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Harmonic and Anharmonic Vibrational Frequency Calculations with the Double-Hybrid B2PLYP Method: Analytic Second Derivatives and Benchmark Studies

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Abstract: This work aims to provide reliable benchmark data on the accuracy of harmonic and anharmonic vibrational frequencies computed with the B2PLYP double-hybrid density functional method. The exchange-correlation contributions required for the B2PLYP analytical second derivatives are presented here, which allow for the effective calculation of harmonic frequency as well as cubic and semidiagonal quartic force fields. The latter, in turn, are necessary to compute the anharmonic vibrational frequencies with the perturbative approach (VPT2). The quality of harmonic vibrational frequencies computed in conjunction with basis sets of double- to quadruple-ζ quality has been checked against reference data from the F38 benchmark set. Then, for an additional set of small closed- and open-shell systems, both harmonic frequencies and anharmonic contributions computed at the B2PLYP/N07D and the B2PLYP/aug-cc-pVTZ levels have been compared to their CCSD(T) counterparts. Moreover, for selected medium-size molecules (furan, pyrrole, thiophene, uracil, anisole, phenol, and pyridine), anharmonic frequencies have been compared to well established experimental results. Such benchmark studies have shown that the B2PLYP/N07D model provides good quality harmonic frequencies and describes correctly anharmonic contributions, the latter being of similar accuracy to their B3LYP/N07D counterparts, but obtained at significantly larger computational cost. Additionally, increased accuracy can be obtained by adopting hybrid models where the B2PLYP/N07D anharmonic contributions are combined with harmonic frequencies computed with more accurate quantum mechanical (QM) approaches or by B2PLYP with larger basis sets. This work confirmed also that most of the recently developed density functionals are significantly less suited for vibrational computations, while the B2PLYP method can be recommended for spectroscopic studies where a good accuracy of vibrational properties is required.

1. Introduction

Computational chemistry experiments have already been proven to deliver highly accurate results for small mole-cules,[1−5] clearly demonstrating their usefulness as tools for the prediction and understanding of many kinds of spectroscopic properties of molecular systems. At present, it is widely recognized that, for semirigid molecules, the computation of vibrational frequencies by a second-order perturbative approach (VPT2)[6,7] can be applied even for quite large systems to support reliable interpretation of spectroscopic measurements. In particular, VPT2 computations coupled with semidiagonal quartic force fields evaluated at the CCSD(T) (coupled clusters with single, double, and

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perturbative inclusion of triple excitations[8]) level in conjunction with basis sets of at least triple-ζ quality usually provide results with an accuracy on the order of $10-15$ cm^{-1} for the fundamental transitions.[9−21] However, computations at the CCSD(T) level are still limited to small systems, so that the extension of accurate computational studies to larger systems requires cheaper yet reliable electronic structure methods. In this respect, the density functional theory (DFT) stands as a valuable route, and several VPT2 computations based on the DFT anharmonic force fields have been reported for small and medium-sized semirigid molecules.[22−27] Among the functionals tested, hybrid ones provide satisfactory results when coupled to basis sets of at least double-ζ plus polarization quality supplemented by diffuse sp functions. However, as we recently pointed out,[28,29] computation of the vibrational frequencies turned out to be a particularly challenging task, even for newly developed density functionals. As a matter of fact, some of the most successful last-generation functionals (M06-2X and ωB97X) provided quite disappointing results, showing that vibrational properties should not be overlooked while optimizing parameters in this kind of functional.

Recently, some of us have presented a DFT/N07D model[30−32] which, for density functionals like B3LYP,[33] CAM-B3LYP,[34] and PBE0,[35] provides results of remarkable quality for a broad range of spectroscopic parameters (ESR, IR, UV, ECD).[36−38] In the search for a computational approach able to reproduce different spectroscopic properties with consistent accuracy, the double-hybrid B2PLYP[39] method appears as a promising alternative, as it has already been shown to provide accurate results even for excited electronic states,[40] including challenging topics like electronic circular dichroism.[41] In this work, we test the performance of B2PLYP in the evaluation of vibrational properties, which represents an issue for several functionals, preventing their systematic use in computational spectroscopy. For this purpose, both harmonic and anharmonic vibrational frequencies will be computed using the B2PLYP approach. At this point, is should be remembered that anharmonic VPT2 computations require cubic and semidiagonal quartic force fields, which in turn can be effectively determined via numerical differentiation of analytically evaluated force constants.[7,13,42,43] In this respect, anharmonic computations with the B2PLYP method have become feasible thanks to the development and implementation of the B2PLYP analytical 2nd derivatives (see section 2). Concerning the validation of the B2PLYP vibrational properties, and further extension of the DFT/N07D model, VPT2 computations with the B2PLYP method have been performed in conjunction with the N07D basis set for all systems. It should be noted that, in the case of B3LYP computations, the basis set extension beyond N07D has a negligible effect on the accuracy of vibrational properties.[29] However, in the case of B2PLYP, it can be expected that significantly larger basis sets are required due to the MP2 contribution. For this purpose, the quality of the B2PLYP/N07D harmonic frequencies has been assessed by comparison with the results obtained at the CCSD(T) level and from experimental data, while the basis set convergence has been checked by

extending the basis set to aug-cc-pVTZ (AVTZ) and/or aug-cc-pVQZ (AVQZ). Next, the performance of the B2PLYP/N07D model in evaluating the anharmonic contributions has been tested for a set of small closed- and open-shell systems by comparison to quartic force fields at the B2PLYP/AVTZ and CCSD(T) levels of theory. Moreover, for larger systems, the quality of the anharmonic frequencies computed with the B2PLYP/N07D and hybrid models has been assessed relative to state-of-the art experimental results. Finally, the accuracy of the vibrational properties computed with several other density functionals has been evaluated, in order to validate further the conclusions drawn on the basis of a smaller set of data.[28,29]

The paper is organized as follows. Section 2 describes the exchange-correlation contributions required by the formalism of the analytical second derivatives of the B2PLYP energies. The details on the computational models applied to the determination of structures and harmonic and anharmonic vibrations are gathered in Section 3. Section 4 reports the benchmark results on vibrational properties computed at the B2PLYP/N07D level. Harmonic frequencies for the molecules from the F38 benchmark set are reported in section 4.1. VPT2 computations for small closed- and open-shell systems validated by comparison with accurate results at the CCSD(T) level are collected in section 4.2. Additionally, B2PLYP/N07D and hybrid B2PLYP//AVTZ/N07D VPT2 anharmonic frequency results are compared to experimental data in section 4.3. Finally, our conclusions on the accuracy of B2PLYP and other DFT approaches in computing vibrational properties are presented in section 4.4.

2. Exchange-Correlation Contributions to the B2PLYP Analytic Second Derivative

B2PLYP belongs to the family of so-called "double-hybrid" methods, which are essentially a second-order perturbation (PT2) treatment of the correlation energy. When the results of a Hartree−Fock (HF) self-consistent field (SCF) calculation are used as a zeroth-order reference, the PT2 approach corresponds to the well-known MP2 method. However, the results of a DFT Kohn−Sham (KS) SCF can be used as a reference as well, and by a suitable (semiempirical) scaling of the PT2 contribution to the energy, a significant improvement in the accuracy of the method can be achieved.[39,44] Therefore, the formalism of the derivatives of the KS-PT2 method (and of B2PLYP in particular) is best understood as a combination of the KS-SCF and MP2 first and second derivatives.

In the following, we will describe only and all of the exchange-correlation (XC) terms required to evaluate the second derivatives of the KS-PT2 energy. The interested reader is invited to review refs 45−47, which describe the details of the evaluation of the first and second derivatives of the KS-SCF energy, and refs 48−50, where the MP2 first derivatives are illustrated. Moreover, a presentation of the overall formalism of the MP2 energy second derivatives can be found in refs 51−53, while the first derivatives of the KS-PT2 method have been recently reported in ref 54. Finally, the exchange-correlation terms involved in any "post-KS" gradient (and thus also in the B2PLYP gradient) have been

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described in detail in connection with the implementation of the time-dependent DFT (TD-DFT) gradient in ref 55. The complete formalism of the KS-PT2 2nd derivatives, including frozen-core approximation and solvent effects by means of the polarizable continuum model (PCM),[56,57] will be presented in a more organic form in a forthcoming paper.

In order to concisely write the various exchange-correlation (XC) contributions to the KS-PT2 energy and its derivatives, it is necessary to introduce some notation. First, we write the XC contribution to the KS-SCF energy as

$$E_{xc} = w\mathscr{F}[\mathbf{v}_I] \tag{1}$$

where we assume an integration grid point index on both the integration weights w and the functional values $\mathscr{F}$, and we assume the required sum over the grid points. The functional itself depends on a set of variables $\{\mathbf{v}_I\}$[55] which typically include the density ρ, the density gradient $\nabla\rho$, the kinetic energy density τ, and the Laplacian of the density $\nabla^2\rho$, i.e.,

$$\{\mathbf{v}_I\} = \{\rho, \nabla\rho, \tau, \nabla^2\rho\} \tag{2}$$

Note that all of the elements of the set $\{\mathbf{v}_I\}$ are linear in a one-particle density matrix $\mathbf{P}$ according to

$$\mathbf{v}_I[\mathbf{P}] = \sum_{\mu\nu} P_{\mu\nu} \mathbf{v}_{I,\mu\nu} \tag{3}$$

where $\mathbf{v}_{I,\mu\nu} = \chi_\mu\chi_\nu$ for the density, $\mathbf{v}_{I,\mu\nu} = \nabla(\chi_\mu\chi_\nu)$ for the density gradients, $\mathbf{v}_{I,\mu\nu} = (\nabla\chi_\mu)\cdot(\nabla\chi_\nu)$ for the kinetic energy density, and $\mathbf{v}_{I,\mu\nu} = \nabla^2(\chi_\mu\chi_\nu)$ for the Laplacian of the density. The set $\{\chi_\mu\}$ represents the atomic orbital (AO) basis set. The functional $\mathscr{F}$ is usually written as depending on the squared norms of the density gradient, i.e., $\gamma_{\sigma\sigma'} = (\nabla\rho_\sigma)\cdot(\nabla\rho_{\sigma'})$, where σ and σ' are spin labels. However, for the sake of a more concise notation, we will assume that the chain rule has been applied to the functional derivatives to obtain derivatives with respect to the elements of the set $\{\mathbf{v}_I\}$.

The first derivative of the XC energy is well-known[45] to be

$$E_{xc}^x = w^x\mathscr{F} + w\mathscr{F}^I\mathbf{v}_I^{(x)} \tag{4}$$

where w^x represents the first derivatives of the integration weights, $\mathscr{F}^I$ is the first derivative of the functional with respect to the Ith variable, and a sum over I is implied. Also, with the parentheses, we indicate the *explicit* dependence of the variables through the basis function, i.e.,

$$\mathbf{v}_I^{(x)} = \sum_{\mu\nu} P_{\mu\nu} \mathbf{v}_{I,\mu\nu}^x \tag{5}$$

The corresponding XC energy second derivatives[45,46] can be written as

$$\begin{aligned}
E_{xc}^{xy} = \ & w^{xy}\mathscr{F} + w^x\mathscr{F}^I\mathbf{v}_I^{(y)} + w^y\mathscr{F}^I\mathbf{v}_I^{(x)} + w\mathscr{F}^{IJ}\mathbf{v}_I^{(x)}\mathbf{v}_J^{(y)} + w\mathscr{F}^I\mathbf{v}_I^{(x,y)} \\
& + w^x\mathscr{F}^I\mathbf{v}_I^{[y]} + w\mathscr{F}^{IJ}\mathbf{v}_I^{(x)}\mathbf{v}_J^{[y]} + w\mathscr{F}^I\mathbf{v}_I^{(x)[y]}
\end{aligned} \tag{6}$$

where the first five terms on the right-hand side involve *explicit* dependence of the weights and the variables on the perturbations, while the last three terms account for the

implicit dependence of the variables on the density derivative, which we indicate using the square brackets

$$\mathbf{v}_I^{[x]} = \mathbf{v}_I[\mathbf{P}^x] = \sum_{\mu\nu} P_{\mu\nu}^x \mathbf{v}_{I,\mu\nu} \tag{7}$$

Note that the last three terms in eq 6 can be also written as follows

$$\sum_{\mu\nu} P_{\mu\nu}^y (w^x\mathscr{F}^I\mathbf{v}_{I,\mu\nu} + w\mathscr{F}^{IJ}\mathbf{v}_J^{(x)}\mathbf{v}_{I,\mu\nu} + w\mathscr{F}^I\mathbf{v}_{I,\mu\nu}^x) = \langle\mathbf{P}^y\mathbf{G}_{xc}^{(x)}\rangle \tag{8}$$

i.e., like the trace of the density derivative $\mathbf{P}^y$ with the XC portion of the skeleton Fock matrix derivative. The occupied-virtual block of the density derivative $\mathbf{P}_{ov}^x$ is the solution of the couple-perturbed KS (CP-KS) equations, whose right-hand side involves the skeleton Fock matrix derivative and the additional XC term

$$\mathbf{G}_{xc}[\mathbf{P}_{oo}^x] = -w\mathscr{F}^{IJ}\mathbf{v}_J[\mathbf{S}_{oo}^x]\mathbf{v}_{I,\mu\nu} \tag{9}$$

where[58] $\mathbf{S}_{oo}^x = -\mathbf{P}_{oo}^x$, while the left-hand side includes the corresponding XC term, which depends on the unknown quantity $\mathbf{P}_{ov}^x$, i.e.

$$\mathbf{G}_{xc}[\mathbf{P}_{ov}^x] = w\mathscr{F}^{IJ}\mathbf{v}_J[\mathbf{P}_{ov}^x]\mathbf{v}_{I,\mu\nu} \tag{10}$$

In addition to the terms in eq 6, there is also an XC contribution to the total energy second derivatives, namely, through the $\langle\mathbf{W}^y\mathbf{S}^x\rangle$ trace, where the derivatives of the energy-weighted matrix express the dependence of the SCF orbital energies on the perturbations, which is assembled from the complete $\mathbf{P}^x$ and $\mathbf{F}^x$ matrices.

On the other hand, the XC contributions to the KS-PT2 gradient,[54] or more generally speaking to any "post-KS" gradient,[55] assume the following form:

$$\begin{aligned}
E_{xc}^{KS\text{-}PT2(x)} = \ & w^x\mathscr{F} + w\mathscr{F}^I\mathbf{v}_I^{(x)} + \langle\gamma\mathbf{G}_{xc}^{(x)}\rangle - \langle\mathbf{S}^x\mathbf{G}_{xc}[\gamma]\rangle \\
= \ & w^x(\mathscr{F} + \mathscr{F}^I\mathbf{v}_I[\gamma]) + w(\mathscr{F}^I + \mathscr{F}^{IJ}\mathbf{v}_J[\gamma])\mathbf{v}_I^{(x)} \\
& + w\mathscr{F}^I\mathbf{v}_I^{(x)}[\gamma] - w\mathscr{F}^{IJ}\mathbf{v}_J[\gamma]\mathbf{v}_I[\mathbf{S}^x]
\end{aligned} \tag{11}$$

where γ is the correlation contribution to the one-particle density matrix, back-transformed to the AO basis. The occupied-virtual block of γ is found by solving the so-called Z-vector equations. These are CP-KS equations whose right-hand side involves the KS-PT2 Lagrangian,[54] which is indeed identical to the MP2 Lagrangian[48] since the KS-PT2 energy $E^{KS\text{-}PT2}$ does not involve any explicit XC energy term beyond the KS-SCF level. The last term on the right-hand side of eq 11 represents the trace of the overlap matrix derivative $\mathbf{S}^x$ with the correlation contribution to the appropriate energy-weighted density matrix $\mathbf{W}^{KS\text{-}PT2}$.

Finally, the XC contributions to the KS-PT2 energy second derivatives are

$$\begin{aligned}
E_{xc}^{\text{KS-PT2}(x,y)} = & \ w^{xy}(\mathscr{F} + \mathscr{F}^{\text{I}}\mathbf{v}_{\text{I}}[\boldsymbol{\gamma}]) + w^{x}[(\mathscr{F}^{\text{I}} + \mathscr{F}^{\text{I,J}}\mathbf{v}_{\text{J}}[\boldsymbol{\gamma}])\mathbf{v}_{\text{I}}^{(y)} + \\
& \ \mathscr{F}^{\text{I}}\mathbf{v}_{\text{I}}^{(y)}[\boldsymbol{\gamma}]] + w^{y}[(\mathscr{F}^{\text{I}} + \mathscr{F}^{\text{I,J}}\mathbf{v}_{\text{J}}[\boldsymbol{\gamma}])\mathbf{v}_{\text{I}}^{(x)} + \mathscr{F}^{\text{I}}\mathbf{v}_{\text{I}}^{(x)}[\boldsymbol{\gamma}]] + \\
& \ w[(\mathscr{F}^{\text{I,J}} + \mathscr{F}^{\text{I,J,K}}\mathbf{v}_{\text{K}}[\boldsymbol{\gamma}])\mathbf{v}_{\text{I}}^{(x)}\mathbf{v}_{\text{J}}^{(y)} + \mathscr{F}^{\text{I,J}}(\mathbf{v}_{\text{I}}^{(x)}\mathbf{v}_{\text{J}}^{(y)}[\boldsymbol{\gamma}] + \\
& \ \mathbf{v}_{\text{I}}^{(y)}\mathbf{v}_{\text{J}}^{(x)}[\boldsymbol{\gamma}]) + (\mathscr{F}^{\text{I}} + \mathscr{F}^{\text{I,J}}\mathbf{v}_{\text{J}}[\boldsymbol{\gamma}])\mathbf{v}_{\text{I}}^{(x,y)} + \mathscr{F}^{\text{I}}\mathbf{v}_{\text{I}}^{(x,y)}[\boldsymbol{\gamma}]] + \\
& \ \langle \mathbf{P}^{y}\mathbf{G}_{xc}^{(x)}[\boldsymbol{\gamma}]\rangle + \langle \boldsymbol{\gamma}^{y}\mathbf{G}_{xc}^{(x)}\rangle - \langle \mathbf{S}^{xy}\mathbf{G}_{xc}[\boldsymbol{\gamma}]\rangle - \langle \mathbf{S}^{x}\mathbf{G}_{xc}^{(y)}[\boldsymbol{\gamma}]\rangle - \\
& \ \langle \mathbf{S}^{x}\mathbf{G}_{xc}^{[y]}[\boldsymbol{\gamma}]\rangle - \langle \mathbf{S}^{x}\mathbf{G}_{xc}[\boldsymbol{\gamma}^{y}]\rangle \rangle \quad (12)
\end{aligned}$$

where

$$\begin{aligned}
\mathbf{G}_{xc}^{(x)}[\boldsymbol{\gamma}] = & \ w^{x}(\mathscr{F}^{\text{I}} + \mathscr{F}^{\text{I,J}}\mathbf{v}_{\text{J}}[\boldsymbol{\gamma}])\mathbf{v}_{\text{I},\mu\nu} \\
& + w[(\mathscr{F}^{\text{I,J}} + \mathscr{F}^{\text{I,J,K}}\mathbf{v}_{\text{K}}[\boldsymbol{\gamma}])\mathbf{v}_{\text{J}}^{(x)} + \mathscr{F}^{\text{I,J}}\mathbf{v}_{\text{J}}^{(x)}[\boldsymbol{\gamma}]]\mathbf{v}_{\text{I},\mu\nu} \\
& + w(\mathscr{F}^{\text{I}} + \mathscr{F}^{\text{I,J}}\mathbf{v}_{\text{J}}[\boldsymbol{\gamma}])\mathbf{v}_{\text{I},\mu\nu}^{x} \quad (13)
\end{aligned}$$

and

$$\mathbf{G}_{xc}^{[x]}[\boldsymbol{\gamma}] = w\mathscr{F}^{\text{I,J,K}}\mathbf{v}_{\text{K}}[\boldsymbol{\gamma}]\mathbf{v}_{\text{J}}[\mathbf{P}^{x}]\mathbf{v}_{\text{I},\mu\nu} \quad (14)$$

In order to completely evaluate eq 12, the full derivative $\boldsymbol{\gamma}^{x}$ of the correlation contribution to the one-particle density matrix must be computed. The occupied−occupied and virtual−virtual blocks of $\boldsymbol{\gamma}^{x}$ depend on products of PT2 amplitudes and amplitudes derivatives. The latter can be assembled from undifferentiated amplitudes and orbital energies, two-electron integral derivatives, and the derivatives of the Fock operators (see, e.g., eq 39 in ref 53). These are the derivatives of the Fock matrix in the canonical molecular orbital basis, which are no longer diagonal matrices and include automatically the proper XC contributions, once the nuclear coordinate CP-KS equations have been solved and the full $\mathbf{P}^{x}$ and $\mathbf{F}^{x}$ matrices are available. Thus, the only remaining piece is the occupied-virtual block of $\boldsymbol{\gamma}^{x}$, which is the solution of the *derivative* Z-vector equations, whose right-hand side involves the derivatives of the MP2 Lagrangian[51−53] and all the terms from the derivatives of the left-hand side which do not involve the unknowns $\boldsymbol{\gamma}_{\text{ov}}^{x}$, i.e., the quantities in eqs 13 and 14 together with the additional term

$$w\mathscr{F}^{\text{I,J}}\mathbf{v}_{\text{J}}[\boldsymbol{\gamma}_{\text{oo}}^{x} + \boldsymbol{\gamma}_{\text{vv}}^{x}]\mathbf{v}_{\text{I},\mu\nu} \quad (15)$$

3. Computational Details

Density functional theory computations have been carried out using the double-hybrid B2PLYP[39] method in conjunction with the recently developed polarized double-ζ N07D[30−32,59] and aug-cc-pVXZ (X = T, Q)[60,61] basis sets. The N07D basis set has been constructed by adding a reduced number of polarization and diffuse functions to the 6-31G set (see refs 30 and 31 for details), leading to an optimum compromise between reliability and computational cost.

All structures have been optimized using tight convergence criteria, followed by the computation of the anharmonic frequencies by means of the VPT2 approach,[6,7] as implemented in the Gaussian package.[62] Semidiagonal quartic force fields have been evaluated by numerical differentiation (with a standard 0.025 Å step) of analytical second derivatives.[42] Since VPT2 computations are sensitive to the proper treatment of the Fermi resonances, it is crucial to automatically neglect nearly singular contributions (deperturbed

computations). This is performed by effectively removing interactions in the second-order treatment, which are more properly treated in the first-order. For this purpose, our VPT2 implementation[7] makes use of the criteria proposed by Martin and Boese,[25] through an automated scheme that has already been shown to provide accurate results, at least for fundamental bands.[63] Additionally, in some cases, the hybrid CCSD(T)/DFT or DFT AVTZ/N07D approaches have also been applied to evaluate the anharmonic frequencies, and two possible routes have been implemented. In the simpler one (DPT2), the harmonic frequencies computed at the higher level of theory (CCSD(T), B2PLYP/AVTZ) are *a posteriori* corrected by the anharmonic contributions ($\Delta\nu$) derived from VPT2 computations performed at the lower level: $\nu_{\text{Higher/Lower}} = \omega_{\text{Higher}} + \Delta\nu_{\text{Lower}}$. Such an approximation, in particular within the CCSD(T)/DFT scheme, has been already validated for several closed- and open-shell systems (see for instance refs 29, 64−67). The second route introduces the harmonic frequencies evaluated at the higher level directly into the VPT2 computations along with the 3rd and 4th order force constants obtained at the lower level of theory. Such an approach is available in the Gaussian package through the InDerAU and InFreq options, with harmonic frequencies computed at the higher level of theory listed in the input stream (a feature available in the standard package[68]) or with the corresponding Hessian matrix read from the checkpoint file. For the latter case, an automatic procedure which compares normal modes computed by the two levels of theory and replaces harmonic data accordingly is introduced in this work. Such an implementation facilitates the application of a hybrid InFreq route for large systems for which the ordering of several closely lying vibrations might be exchanged. It should be noted that the InFreq procedure might significantly improve the quality of the results in difficult cases, i.e., when large discrepancies between harmonic frequencies computed at two levels of theory or Fermi resonances are present.

In addition to the computations with the B2PLYP method, we decided to benchmark the performances of other density functionals, in order to confirm the findings obtained in several case studies[28,29] where an unsatisfactory description of vibrational frequencies had been found out. In this context, a broad range of recently introduced density functionals, namely, M06/M06-2X,[69,70] the ωB97 family,[71,72] HSE06,[73] and LC-ωPBE,[74] has been considered. For the sake of completeness, standard functionals like B3LYP,[33] CAM-B3LYP,[34] and B97-1[75] and the parameter-free PBE0[35] have also been included in our tests. All calculations have been performed with a locally modified version of the Gaussian suite of quantum chemistry programs.[62]

4. Validation of the B2PLYP Method for the Calculation of Vibrational Frequencies

4.1. Harmonic Vibrational Frequencies for Small Molecules from the F38 Database. The present work is devoted to the validation of the B2PLYP/N07D model for the computation of vibrational frequencies. Thus, it is appropriate to start the analysis discussing the accuracy of

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Table 1. Harmonic (ω) Vibrational Frequencies (in cm^{-1}) Computed with the B2PLYP and B3LYP Functionals and the N07D or aug-cc-pVTZ(AVTZ) (for B2PLYP also aug-cc-pVQZ(AVQZ)) Basis Sets for Molecules from the F38 Benchmark Set, and Compared to the F38 Reference Data

			B2PLYP			B3LYP	
		exp.[a]	N07D	AVTZ	AVQZ	N07D	AVTZ
H$_2$	ω_1	4401	4501	4464	4461	4451	4418
CH$_4$	ω_1	1367	1361	1353	1352	1342	1339
	ω_2	1583	1576	1576	1575	1557	1557
	ω_3	3026	3068	3050	3050	3037	3028
	ω_4	3157	3191	3162	3163	3150	3130
NH$_3$	ω_1	3478	3517	3489	3492	3485	3469
	ω_2	1084	1028	1037	1034	999	1025
	ω_3	3597	3660	3617	3621	3621	3588
	ω_4	1684	1682	1673	1674	1666	1664
H$_2$O	ω_1	1649	1652	1635	1637	1641	1627
	ω_2	3832	3832	3813	3823	3814	3796
	ω_3	3943	3951	3924	3934	3922	3899
HF	ω_1	4139	4096	4099	4107	4071	4070
CO	ω_1	2170	2155	2154	2161	2205	2207
N$_2$	ω_1	2359	2351	2341	2346	2453	2448
F$_2$	ω_1	917	970	1016	1012	1023	1050
C$_2$H$_2$	ω_1	624	588	643	649	622	666
	ω_2	747	765	766	762	772	770
	ω_3	2008	2025	2024	2025	2063	2068
	ω_4	3415	3457	3429	3432	3429	3412
	ω_5	3495	3550	3530	3524	3531	3517
HCN	ω_1	727	753	745	745	768	759
	ω_2	2127	2129	2125	2129	2198	2200
	ω_3	3443	3495	3460	3456	3473	3444
H$_2$CO	ω_1	2937	2951	2930	2928	2901	2885
	ω_2	1778	1790	1782	1786	1819	1813
	ω_3	1544	1543	1538	1540	1529	1530
	ω_4	1188	1192	1201	1204	1188	1198
	ω_5	3012	3023	2992	2991	2967	2940
	ω_6	1269	1269	1268	1272	1260	1263
CO$_2$	ω_1	673	660	666	668	666	674
	ω_2	1353	1343	1341	1345	1370	1369
	ω_3	2392	2400	2384	2392	2416	2400
N$_2$O	ω_1	596	572	599	608	592	617
	ω_2	1298	1310	1298	1301	1337	1324
	ω_3	2282	2271	2259	2279	2352	2340
Cl$_2$	ω_1	560	540	551	555	532	537
OH	ω_1	3738	3758	3737	3748	3712	3695
	MIN		−56	−47	−50	−85	−72
	MAX		100	99	95	106	133
	MUE		23	18	17	33	33

[a] Benchmark harmonic frequency values as compiled in refs 70 and 76 on the basis of data from refs 78−80.

harmonic frequencies with reference to the recently introduced benchmark set F38,[70] designed to cover a broad range of frequencies for small molecules. It has been applied here to assess the accuracy of harmonic vibrational frequencies for several density functional[70,76,77] methods. The F38 reference set of data is based on the best experimental harmonic frequencies,[78,79] with the single exception for the umbrella mode of the NH$_3$, which is taken from a CCSD(T)/cc-pVQZ calculation.[80] It should be noted that, for consistency with the available benchmark studies, Table 1 compares harmonic frequencies computed at the B2PLYP level to the original F38 reference data,[70] while in section 4.2 we report the best theoretical harmonic frequencies up to date for some molecules from the F38 database. However, the best experimental and theoretical values for these molecules (H$_2$O,[81] NH$_3$,[83] and H$_2$CO[83]) are very similar, with an

average deviation of 6 cm^{-1} only. The results presented in Table 1 clearly show the good overall accuracy of the harmonic frequencies computed by the B2PLYP/N07D model, which are off by only 1.5% on average from the reference, with a maximum error of about 5%. In absolute values, this corresponds to a mean unsigned error (MUE) of about 23 cm^{-1}, and maximum negative (MIN) and positive (MAX) discrepancies of −56 cm^{-1} and 100 cm^{-1}, respectively, with the single absolute deviation above 60 cm^{-1} observed for the H−H stretching frequency in H$_2$. Additionally, it can be noted that slightly higher absolute deviations are observed for frequencies above 2500 cm^{-1}. The separate analysis performed for frequencies above and below this threshold led to MUEs of 37 cm^{-1} and 15 cm^{-1}, respectively. The results presented in Table 1 show also that the extension of the basis set up to aug-cc-pVTZ, or even aug-cc-pVQZ (with the exception of the F$_2$ molecule), leads in most cases to a slightly superior agreement with the reference data with a MUE of 18 cm^{-1} and 17 cm^{-1}, respectively. Such an effect is most pronounced for the frequencies above 2500 cm^{-1}, and in the extreme case of the H$_2$ molecule, the extension of the basis set improves the agreement by about 50%. It is worth adding that the frequencies computed with the aug-cc-pVTZ and aug-cc-pVQZ basis sets agree on average to 5 cm^{-1}, with a maximum discrepancy of 20 cm^{-1}, confirming that frequency calculations approach the basis set convergence at the AVTZ level. Indeed, the MP2 contribution to B2PLYP causes the computed harmonic frequencies to be not fully converged with respect to the basis set at the N07D level. However, comparison of the results obtained with the double-ζ N07D (58 basis functions for Cl$_2$) and aug-cc-pVQZ (168 basis functions for Cl$_2$) basis sets shows that the error compensation allows the B2PLYP/N07D model to deliver good quality harmonic frequencies. The above arguments are confirmed by the data gathered in Table 1, which point out that, for the standard B3LYP functional, no overall improvement is obtained going from N07D to the more computationally demanding AVTZ basis set, as already shown by the comparison of the harmonic frequencies computed with B3LYP using basis sets of both double- and triple-ζ quality.[65] Additionally, it can be observed that the B2PLYP method outperforms the B3LYP functional, in line with preliminary studies by Grimme.[39] In fact, for the F38 database, B2PLYP/N07D shows a MUE about 30% smaller than B3LYP/N07D (34 cm^{-1}). Thus, despite the fact that particularly difficult cases and/or a need of extreme accuracy might require CCSD(T) computations with extended basis sets, the overall impression is that the B2PLYP stands as the most accurate DFT model to compute harmonic frequencies.

4.2. Anharmonic Vibrational Frequencies for Small Closed- and Open-Shell Systems: B2PLYP vs CCSD(T). In a next step, we compare results provided by the B2PLYP method with those obtained at the CCSD(T) level, with extended basis sets, in order to dissect the overall accuracy of the vibrational frequencies into harmonic and anharmonic contributions. In this respect, we have chosen a set of closed- and open-shell molecules, for which the accuracy of CCSD(T) results has been confirmed by a comparison with experimental data.[5,29,81−83,87−89] As we did in the previous

Table 2. Harmonic (ω) and Anharmonic (ν) Vibrational Frequencies (in cm^{-1}) Computed at the B2PLYP/N07D, B2PLYP/AVTZ, and Hybrid CC+DFT Levels for Selected Closed- and Open-Shell Systems, Compared to the Best Available Theoretical Results Computed at Coupled Cluster Levels

	B2PLYP						CCSD(T)	
	ω	ν	νCC+DFT[a]	ω	ν	νCC+DFT[a]	ω	ν
H$_2$O		N07D			AVTZ		CBS(67)/PES[b]	
ν_1	3832	3659	3663	3812	3645	3669	3836	3659
ν_2	1652	1598	1596	1635	1582	1598	1650	1596
ν_3	3951	3766	3761	3924	3744	3766	3946	3758
HCO		N07D			AVTZ		CBS/aCV[c]	CBS+ QZ[c]
ν_1	2724	2483	2476	2708	2458	2466	2717	2460
ν_2	1892	1868	1880	1886	1862	1881	1905	1878
ν_3	1120	1087	1088	1112	1077	1084	1120	1093
FCO		N07D			AVTZ		augVQZ[d]	augVTZ[d]
ν_1	1896	1834	1838	1888	1849	1861	1900	1864
ν_2	1019	978	1012	1037	1009	1026	1054	1025
ν_3	619	608	623	628	617	623	634	624
H$_2$CO		N07D			AVTZ		AVTZ(F12a)[e]	
ν_1	2951	2794	2775	2930	2775	2778	2933	2784
ν_2	1790	1760	1747	1782	1752	1747	1777	1747
ν_3	1543	1509	1498	1538	1505	1499	1532	1498
ν_4	1192	1175	1170	1201	1184	1170	1187	1167
ν_5	3023	2842	2823	2992	2842	2853	3004	2849
ν_6	1268	1248	1247	1268	1246	1246	1267	1246
H$_2$O$_2$		N07D			AVTZ		AVTZ(F12a)[e]	
ν_1	3788	3598	3606	3777	3590	3609	3796	3606
ν_2	1431	1390	1395	1431	1386	1391	1436	1393
ν_3	909	877	881	930	901	883	913	880
ν_4	389	357	351	376	310	317	384	378
ν_5	3788	3601	3609	3777	3594	3613	3796	3608
ν_6	1324	1272	1278	1321	1262	1270	1329	1280
NH$_3$		N07D			AVTZ		cc-pwCVQZ[f]	
ν_1	3517	3372	3344	3488	3348	3348	3489	3342
ν_2	1028	938	986	1037	954	993	1076	1001
ν_3	3660	3490	3449	3617	3450	3452	3619	3444
ν_4	1682	1635	1633	1673	1626	1633	1680	1635
PH$_3$		N07D			AVTZ		cc-pwCVQZ[f]	
ν_1	2427	2328	2329	2427	2328	2329	2429	2331
ν_2	1031	1009	996	1018	998	997	1017	997
ν_3	2439	2329	2327	2437	2327	2327	2437	2336
ν_4	1152	1127	1122	1150	1123	1121	1147	1122
F$_2$CN		N07D			AVTZ		augVQZ[g]	aVQZ+ augVTZ[g]
ν_1	1809	1787	1790	1796	1775	1790	1811	1781
ν_2	960	946	960	967	953	960	974	957
ν_3	544	538	547	547	542	547	552	546
ν_4	673	667	674	687	681	673	679	673
ν_5	1252	1219	1262	1261	1228	1262	1295	1262
ν_6	493	489	497	500	496	497	501	496
NH$_3^+$		N07D			AVTZ		VQZ[h]	
ν_1	3395	3252	3231	3372	3234	3237	3375	3231
ν_2	873	928	921	864	922	923	865	910
ν_3	3590	3419	3388	3552	3393	3400	3559	3388
ν_4	1557	1523	1517	1548	1507	1510	1551	1507
PH$_3^+$		N07D			AVTZ		VQZ[h]	
ν_1	2501	2406	2402	2505	2419	2410	2497	2400
ν_2	745	667	673	748	674	678	751	670
ν_3	2577	2482	2474	2584	2492	2476	2568	2469
ν_4	2577	2471	2463	2584	2494	2478	2568	2469
ν_5	1058	1036	1032	1056	1037	1035	1054	1029
ν_6	1059	1035	1030	1056	1037	1035	1054	1029
C$_2$H$_3$		N07D			AVTZ		AVTZ(PES/S)[i]	
ν_1	3290	3267	3242	3267	3129	3105	3242	3108
ν_2	3211	3053	3016	3178	3024	3021	3174	3016
ν_3	3109	2946	2907	3077	2917	2910	3070	2901
ν_4	1679	1659	1590	1667	1647	1590	1610	1576
ν_5	1412	1378	1356	1405	1370	1355	1390	1355
ν_6	1069	1019	1014	1061	1010	1013	1064	1015
ν_7	728	695	683	716	681	683	717	688
ν_8	932	920	895	935	921	893	907	892
ν_9	821	809	787	828	812	784	799	793
MIN	−48	−63	−27	−39	−68	−61		
MAX	69	83	17	57	71	14		
MUE	16	18	4	10	11	4		

[a] Anharmonic corrections at the B2PLYP/N07D level. [b] Ref 81. [c] Ref 87. [d] Ref 29. [e] Ref 83. [f] Ref 82. [g] Ref 5. [h] Ref 88. [i] Analytic harmonic frequencies and anharmonic results from VCI calculations using five-mode potential coupling based on a full-dimensional PES computed at the RCCSD(T)/aug-cc-pVTZ level. For details on PES/S, see ref 89.

section, we start the analysis of vibrational data by discussing harmonic frequencies, It should be noted that discrepancies in the former term can be reduced by applying hybrid CC/DFT schemes, which are also presented in Table 2. First,

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considering the accuracy of harmonic frequencies, it is immediately apparent that the conclusions drawn in section 4.1 are, in general terms, confirmed. Namely, the values computed at the B2PLYP/N07D level agree well with the most accurate calculations, with a MUE of 16 cm^{-1}, and further improvement (MUE of 10 cm^{-1}) can be achieved by using the aug-cc-pVTZ basis set. Similarly, anharmonic frequencies computed at the B2PLYP/N07D level show a MUE of 18 cm^{-1}, while the extension of the basis set to aug-cc-pVTZ leads to a MUE of 11 cm^{-1}. Additionally, a significant improvement is achieved through hybrid approaches with harmonic frequencies computed at the CCSD(T) level, which lead to a MUE of 4 cm^{-1} with respect to the anharmonic data computed entirely at the CCSD(T) level. Such a finding confirms the remarkable accuracy of the anharmonic force fields computed with the B2PLYP method, showing also that an improved accuracy can be achieved by using harmonic frequencies of coupled cluster quality. It should be underlined that both hybrid models, which differ by the computational cost associated with the size of the basis set, provide equally accurate results. This demonstrates clearly that the better agreement for the vibrational frequencies computed with the AVTZ basis set should be attributed uniquely to the higher accuracy of the harmonic component. In summary, a direct comparison with accurate computations at the CCSD(T) level clearly shows that the B2PLYP/N07D model provides harmonic frequencies of good accuracy and leads to a description of the anharmonic contributions in agreement with more accurate QM methods. However, it should be noted that results of equivalent accuracy can be delivered by hybrid approaches with anharmonic force fields obtained using the less computationally demanding B3LYP/N07D method.[29]

4.3. Anharmonic Vibrational Frequencies of Larger Molecules Computed with B2PLYP/N07D and Hybrid Schemes. In this section, the performances of the B2PLYP method will be checked against well established experimental data for medium-size molecules. In this respect, we have chosen a set of organic aromatic systems, namely, pyridyne, furan, pyrrole, thiophene, uracil, phenol, and anisole, for which previous calculations of anharmonic frequencies using the B3LYP or the B97-1 density functionals resulted in a very good agreement with the experimental results.[23−25,63,84−86] In this work, both the B2PLYP/N07D model and a hybrid scheme with harmonic frequencies refined through B2PLYP/AVTZ calculations have been tested. For the latter, corrections have been applied to all normal modes or only to normal modes above 2500 cm^{-1}, in line with the findings reported in section 4.1 which displayed a larger basis set dependence for higher harmonic frequencies. Table 3 reports the mean unsigned errors with respect to the experimental data, along with maximum (negative and positive) deviations for all molecules considered. Figure 1 shows differences between computed and experimental frequencies for all normal modes of pyridyne, furan, pyrrole, thiophene, uracil, phenol, and anisole, which are listed in order of increasing wavenumber. First, it can be observed that the overall agreement of the B2PLYP/N07D anharmonic frequencies with the reference data is very good, i.e., in the range of 9−15 cm^{-1} for all the

Table 3. Mean Absolute Errors (MUE), Maximum Negative (MIN) and Positive (MAX) Deviations of Anharmonic Vibrational Frequencies (in cm^{-1}) Computed with the B2PLYP/N07D and Hybrid B2PLYP/(AVTZ/N07D) Models As Compared to the Experimental Data[a]

	N07D			AVTZ/N07D			AVTZ>2500[b]/ N07D		
	MUE	MIN	MAX	MUE	MIN	MAX	MUE	MIN	MAX
pyridine	9	−22	40	17	−35	53	10	−35	40
furan	9	−11	29	9	−14	55	5	−11	7
pyrrole	10	−7	32	11	−20	43	6	−11	28
thiophene	12	−10	34	6	−8	29	7	−10	21
uracil	11	−41	31	8	−12	27	9	−41	31
phenol	12	−18	70	13	−26	65	11	−27	70
anisole	15	−10	48	15	−51	72	12	−51	48
average all	11	−17	41	11	−24	49	9	−27	35

[a] Experimental data are taken from (and references therein): pyridine, ref 90; furan and pyrrole, ref 91; thiophene, ref 92; uracil, ref 93; phenol, ref 94; anisole, ref 86. [b] Hybrid scheme applied to normal modes with frequencies above 2500 cm^{-1}, see text for details.
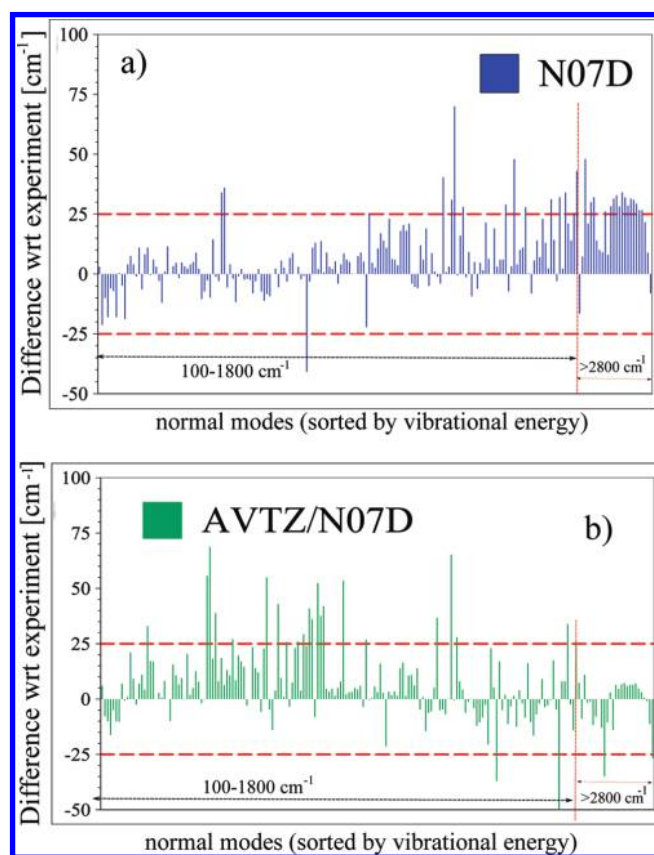

Figure 1. Performance of the B2PLYP/N07D (panel a) and hybrid B2PLYP/(AVTZ/N07D) (panel b) models for the prediction of anharmonic frequencies. The relative absolute discrepancies with respect to experimental results are shown for all normal modes of pyridyne, furan, pyrrole, thiophene, uracil, phenol, and anisole, which are listed according to the increasing wavenumbers (in cm^{-1}).

molecules studied, corresponding to an average of 11 cm^{-1}. Moreover, as shown in Figure 1, despite maximum positive and negative discrepancies of 70 cm^{-1} and −41 cm^{-1}, respectively, the computed anharmonic frequencies are within 25 cm^{-1} of the experimental references, for almost all of the normal modes. Somewhat larger discrepancies are

Table 4. Mean Absolute Errors (MUE), Maximum Negative (MIN), and Positive (MAX) Deviations of Harmonic Vibrational Frequencies (in cm^{-1}) Computed with Several DFT/N07D Models for Molecules from the F38 Benchmark Set, and Compared to the F38 Reference Data

	MUE	MIN	MAX
CAM-B3LYP	52	−110	129
PBE0	50	−86	140
LC-ωPBE	74	−135	192
M06	57	−124	134
M06-2X	66	−77	163
HSE06	50	−86	138
ωB97	62	−93	159
ωB97X	60	−97	152
B97-1	33	−81	61

observed in the high frequency region of the spectrum. However, the relative deviation from experiment remains within 2% even for these frequencies, with only four frequencies above 1000 cm^{-1} exceeding this limit. It can be noted that a significant improvement of the absolute values in the high frequency region is achieved through a hybrid scheme, where the harmonic component is corrected using B2PLYP/aug-cc-pVTZ results. However, the hybrid scheme does not provide a systematic improvement for every normal mode; thus, the overall accuracy of the B2PLYP/(AVTZ/N07D) (referred to as AVTZ/N07D later on) model does not change with respect to the straightforward B2PLYP/N07D approach. On the other hand, it is possible to apply harmonic frequency refinements only to the high frequency normal modes (>2500 cm^{-1}); such a scheme effectively improves the agreement with respect to the experiment and should be considered when a good accuracy in the high frequency region of the spectrum is of particular importance. Thus, it can be concluded that the B2PLYP/N07D model provides very reliable anharmonic frequencies and can be safely applied to spectroscopic studies. However, it should also be

noted that the good overall accuracy of the B2PLYP/N07D and the hybrid AVTZ/N07D models is comparable to that obtained by less expensive anharmonic B3LYP/N07D calculations.

4.4. Accuracy of Harmonic and Anharmonic Vibrational Frequencies Computed with Other DFT/N07D Models. For the sake of completeness, we have investigated the performances of other density functional approaches using the N07D basis set. The same scheme as applied in the previous sections is used here. First, we assessed the accuracy of the harmonic frequencies with respect to the results from the F38 database. Table 4 collects the results obtained by means of some last generation DFT functionals not considered in the work of Zhao and Truhlar,[70,77] along with a few standard functionals, which are among the most popular ones. First, it should be noted that the B3LYP, PBE0, M06, and M06-2X functionals together with the N07D basis set yield harmonic frequencies of accuracy essentially equivalent to the one reported in refs 70 and 77. Additionally, among all the density functionals tested either here or in the work by Zhao and Truhlar,[70,77] only B3LYP, B97-1, and B2PLYP yield harmonic frequencies with the accuracy required for spectroscopic studies, and the B2PLYP method shows clearly the best results. As a next step, it seemed interesting to check also the quality of the cubic and semidiagonal quartic force fields computed with the recently developed density functionals. In this respect, the accuracy of anharmonic contributions has been assessed by comparison with their CCSD(T) counterparts for a few selected molecules, namely, H$_2$O, NH$_3$, PH$_3$, and F$_2$CN. This set of molecules has been chosen in view of the superior accuracy of anharmonic frequencies obtained with the hybrid CCSD(T)/B2PLYP scheme. The quality of the anharmonic force fields has been checked by inspection of the relative discrepancies between $\Delta\nu_{PT2}$'s computed at the DFT and CCSD(T) levels, respectively. Figure 2 shows a plot of the differences in $\Delta\nu_{PT2}$
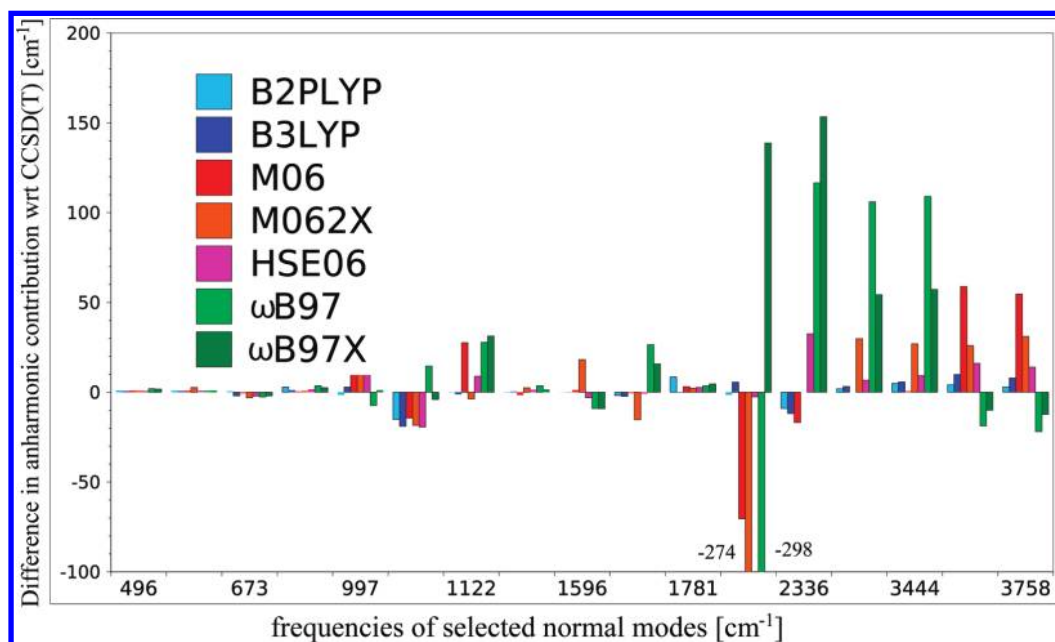

Figure 2. Performance of different density functionals for the prediction of the anharmonic contribution. The relative discrepancies with respect to the values computed at the CCSD(T) level are shown for each normal mode of H$_2$O, NH$_3$, PH$_3$, and F$_2$CN and are listed according to their wavenumbers (in cm^{-1}).

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Table 5. Mean Absolute Errors (MUE), Maximum Negative (MIN) and Positive (MAX) Deviations of Anharmonic Vibrational Frequencies (in cm^{-1}) Computed with Several DFT/N07D Models and Compared to the Experimental Data[a]

	pyridine	furan	pyrrole	thiophene	all
			MUE		
B2PLYP	9	9	10	12	10
B3LYP	9	5	6	7	7
CAM-B3LYP	19	22	21	20	20
PBE0	14	15	18	14	15
LC-ωPBE	28	44	47	35	39
M06	18	13	24	22	19
M06-2X	29	37	50	17	33
HSE06	12	16	20	11	15
ωB97	25	20	20	36	25
ωB97X	25	20	20	26	23
B97-1	13	5	5	9	8
			MIN		
B2PLYP	−22	−11	−7	−10	−13
B3LYP	−33	−15	−16	−19	−21
CAM-B3LYP	−9	6	7	3	2
PBE0	−19	−7	−4	−9	−10
LC-ωPBE	0	14	8	9	8
M06	−39	−17	−118	−63	−59
M06-2X	−18	−7	−15	−17	−14
HSE06	−20	−4	−4	−10	−9
ωB97	−53	−10	−21	4	−20
ωB97X	−50	1	−10	3	−14
B97-1	−47	−14	−13	−20	−24
			MAX		
B2PLYP	40	29	32	34	34
B3LYP	24	5	24	14	17
CAM-B3LYP	46	49	57	51	51
PBE0	75	31	43	40	47
LC-ωPBE	86	92	85	95	90
M06	74	50	55	29	52
M06-2X	136	137	298	56	157
HSE06	71	39	44	38	48
ωB97	74	75	72	82	76
ωB97X	59	70	68	65	66
B97-1	22	4	18	8	13

[a] Experimental data from refs (and references therein): pyridine, ref 90; furan and pyrrole, ref 91; thiophene, ref 92.

between DFT and CCSD(T) for each normal mode of selected molecules, which are listed according to their wavenumbers (in cm^{-1}). First, it is clear that anharmonic corrections at the B2PLYP level agree very well with the reference data, as discussed in section 4.2. Similar results can be observed for B3LYP, further supporting the well-known good quality of the B3LYP/N07D force fields. The other density functionals show different trends, considering that only HSE06 performs in a qualitatively correct way, while functionals belonging to the M06 and the ωB97 families provide unreliable anharmonic corrections. Finally, we assessed the overall accuracy of the anharmonic vibrational frequencies computed by all of the DFT/N07D models considered in this work. For this purpose, Table 5 reports the mean unsigned errors and maximum deviations with respect to experimental data for pyridine, furan, pyrrole, and thiophene. These results show clearly that, among last generation DFT models, only the B2PLYP method (as discussed above) provides anharmonic frequencies in good agreement with experimental results, consistent with the accuracy of harmonic contributions and anharmonic correc-

tions discussed above. Moreover, the good performances of the B3LYP and the B97-1 functionals, when used in conjunction with the N07D basis set, are confirmed. In fact, for both functionals, the MUE is lower than 8 cm^{-1}. Qualitatively correct frequencies are also predicted by the PBE0 and HSE06 functionals, both showing MUEs of about 15 cm^{-1}. All of the other DFT models considered yield MUEs in the range of 20−40 cm^{-1} and also show larger absolute discrepancies. Overall, the results presented in this section show that most of the recently developed density functionals are significantly less accurate in the calculation of vibrational frequencies, confirming the conclusions drawn in refs 28 and 29, on the basis of a smaller benchmark set. On the other hand, the B2PLYP method should be preferred for spectroscopic studies where a good accuracy of the vibrational properties is required.

5. Conclusions

In this work, we presented a concise exposition of the formalism of the analytic second derivatives for the double-hybrid B2PLYP method, along with an assessment of their accuracy in the calculation of vibrational properties. To that end, the computed harmonic vibrational frequencies have been compared with the best experimental estimates from the established F38 benchmark set. Additionally, for several small closed- and open-shell systems, both harmonic frequencies and anharmonic corrections have been compared to their CCSD(T) counterparts, while, for larger systems, the quality of the calculated frequencies has been evaluated by comparison with experimental data. It has been shown that B2PLYP yields harmonic frequencies substantially more accurate than other approaches rooted in the density functional theory, and in this respect, it outperforms the B3LYP functional. However, such an improved accuracy is achieved at a significantly increased computational cost, caused by the second-order perturbation treatment of the electron correlation and the slower convergence with respect to the basis set. Nevertheless, when high quality harmonic contributions are required, the availability of the B2PLYP analytic second derivatives shall improve the current state-of-the-art accuracy for significantly larger systems. In addition to accurate harmonic frequencies, the numerical differentiation of the B2PLYP analytic second derivatives provides also cubic and semidiagonal quartic force fields of good quality. However, in this case, despite the significantly larger computational cost, no clear improvement over calculations employing anharmonic force constants obtained at the B3LYP level has been observed. Additionally, in this work, it has been further confirmed that some of the otherwise successful last generation functionals (the M06 and ωB97X families) do not provide sufficiently accurate vibrational properties, concerning both harmonic frequencies and anharmonic contributions. For such reasons, it seems that the most cost-effective approach is currently to add anharmonic corrections calculated at the B3LYP level to harmonic force fields obtained using more sophisticated computational models, like, e.g., CCSD(T) or B2PLYP with large basis sets. In this respect, the B2PLYP/AVTZ//B3LYP/N07D approach combines the feasibility of accurate harmonic frequency computations with the possibility of taking into account the vibrational effects

beyond the harmonic approximation even for quite large systems of biological and/or technological interest.

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