{\alpha\beta}^r q_r J_\alpha J_\beta + 1/2\sum_{\alpha,\beta}\sum_{rs} B_{\alpha\beta}^{rs} q_r q_s J_\alpha J_\beta - 2\sum_\alpha B_\alpha J_\alpha j_\alpha. \tag{15}$$

Fourth-order perturbation theory with respect to selected components of this Hamiltonian leads to an effective rotational Hamiltonian matrix inclusive of all quartic and sextic centrifugal distortion constants, from which vibrotational eigenfunctions $|v_{jJ}\rangle$ and energies are obtained.[27] In particular, the effective rotational Hamiltonian in its reduced asymmetric form (referred to as A in the following) in the I_r representation (i.e., in the Eckart orientation with the axes choice leading to $I_X < I_Y < I_Z$) is

$$\begin{aligned}\mathbf{H}_{\rm eff}^{nJ} = &\sum_\alpha B_\alpha^n J_\alpha^2 - \Delta_J \mathbf{J}^4 - \Delta_{Jk}\mathbf{J}^2\mathbf{J}_z^2 - \Delta_k \mathbf{J}_z^4 \\ &- 1/2[(\delta_J \mathbf{J}^2 + \delta_k \mathbf{J}_z^2),(\mathbf{J}_+^2 + \mathbf{J}_-^2)]_+ + \mathbf{\Phi}_J \mathbf{J}^6 \\ &+ \mathbf{\Phi}_{Jk}\mathbf{J}^4\mathbf{J}_z^2 + \mathbf{\Phi}_{Jk}\mathbf{J}^2\mathbf{J}_z^4 + \mathbf{\Phi}_k \mathbf{J}_z^6 \\ &+ 1/2[(\phi_J \mathbf{J}^4 + \phi_{Jk}\mathbf{J}^2\mathbf{J}_z^2 + \phi_k \mathbf{J}_z^4),(\mathbf{J}_+^2 + \mathbf{J}_-^2)]_+,\end{aligned} \tag{16}$$

where B_α^n is the effective rotational constant around axis α for the vibrational state n,

$$B_\alpha^n = B_\alpha^e - \sum_i a_i^\alpha (n_i + 1/2), \tag{17}$$

the constant a_i^α is defined below, and explicit expressions for all the other constants can be given in terms of quartic centrifugal distortion constants $\tau_{\alpha\beta\gamma\delta}$,

$$\tau_{\alpha\beta\gamma\delta} = -\frac{\hbar^4}{2hcI_\alpha I_\beta I_\gamma I_\delta}\sum_k \frac{I_{\alpha\beta}^k a_{\gamma\delta}^k}{\lambda_k}, \tag{18}$$

where $I_{\alpha\beta}^k$ is an inertial derivative

$$I_{\alpha\beta}^k = \left(\frac{\partial I_{\alpha\beta}}{\partial Q_k}\right)_e. \tag{19}$$

It is noteworthy that the quartic centrifugal distortion constants depend only on the quadratic (harmonic) part of the vibrational Hamiltonian and are expected to be about four orders of magnitude smaller than the corresponding rotational constants.[27,28] Furthermore, only terms with at most two different indices influence the rotational Hamiltonian to first order. In particular, in the Kivelson-Wilson formalism[29] the vibrationally averaged rotational constants for the ground vibrational state used to fit the observed energy levels are

$$B_\alpha'^0 = B_\alpha^0 + \tfrac{1}{4}(3\tau_{\beta\gamma\beta\gamma} - 2\tau_{\gamma\alpha\gamma\alpha} - 2\tau_{\alpha\beta\alpha\beta}), \tag{20}$$

$$B_\beta'^0 = B_\beta^0 + \tfrac{1}{4}(3\tau_{\gamma\alpha\gamma\alpha} - 2\tau_{\alpha\beta\alpha\beta} - 2\tau_{\beta\gamma\beta\gamma}), \tag{21}$$

$$B_\gamma'^0 = B_\gamma^0 + \tfrac{1}{4}(3\tau_{\alpha\beta\alpha\beta} - 2\tau_{\beta\gamma\beta\gamma} - 2\tau_{\gamma\alpha\gamma\alpha}), \tag{22}$$

and the asymmetry parameter σ is defined as

$$\sigma = \frac{2B_\alpha'^0 - B_\beta'^0 - B_\gamma'^0}{B_\beta'^0 - B_\gamma'^0}. \tag{23}$$

The quartic centrifugal distortion constants appearing in the Kivelson-Wilson formalism[29] for an asymmetric top are

$$D_J = -\tfrac{1}{32}[3\tau_{\beta\beta\beta\beta} + 3\tau_{\gamma\gamma\gamma\gamma} + 2(\tau_{\beta\beta\gamma\gamma} + 2\tau_{\beta\gamma\beta\gamma})], \tag{24}$$

$$D_K = D_J - \tfrac{1}{4}[\tau_{\alpha\alpha\alpha\alpha} - (\tau_{\alpha\alpha\beta\beta} + 2\tau_{\alpha\beta\alpha\beta}) - (\tau_{\gamma\gamma\alpha\alpha} + 2\tau_{\gamma\alpha\gamma\alpha})], \tag{25}$$

$$D_{JK} = -D_J - D_K - \frac{1}{4}\tau_{\alpha\alpha\alpha\alpha}, \tag{26}$$

$$R_5 = -\tfrac{1}{32}[\tau_{\beta\beta\beta\beta} - (\tau_{\gamma\gamma\gamma\gamma} - 2(\tau_{\alpha\alpha\beta\beta}) + 2\tau_{\alpha\beta\alpha\beta}) + 2(\tau_{\gamma\gamma\alpha\alpha} + 2\tau_{\gamma\alpha\gamma\alpha})], \tag{27}$$

$$R_6 = \tfrac{1}{64}[\tau_{\beta\beta\beta\beta} + \tau_{\gamma\gamma\gamma\gamma} - 2(\tau_{\beta\beta\gamma\gamma} + 2\tau_{\beta\gamma\beta\gamma})], \tag{28}$$

and

$$\delta_J = -\tfrac{1}{16}(\tau_{\beta\beta\beta\beta} - \tau_{\gamma\gamma\gamma\gamma}). \tag{29}$$

Watson[30,31] has shown that only five linear combinations of the τ constants can be determined experimentally from spectra. In his reduced form of the Hamiltonian given above, the five independent centrifugal distortion constants are related to the quantities defined above by

$$\Delta_J = D_J - 2R_6, \tag{30}$$

$$\Delta_{JK} = D_{JK} + 12R_6, \tag{31}$$

$$\Delta_K = D_K - 10R_6, \tag{32}$$

$$\delta_J = \delta_J, \tag{33}$$

and

$$\delta_K = -2R_5 - 4\sigma R_6. \tag{34}$$

The ξ and a terms will be now given by slightly non standard expressions, based on normal coordinates rather than on their reduced counterparts, since this allows to avoid complex numbers when dealing with transition states rather than energy minima. This extension gives also access to anharmonic

evaluations of reaction rates through the semiclassical approximations developed by Miller and co-workers.[32]

$$A\xi_0=\sum_{i=1}^{f}\frac{\mathbf{\Phi}_{iiii}}{\lambda_i}-7/9\sum_{i=1}^{f}\frac{\mathbf{\Phi}_{iii}^2}{\lambda_i^2}+3\sum_{i=1}^{f}\sum_{j\neq i=1}^{f}\frac{\mathbf{\Phi}_{ijj}^2}{\lambda_j(4\lambda_j-\lambda_i)}$$
$$-16\sum_{i=1}^{f}\sum_{j>i}^{f}\sum_{k>j}^{f}\frac{\mathbf{\Phi}_{ijk}^2}{\Delta_{ijk}}-16$$
$$\times\sum_{\alpha=x,y,z}\mu_{\alpha\alpha}^0\left[1+2\sum_{i=1}^{f}\sum_{j>i}^{f}(\zeta_{ij}^{\alpha})^2\right], \tag{35}$$

$$B_i\xi_{ii}=\mathbf{\Phi}_{iiii}-\frac{5\mathbf{\Phi}_{iii}^2}{3\lambda_i}-\sum_{j\neq i=1}^{f}\frac{(8\lambda_i-3\lambda_j)\mathbf{\Phi}_{iij}^2}{\lambda_j(4\lambda_i-\lambda_j)} \tag{36}$$

$$C_{ij}\xi_{ij}=\mathbf{\Phi}_{iijj}-\frac{2\mathbf{\Phi}_{iij}^2}{4\lambda_i-\lambda_j}-\frac{2\mathbf{\Phi}_{ijj}^2}{4\lambda_j-\lambda_i}-\frac{\mathbf{\Phi}_{iii}\mathbf{\Phi}_{ijj}}{\lambda_i}-\frac{\mathbf{\Phi}_{jjj}\mathbf{\Phi}_{iij}}{\lambda_j}$$
$$+\sum_{k\neq i\neq j=1}^{f}\left[\frac{2(\lambda_i+\lambda_j-\lambda_k)\mathbf{\Phi}_{ijk}^2}{\Delta_{ijk}}-\frac{\mathbf{\Phi}_{iik}\mathbf{\Phi}_{jjk}}{\lambda_k}\right]$$
$$+4(\lambda_i+\lambda_j)\sum_{\alpha=x,y,z}\mu_{\alpha\alpha}^0(\zeta_{ij}^{\alpha})^2, \tag{37}$$

where $A=64hc$, $B_i=16hc\lambda_i$, $C_{ij}=4hc(\lambda_i\lambda_j)^{1/2}$, and

$$\Delta_{ijk}=\lambda_i^2+\lambda_j^2+\lambda_k^2-2[\lambda_i\lambda_j+\lambda_i\lambda_k+\lambda_j\lambda_k]. \tag{38}$$

Although specialized equations are available for non Abelian symmetry groups involving degenerate frequencies,[33,34] the above equations can be used in those cases too, provided that the masses (or the coordinates) of one or more nuclei are changed very slightly in order to break degeneracy.

It is then possible to factorize potentially divergent terms (which can occur, of course, only for real frequencies) as follows:

$$\frac{1}{\Delta_{lmn}}=-\frac{1}{8\omega_l\omega_m\omega_n}\left[\frac{1}{\omega_l+\omega_m+\omega_n}-\frac{1}{\omega_l+\omega_m-\omega_n}\right.$$
$$\left.-\frac{1}{\omega_l+\omega_n-\omega_m}-\frac{1}{\omega_m+\omega_n-\omega_l}\right], \tag{39}$$

$$\frac{1}{4\lambda_l-\lambda_m}=\frac{1}{4\omega_l(2\omega_l+\omega_m)}+\frac{1}{4\omega_l(2\omega_l-\omega_m)}, \tag{40}$$

$$\frac{8\lambda_l-3\lambda_m}{4\lambda_l-\lambda_m}=2+\frac{\omega_m}{2(2\omega_l+\omega_m)}-\frac{\omega_m}{2(2\omega_l-\omega_m)}, \tag{41}$$

$$\frac{\lambda_l+\lambda_m-\lambda_n}{\Delta_{lmn}}=-\frac{1}{4\omega_n}\left[\frac{1}{\omega_l+\omega_m+\omega_n}-\frac{1}{\omega_l+\omega_m-\omega_n}\right.$$
$$\left.+\frac{1}{\omega_l-\omega_m+\omega_n}-\frac{1}{\omega_l-\omega_m-\omega_n}\right]. \tag{42}$$

Note that there is a typographic error in the expression for $1/\Delta_{lmn}$ given in Ref. 35: the correct expression is given here above.

Next, fundamental vibrational frequencies ν_i, overtones $[2\nu_i]$, combination bands $[\nu_i\nu_j]$, and zero-point energy (ZPE) are given by

$$\nu_i=\omega_i+2\xi_{ii}+\frac{1}{2}\sum_{j\neq i}\xi_{ij}, \tag{43}$$

$$[2\nu_i]=2\omega_i+6\xi_{ii}+\sum_{j\neq i}\xi_{ij}=2\nu_i+2\xi_{ii}, \tag{44}$$

$$[\nu_i\nu_j]=\omega_i+\omega_j+2\xi_{ii}+2\xi_{jj}+2\xi_{ij}+\frac{1}{2}\sum_{l\neq i,j}(\xi_{il}+\xi_{jl})$$
$$=\nu_i+\nu_j+\xi_{ij}, \tag{45}$$

$$\mathrm{ZPE}=\xi_0+\frac{1}{2}\sum_i\left(\omega_i+\frac{1}{2}\xi_{ii}+\sum_{j>i}\frac{1}{2}\xi_{ij}\right). \tag{46}$$

It has been already pointed out[35] that the ZPE cannot be expressed in terms of the ω_i only, but it can be rewritten as

$$\mathrm{ZPE}=\frac{1}{2}(\mathrm{ZPE}_H+\mathrm{ZPE}_F)+\xi_0-\frac{1}{4}\sum_i\xi_{ii}, \tag{47}$$

where

$$\mathrm{ZPE}_H=\frac{1}{2}\sum_i\omega_i \tag{48}$$

$$\mathrm{ZPE}_F=\frac{1}{2}\sum_i\nu_i. \tag{49}$$

In an analogous way, one gets

$$\lambda_k^{1/2}a_k^{\beta}=-2B_\beta^2\left[\sum_\gamma\left(\frac{3(a_k^{\beta\gamma})^2}{4I\gamma\gamma}\right)+\sum_l(\zeta_{kl}^{\beta})^2\left(\frac{3\lambda_k+\lambda_l}{\lambda_k-\lambda_l}\right)\right.$$
$$\left.+\pi\left(\frac{c}{h}\right)^{1/2}\sum_l\frac{\Phi_{kkl}a_l^{\beta\beta}}{\lambda_l}\right]. \tag{50}$$

Note that in such a perturbation formula, the rotational constants B_α are the equilibrium constants of the nonvibrating molecule, viz., B_α^e. Many experimental analyses use, to a good approximation, $B_\alpha'^0$, instead, which contain effects due to zero-point vibrations and centrifugal distortion. This explains at least part of the small discrepancies between "experimental" and computed values in the results presented in the following section.

The first contribution in the above equation is a moment-of-inertia correction term, the second term is due to Coriolis interactions, and the last term is an anharmonic correction. The Coriolis coupling term has a resonance when ω_k is close to ω_l. By contrast, as already recognized,[36,37] the summed Coriolis coupling term

$$-\sum_k\lambda_k^{1/2}a_k^{\beta}(\mathrm{Coriolis})=\sum_k 2B_\beta^2\sum_l(\zeta_{kl}^{\beta})^2\left(\frac{3\lambda_k+\lambda_l}{\lambda_k-\lambda_l}\right)$$
$$=-\sum_{l>k}\frac{2B_\beta^2(\zeta_{kl}^{\beta})^2(\omega_k-\omega_l)^2}{\omega_l(\omega_k+\omega_l)} \tag{51}$$

does not have a resonance contribution. In cases of Coriolis resonance, therefore, the summed Coriolis contribution is unaffected by the resonance and may be safely calculated. On the other hand, it is far from clear *a priori* which Fermi

TABLE I. Computed and experimental geometries (angstroms and degrees), dipole moments (D), vibration-rotation interaction constants (α in cm^{-1}), and rotational constants (A, B, and C, in cm^{-1}) for water.

	SCF/DZP[a]	BLYP[b]	B97-2[b]	B3LYP[b]	MP2[b,c]	Expt.[d]
OH_e	0.9457	0.9719	0.9567	0.9619	0.9614	0.9576
OH_0	0.9588	0.9873	0.9710	0.9764	0.9759	0.9724
HOH_e	106.16	104.47	104.77	105.08	104.11	104.51
HOH_0	106.18	104.39	104.74	105.04	103.97	104.50
Dipole	2.1329	1.8033	1.8473	1.8411	1.8701	1.8546
a_1^a	0.5855	0.6818	0.6747	0.6601	0.6773	0.750
a_2^a	−2.8425	−2.6241	−2.7426	−2.7702	−2.5333	−2.941
a_3^a	1.1004	1.1759	1.1440	1.1655	1.1177	1.253
a_1^b	0.2170	0.2273	0.2226	0.2214	0.2097	0.238
a_2^b	−0.1528	−0.1420	−0.1528	−0.1430	−0.1749	−0.160
a_3^b	0.1020	0.0995	0.0989	0.0977	0.0920	0.078
a_1^c	0.1617	0.1798	0.1728	0.1735	0.1721	0.202
a_2^c	0.1372	0.1446	0.1417	0.1423	0.1433	0.139
a_3^c	0.1319	0.1438	0.1405	0.1404	0.1388	0.145
A_e	29.1839	26.5759	27.6220	27.5168	26.9465	27.4097
B_e	14.6301	14.1725	14.5639	14.3473	14.5560	14.5895
C_e	9.7448	9.2370	9.5360	9.4303	9.4445	9.5310
A_0	29.7613	26.9608	28.0976	27.9891	27.3157	27.8787
B_0	14.5470	14.0745	14.4795	14.2592	14.4926	14.5115
C_0	9.5295	9.0069	9.3085	9.2022	9.2175	9.2880

[a]The results differ by not more than 1 on the last digit from those of Ref. 11.
[b]aug-cc-pvTZ basis set.
[c]Frozen core.
[d]From Ref. 45.

resonances are to be included in the analysis of purely vibrational terms. The usual empirical criterium based on a threshold for the differences $(2\omega_i-\omega_j)$ (Fermi type 1 resonance) or $(\omega_i+\omega_j-\omega_k)$ (Fermi type 2 resonance) does not take into account that the error in the perturbative treatment depends also on the numerator. A viable solution to this problem has been suggested by Martin and co-workers,[38] who derived simple formulas giving fairly good estimates of the differences between explicitly including a Fermi resonance and absorbing it into the anharmonicity constants. Recasted in the present formalism they read

$$\Delta_{ik}^1=\frac{\phi_{iik}^4}{256(2\omega_i-\omega_k)^3}, \tag{52}$$

TABLE II. Quartic (Δ and R_6) and sextic (Φ and ϕ) centrifugal distortion constants, asymmetry parameter σ, and differences between harmonic and fundamental wave numbers Δ in cm^{-1} for water.

	SCF/DZP[a]	SCF/DZP[b]	B97-2[c]	B3LYP[c]	MP2[c]	Expt.[d]
$10^6\Delta_J$	1039.9	1040.1	1134.1	1136.2	1183.5	1254.0
$10^6\Delta_{JK}$	−4825.0	−4826.2	−4840.2	−4955.9	−5140.3	−5767.7
$10^6\Delta_K$	27219.4	27226.0	25826.3	26705.4	2527.6	32465.5
$10^6\delta_J$	412.6	412.7	450.4	451.6	476.2	507.4
$10^6\delta_K$	426.6	426.3	406.4	402.9	315.8	1369.3
10^6R_6	−89.06	−89.08	−98.39	−98.93	−105.1	/
$10^6\Phi_J$	0.366	0.366	0.437	0.440	0.483	0.522
$10^6\Phi_{JK}$	−2.354	−2.410	−2.816	−2.841	−3.141	−1.400
$10^6\Phi_{KJ}$	−8.490	−8.309	−7.816	−8.562	−7.188	−17.0
$10^6\Phi_K$	76.962	76.862	72.868	78.283	68.544	124.5
$10^6\phi_J$	0.181	0.181	0.216	0.218	0.239	0.260
$10^6\phi_{JK}$	−0.386	−0.442	−0.533	−0.540	−0.638	−0.841
$10^6\phi_K$	11.526	11.473	11.427	11.929	11.347	36.59
σ	7.059	6.958	6.249	6.357	5.859	6.109
Δ_1	−167	−168	−162	−165	−169	−176
Δ_2	−57	−57	−50	−52	−50	−52
Δ_3	−178	−179	−177	−179	−181	−187

[a]From Ref. 11.
[b]This work.
[c]aug-cc-pvTZ basis set.
[d]From Ref. 45.

TABLE III. Harmonic frequencies ω and anharmonic constants $\mathbf{x}_{ij}$ in cm^{-1} for the transition state governing D_2 elimination from D_2CO obtained using the DZP basis set of Ref. 44.

	MP2[a]	MP2[b]	MP2[c]	MP2[d]	B97-2[c]	B97-2[d]
ω_1	1579i	1579i	1579i	1579i	1498i	1498i
x_{11}	−6.7	−6.6	−6.6	−6.6	−8.4	−8.4
x_{21}	−57.2i	−57.4i	−57.4i	−57.3i	−43.9i	−43.9i
x_{31}	−3.3i	−3.4i	−3.4i	−3.4i	−7.1i	−7.1i
x_{41}	14.6i	14.6i	14.6i	14.6i	20.0i	20.0i
x_{51}	2.9i	2.9i	2.9i	2.9i	4.7i	4.7i
x_{61}	−28.2i	−28.2i	−28.3i	−28.3i	−24.7i	−24.8i
ω_2	2478	2478	2478	2478	2463	2463
x_{22}	−15.0	−14.8	−14.8	−14.9	−14.9	−14.9
x_{32}	−19.6	−19.6	−19.6	−19.7	−21.3	−21.3
x_{42}	1.2	1.2	1.2	1.2	0.8	0.8
x_{52}	0.8	0.9	0.9	0.9	4.0	4.0
x_{62}	−14.9	−15.3	−15.3	−15.2	−14.4	−14.5
ω_3	1730	1730	1730	1730	1783	1783
x_{33}	−7.5	−7.5	−7.5	−7.5	−7.6	−7.6
x_{43}	−16.0	−16.1	−16.1	−16.1	−18.7	−18.7
x_{53}	−16.9	−16.9	−16.9	−16.9	−15.8	−15.8
x_{63}	1.8	2.2	2.2	2.2	4.3	4.3
ω_4	1125	1125	1125	1125	1099	1099
x_{44}	−13.8	−13.8	−13.8	−13.8	−12.2	−12.2
x_{54}	−1.0	−1.0	−1.0	−1.0	−31.9	−31.8
x_{64}	−4.2	−4.2	−4.2	−4.2	−4.3	−4.3
ω_5	660	660	660	660	650	650
x_{55}	−1.9	−1.9	−1.9	−1.9	−2.0	−2.0
x_{65}	1.9	2.3	2.3	2.3	2.5	2.5
ω_6	698	698	698	698	703	703
x_{66}	−3.1	−3.3	−3.3	−3.3	−2.7	−2.8

[a]From Ref. 44.
[b]This work, step=0.005 Å.
[c]This work, step=0.010 Å.
[d]This work, step=0.025 Å.

$$\Delta_{ijk}^2=\frac{\phi_{ijk}^4}{64(\omega_i+\omega_j-\omega_k)^3}, \tag{53}$$

$$\Delta\alpha_{ij}^{\beta}=\frac{B_\beta^2}{\omega_i\omega_j}(\zeta_{ij}^{\beta})^2\frac{(\omega_i+\omega_j)^2}{\omega_i-\omega_j}, \tag{54}$$

and Δ values of 10 cm^{-1} are the default options in the latest version of the implemented algorithm.

At the same level of perturbation, vibrationally averaged properties $\langle P\rangle$ are given by[39,40]

$$\langle P\rangle_n=P_e+\sum_i \alpha_i\langle Q_i\rangle_n+\sum_{ij}\beta_{ij}\langle Q_iQ_j\rangle_n, \tag{55}$$

$$\langle Q_i\rangle_n=-\frac{\hbar}{4\omega_i^2}\sum_j\frac{\Phi_{ijj}}{\omega_j}\left(n_j+\frac{1}{2}\right), \tag{56}$$

$$\langle Q_iQ_j\rangle_n=-\frac{\hbar}{2\omega_i}\delta_{ij}\left(n_j+\frac{1}{2}\right), \tag{57}$$

where

$$\alpha_i=\left(\frac{\partial P}{\partial Q_i}\right)_e,\quad \beta_{ij}=\left(\frac{\partial^2 P}{\partial Q_i\partial Q_j}\right)_e, \tag{58}$$

and δ_{ij} is the Kronecker delta. The average values at 0 K (r_z

TABLE IV. Harmonic ω and fundamental ν wave numbers, and anharmonic corrections Δ to the wave numbers (cm^{-1}) for water. All the computed values have been obtained by the aug-cc-pVTZ basis set and the compilation of experimental values has been taken from Ref. 11.

	BLYP	HCTH	B3LYP	B98	B97-2	PBE0	B1B95	MP2	Expt.
ω_1	3655	3785	3796	3836	3860	3856	3836	3822	3832
ω_2	1596	1620	1627	1634	1645	1633	1628	1628	1648
ω_3	3757	3897	3899	3940	3968	3961	3941	3948	3943
ν_1	3480	3614	3631	3678	3701	3698	3686	3653	3657
ν_2	1543	1571	1575	1583	1594	1582	1578	1578	1595
ν_3	3567	3710	3720	3768	3794	3789	3778	3767	3756
Δ_1	−175	−171	−165	−158	−159	−171	−150	−169	−175
Δ_2	−53	−49	−52	−51	−51	−51	−50	−50	−53
Δ_3	−200	−187	−179	−172	−172	−172	−163	−181	−187

TABLE V. Harmonic ω and fundamental ν wave numbers, and anharmonic corrections Δ to the wave numbers (cm^{-1}) for water. The labels aug-TZ, aug-DZ, and TZ refer to aug-cc-pvTZ, aug-cc-pvDZ, and cc-pvTZ basis sets, respectively. The compilation of experimental values has been taken from Ref. 11.

	MP2			B97-2				
	aug-TZ	aug-DZ	6-31+G**	aug-TZ	aug-DZ	TZ	6-31+G**	Expt.
ω_1	3822	3803	3867	3860	3857	3866	3880	3832
ω_2	1628	1622	1623	1645	1639	1655	1626	1648
ω_3	3948	3937	4014	3968	3971	3971	4008	3943
ν_1	3653	3621	3688	3701	3684	3704	3720	3657
ν_2	1578	1573	1571	1594	1590	1606	1578	1595
ν_3	3767	3744	3821	3794	3786	3795	3832	3756
Δ_1	−169	−182	−179	−159	−173	−162	−160	−175
Δ_2	−50	−49	−52	−51	−49	−49	−48	−53
Δ_3	−181	−193	−193	−172	−185	−176	−176	−187

structure) are obtained by setting all the $n_i=0$, whereas the values at T K (r_α structure when $T=298.15$ K) can be obtained in a first approximation (using the harmonic oscillator partition function) by the replacement,

$$(n_i+1/2)\rightarrow\coth\left(\frac{\hbar\omega_i}{2k_BT}\right), \tag{59}$$

where K_B is the Boltzmann constant.

At the r_z structure the value of the property P is

$$P_\alpha=P(\langle Q\rangle_0)=P_e+\sum_i \alpha_i\langle Q_i\rangle+1/2\sum_{ij} \beta_{ij}\langle Q_i\rangle\langle Q_j\rangle + \cdots \tag{60}$$

and thus the average value can be written as

$$\langle P\rangle_0=P_z+\frac{1}{2}\sum_{ij} \beta_{ij}(\langle Q_iQ_j\rangle_0-\langle Q_i\rangle_0\langle Q_j\rangle_0)+\cdots. \tag{61}$$

Hence, to first order of Q_i and retaining only the principal harmonic and anharmonic contributions,

$$\langle P\rangle_0=P_e+(P_z-P_e)+\langle P_2\rangle \tag{62}$$

with

$$\langle P_2\rangle=\frac{1}{2}\sum_i \beta_{ii}\langle Q_i^2\rangle. \tag{63}$$

This paves the route for effective computations in which equilibrium values are obtained at a very high computational level, whereas vibrational corrections are estimated by cheaper models.

III. RESULTS AND DISCUSSION

As mentioned above, our standard implementation can be used for all the quantum mechanical procedures for which analytical second derivatives are available. In the framework of the Gaussian code[26] this includes HF,[41] KS,[42] and MP2.[43] Some examples for all these procedures will be given in this section. The first step has been to check the results for different rovibrational terms with reference to the SCF results of Ref. 11 for H_2O concerning energy minima and to the MP2 results of Ref. 44 for D_2CO concerning transition states (TSs). Geometries and harmonic frequencies are identical to those of the reference computations, whereas Tables I–III show that at most slight differences are obtained for anharmonic terms due to different numerical implementations.

TABLE VI. Harmonic frequencies, fundamental wave numbers, and anharmonic corrections (cm^{-1}) computed for ethylene using the aug-cc-PVTZ basis set and DFT (B97-2) or CC [CCSD(T)] methods. The compilation of experimental values has been taken from Ref. 11.

	Harmonic			Anharmonic			Difference			
Symmetry	DFT	CC	Expt.	DFT	CC	Expt.	DFT	DFT[a]	CC	Expt.
a_g	3166	3157	3156	3037	3017	3022	−129	−134	−141	−127
a_g	1699	1672	1656	1666	1622	1625	−33	−35	−51	−32
a_g	1383	1369	1372	1359	1341	1344	−24	−24	−28	−28
a_u	1065	1047	1045	1046	1026	1026	−19	−20	−21	−21
b_{1g}	3225	3219	3207	3075	3076	3083	−140	−141	−143	−146
b_{1g}	1243	1242	1248	1225	1223	1222	−18	−21	−19	−23
b_{1u}	981	967	968	971	949	949	−10	−13	−18	−20
b_{2g}	983	942	960	973	929	940	−10	−11	−13	−19
b_{2u}	3253	3246	3239	3116	3100	3105	−147	−145	−146	−129
b_{2u}	828	823	844	831	82	826	3	7	−1	−17
b_{3u}	3149	3139	3130	2999	2979	2989	−150	−150	−160	−158
b_{3u}	1475	1479	1472	1441	1440	1442	−36	−33	−39	−29

[a]B3LYP/6-31G(d).

TABLE VII. Harmonic frequencies, fundamental wave numbers, and anharmonic corrections (cm^{-1}) computed by different methods for *s* tetrazine. The compilation of experimental values has been taken from Ref. 49 except for the $1a_g$ mode, which is taken from Ref. 50.

	Harmonic			PT2			
Symmetry	CCSD(T)[a]	B97-1[b]	B3LYP[c]	B97-1[b]	B3LYP[d]	CCSD(T)[d]	Expt.
a_g	3226	3192	3222	3073(119)	3083(139)	3087	3090
a_g	1457	1473	1486	1424(49)	1436(50)	1407	1415
a_g	1025	1047	1050	1024(23)	1028(22)	1003	1009
a_g	745	751	755	741(10)	745(10)	735	736
b_{1u}	3225	3191	3221	3070(121)	3082(139)	3086	3086
b_{1u}	1216	1231	1233	1204(27)	1207(26)	1190	1204
b_{1u}	1098	1096	1098	1079(17)	1081(17)	1081	1093
b_{2u}	1470	1478	1474	1445(33)	1442(32)	1438	1448
b_{2u}	1137	1147	1153	1112(35)	1113(40)	1097	1108
b_{2u}	927	969	997	927(42)	955(42)	875	883
b_{3g}	1561	1560	1565	1511(49)	1516(49)	1512	1525
b_{3g}	1323	1325	1323	1294(31)	1294(29)	1294	1290
b_{3g}	640	650	648	645(5)	644(4)	636	640
a_u	346	344	351	336(8)	344(7)	339	335
b_{2g}	996	999	994	977(22)	974(20)	976	994
b_{2g}	816	829	826	814(15)	813(13)	803	801
b_{3u}	921	930	926	911(19)	907(19)	902	929
b_{3u}	270	250	259	244(6)	251(8)	262	254

[a]ANO-4321 basis set from Ref. 22.
[b]TZ2P basis set from Ref. 22.
[c]This work TZ2P′ basis set.
[d]B3LYP/6-31G(*d*) anharmonic corrections.

Note that the present convention for the sign of imaginary elements of the *x* matrix for TSs is opposite to that employed in Ref. 44.

The results of Table III show also that the choice of the stepsize for the numerical differentiation of second derivatives is less critical than previously suggested, thanks to quite strict convergence criteria both of SCF and coupled perturbed steps, improved DFT grids, and averaging of equivalent force constants. This justifies the choice of 0.01 Å as the standard step size for all kinds of computations. Harmonic and fundamental frequencies obtained by different methods for H_2O are compared in Table IV to experimental values.[45] The most apparent feature is that harmonic frequencies obtained by hybrid functionals (B3LYP,B98,B97-2,B1B95) are significantly better than those issuing from conventional functionals even including kinetic energy contributions (BLYP,HCTH). The choice between different hybrid functionals is difficult and somewhat dependent on the molecule and kind of vibration (vide infra). On the other hand, anharmonic corrections are much more stable and in good agreement with experimental results. Harmonic and anharmonic frequencies of water obtained at the MP2 and B97-2 levels using different basis sets are compared in Table V.[46] It is quite apparent that converged harmonic values can be obtained only using quite large basis sets. On the other hand, the relatively small 6-31+G(d,p) basis set performs a very good job for anharmonic corrections, especially in the framework of DFT methods. All these results suggest that the coupling of harmonic frequencies computed at a very high level (concerning both QM method and basis set) with anharmonic corrections computed by a relatively cheap model (typically hybrid functionals and 6-31G(d) basis set augmented by diffuse functions on electronegative atoms and *p* functions on hydrogens bonded to them) could provide a very effective procedure for medium size molecules. Table VI allows to evaluate this approach in the case of ethylene, which is a quite demanding system.[47,48] It is apparent that extension of the basis set above the 6-31G(d) level and/or use of functionals different from the standard B3LYP one have a negligible effect on the quality of the computed anharmonic corrections, which are, furthermore, remarkably close to their CCSD(T)/cc-pVTZ counterparts. This is not the case, of course, for harmonic frequencies and intensities, which benefit from careful choice of the computational model. From another point of view, it should be noted that a very inaccurate value is obtained for ν_{11}, unless the well known (e.g., Ref. 48) very strong Fermi type 2 resonance with $\nu_2+\nu_{12}$ is taken into account. For $K_{2,11,12}$ two very different experimental values are available, namely, 113.4 and 44.85 cm^{-1}.[47] Our computed value (124.2 cm^{-1}) is in close agreement with the CCSD(T) result (125.7 cm^{-1}) and definitely favors the former experimental value.

The study of larger molecules requires further approximations. In the absence of hydrogen bridges, several studies are showing that the anharmonic corrections obtained by hybrid density functionals in conjunction with the 6-31G(d) basis set are quite reliable and can be safely added to harmonic force fields obtained at more refined levels.[21,24] For purposes of illustration, Table VII collects the results obtained at this level for *s*-tetrazine. The errors with respect to experimental results[49,50] are typical of this kind of computations.[23] It is noteworthy that B3LYP and CCSD(T) harmonic frequencies are quite close except for the $3B_{2u}$ Kekulé mode, which is overestimated by 70 cm^{-1} at the

TABLE VIII. Fundamental wave numbers (cm^{-1}) and (in parenthesis) IR intensities ($km\,mol^{-1}$) for phenoxy radical.

Symmetry	Harmonic[a]	PT2[a]	Harmonic[b]	PT2[b]	Harmonic[c]	Expt.[d]
$A1$	3223(0.4)	3102	3217(1.1)	3096	3217(1.1)	
	3210(20.5)	3075	3207(14.7)	3072	3206(12.9)	
	3188(0.6)	3038	3185(0.6)	3035	3185(0.6)	
	1603(34.0)	1564	1592(37.8)	1553	1591(37.8)	1557
	1498(14.9)	1469	1490(27.4)	1461	1490(27.0)	1505
	1433(0.0)	1406	1421(0.3)	1394	1421(0.2)	1398
	1175(0.4)	1161	1168(0.3)	1154	1166(0.4)	1157
	1018(0.0)	1001	1011(0.2)	994	1011(0.2)	990
	986(1.8)	969	982(2.2)	965	982(2.1)	
	811(2.0)	798	808(2.2)	795	808(1.9)	801
	531(2.2)	525	529(2.4)	523	529(2.5)	528
$A2$	975(0.0)	964	982(0.0)	971	986(0.0)	
	808(0.0)	794	802(0.0)	788	803(0.0)	
	380(0.0)	374	378(0.0)	372	379(0.0)	
$B1$	995(0.2)	980	993(0.4)	978	999(0.1)	
	922(7.6)	908	922(7.6)	908	927(8.2)	
	796(38.7)	786	791(49.4)	781	799(41.2)	
	658(28.1)	648	648(40.9)	638	652(43.5)	
	486(0.2)	478	481(0.8)	473	481(0.9)	
	196(2.6)	190	189(2.7)	183	190(2.8)	
$B2$	3221(11.7)	3087	3215(7.8)	3081	3214(6.5)	
	3195(12.0)	3062	3191(9.2)	3058	3191(8.4)	
	1564(3.8)	1529	1551(3.0)	1516	1550(3.2)	
	1458(3.2)	1425	1448(4.4)	1415	1448(4.3)	
	1352(7.5)	1329	1347(7.4)	1324	1347(7.1)	
	1289(5.8)	1262	1283(5.7)	1256	1284(5.6)	
	1176(1.0)	1162	1167(1.5)	1153	1164(1.4)	
	1098(7.2)	1083	1092(8.2)	1077	1090(7.8)	
	598(0.6)	592	596(0.4)	590	596(0.5)	
	444(5.2)	441	444(4.4)	441	444(4.4)	

[a]6-31G(d).
[b]6-31+G(d,p).
[c]6-31+G(d,p)+FIP d function on C,N taken from Ref. 23.
[d]From Ref. 51.

B3LYP level (997 vs 927 cm^{-1}). Furthermore, combination of CCSD(T) harmonic frequencies and B3LYP anharmonic corrections and (with the exception of the above Kekulé mode) full B3LYP computations lead to remarkable agreement with experimental data, the only disagreement larger than 20 cm^{-1} concerning the $1B_{3u}$ mode.

While DFT and MP2 approaches provide comparable results for closed-shell systems (although converged results often require somewhat larger basis sets at the MP2 level) the situation is different for open-shell species, where spin contamination often becomes an issue for unrestricted post-Hartree-Fock methods, whereas this is not the case for unrestricted DFT approaches. Typical DFT results are shown in Table VIII for the phenoxy radical, whose significant multireference character precludes the use of single reference post-HF methods. Although only few bands were detected experimentally,[51,52] the agreement seems of the same quality as for closed-shell systems. Furthermore addition of diffuse polarization functions to the 6-31+G(d) basis set does not alter significantly the computed harmonic frequencies and IR intensities. This is quite interesting since it has been previously shown that the larger basis set performs a very good job in the reproduction of polarizabilities and IR intensities.[23]

Together with vibrational spectra, the implemented code provides vibrationally averaged values of properties (including geometrical parameters) and anharmonic corrections to thermodynamic functions. While these aspects will be dealt with in specific studies,[35,53] the vibrationally averaged geometry of water reported in Table I illustrates the quality of typical computations.

The results reported so far show, in my opinion, that one disposes of a quite robust and effective procedure for the routine study of semirigid molecules even in the presence of Fermi resonances. In such circumstances the present PT2 approach is, at least, competitive with the VSCF approach and its perturbative extension. There are, however, a number of situations where the present approach is not sufficient. A very simple example is provided by the out of plane motion of amide groups, where a straightforward perturbative treatment leads to completely unrealistic values. A viable way out for these cases is offered by an integrated perturbative-variational approach. A pilot version of the algorithm has already been coded and its first applications seem quite

promising. Even taking this remark into account, several interesting systems can be already studied in a proper way by the present perturbative algorithm.

IV. CONCLUSION

This paper compares the vibrational frequencies of a number of molecules obtained at the harmonic level with their counterparts issuing from a second-order perturbative treatment based on quadratic, cubic, and semidiagonal quartic force constants. The results show that the latter model is very useful and reasonably accurate for approximate calculations of low lying vibrational levels. Furthermore, accurate band origins can be effectively computed at the DFT level with medium size basis sets without any ad hoc scaling. The whole algorithm has been included as a black box procedure in the G03 package.

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