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ARTICLE *in* JOURNAL OF COMPUTATIONAL CHEMISTRY · MARCH 2005

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Vibrational Computations Beyond the Harmonic Approximation: Performances of the B3LYP Density Functional for Semirigid Molecules

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Received 9 July 2004; Accepted 21 October 2004

DOI 10.1002/jcc.20170

Published online in Wiley InterScience (www.interscience.wiley.com).

Abstract: The performances of the B3LYP density functional in the computation of harmonic and anharmonic frequencies were tested using 14 standard basis sets of double and triple zeta quality for a set of semirigid molecules containing from 4 to 12 atoms. The quality of the results is assessed by comparison with the most reliable computations available in the literature. The study reveals that the relatively cheap 6-31+G(d,p) basis set performs a very good job for harmonic frequency calculations and that B3LYP anharmonicities are in close agreement with the reference values irrespective of the basis set used. On these grounds "hybrid force fields" are proposed to achieve the best compromise between computer time and quality of the results.

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Key words: vibrational frequencies; B3LYP density functional; hybrid force fields; basis sets; performances

Introduction

Thanks to the progresses in hardware and software, the *a priori* prediction of accurate low-lying vibrational levels of semirigid polyatomic molecules is becoming a viable task. It is now well established that the computation of quartic force fields at the CCSD(T) (Coupled Clusters with Single, Double, and perturbative inclusion of Triple excitations) level with basis sets of at least spdf quality followed by an effective second order perturbative treatment^{1–3} can reach an accuracy of the order of 10 cm^{−1} for fundamental transitions (see ref. 4, and references therein). Although the perturbative vibrational treatment remains highly cost effective for quite large systems, the unfavorable scaling of the CCSD(T) model with the number of active electrons limits the determination of quartic force fields to molecules containing at most five to six atoms.

Recently, several authors have reported anharmonic force fields for small^{5–7} and medium-size^{8–12} semirigid molecules computed by methods rooted in the density functional theory (DFT).¹³ Among the functional tested (LDA,^{14,15} BLYP,^{16,17} BP86,^{16,18} B3LYP,^{19,20} B97-1²¹), the B3LYP and B97-1 models provide quite impressive results (absolute errors close to 10 cm^{−1}) for

several heteroaromatic systems. Moreover, DFT anharmonic corrections to CCSD(T) harmonic force fields further improve the agreement with experimental data.¹⁰ In particular, Boese et al.²² claimed that "basis set of triple-zeta quality are preferable over basis sets of double-zeta quality when doing calculations employing DFT," and that the B97-1 functional outperforms the B3LYP approach when using the TZ2P and cc-pVTZ basis sets.²² However, the anharmonic force fields of pyrrole, furan, and the whole azabenzene series obtained by the B3LYP density functional coupled to a basis set of double-zeta quality^{11,12} are of comparable accuracy to those obtained at the B97-1/TZ2P^{9,10} level.

On these grounds, we thought it interesting to test the performances of the widely used B3LYP functional coupled to standard basis sets of double- and triple-zeta quality for the computation of harmonic frequencies and anharmonic corrections issuing from a second order perturbative treatment.¹ The quality of the results is assessed by comparison with very reliable CCSD(T)^{4,23–27} computations available in the literature for H₂CO (Formaldehyde), H₂CS (Thioformaldehyde), H₂CN (methylenimine), C₂H₄ (Ethyl-

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Table 1. Basis Sets Used in This Study Together with cc-pVDZ and cc-pVTZ.

Acronym	dzp	dzpd	dzpdT	dzpp	dzppd	dzppdT
Description	6-31G(d)	6-31G(d) + diff on X	6-31+G(d)	6-31G(d,p)	6-31G(d,p) + diff on X	6-31+G(d,p)
Acronym	tzp	tzpd	tzpdT	Tzpp	tzppd	tzppdT
Description	6-311G(d)	6-311G(d) + diff on X	6-311+G(d)	6-311G(d,p)	6-311G(d,p) + diff on X	6-311+G(d,p)

+ diff on X: sp diffuse functions on each heteroatom if any.

ene), s-tetrazine, and benzene. Although the set of molecules is quite limited, the double requirement of availability of refined CCSD(T) computations and validity of a second-order perturbative vibrational treatment restricts the number of available systems quite significantly. At the same time we refrain from a direct comparison with experimental results because separation between harmonic and anharmonic contributions is often difficult. Even with these limitations in mind, we think that the present study can provide interesting insights about the reliability of anharmonic force fields obtained at the DFT level.

Computational Details

All computations have been performed with the G03 system of programs²⁸ using the B3LYP functional and the 14 standard basis sets summarized in Table 1.

Details about the implementation of anharmonic computations are given elsewhere.¹ Here, we only recall that starting from an optimized geometry, it is possible to build by effective numerical differentiation²⁹ third and semidiagonal fourth derivatives for any computational model for which analytical second derivatives are available, and next to evaluate vibrational frequencies using second-order perturbation theory (hereafter PT2). Note that, as explained elsewhere,¹ at least in the absence of low-frequency modes, the best compromise between different error sources is obtained using a step size of 0.010 Å in the numerical differentiation of harmonic frequencies, tight geometry optimizations, and fine grids (at least 99 radial and 590 angular points) in both self-consistent field (SCF) and coupled perturbed Kohn–Sham (CPKS) computations. It is well known that PT2 computations are plagued by Fermi resonances; however, our implementation automatically neglects nearly singular contributions (deperturbed computations), thus effectively removing interactions in the second-order treatment, which are more properly treated in first order. This is accomplished by direct diagonalization of the corresponding part of the Hamiltonian matrix. The selection criteria, namely the zero-order energy difference between two resonant states (Δ_1) and the guess of the difference between explicitly including a Fermi resonance and absorbing it into the anharmonicity constant (Δ_2 , as described in refs. 1 and 4) are manually set up in the present study in order to fit the *modus operandi* of the calculations taken as references.

Finally, hybrid H/L or M/L results are obtained using high level (H) or medium level (M) second derivatives and low level (L) third and fourth derivatives in the equations giving the x matrix ele-

ments, which in turn, provide anharmonic corrections^{1,2,7} to high-level harmonic frequencies.

Results and Discussion

For each basis set of Table 1, the harmonic frequencies of H₂CO, H₂CS, CH₂NH, and C₂H₄ computed at the B3LYP level of theory are compared to their CCSD(T)/cc-pVTZ counterparts^{4,23–25} and gathered in terms of average absolute error and maximum error. The results reported in Figure 1 show average absolute errors ranging between 12 and 24 cm⁻¹. Quite surprisingly, a better agreement with the reference calculations is obtained when using double zeta basis sets followed by triple zeta and correlation-consistent families. Addition of polarization functions on hydrogen atoms improves the results by about 10% for double zeta basis sets, but worsens somewhat the performances of triple zeta basis sets. It has been observed that for DFT methods addition of diffuse functions to polarized split valence basis sets leads to remarkable improvements of structural, energetic, and spectroscopic parameters.^{30,31} Our results show that this is also the case for harmonic frequencies since the inclusion of diffuse functions on heteroatoms, or slightly better, on all nonhydrogen atoms reduces the maximum error by at least 20 cm⁻¹. Among the harmonic frequencies involving the largest discrepancies, one can observe (see Table 2) that the C=X stretching modes (X: first row heteroatom) are overestimated by 30 to 70 cm⁻¹. Although addition of diffuse functions greatly enhances the results, the error remains significant

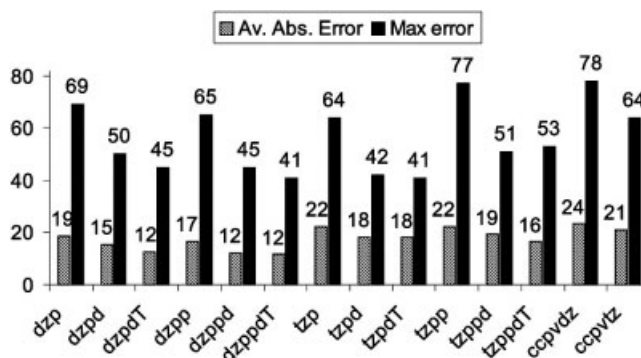


Figure 1. Average absolute error and maximum error w.r.t. CCSD(T)/cc-pVTZ results for B3LYP harmonic frequencies (cm⁻¹) of the small size systems H₂CO, H₂CS, H₂CNH, and C₂H₄.

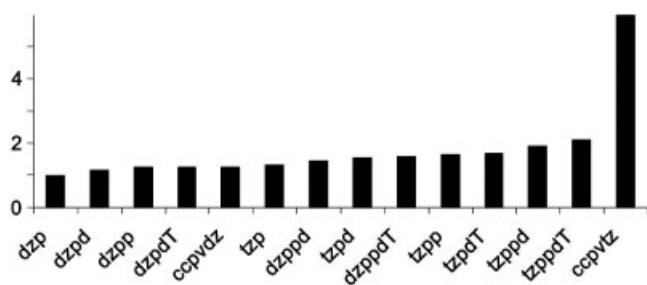
Table 2. Reference Harmonic Values (ω_{ref}) and Errors by Different Basis Sets at the B3LYP Level for the Most Problematic Harmonic Frequencies in the Series of Molecules Considered in the Present Study.

ω_{ref}	dzp	dzpd	dzpdT	dzpp	dzppd	dzppdT	tzp	tzpd	tzpdT	tzpp	tzppd	tzppdT	ccpvdz	ccpvtz
Stretching C=O and C=N														
1781 ^a	69	47	42	65	43	38	54	42	40	46	35	34	52	43
1675 ^a	61	50	45	58	45	41	46	39	38	39	34	32	43	38
Stretching CH (H ₂ CO)														
2995 ^a	-28	10	-5	-40	-3	-16	-64	-37	-2	-77	-51	-15	-78	-64
2929 ^a	-12	11	2	-31	-6	-15	-49	-33	-35	-60	-44	-45	-64	-52
Stretching CH (CH ₂ NH)														
3152 ^a	-8	11	2	-20	-2	-9	-41	-28	-30	-52	-38	-40	-47	-49
3052 ^a	-11	0	-9	-24	-12	-20	-45	-35	-38	-50	-40	-42	-49	-42
Stretching CH s-tetrazine														
3226 ^b	6	17	12	-7	4	1	-19	-12	-15	-27	-23	-24	-25	-29
3225 ^b	5	17	12	-7	4	1	-20	-12	-15	-27	-23	-24	-26	-30
Stretching CH benzene														
3210 ^b	1	1	-2	-2	-2	-3	-19	-19	-20	-20	-20	-19	-9	-18
3200 ^b	0	0	-2	-3	-3	-3	-21	-21	-21	-20	-20	-19	-10	-18
3183 ^b	1	1	-1	-2	-2	-1	-20	-20	-20	-19	-19	-18	-9	-16
3173 ^b	2	2	0	-1	-1	-1	-20	-20	-20	-19	-19	-17	-10	-16
Kekulé and aka-kekulé modes														
1326 ^b	30	30	29	29	29	27	12	12	13	9	9	10	31	9
927 ^b	62	72	67	61	71	67	36	41	41	35	40	40	66	38

^aCCSD(T)/cc-pVTZ.^bCCSD(T)/ANO-4321.

and seems an intrinsic shortcoming of the B3LYP functional, which should persist in the treatment of larger molecular systems. Interestingly, the =CH stretching modes, quite poorly represented by the Pople triple zeta and correlation-consistent families, are much better described by a double zeta basis set and come into close agreement with the reference values when using the 6-31+G(d) basis set.

Another important issue from a practical point of view is the computer time required by a specific basis set. Figure 2 shows that for small molecules the cc-pVTZ set is between three and five times slower than the other basis sets. Although part of this effect

**Figure 2.** Relative computer times for the calculation of PT2 frequencies of H₂CNH at the B3LYP level by different basis sets.

is related to the G03 implementation, which does not treat in a very effective way generally contracted basis sets, the comparable performances of different triple-zeta basis sets in DFT computations (at variance with the significantly improved accuracy of the correlation consistent basis sets in post-Hartree-Fock computations) do not justify, in our opinion, the systematic use of the cc-pVTZ set. Although for larger molecules the spread in computer times between the other basis sets would be significantly larger, we do not think that this would be sufficient to reverse a choice based on the relative accuracy.

Concerning the larger molecules considered here, that is, benzene and s-tetrazine, the CCSD(T)/ANO-4321 harmonic results were taken as refs. 26 and 27, because in the case of benzene³² they are in better agreement with experimentally derived harmonic frequencies than results obtained with the cc-pVTZ' basis set (d functions on hydrogen removed). Figure 3 shows that the average absolute error for these systems is nearly halved with respect to that obtained for small size systems, and that the discrepancies between the different basis sets are correspondingly smoothed. As mentioned in the caption of Figure 3, the results for "Kekulé modes" are removed from the statistical analysis. Because these vibrations correspond to stretchings towards one of the two limiting localized structures, the errors provided by the B3LYP functional are of the same order as those observed for C=X stretchings

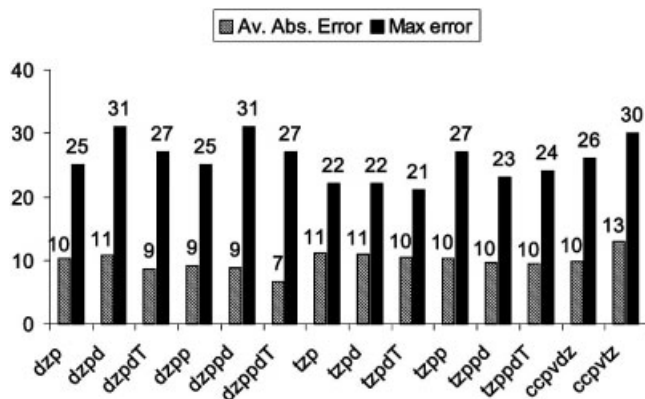


Figure 3. Average absolute error and maximum error w.r.t. CCSD(T)/ANO-4321 results for B3LYP harmonic frequencies (cm^{-1}) of the middle size system s-tetrazine and benzene. The Kekulé modes have been removed from the analysis (see text).

in the case of small size systems. Here, triple zeta basis sets are significantly more accurate, reducing the error by a factor of 2 and 3 for s-tetrazine and benzene, respectively. Nevertheless, these basis sets systematically underestimate the frequency of $=\text{CH}$ stretchings by about $20\text{--}30\text{ cm}^{-1}$, whereas the error is in most cases significantly lower than 10 cm^{-1} when using double zeta basis sets.

Although the origin of the two types of error is different (limitations of the functional for CH stretchings, and limitations of double-zeta basis sets for the other modes) from a pragmatic point of view (and pending the development of improved functionals), B3LYP/6-31+G(d,p) appears the most effective computational model.

Figure 4 compares B3LYP and CCSD(T) anharmonic corrections to CCSD(T) harmonic frequencies of H_2CO , H_2CS , H_2CNH , and C_2H_4 calculated by the vibrational PT2 approach. The same resonances considered in the original CCSD(T) studies have been selected and treated by a variational approach: (1) for H_2CO a pure perturbative approach has been used. (2) The significant Darling–Dennison resonance between the out of plane and the SCH asym-

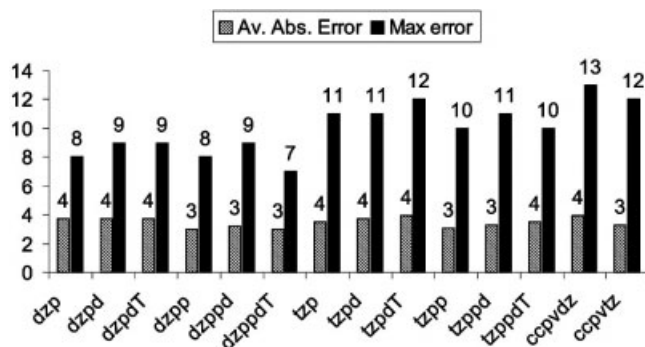


Figure 4. Average absolute error and maximum error w.r.t. CCSD(T)/cc-pVTZ results for B3LYP anharmonicities (cm^{-1}) of the small size systems H_2CO , H_2CS , H_2CNH , and C_2H_4 .

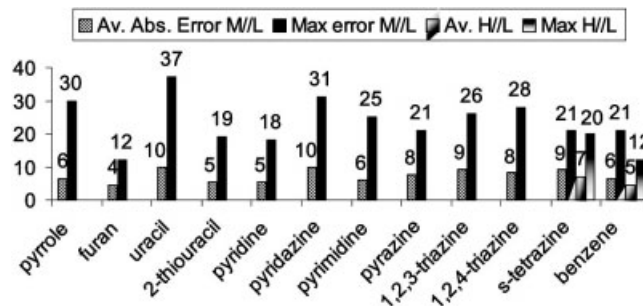


Figure 5. Average absolute error and maximum error (cm^{-1}) w.r.t. experimental results of the fundamental transitions calculated by different hybrid force fields for heteroaromatic systems. The harmonic/anharmonic hybrid force fields are: H:CCSD(T)/ANO-4321; M: B3LYP/dzppdt; L: B3LYP/dzp. Kekulé and $\text{C}=\text{O}$ modes (when present) have been removed from the analysis (see text).

metric bending has been considered for H_2CS . (3) CH_2NH is a 9×9 resonance matrix problem involving a Fermi type 1 resonance for two states whose deperturbed values differ by less than 1 cm^{-1} . Unfortunately, our results provide an inversion in the energetic order with a discrepancy approaching 10 cm^{-1} : as a consequence, this extreme case is simply removed from the analysis. (4) For ethylene, the very strong Fermi type 2 resonance ($\nu_{\text{CH asym. stretch.}}/\nu_{\text{CC stretch.}} + \nu_{\text{asym. HCH bend.}}/2\nu_{\text{sym. HCH wag.}}$) as well as the milder type 1 resonance ($\nu_{\text{CC stretch.}}/2\nu_{\text{sym. HCH wag.}}$) have been taken into account. The statistical analysis speaks for itself: it shows that the B3LYP functional is able to reproduce CCSD(T) anharmonicities with an error lower than 4 cm^{-1} and that, as observed in previous studies,^{11,33} basis set extension above the 6-31G(d) level leads to negligible variations of computed frequencies.

For even larger molecules, both harmonic and anharmonic contributions must be obtained at the DFT level (M/L approach). Although the reliability is, of course, reduced, a number of investigations is showing that for semirigid molecules hybrid functionals coupled to medium-size basis sets could be sufficient for most interpretative studies.^{11,12,33}

For purposes of illustration, Figure 5 summarizes the errors between frequencies computed by the M/L approach and their experimental counterparts. For benzene and s-tetrazine, anharmonic frequencies based on CCSD(T)/ANO-4321 harmonic reference (H/L approach) are also reported. The average errors range between 4.3 and 9.9 cm^{-1} , showing that the (M/L) approach paves the route toward the semiquantitative study of larger semirigid molecules. Although the CCSD(T) method is definitely more accurate, the cases of benzene and s-tetrazine confirm that this level of theory is required at most for the harmonic force field, because DFT anharmonic corrections are largely sufficient also for quantitative studies of IR spectra.

Conclusion

The ability of the B3LYP functional to approach CCSD(T)/spdf computations of harmonic and anharmonic frequencies was tested using 14 standard basis sets of double and triple zeta quality for a

set of semirigid molecules containing from 4 to 12 atoms. In this framework, our study shows that the relatively cheap 6-31+G(d,p) basis set performs a very good job, providing an average absolute error below 12 cm^{-1} for the harmonic frequencies of small size molecules and below 7 cm^{-1} for representative aromatic compounds. Furthermore, it has been observed that B3LYP anharmonicities match their CCSD(T) counterparts with an average error of 3 cm^{-1} irrespective of the basis set used. As a matter of fact, the 6-31+G(d,p) basis set represents an effective choice to investigate vibrational properties of semirigid molecules by the B3LYP functional. Concerning “hybrid force fields” in which harmonic and anharmonic parts are computed at different levels of theory, we propose the CCSD(T)/spdf//B3LYP/6-31G(d) and B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) approaches for small size molecules and larger systems, respectively, to achieve the best compromise between computer time and quality of results.

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