

Comparison of the Numerical Stability of Methods for Anharmonic Calculations of Vibrational Molecular Energies

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Abstract: On model examples, we compare the performance of the vibrational self-consistent field, variational, and four perturbational schemes used for computations of vibrational energies of semi-rigid molecules, with emphasis on the numerical stability. Although the accuracy of the energies is primarily dependent on the quality of the potential energy surface, approximate approaches to the anharmonic vibrational problem often do not converge to the same results due to the approximations involved. For furan, the sensitivity to variations of the anharmonic potential was systematically investigated by adding random noise to the cubic and quartic constants. The self-consistent field methods proved to be the most resistant to the potential variations. The second order perturbational techniques are sensitive to random degeneracies and provided the least stable results. However, their stability could be significantly improved by a simple generalization of the perturbational formula. The variational configuration interaction is practically limited by the size of the matrix that can be diagonalized for larger molecules; however, relatively fewer states need to be involved than for smaller ones, in favor of the computing.

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Key words: anharmonic vibrational energies; vibrational self-consistent field; second-order perturbation; numerical stability; vibrational spectroscopy

Introduction

Computations of the vibrational molecular energies beyond the harmonic limit appear necessary for many important systems including biologically relevant molecules,^{1,2} solute-solvent complexes,³ and industrially important compounds.⁴ Particularly, the involvement of the anharmonic part is imperative for studies of spectral temperature dependencies and molecular stability.⁵ For semi-rigid molecules many methods have been developed,⁶ based primarily on perturbation calculus^{7–9} or vibrational self-consistent field (VSCF).^{10–12} Except of small systems, nuclear potentials (potential energy surfaces) used in these computations as input parameters are known only approximately as they usually depend on the ab initio approximation of the electronic problem. The errors in the potential frequently transfer differently into the errors of the vibrational energies if also approximate vibrational schemes are used. Therefore, in this study, we try to compare various approaches and concentrate on the stability of the vibrational energies obtained by various methods. It turns out that small and big molecules behave differently. The latter are notoriously affected by the random degeneracies of the

vibrational energy levels, which inhibits application of the perturbation calculus. For such cases we propose a generalization of the second-order formula as outlined below. Our implementations of the VSCF, variational (vibrational configuration interaction, VCI), and second-order perturbation (PT) methods in one program package enabled us to make a consistent comparison.

In the next section working equations for the VCI, VSCF, and PT approaches are outlined. Then their performances are tested and discussed for two and three-dimensional analytical potentials used for calibration of the anharmonic calculus previously.¹² These tests are followed by applications to real molecules, furan, formaldehyde, and α -pinene. For furan, systematic noise was added in various ways to the ab initio potential so that the numerical stability of the vibrational algorithms could be analyzed. Finally, dependence of VCI energies on the basis set size is analyzed.

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Methods

For semi-rigid molecules the nuclear potential V can be expanded in a Taylor series around the equilibrium geometry. For example, in the vibrational normal-mode coordinates (Q_i) and the atomic units,

$$V(Q_1, \dots, Q_M) = \sum_{i=1}^M \frac{\omega_i^2}{2} Q_i^2 + \frac{1}{6} \sum_{i=1}^M \sum_{j=1}^M \sum_{k=1}^M c_{ijk} Q_i Q_j Q_k + \frac{1}{24} \sum_{i=1}^M \sum_{j=1}^M \sum_{k=1}^M \sum_{l=1}^M d_{ijkl} Q_i Q_j Q_k Q_l + \dots, \quad (1)$$

where M is the number of the modes.¹³ For simplicity we neglect other anharmonic and rotation-vibration interaction terms stemming from the kinetic energy operator. To approach the solution of the Schrödinger equation,

$$\left(-\frac{1}{2} \sum_{i=1 \dots M} \frac{\partial^2}{\partial Q_i^2} + V \right) \Psi = E \Psi,$$

we implemented the VSCF, PT, and VCI approximations as follows.

Vibrational Self-Consistent Field

Following the usual procedure^{1,10} the wavefunction was expressed as a product of one-dimensional parts,

$$\Psi(Q_1, \dots, Q_M) \approx \prod_{i=1}^M \psi_i(Q_i), \quad (2)$$

and the potential as a sum of effective potentials,

$$V(Q_1, \dots, Q_M) \rightarrow \sum_{i=1}^M v_i(Q_i), \quad (3)$$

with

$$v_i(Q_i) = \left\langle \prod_{j=1, j \neq i}^M \psi_j(Q_j) \left| V(Q_1, \dots, Q_M) \right| \prod_{k=1, k \neq i}^M \psi_k(Q_k) \right\rangle.$$

Note, that a general VSCF approach is not dependent on the Taylor expansion (1) of the potential; the Taylor form, however, was used here for the sake of comparison with the other methods. Under the assumption of the separability the Schrödinger equation divides into a sum of effective 1D equation,

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + v_i(Q_i) \right) \psi_i(Q_i) = e_i \psi_i(Q_i), \quad (4)$$

where $i = 1 \dots M$, and can be easily solved in a harmonic oscillator basis. Because of the dependence of the effective potentials

on the resultant wavefunction, the solving has to be repeated “self-consistently” until the energy values (e_i) stabilize. Also, a self-interaction correction term has to be subtracted from the energy sum, in order to obtain molecular energy of a physical relevance,

$$E = \sum_{i=1 \dots M} e_i - (M-1) \langle \Psi | V | \Psi \rangle. \quad (5)$$

As the excited states can be treated only approximately within the VSCF scheme two alternate approaches were implemented. First, only the lowest-energy (ground) states (ψ_i) were used for determining the potential in eq. (3) (which is referred to as **gVSCF**), while in the second approximation (“**eVSCF**”) excited states were included in the averaging. Thus, in the **gVSCF** method, resultant set of excited states is orthogonal, but not self-consistent. On the contrary, in **eVSCF** the self-consistency holds at the expense of the orthogonality. The **gVSCF** computation requires only one set of the self-consistent iterations for the ground state, while this has to be repeated for each excited state in **eVSCF**.

Second-Order Perturbation

The cubic and quartic terms in eq. (1) are often small (in terms of their influence on the energies of interest) and, with respect to the harmonic solutions, can be treated as a perturbation potential directly. Also for the VSCF wave functions, the perturbation can be defined, in analogy to the electronic MP2 theory,¹⁴ as a difference between the exact and the VSCF potential,

$$W = V - \sum_{i=1 \dots M} v_i. \quad (6)$$

Note, that for VSCF formula 5 is correct to the first order. A second-order correction can be obtained from a standard perturbation calculus as

$$E_n^{(2)} = \sum_{m \neq n} \frac{|W_{nm}|^2}{E_n - E_m}, \quad (7a)$$

with $W_{nm} = \langle n | W | m \rangle$. The division by the energy difference in eq. (7a) makes the second-order perturbation (**PT2**) numerically unstable because of random degeneracies. Simple treatment based on separation of the degenerate and non-degenerate states was proposed previously.¹⁵ Here we explore a differently modified algorithm, replacing the **PT2** formula 7a for all states by

$$E_n^{(2)} = \frac{1}{2} \sum_{m \neq n} \left[E_m - E_n + W_{mm} - W_{nn} \pm \sqrt{(E_m - E_n + W_{mm} - W_{nn})^2 + 4|W_{nm}|^2} \right] \quad (7b)$$

where the + sign holds for $E_n > E_m$ and –sign for $E_n < E_m$. It can be easily verified that the formula 7b provides exact solu-

tions for two-state (n,m) system including the degenerate case, while for small perturbations ($W \rightarrow 0$) its polynomial expansion is equal to 7a up to the second powers of W .

Vibrational Configuration Interaction

If the wavefunction is expressed as a sum of harmonic oscillator functions, we obtain a solution of the Schrödinger equation directly by the Hamiltonian diagonalization. As this method is limited by the size of the matrix that must be diagonalized, number of the harmonic states (j) must be restricted. They can be selected, for example, based on of the ratio $\eta = |W_{fi}/E_f - E_j|$, bigger than given limit for at least some ground or fundamental state f . Although indirect iterative diagonalization methods¹⁶ (not used in the present study) enable to increase the number of the states significantly, for larger molecules some selection is always necessary. In addition, the speed of the diagonalization, mostly scaled as M^3 , becomes the limiting factor for such cases. For our tests we systematically increased the number the states varying the perturbation parameter η . Because the force field (1) was expanded up to the quartic terms, states with a maximum of five excitations were considered in VCI, similarly as for the methods described above. For example, a non-zero force constant d_{1123} in a three mode system can make the matrix element $\langle 001|V|212\rangle$ non-zero, mediating thus an interaction of $1 \times$ excited normal mode number 3 ($|001\rangle$) and the state with 2, 1, and 2 excitations on modes 1, 2, and 3 ($|212\rangle$). By similar arguments we could deduce that a six-time excited state (e.g. $|213\rangle$) would have probably a negligible effect on the $|000\rangle \rightarrow |001\rangle$ fundamental transition, etc.

Computations

For equilibrium geometries of the model molecules analytical second derivatives were calculated by the Gaussian program,¹⁷ while the third and fourth derivatives were obtained by a numerical differentiation, using a step of 0.025 Å (0.07 Å for α -pinene). The normal mode derivatives were calculated from the Cartesian constants. The geometries were obtained as local energy minima for each approximation used, that is for the Becke3LYP(B3L)^{18,19}/6-311++G**, B3L/6-31G*, and MP2/6-311++G* methods. Only semi-diagonal quartic constants with two and more identical indices (e.g. d_{ijkk}) were considered. Anharmonic interactions of some lowest strongly anharmonic modes were neglected in the computations (one for furan, ring torsion calculated at 610 cm⁻¹, five for α -pinene, CH₃ rotation, and wagging modes²⁰ within 0–229 cm⁻¹).

Results and Discussion

Model Potentials

To test our programs as well as to investigate the behavior of the different anharmonic approaches for small systems, we selected model two- and three-dimensional potentials introduced previously.^{10–12} In Table1, state energies computed using the harmonic, gVSCF, eVSCF, and perturbational [eq. (7a)] methods are compared with (exact) VCI results. We see that any method

Table 1. State Energies Obtained for Two Model Potentials by Various Methods.

Method	State ^a				
	$ 00\rangle$	$ 20\rangle$	$ 000\rangle$	$ 010\rangle$	$ 101\rangle$
E-E(VCI)					
Harmonic part	0.00837	0.05313	0.00625	0.02814	0.02328
gVSCF	0.00084	0.00564	0.00128	0.01259	0.00793
eVSCF	0.00084	0.00546	0.00128	0.00618	0.00478
Harmonic/PT2 ^b	0.00031	0.00469	0.00013	0.00103	0.00116
gVSCF/PT2 ^b	0.00001	0.00045	0.00002	0.00036	0.00053
eVSCF/PT2 ^b	0.00001	0.00008	0.00002	0.00012	0.00009
E(VCI)					
VCI	0.99163	2.03085	1.49375	2.77186	3.17672

^aQuantum numbers are specified for the Henon–Heiles two- and Christoffel three-dimensional dimensionless potentials, as implemented in Refs. 11 and 12 (there is a misprint in the definition of the 3D potential in the latter reference, for this case the original work¹¹ was followed).

^bFormula 7a.

involving the anharmonic part of the potential reduces the error. The VSCF methods are slightly inferior to the simple (harmonic) perturbation theory. However, as found also in previous studies,¹² application of the PT2 theory within the VSCF reduces the overall error significantly. For the ground states ($|00\rangle$, $|000\rangle$) the gVSCF and eVSCF approaches obviously provide the same numbers. For the excited states the plain eVSCF approach gives consistently smaller errors by ~ 3 –50% than gVSCF. The difference is even emphasized when the self-consistent methods are coupled with the perturbational approach, as the eVSCF/PT2 errors of excited energies are several times smaller than for gVSCF/PT2. This may reflect the fact that the gVSCF/PT2 approach bases the perturbation expansion on unperturbed ground state wave functions, not variationally optimal for the excited states. However, even the gVSCF/PT2 calculus seems to be significantly better than the direct application of the perturbation theory to harmonic solutions.

Ab Initio Potential Variation

To investigate possible effects of usual ab initio potential variations on the vibrational energies, we calculated three different vibrational potentials of furan: in vacuum and with the COSMO^{21,22} solvent models, using the B3L approximation, and in vacuum at the MP2 level, all with the 6-311++G** basis. No significant differences in the equilibrium geometries were observed, bond lengths varied less than by 0.01 Å, which contrasts with the force field changes. An inspection of the cubic and quartic field, for example, revealed that for larger constants the variations caused by the solvent inclusion are typically smaller than about 5%. For small constants (smaller than about 10% of the maximal cubic or quartic term), however, no correlation between the vacuum and COSMO values was observed. Supposedly these differences are largely numerical artifacts of the calculation and do not reflect physical changes that occur in the potential when the molecule is submerged into water. In any case, for computation of the vibrational energies beyond the har-

Table 2. Average Differences of Vibrational Energies of the Fundamental Transitions in Furan Obtained with the B3L, MP2, and B3L/COSMO (H₂O) Force Fields, as Calculated by Various Vibrational Methods.

Method	E(B3L/COSMO)-E(B3L)			E(B3L)-E(MP2)		
	δ_{AVE}	$ \delta _{AVE}$	$ \delta _{MAX}$	δ_{AVE}	$ \delta _{AVE}$	$ \delta _{MAX}$
Harmonic	-3	12	25	3	31	127
gVSCF	-6	15	29	-18	23	59
eVSCF	-6	15	29	-18	22	57
Harmonic/PT2 ^a	-5 (-7)	25 (15)	101 (27)	4 (-13)	46 (31)	179 (76)
gVSCF/PT2 ^a	-8 (-7)	14 (15)	26 (26)	-14 (-16)	20 (22)	61 (61)
eVSCF/PT2 ^a	-14 (-2)	21 (20)	105 (79)	-11 (-21)	25 (26)	94 (88)
VCI ^b	-9	14	30	-25	32	115

δ_{AVE} , $|\delta|_{AVE}$, and $|\delta|_{MAX}$: average plain, absolute, and maximal deviations in cm^{-1} .

^aFormula 7b was used for the values in parentheses.

^b1000 states ($\eta > \sim 0.001$).

monic limit we obviously desire a method that does not unrealistically magnify such a noise. The calculated average frequency differences are summarized in Table 2. Apparently, both the **gVSCF** and **eVSCF** methods provide rather conservative estimates of energy changes under the force field variations (B3L \rightarrow B3L/COSMO or B3L \rightarrow MP2). The changes are close to those obtained by the VCI method, in terms of systematic and absolute deviations. Interestingly, while the VCI maximal deviation (30 cm^{-1}) is comparable with that obtained by VSCF (29 cm^{-1}) for the B3L \rightarrow B3L/COSMO force field change, the VCI method leads to a notably larger maximal deviation of 115 cm^{-1} for the B3L \rightarrow MP2 variations. Further increase of the number of the states involved in VCI (from 1000 to 4000) brought only minor energy changes of the order of 1 cm^{-1} .

More importantly, direct application of the perturbation formula 7a leads to rather unrealistic variations of the energies; this is apparent namely from the values of the absolute and maximal deviations (up to 179 cm^{-1} for harmonic/PT2). The gVSCF/PT2 combination seems to provide somewhat more stable results than harmonic/PT2. Because the average deviations remain reasonable we can conclude that the PT2 method even for such a simple molecule effectively generates random errors in calcu-

lated energies due to near degeneracies. The erratic behavior of the PT2 method; however, can be eliminated by using the generalized formula 7b. Indeed, in this case, the frequency changes given in parentheses in Table 2 are more realistic and also consistent with the VSCF and VCI values.

An example of the effect of the ab initio potential variation on the furan modes 2–7 is depicted in Figure 1. The B3L and MP2 vacuum force fields are compared. For modes 2 and 7, out and in plane deformations of the carbonyl five-member ring respectively, the two ab initio methods provide similar force fields. However, the harmonic approximation and the DFT (B3L) method are known to be inadequate for an exact description of the C–H out of plane bending in the neighborhood of a conjugated electronic π -system. For modes 3–6 involving this motion, similarly as for the N–H bending in the amide group,²³ rather complicated mixing of the σ and π electrons takes place and the MP2 computation may be more appropriate. Already the harmonic DFT and MP2 frequencies for the four bending modes differ significantly, up to 130 cm^{-1} for the mode number 6. This nature of the vibrations clearly transmits differently to the other vibrational differences given in Figure 1. The nearly harmonic modes 2 and 7, where additionally the DFT and MP2

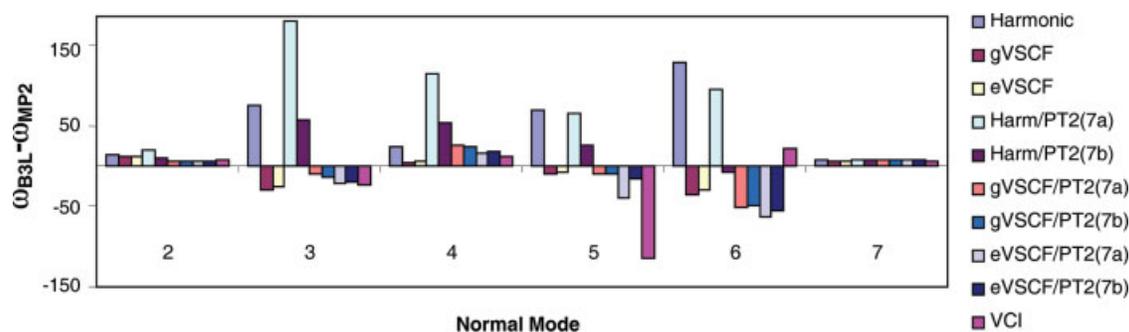


Figure 1. Differences between furan vibrational energies calculated with the B3L and MP2 force fields, for fundamental transitions 2–7, as obtained by the 10 various approaches to the vibrational problem indicated at the right hand side. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 3. Frequency Differences (cm^{-1}) Caused by Random Noise in the Anharmonic Potential (B3L/6-311++G**) of Furan.

Method	Absolute noise " $c \pm \Delta$ "		Relative noise " $c \times (1 \pm \Delta)$ "	
	$ \delta _{\text{AVE}}$	$ \delta _{\text{MAX}}$	$ \delta _{\text{AVE}}$	$ \delta _{\text{MAX}}$
gVSCF	20	84	11	123
eVSCF	22	96	12	180
Harmonic/PT2 ^a	136 (81)	1538 (185)	12 (12)	141 (125)
gVSCF/PT2 ^a	295 (83)	16245 (235)	16 (13)	501 (208)
eVSCF/PT2 ^a	273 (94)	42285 (310)	23 (15)	567 (199)
VCI ^b	38	187	14	200

Averages for sets of 20 computations.

^aFormula 7b was used for the values in parentheses.

force fields are similar, are not affected by the treatment of the anharmonic problem, while the modes 3–6 are more sensitive. As an extreme case, the B3L frequency of mode number 3 is bigger by 180 cm^{-1} than the MP2 value if calculated with the harmonic/PT2 method (formula 7a). This is partially an artifact of the perturbational calculus, but can be improved by the simplified degeneracy treatment (formula 7b) only incompletely. A similar situation occurs for the mode number 6. From the point of the computational efficiency and reliability, it seems reasonable to prefer the VSCF methods over the plain PT2, as the for-

mer quickly provides energy corrections mostly consistent with the VCI results.

Random Potential Changes

To investigate the influence of the potential variations on vibrational energies more systematically, the B3L/6-311++G** furan force field was arbitrarily modified. Firstly, random increments were added to all anharmonic normal mode constants pertaining to the dimensionless normal-mode coordinates q_i , $q_i = \sqrt{\omega_i} Q_i$.¹³ Increments within $(-0.00031, 0.00031)$ hartree were used for both cubics and quartics. As an alternate option, relative sizes of the constants were modified up to 30% of their ab initio values. Supposedly, both modifications are relevant, because smaller anharmonic constants are usually produced with significantly larger relative errors than the bigger ones. For each modification type a series of 20 computations was performed, and the vibrational energies obtained by various anharmonic methods were compared with the unperturbed values.

The frequency changes caused by the two types of random perturbations are summarized in Table 3. Similarly as for the force field differences investigated in Table 2, the VSCF methods are least sensitive to the noise and tend to smooth the potential variations. Interestingly however, as can be seen in Table 3, the behavior of the absolute and relative noise perturbations differ. For the former, the simple perturbation formula (7a) produces clearly worst artifacts, which can be removed by the

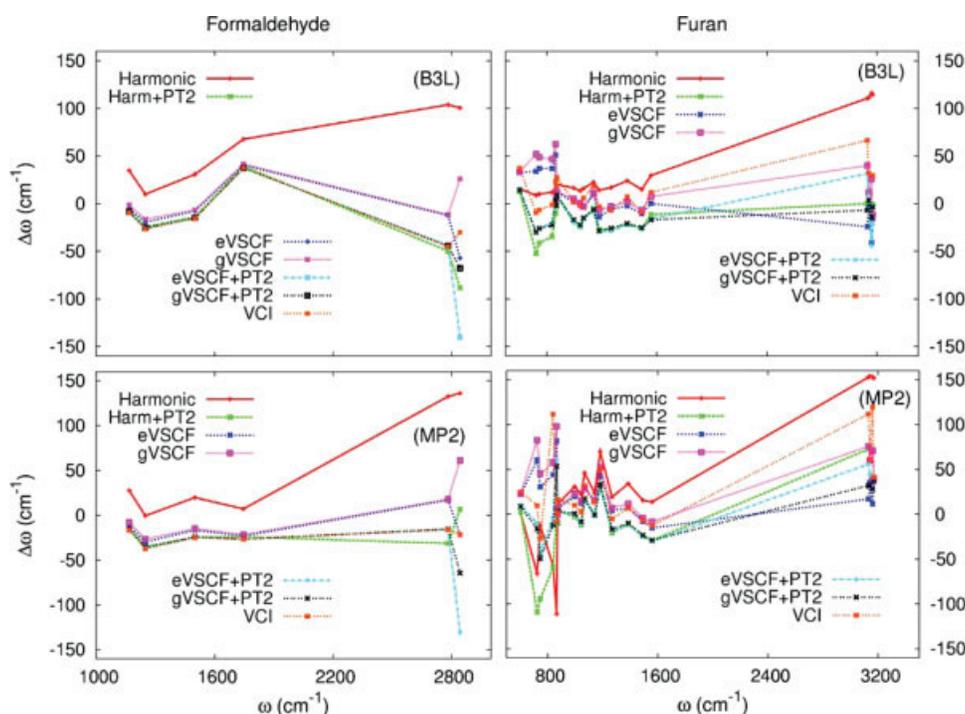


Figure 2. Comparison of the errors of vibrational frequencies computed by different methods for B3L (top) and MP2 (bottom) force field of formaldehyde (on the left) and furan (right hand side). Experimental formaldehyde²⁶ and furan²⁷ frequencies were used as a reference, the 6-311++G** basis used in the force field computations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

degeneracy correction (7b); the pure VSCF and VCI methods remain the most stable. For the relative noise, the corrected perturbational calculus provides energy changes more in line with the (supposedly correct) VCI values. The advantage of the combined VSCF/PT2 over uncorrected harmonic/PT2 method observed for the various ab initio force fields in Table 2 does not seem to be conserved for the random noise perturbations where the harmonic/PT2 approach appears slightly but consistently more stable. The eVSCF/PT2 method is somewhat more prone to the random noise than gVSCF/PT2, probably because of bigger volatility of the excited states to the potential changes. A problematic convergence behavior of the perturbation methods with the VSCF was also observed previously;^{24,25} however, the harmonic/PT2 computations may presumably exhibit similar difficulties as the degeneracies occur randomly.

Molecular Size

The numerical stability of the vibrational computations becomes crucial for larger molecules. This can be seen in Figure 2 where deviations of calculated (B3L/6-311++G**) frequencies from the experimental values^{26,27} of formaldehyde and furan are plotted for individual fundamental transitions. The DFT (B3L) computations presented at the upper part of the figure were repeated with the MP2 force field and are plotted at the bottom. For formaldehyde, similarly as for the model potentials mentioned above, the anharmonic methods converge to common values,

mostly better than those obtained by the harmonic approximation. An exception is the highest-frequency mode where the eVSCF method provides a frequency very close to the experiment and the PT2 correction (7b) destroys this agreement. For furan; however, various anharmonic methods provide very different results and often do not correct the harmonic values at all. Especially for the lowest-frequency modes the perturbational, but also pure VSCF methods, cause unrealistic frequency deviations and thus the benefit of correcting the anharmonicity is overshadowed by numerical artifacts. Obviously, the quality of the computed frequencies is also dependent on the quality of the ab initio force field, detailed analysis of which goes beyond the scope of this work. Nevertheless, it should be noted that the DFT methods are generally believed to be less sensitive to potential variations, providing reasonable harmonic frequencies, but are not able to capture the anharmonic effects to the same accuracy as the accurate wavefunction methods (MP2, CCSD(T)).²⁸ Because of the great many of available DFT functionals; however, it is difficult to generalize particular cases; for example, a very good performance of the DFT for the anharmonic force fields was observed for azabenzenes recently.²⁹ For the formaldehyde presented in Figure 2 the MP2 computations seem to be more appropriate, while for furan the B3L results are closer to experiment.

Unlike for the perturbational and VSCF methods, accuracy of the VCI energies can be systematically improved up to the Schrödinger limit by increasing the vibrational basis set size.

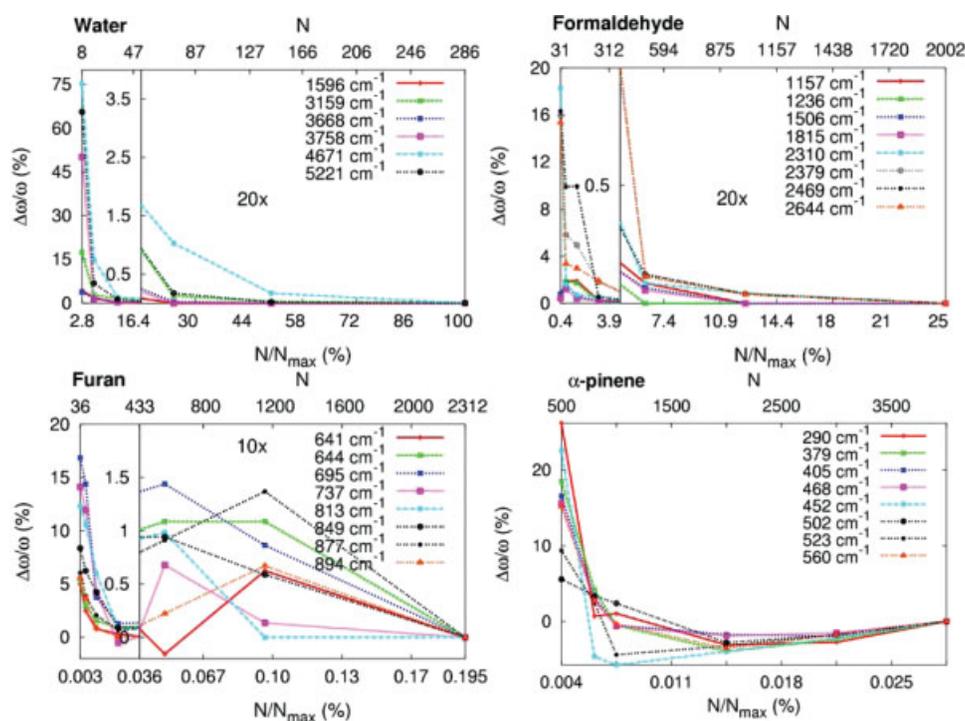


Figure 3. Convergence of the VCI energies. For selected vibrational levels in water, formaldehyde, furan and α -pinene the dependencies of the energy differences (cm^{-1}) from the best calculation on the number of the states involved are plotted. The B3L/6-31G** force fields and the maximum of 286, 2002, 2312, and 4000 vibrational functions (for H_2O , H_2CO , furan and α -pinene, respectively) were used. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 4. Errors of Fundamental Frequencies (cm^{-1}) of α -pinene Obtained with the Becke3LYP/6-31G** Force Field.

Method	C—H stretching			Mid ir			Entire region		
	δ_{AVE}	$ \delta _{\text{AVE}}$	$ \delta _{\text{MAX}}$	δ_{AVE}	$ \delta _{\text{AVE}}$	$ \delta _{\text{MAX}}$	δ_{AVE}	$ \delta _{\text{AVE}}$	$ \delta _{\text{MAX}}$
Harmonic	153	153	174	29	30	76	55	55	174
gVSCF	15	98	89	23	21	60	21	27	89
eVSCF	-12	33	81	21	21	49	14	23	81
Harmonic/PT2 ^a	10 (3)	34 (17)	116 (40)	-9 (-4)	16 (10)	220 (46)	-2 (-4)	37 (11)	605 (47)
gVSCF/PT2 ^a	16 (-4)	37 (15)	140 (37)	-2 (-3)	11 (9)	47 (45)	2 (-3)	17 (10)	140 (45)
eVSCF/PT2 ^a	43 (-8)	98 (18)	605 (47)	-14 (-3)	21 (9)	423 (44)	-5 (-2)	19 (12)	220 (46)
VCI ^b	127	128	213	83	83	113	92	92	213

Frequencies were compared to experiment in Refs. 30 (mid ir region) and 31 (matrix experiment, C—H stretching region).

^aIn parentheses, values obtained with the generalized formula 7b are given.

^b4000 states included, with $\eta < 0.02$.

Additionally, VCI fundamental and combination states can be easily obtained at once. As aforementioned, however, only a small fraction of the states formally interacting with the fundamental transitions of interest can be included for big molecules. Therefore, in Figure 3, we look at the convergence of the VCI energies with respect to the fraction of the 5-times excited vibrational states needed for a balanced second-order correction to the fundamental transitions in water, formaldehyde, furan, and α -pinene. The energy differences (in %) are related to those obtained with the biggest vibrational basis used. Clearly, if a small fraction of the states is included, larger frequency deviations occur. Combination transitions also included in the graphs behave similarly as the fundamentals. Nevertheless the relative number of the states needed for reasonably precise results is smaller for larger molecules. For example, for water 16% of the states need to be included to achieve errors smaller than 2%, while for formaldehyde and furan it is about 7 and 4% of all states, respectively. It is obviously dangerous to approximate the dependence for α -pinene in Figure 3, when only such a tiny fraction of the states is considered. Nevertheless, relative frequency changes for strongly anharmonic modes (not included) are even smaller, and certainly the fraction of the states that must be considered in order to produce comparable effect is again much smaller than for the previous systems. Thus, from the point of practical computations, application of VCI with reasonably-chosen basis set may be meaningful even for larger molecules.

For α -pinene, as an example of a bigger molecule, we also compare the performance of the vibrational methods in Table 4, in terms of average deviations of calculated frequencies from the experiment.^{30,31} The experimental values are preferred as a fully converged VCI computation appears unrealistic, even with the indirect diagonalization schemes.¹⁶ It is important to note that $(M + 4)!/(5!(M - 1)!)$ states must be included to produce the balanced second-order correction for the fundamental transitions and the quartic potential (1), which makes the computational time of the diagonalization proportional to $\sim(M^5)^3 = M^{15}$. Thus we have to accept that the error of the VCI computation is caused by the basis set incompleteness. On the other hand, all the other schemes lead to improvement of the harmonic frequencies. Additionally, we can observe a different

behavior in the high and low(mid)-frequency region; in the former even the VCI is partially beneficial. On the contrary, for the transitions in the mid ir, the convergence of the VSCF and PT2 is very convincing. The VSCF/PT2 (uncorrected) methods provide best performance and are followed by the harmonic/PT2 combination and the plain VSCF schemes. This corresponds to the behavior of the benchmark potentials in Table 1 only approximately; particularly the harmonic/PT2 method provided much bigger energy errors than the VSCF/PT2 computations for the benchmarks. For the α -pinene, the generalized PT2 formula leads to further improvement of the energies and provides virtually identical results for both harmonic and VSCF functions. For the high-frequency C-H stretching modes the behavior slightly differ as the combination of the VSCF and perturbational technologies is beneficial only with the degeneracy correction.

Conclusions

We have implemented and extended some of the computational methods suitable for calculating molecular vibrational energies of semi-rigid molecules beyond the harmonic approximation. On the model examples the performance was analyzed with emphasis on the numerical stability. The results indicated that the algorithms behave differently under different circumstances and should not be applied universally. For example, the VSCF procedure was found to be the most stable with respect to the minor potential variations and also provided the anharmonic part of the vibrational energies only with a relatively minor computational effort. However, the combination of the VSCF with the standard perturbational calculus was found beneficial only for nearly harmonic problems, such as the benchmark potential or mid ir vibrations of α -pinene. For small systems the eVSCF variant provided somewhat better frequencies for the excited states than the gVSCF. The usual second-order perturbational formula seems to be almost unusable for everyday use due to the random degeneracies. Thus, however, could be improved significantly by the modification based on the two-state degenerate model. The conventional VCI results are often hampered by incompleteness of the basis set for bigger molecules, yet a relatively tiny frac-

tion of the basis states subjected to VCI may be already beneficial and improves the agreement with the experiment.

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