Impact of Local and Density Fitting Approximations on Harmonic Vibrational Frequencies

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Harmonic vibrational frequencies are computed using second-order Møller−Plesset perturbation theory (MP2) with and without local (LMP2) and density fitting (DF) approximations. Results for a test set of 17 small and medium size molecules (366 normal modes) are presented, and frequency scaling factors for LMP2 in combination with two different basis sets are determined. Comparison of the MP2 and LMP2 frequencies with experimental data reveals that the introduction of local approximations leads to a slightly better agreement with experiment. This is attributed to the reduction of basis set superposition errors in local calculations. Introduction of DF approximations within the LMP2 formalism leads to negligible deviations but significantly reduces the computational cost. These facts extend the applicability of the method to larger systems with large basis sets. As an example, the method is applied to a full DF-LMP2/cc-pVTZ frequency calculation for testosterone (49 atoms).

1. Introduction

Calculations of harmonic vibrational frequencies have been used in molecular spectroscopy for more than 50 years.[1] Despite the restrictions imposed by the harmonic approximation, the calculation of harmonic frequencies and normal modes is still the initial step in more accurate simulations of vibrational spectra.[2−4] Generally, the calculated values of harmonic vibrational frequencies depend sensitively on the shape of the potential energy surface (PES) near the equilibrium structure, and therefore, their comparison to experimental data represents a sensitive test for the quality of the particular electronic structure method. Results of good accuracy can often be obtained with density functional theory (DFT), but high-level electron correlation methods are necessary to obtain frequencies which agree within a few wavenumbers with experimental values. Unfortunately, due to the steep scaling of the computational resources with the molecular and basis set sizes, accurate calculations for large molecules are exceedingly expensive and often impossible.

The steep scaling with molecular size can be reduced using local approximations as proposed by Pulay[5−9] and further developed in our[10−19] group. Linear scaling of the CPU time with molecular size has been achieved for all standard closed-shell single reference methods,[13−17] and this makes it now possible to apply high-level methods to much larger molecules than with conventional methods. An important question is how much the local approximations affect the results. Previous studies showed that local Møller−Plesset perturbation theory (LMP2) optimized geometries are essentially identical to conventional MP2 structures, with a tendency for LMP2 to yield slightly longer bond lengths.[20] The deviations in geometrical parameters were almost basis set independent. LMP2 and MP2 harmonic vibrational frequencies were found to be mostly in close agreement as well. An exception is acetylene, where the values predicted by LMP2 are in better agreement with experiment.[21] This effect can be attributed to the reduction of the intramolecular basis set superposition error (BSSE) in local calculations.[22,23] In the present work, we will give further evidence that the reduction of the BSSE improves the computed frequencies for certain modes.

The second problem, namely, the steep scaling of the computational cost with basis set size per atom, can be reduced by density fitting (DF) approximations. Boys and Shavitt were probably the first who used this technique to compute intractable three-center Slater integrals in calculations on the H_3 molecule.[24] Further early use was mostly in DFT calculations. Fitting of the entire density in an auxiliary basis set[25−28] leads to a reduction from $\mathcal{O}((N_{AO}/N_{atom})^4)$ to $\mathcal{O}((N_{AO}/N_{atom})^3)$ scaling and much cheaper evaluation of the Coulombic operator. Feyereisen et al. generalized the DF approach to MP2.[29,30] Similar approximations were later implemented by several authors for various methods.[31−40] Particularly useful and important for these developments was the optimization of accurate fitting basis sets for DFT, HF (Hartree−Fock), and MP2.[41−44] Recent work in our group has demonstrated that the DF method can be combined with local approximations,[38,40,45] leading to very efficient low-order scaling methods. The availability of analytical DF-LMP2 energy gradients[45] makes it now possible to test the effect of local DF approximations on equilibrium structures and vibrational frequencies.

There are various sources of errors in harmonic frequency calculations which typically cause overestimation in comparison to the experimental frequencies. Most important are missing correlation contributions caused by truncation of the one-electron and *N*-electron basis sets. Another source of error is the overall neglect of anharmonicity. To obtain a better agreement between calculated and observed frequencies, scaling procedures are often used. The simplest is to multiply the frequencies using one or two scaling factors.[46−48] These factors are derived by least-squares fitting to experimental data and are used whenever there is a need for a quick preliminary assignment of vibrational spectra. Such corrections are made possible by the fact that the overestimation of the frequencies is rather uniform, at least in some parts of the spectra.

In the present work, we investigate the effect of local and DF approximations on harmonic vibrational frequencies. The

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calculations are restricted to MP2 theory, but it can be expected that similar results would be obtained for higher-order methods if the same approximations are made. In section 3, a brief introduction to the methods and approximations will be given. Results for a set of benchmark molecules will be presented in section 4.

2. Theoretical Methods and Computational Details

The methods applied in this work have been described in detail in previous papers[10,13,28,40,45] and will therefore be only briefly reviewed here. All calculations were done with a development version of the MOLPRO[49] package of ab initio programs.

2.1. Local Correlation Methods. In local correlation methods as originally proposed by Pulay[5] and used in the present work, the occupied orbitals (LMOs) are localized using standard procedures as proposed by Boys[50,51] or Pipek and Mezey.[52] The latter method has some advantages, in particular for computing analytical energy gradients[20,45,53] and is therefore employed here. The virtual space is spanned by projected atomic orbitals (PAOs), which are obtained from the basis functions (AOs) by projecting out the occupied orbital space.[5] Since the LMOs and PAOs are local, it is possible to restrict the excitations to pair-specific subspaces of PAOs (domains) and to neglect correlations of distant orbital pairs. In higher correlation methods, such as LCCSD(T), a hierarchy of approximations dependent on the importance of electron pairs can be introduced, but in the current work, which is restricted to LMP2, there is only one class of pairs. The introduction of domains and the neglect of distant pairs lead to linear scaling in LMP2.[13]

The domains were determined using the procedure of Boughton and Pulay[22] using a completeness criterion of 0.98. Distant pairs were defined on the basis of the minium distance between the atoms in the two different LMOs forming the pair. For more details, we refer to previous work.[10,13] Particular care must be taken in calculations of highly symmetric aromatic systems such as benzene, in which localization of the π-electrons is not unique, that is, a parameter in localization space is redundant. This can lead to artifical results if the molecule is distorted in geometry optimizations or frequency calculations. This problem can easily be avoided, however, by merging the orbital domains which correspond to the redundant set of LMOs. The energy and gradients are then invariant with respect to unitary orbital transformations within the redundant set. In the case of benzene, this leads to full π-domains, that is, the domains for all three π-orbitals comprise all PAOs arising from carbon basis functions. Such merging can be done automatically and is recommended whenever two orbital domains overlap by two or more atoms.

When computing the Hessian by finite differences of analytical gradients, as done in the present work, it is important to make sure that the domains do not change for the different geometry displacements, that is, that the PES is perfectly smooth. This can be achieved by freezing the domains. In complete analogy to DFT, where a similar problem concerns the grid on which the functional is evaluated, we freeze the domains in the geometry optimization once a certain accuracy (step length smaller than 0.05 a_0) has been reached. Similarly, in a Hessian calculation, the domains are determined at the equilibrium structure and then frozen. If local DF procedures are used (see below), this also applies to the fitting domains used in the HF, LMP2, and coupled-perturbed HF (CPHF).

2.2. Density Fitting. Despite linear scaling, the bottleneck of the LMP2 method is the evaluation and transformation of the two-electron repulsion integrals. Since this step scales as $\mathcal{O}((N_{\mathrm{AO}}/N_{\mathrm{atom}})^4)$, this problem is particularly severe if large basis sets are used. The evaluation and transformation of the integrals can be much sped up using DF approximations, as first used in the context of MP2 by Vahtras, Almlöf, and Feyereisen.[29,30] In conventional MP2 with canonical orbitals, this does not reduce the $\mathcal{O}(N^5)$ scaling with molecular size but lowers the pre-factor and the scaling with basis set size per atom from quartic to cubic. In the LMP2 case, the use of domains and the neglect of distant pairs immediately lead to $\mathcal{O}(N^2)$ scaling with molecular size. Furthermore, the local character of the excitations allows for the use of domains in the fitting basis, which leads to linear ($\mathcal{O}(N)$) scaling.[38] Similar approximations can be made in the preceding DF-HF calculations[40] and in the calculation of analytical energy gradients.[45] It has been shown in our previous work that these approximations lead to dramatic savings but hardly affect computed energy differences and optimized structures. In the present paper, we will investigate whether the same applies to computed vibrational frequencies. It will in fact be demonstrated that the errors caused by neglecting distant pairs and using (local) DF approximations in the HF and LMP2 are negligible.

In all density fitting calculations reported in this paper (both for the cc-pVDZ and cc-pVTZ orbital basis sets), we used the cc-pVTZ/JKFIT and cc-pVTZ/MP2FIT fitting basis sets of Weigend and Hättig et al.[42−44] in the DF-HF and DF-LMP2 calculations, respectively.

2.3. Parallelization. In the current work, the Hessian has been computed using finite differences of analytical gradients, since the implementation of analytical second derivatives for DF-LMP2 would be very complicated. Also, the savings would probably not be very significant, since for all 3N degrees of freedom the Fock matrix derivatives would have to be computed and stored (N is the number of atoms). Furthermore, 3N sets of CPHF and coupled-perturbed localization (CPL) equations would have to be solved. These steps would probably dominate as much as the 6N HF and CPHF calculations in finite difference calculations, and this cannot be much improved by local approximations.

Another advantage of using finite differences is the fact that many basically independent calculations are needed. This makes it easily possible to implement an “embarrassingly parallel” algorithm, in which each displacement can be computed on a different processor.[54] In our implementation within MOLPRO,[49] a dynamical task scheduling algorithm is used and no synchronization is necessary before the Hessian is completed. The energies and gradients are stored in global arrays,[55] which can be accessed independently (one sided) from each processor. Whenever processor 0 gets a new task, the results of all finished tasks are read from the global array and written to a file, which makes restarts possible. Data integrity in the GA is ensured using fences and locks, which prevent access to the GA for the other processors while a processor reads or writes data. In principle, if a sufficient number of processors is available on a compute cluster, a speedup of 6N is possible. This method has been used in the present work to compute the harmonic vibrational frequencies for a molecule with 49 atoms at the DF-LMP2/cc-pVTZ level.

2.4. Frequency Scaling Procedure. Due to the neglect of anharmonicity, a direct comparison of computed frequencies and experimental frequencies leads to large errors (in particular for the high-frequency CH stretching modes) and is therefore meaningless. However, as pointed out in the Introduction, the anharmonicity effects are to a good approximation proportional

TABLE 1: Scaling Factors and Error Analysis for the Test Set of Molecules

	cc-pVDZ			cc-pVTZ		
	MP2	LMP2	DF-LMP2	MP2	LMP2	DF-LMP2
λ^a	0.954	0.955	0.955	0.955	0.956	0.956
SSD/cm^{-2}	446749	408093	408497	338198	307787	308415
rms/cm^{-1}	35.7	34.1	34.1	31.0	29.6	29.6
MAD/cm^{-1}	109.6	112.0	111.8	109.6	110.6	110.7
$\lambda_1{}^b$	0.976	0.976	0.976	0.974	0.974	0.974
$\lambda_2{}^b$	0.946	0.947	0.947	0.947	0.949	0.949
SSD/cm^{-2}	216888	197228	197949	160035	157133	157474
rms/cm^{-1}	24.9	23.7	23.7	21.4	21.2	21.2
MAD/cm^{-1}	114.5	116.8	117.8	116.3	117.3	117.4
$\lambda_1{}^c$	0.990	0.988	0.988	0.981	0.977	0.977
$\lambda_2{}^c$	0.973	0.974	0.973	0.972	0.973	0.973
$\lambda_3{}^c$	0.946	0.947	0.947	0.947	0.949	0.949
SSD/cm^{-2}	201858	185995	186330	156081	155946	156248
rms/cm^{-1}	24.0	23.0	23.0	21.1	21.1	21.1
MAD/cm^{-1}	110.1	113.9	113.3	113.6	115.9	116.0

[a] Complete spectra. [b] Spectra are divided in two regions ($\omega_1 < 1800$ cm$^{-1} \leq \omega_2$.) [c] Spectra are divided in three regions ($\omega_1 < 1000$ cm$^{-1} \leq \omega_2 < 1800$ cm$^{-1} \leq \omega_3$.)

to the frequency, and therefore, the agreement between theory and experiment can be much improved by scaling procedures. Scaling was carried out using a least-squares procedure by minimizing the residuals[48]

$$\Delta = \sum_i (\lambda \nu_i^{\mathrm{calc}} - \nu_i^{\mathrm{obs}})^2 \tag{1}$$

where $\nu_i{}^{\mathrm{calc}}$ is the ith calculated harmonic frequency and $\nu_i{}^{\mathrm{obs}}$ is the corresponding experimental fundamental. λ is the scaling factor which is optimized to minimize Δ. Since the magnitude of the errors of harmonic vibrational frequencies often depends on the spectral region, we determined three different sets of scaling factors. First, we computed a single scaling factor for the complete spectra. Second, we divided the spectra into two regions ($\omega_1 < 1800$ cm$^{-1} \leq \omega_2$) and finally into three regions ($\omega_1 < 1000$ cm$^{-1} \leq \omega_2 < 1800$ cm$^{-1} \leq \omega_3$). In the latter, two cases different scaling factors for each region were used. In each case, the root-mean-square (rms) error, the maximum absolute error (MAD), and the total sum of squares of deviations (SSD) were determined in order to compare the scalability of the results for the different electronic structure methods (MP2, LMP2, and DF-LMP2) used in this work.

3. Results and Discussion

3.1. Benchmark Calculations. To evaluate and compare the accuracy of the computed harmonic vibrational frequencies for various methods, the following test set of 17 molecules was used: acetone (C_{2v}), azetidine (C_s), benzaldehyde (C_s), butatriene (D_{2h}), chloroethylene (C_s), ethylene (D_{2h}), fluorobenzene (C_{2v}), formaldehyde (C_{2v}), formic acid (C_s), furan (C_{2v}), furazane (C_{2v}), methanol (C_s), phenol (C_s), pyridine (C_{2v}), pyrrol (C_{2v}), tropone (C_{2v}), and water (C_{2v}). The total number of investigated normal modes was 366. Symmetry was used to reduce the computational effort in the canonical MP2 calculations, while all LMP2 calculations had to be performed in C_1 symmetry, since the LMOs are not symmetry adapted.

Harmonic vibrational frequencies were calculated at the MP2 and LMP2 levels with and without the DF in combination with the cc-pVDZ and cc-pVTZ basis sets.[56] All geometries were reoptimized for each basis set and method. The calculated harmonic frequencies were scaled as described in section 3.4. The comparison of calculated and experimental frequencies was performed in a careful fashion by checking the particular symmetry species and intensities in order to ensure correct assignments.

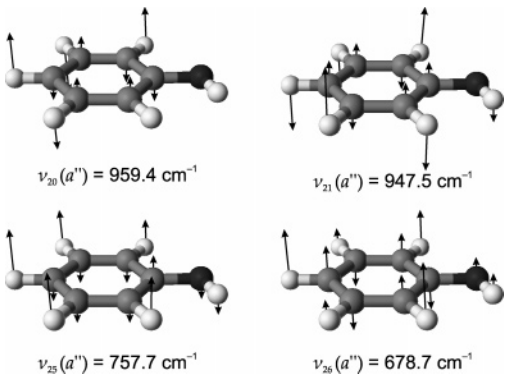

Figure 1. Normal modes of phenol calculated at the MP2/cc-pVTZ level.

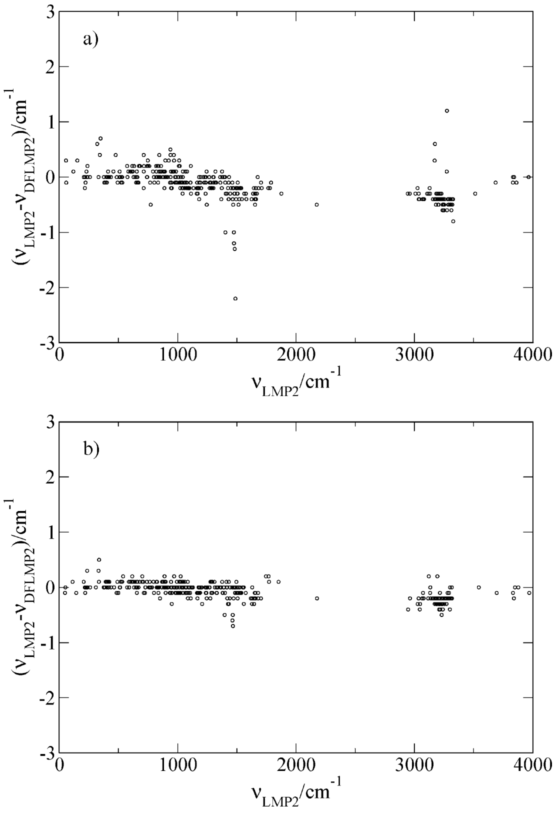

Figure 2. Differences between LMP2 and DF-LMP2 frequencies employing the (a) cc-pVDZ and (b) cc-pVTZ basis sets.

The scaling factors, along with the rms, SSD, and MAE values for all modes of the test set, are presented in Table 1. It is clear that a comparison of these errors for different methods depends on the assumption that the uniform scaling procedure is valid. Previous work has shown, however, that more accurate methods usually lead to smaller errors of the scaled frequencies;[48] similarly, basis set improvements usually reduce the errors. Therefore, we assume here that such comparisons are justified. More pragmatically, one could argue that the method is most useful in practice which leads to smallest errors after scaling, even though this does not necessarily mean that the same method would give also the smallest errors if anharmonic frequencies would be computed and compared directly to experimental data.

For both basis sets used, the scaled LMP2 frequencies are in slightly better agreement with the experimental values than the

TABLE 2: Experimental and Calculated (unscaled) Frequencies for Phenol (cm^{-1})

			cc-pVDZ			cc-pVTZ		
	sym	expt[57]	MP2	LMP2	DF-LMP2	MP2	LMP2	DF-LMP2
ν_1	a'	3655	3831.2	3832.5	3832.6	3840.6	3841.0	3841.2
ν_2	a'	3074	3249.9	3244.5	3244.9	3242.6	3234.5	3234.7
ν_3	a'	3061	3243.1	3238.0	3238.4	3235.8	3228.4	3228.6
ν_4	a'	3052	3229.2	3224.3	3224.7	3222.2	3215.6	3215.7
ν_5	a'	3046	3220.0	3215.8	3216.1	3212.8	3207.3	3207.5
ν_6	a'	3021	3199.5	3196.6	3197.0	3195.0	3189.5	3189.8
ν_7	a'	1609	1672.2	1669.3	1669.6	1660.8	1657.9	1658.1
ν_8	a'	1604	1656.5	1653.3	1653.7	1648.1	1645.6	1645.8
ν_9	a'	1501	1533.7	1532.2	1532.4	1531.9	1532.0	1532.1
ν_{10}	a'	1472	1499.3	1498.7	1498.9	1498.9	1499.6	1499.7
ν_{11}	a'	1361	1482.9	1482.2	1483.5	1469.6	1466.8	1467.5
ν_{12}	a'	1344	1353.5	1358.9	1358.9	1361.5	1367.8	1367.8
ν_{13}	a'	1261	1307.2	1302.9	1303.0	1296.4	1293.2	1293.1
ν_{14}	a'	1197	1213.4	1217.5	1217.5	1202.5	1204.7	1204.7
ν_{15}	a'	1176	1181.9	1182.8	1182.9	1188.8	1189.1	1189.2
ν_{16}	a'	1150	1167.0	1168.1	1168.3	1174.2	1174.6	1174.7
ν_{17}	a'	1070	1090.2	1091.2	1091.4	1093.4	1093.6	1093.7
ν_{18}	a'	1026	1045.0	1044.6	1044.8	1045.5	1045.3	1045.4
ν_{19}	a'	999	1008.8	1012.7	1012.4	1016.5	1019.9	1019.8
ν_{20}	a''	973	947.2	963.0	962.9	959.4	992.2	992.2
ν_{21}	a''	956	937.0	944.1	944.0	947.5	968.2	968.2
ν_{22}	a''	881	872.4	878.4	878.2	885.2	900.3	900.3
ν_{23}	a''	823	823.4	821.0	820.9	827.7	832.4	832.4
ν_{24}	a'	810	826.9	826.5	826.5	827.2	826.5	826.4
ν_{25}	a''	752	747.1	750.4	750.1	757.7	766.0	766.0
ν_{26}	a''	687	632.7	674.0	673.8	678.7	700.7	700.6
ν_{27}	a'	618	618.9	620.3	620.2	620.7	621.8	621.7
ν_{28}	a'	526	525.7	526.4	526.4	528.0	528.5	528.4
ν_{29}	a''	503	505.0	510.4	510.3	512.3	515.0	515.0
ν_{30}	a''	420	409.9	412.6	412.5	415.6	419.5	419.5
ν_{31}	a'	410	399.4	402.0	402.0	402.2	402.5	402.5
ν_{32}	a''	310	333.8	342.5	342.1	331.0	331.5	331.2
ν_{33}	a''	242	228.9	229.9	229.8	229.5	230.6	230.6

MP2 ones. The difference is more pronounced for the cc-pVDZ basis set than for the larger cc-pVTZ one, in particular for the SSD values. Possibly, this is due to the reduction of BSSE effects in the LMP2 method.[22,23] More evidence for this assumption will be given in the next section. As one would anticipate, overall, the errors are substantially smaller for the cc-pVTZ basis than for the cc-pVDZ basis.

Errors introduced by the use of the DF approximation are negligible. As can be seen in Figure 2, the maximum deviations between the LMP2 and DF-LMP2 frequencies are below 2 cm^{-1} for cc-pVDZ and below 1 cm^{-1} for cc-pVTZ. The average deviations amount to -0.14 ± 0.28 and -0.06 ± 0.15 cm^{-1} for cc-pVDZ and cc-pVTZ, respectively. Thus, the DF approximation can be used with confidence.

3.2. Case of Monosubstituted Benzenes. One striking fact arises in the case of all monosubstituted benzene molecules in the set (phenol, benzaldehyde, and fluorobenzene). For some frequencies that belong to out-of-plane normal modes, the differences between the MP2 and LMP2 results were quite significant and much larger than for all other modes. For these modes, the LMP2 results are in much better agreement with the experimental values than the MP2 ones.

As an example, we consider the results for phenol, which are presented in Table 2. In this case, accurate assignments of the experimental bands are available.[57] The calculated values in Table 2 are not scaled and should therefore be larger than the experimental ones by about 5%. However, at the MP2 level, this is not the case for the ν_{20}, ν_{21}, ν_{25}, and ν_{26} modes. As shown in Figure 1, these modes correspond to out-of-plane (a'') CH vibrations. The MP2 values are substantially too small, even at the cc-pVTZ level; the LMP2 values are larger and in better agreement with experiment (taking into account the anharmonicity correction). This effect, which is most pronounced for the ν_{26} mode, is attributed to intramolecular BSSEs, which are expected to be smaller in LMP2 than in MP2. The BSSE leads to an artifical lowering of the energy if the planar symmetry is disturbed and therefore results in frequencies that are too low. Similar findings apply to the other monosubstituted benzenes. It is mainly the reduction of the BSSE and the resulting better basis set convergence in LMP2 which leads to the significantly lower SSD values for the LMP2/cc-pVDZ method.

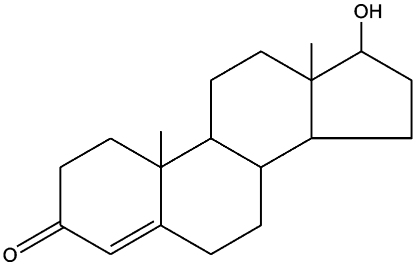

Figure 3. Testosterone.

TABLE 3: Effect of Neglecting Distant Pairs and of Applying Local Fitting Approximations in DF-LMP2 Calculations for Testosterone[a]

	$R_v = 15$	$R_v = 12$	$R_v = 6$	$R_v = 15^c$
number of pairs[a]	1633	1456	822	1633
rms[b]	0.0	0.0	3.9	5.6
MAD[b]	0.0	0.4	4.8	13.0

[a] The total number of pairs for $R_v = \infty$ is 1711. [b] Average and maximum deviations from the $R_v = 15$ calculation in cm^{-1}. [c] Using local fitting in DF-HF, DF-CPHF, and the DF-LMP2 gradient.[45]

3.3. DF-LMP2 Frequency Calculation for Testosterone. The neglect of distant pairs and the use of local fitting approximations can significantly reduce the computational effort for large molecules. These truncations come into effect only for rather large systems and do not affect the results presented in the previous sections. To investigate the impact of these approximations, we applied the DF-LMP2 method to testosterone, using the cc-pVTZ basis set. This molecule has 49 atoms (see Figure 3), leading to a total of 141 normal modes. The number of contracted basis functions is 1022, and all 116 valence electrons were correlated. The parallel implementation described in section 3.3 was used for these calculations, using 6−8 processors.

To study the effect of neglecting distant pairs, we performed three different calculations: one with $R_v = 15\ a_0$ (which is the default in MOLPRO), one with $R_v = 12\ a_0$, and one with $R_v = 6\ a_0$, where R_v is the distance criterion to omit distant pairs. Furthermore, a calculation ($R_v = 15\ a_0$) with local fitting employed in the DF-HF, DF-LMP2, and CPHF steps was performed. All computed frequencies are available as Supporting Information. Correlation energy contributions for pairs with $R > 15$ are in the μH range, and therefore, the calculation for $R_v = 15\ a_0$ should yield virtually identical results as a full calculation.

The rms and MAD values of the deviations from the default calculation ($R_v = 15$, no local fitting) are presented in Table 3. It is found that truncation the pair list at $R_v = 12\ a_0$ has virtually no effect. If all pairs for distances greater than 6 a_0 are neglected, then the maximum error remains below 5 cm^{-1}, even though more than half of the orbital pairs are neglected. Somewhat larger are errors caused by local fitting, as seen in the last column. As discussed in ref 40, this approximation has some effect on the optimized HF orbitals, which in turn affects the gradients and frequencies. The errors could be reduced by increasing the fitting domains, but due to the high cost of these calculations, it was not possible in this work to study this systematically.

It should finally be noted that the computational cost of the LMP2 gradient and frequency calculations is strongly dominated by the Fock matrix evaluations in the HF and CPHF steps. These parts are not affected by the number of correlated electron pairs, and therefore, the neglect of distant pairs saves only 14% of the CPU time in the present case. The local fitting has a somewhat larger effect and saves about 40% of the time, but again, the molecular size is not large enough to make the saving really impressive. With local fitting and the use of rather strict convergence and screening thresholds, the calculation for one displacement took about 8 h of CPU time on an opteron 2.4 GHz processor.

4. Conclusions

Harmonic vibrational frequencies have been computed for a set of 17 molecules using MP2, LMP2, and DF-LMP2 with double and triple-ζ basis sets. To account for anharmonicity effects, the frequencies were scaled with factors determined by least-squares fits to experimental data. The agreement of the scaled results with experiment was found to be better for LMP2 than for MP2, in particular for the smaller basis set. This was traced to be mainly due to some out-of plane vibrations in monosubstituted benzenes. It was found that the MP2 frequencies of such vibrations are substantially too low and rather strongly basis set dependent. The corresponding LMP2 frequencies are larger and thus in better agreement with experiment. Most likely, this is due to the reduction of BSSEs in the LMP2. The BSSE leads to a flattening of the out-of-plane bending potentials and thus to a lowering of the frequencies of such modes.

DF approximations used in the HF and LMP2 have only a negligible effect on the computed frequencies. Thus, such approximations, which strongly reduce the computational effort, in particular for large basis sets, can be trustfully used.

Finally, the DF-LMP2 method was used to compute the vibrational frequencies of testosterone using the cc-pVTZ basis set. It was found that the neglect of distant pairs in the LMP2 hardly affects the results, even if a rather small cutoff criterion of 6 a_0 is used. The neglect of distant pairs reduces the computational effort for the LMP2, but unfortunately, the total CPU time is strongly dominated by the Fock matrix evaluations in the HF and CPHF calculations, so that in the current case the overall time was not much reduced. Thus, further improvements in fast Fock matrix evaluation are most important in order to make the method applicable to even larger molecules.

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Supporting Information Available: Table showing LMP2/cc-pVTZ vibrational frequencies of testosterone. This material is available free of charge via the Internet at http://pubs.acs.org.

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