

# Calculating molecular vibrational spectra beyond the harmonic approximation

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**Abstract** We present a new approach for calculating anharmonic corrections to vibrational frequency calculations. The vibrational wavefunction is modelled using translated Hermite functions thus allowing anharmonic effects to be incorporated directly into the wavefunction whilst still retaining the simplicity of the Hermite basis. We combine this new method with an optimised finite-difference grid for computing the necessary third and fourth nuclear derivatives of the energy. We compare our combined approach to existing anharmonic models—vibrational self-consistent field theory (VSCF), vibrational perturbation theory (VPT), and vibrational configuration interaction theory (VCI)—and find that it is more cost effective than these alternatives. This makes our method well-suited to computing anharmonic corrections for frequencies in medium-sized molecules.

**Keywords** PES · VPT · TOSH · Anharmonic · Vibrational frequencies · Potential energy surface · Perturbation · Nuclear vibration theory · Quartic force field

## 1 Introduction

Infra-red and Raman vibrational spectroscopies are among the most direct probes of molecular structure available. Experimental measurements are relatively straightforward, the techniques are non-destructive, the time-scale can be extremely short and the sensitivity is high. Perhaps their main weakness is that they yield too much information. A

molecule with  $N$  atoms and no symmetry possesses  $3N - 6$  distinct vibrational frequencies and most of these, together with assorted overtones and combinations, will be present in the measured spectrum, making the assignment task a formidable one, even for modest values of  $N$ . For this and other reasons, theoretical modelling of vibrational spectra is potentially valuable, particularly for species with unusual structures or bonding types. The caveat, of course, is that, unless such calculations are sufficiently accurate, they will simply add to the confusion.

The vibrational frequencies are obtained by solving the nuclear Schrödinger wave equation on a Born-Oppenheimer potential energy surface (PES). This surface, which depends on the level of theory used to compute the electronic energy, can be expanded as a Taylor series

$$E(\mathbf{x}) = E(\mathbf{x}_0) + \frac{1}{2!} \sum_{i,j}^{3N} H_{ij} x_i x_j + \frac{1}{3!} \sum_{i,j,k}^{3N} H_{ijk} x_i x_j x_k + \frac{1}{4!} \sum_{i,j,k,l}^{3N} H_{ijkl} x_i x_j x_k x_l + \dots \quad (1)$$

about a stationary point,  $\mathbf{x}_0$ , where the  $x_i$  are nuclear displacement coordinates and the  $\mathbf{H}$  are arrays of derivatives of the energy with respect to these coordinates. For example, the second derivative matrix (Hessian) is given by

$$H_{ij} = \left. \frac{\partial^2 E(\mathbf{x})}{\partial x_i \partial x_j} \right|_{\mathbf{x}=\mathbf{x}_0} \quad (2)$$

The harmonic approximation, which forms the foundation of most vibrational frequency calculations, is obtained by truncating the expansion in Eq. (1) after the second-order terms. The Schrödinger equation for  $N$  nuclei moving in a harmonic potential is separable and can be solved exactly by diagonalis-

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ing the  $3N \times 3N$  mass-weighted Hessian [1]. The  $m = 3N - 6$  non-zero eigenvalues and associated eigenvectors yield the harmonic frequencies,  $\omega_i$ , and normal coordinates  $q_i$ . The vibrational wavefunctions are characterised by  $m$  non-negative quantum numbers and are the simple products

$$\Phi_{\mathbf{n}} = \phi_{n_1}(q_1, \omega_1) \phi_{n_2}(q_2, \omega_2) \cdots \phi_{n_m}(q_m, \omega_m) \quad (3)$$

where the  $\phi_n$  are harmonic oscillator functions

$$\phi_n(q, \omega) = \left( \frac{\sqrt{\omega}}{\sqrt{\pi} 2^n n!} \right)^{1/2} H_n(q\sqrt{\omega}) \exp(-\omega q^2/2) \quad (4)$$

and  $H_n(x)$  is a Hermite polynomial. The vibrational state,  $\Phi_{\mathbf{n}}$  has an energy

$$E_{\mathbf{n}} = \left( n_1 + \frac{1}{2} \right) \omega_1 + \left( n_2 + \frac{1}{2} \right) \omega_2 + \cdots + \left( n_m + \frac{1}{2} \right) \omega_m \quad (5)$$

Several quantum chemistry packages exist that can compute the required second-derivatives analytically for Hartree–Fock and density functional calculations. These analytic derivatives are both more accurate and more efficient than finite-difference methods and allow for the routine computation of harmonic frequencies of moderately large molecular systems.

For many qualitative and semi-quantitative purposes, the harmonic approximation is satisfactory but, with greater computer resources becoming available, going beyond this approximation has become increasingly feasible and has developed into an active area of research [2–19]. Unfortunately, when higher terms in the Taylor expansion are retained the associated Schrödinger equation is no longer separable and near-exact solutions are difficult to obtain for systems with more than three or four atoms [20, 21]. Nonetheless, it is possible to devise systematic approaches that begin with the harmonic approximation and build toward the exact result. Many of these post-harmonic treatments have analogues in electronic structure methodology. For example, vibrational perturbation theory (VPT) [22–24], which treats the higher-order derivatives of the potential as a perturbation on the harmonic potential, and  $n$ th-order vibrational configuration interaction, VCI( $n$ ) [25], which expands the vibrational wavefunction in terms of configurations involving up to  $n$ -quanta. The problem with many of these methods is that their computational cost, particularly the memory requirements, scales poorly with  $m$ . If anharmonic corrections are to be applied routinely, efficient and accurate approximations are required. We address this need in this Paper.

In the following section we introduce a new approach to incorporating anharmonic effects directly into the wavefunction based on transition-optimised shifted Hermite (TOSH)

functions. The wavefunction is a product of harmonic basis functions that have been shifted from their equilibrium position, with the magnitude of the shift being determined from first- and second-order VPT. In Sect. 3 we consider the relative importance of the third- and fourth-order derivatives required to model the anharmonic PES. By focussing only on the derivatives that contribute significantly to the anharmonic corrections, an efficient finite-difference scheme is developed that minimises the number of different geometries that need to be considered. Furthermore, by considering the round-off and truncation errors from the finite-difference formulae, a new prescription for the step size is proposed in Sect. 4. Finally, in Sect. 5, we compare the accuracy and efficiency of our new approach with existing vibrational theories.

## 2 Transition-optimised shifted Hermite theory

Our approach is based on VPT, which we now outline briefly. Using normal coordinates, and retaining up to fourth-order terms in the expansion of the potential in Eq. 1, the nuclear Hamiltonian can be written

$$\hat{H} = \hat{H}_0 + \hat{V} \quad (6)$$

where  $\hat{H}_0$  is the harmonic Hamiltonian

$$\hat{H}_0 = \sum_i^m \left( -\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{\omega_i^2}{2} q_i^2 \right) \quad (7)$$

and  $\hat{V}$  contains the anharmonic terms

$$\hat{V} = \frac{1}{3!} \sum_{i,j,k} \eta_{ijk} q_i q_j q_k + \frac{1}{4!} \sum_{i,j,k,l} \eta_{ijkl} q_i q_j q_k q_l \quad (8)$$

where  $\eta$  are the derivatives of the energy with respect to the normal modes  $q_i$ . If the anharmonic terms in  $\hat{V}$  are small in comparison to those in  $\hat{H}_0$ , then they may be treated as a perturbation and application of Rayleigh–Schrödinger perturbation theory yields a sequence of Vibrational Perturbation theories VPT $n$  ( $n = 1, 2, \dots$ ), that approximate the effects of  $\hat{V}$ . If  $\hat{H}_0$  has eigenfunctions  $\Psi_{\mathbf{n}}$  and energies  $E_{\mathbf{n}}$  given by Eqs. (3) and (5), then perturbation theory gives

$$\begin{aligned} E_{\mathbf{n}}^{(1)} &= E_{\mathbf{n}}^{(0)} + \langle \Psi_{\mathbf{n}} | \hat{V} | \Psi_{\mathbf{n}} \rangle \\ &= \sum_i \omega_i \left( n_i + \frac{1}{2} \right) + \frac{1}{4!} \sum_i \eta_{iiii} \left( \frac{6n_i^2 + 6n_i + 3}{4\omega_i^2} \right) \\ &\quad + \frac{6}{4!} \sum_{j \neq i} \eta_{iijj} \left( \frac{2n_i + 1}{2\omega_i} \right) \left( \frac{2n_j + 1}{2\omega_j} \right) \end{aligned} \quad (9)$$

where  $E_{\mathbf{n}}^{(0)} \equiv E_{\mathbf{n}}$  is the zeroth-order (harmonic) energy of the  $\mathbf{n}$ th vibrational state. The exact expression for VPT2 is

significantly more complicated, however from the second order Rayleigh–Schrödinger expression

$$E_{\mathbf{n}}^{(2)} = E_{\mathbf{n}}^{(1)} + \sum_{\mathbf{k} \neq \mathbf{n}} \frac{|\langle \Psi_{\mathbf{n}} | \hat{V} | \Psi_{\mathbf{k}} \rangle|^2}{E_{\mathbf{n}} - E_{\mathbf{k}}} \quad (10)$$

it can be seen that the equation is manifestly singular if the vibrational state  $\mathbf{n}$  is degenerate and, although this problem can be overcome through the use of the appropriate degenerate perturbation theory [19, 26–29], the expression also behaves poorly if the state is *nearly* degenerate, and this weakness is more difficult to overcome. This well-documented shortcoming of VPT $n$  becomes more acute in larger molecules, where the probability of accidental near-degeneracies and near-resonances is high and leads to divergence of the VPT $n$  expansion. One solution to overcome this problem is to give the nuclei fictitious masses, thus lifting the degeneracies [19]. The disadvantage of this approach is that by breaking the degeneracies the fundamental frequencies no longer retaining their correct symmetry. Despite these drawbacks, VPT is computationally more attractive than other approaches, such as VCI( $n$ ), because of its more modest storage requirements and it has been widely used in theoretical molecular spectroscopy.

The expression for the energy of the  $i$ th vibrational level obtained from second-order perturbation theory is usually approximated [19, 22–24, 27, 30] as:

$$E_i = \sum_j \omega_j \left( n_j + \frac{1}{2} \right) + \sum_{i \leq j} x_{ij} \left( n_i + \frac{1}{2} \right) \left( n_j + \frac{1}{2} \right) \quad (11)$$

where, if rotational coupling is ignored, the anharmonic constants  $x_{ij}$  are given by

$$x_{ij} = \frac{1}{4\omega_i\omega_j} \left( \eta_{iijj} - \sum_k^m \frac{\eta_{iik}\eta_{jjk}}{\omega_k^2} + \sum_k^m \frac{2(\omega_i^2 + \omega_j^2 - \omega_k^2)\eta_{ijk}^2}{[(\omega_i + \omega_j)^2 - \omega_k^2][(\omega_i - \omega_j)^2 - \omega_k^2]} \right) \quad (12)$$

For most systems, higher order terms in (11) make little contribution to the energy and the expansion can be truncated after the second-order terms in the quantum numbers without introducing significant error [31]. Equation (12) also assumes that terms that are quadratic in the fourth-order derivatives do not contribute significantly and have therefore been neglected. The energy of the  $i$ th fundamental vibrational mode is given by:

$$\Delta E_i = \nu_i = \omega_i + \frac{1}{2} \sum_j^m x_{ij} \quad (13)$$

First-order perturbation theory accounts for the effects of the perturbation on the unperturbed wavefunction, whereas second-order perturbation theory begins to model the relaxation of the unperturbed wavefunction in the presence of the perturbation. We now ask a question; can anharmonic effects be introduced into the wavefunction without resorting to second-order perturbation theory? A simple example will demonstrate how this is possible. For a diatomic molecule, the Hamiltonian with a quartic force field (QFF) can be written:

$$\hat{H} = -\frac{1}{2} \frac{\partial^2}{\partial q^2} + \frac{1}{2} \omega^2 q^2 + \frac{1}{3!} \eta_{1111} q^3 + \frac{1}{4!} \eta_{11111} q^4 \quad (14)$$

and the zeroth-order wavefunction is given by Eq. (4). If the origin of this wavefunction is shifted by a small amount,  $\sigma$ , the shape will remain the same, but the asymmetry about the equilibrium geometry can be exploited to allow anharmonic effects to be incorporated into the wavefunction. The shifted wavefunction for the ground vibrational state is

$$\phi_0 = \left( \frac{\omega}{\pi} \right)^{\frac{1}{4}} e^{-\omega(q-\sigma)^2/2} \quad (15)$$

and that for the first excited state is

$$\phi_1 = \left( \frac{4\omega^3}{\pi} \right)^{\frac{1}{4}} (q - \sigma) e^{-\omega(q-\sigma)^2/2} \quad (16)$$

The difference in energy between these vibrational states is

$$\begin{aligned} \Delta E^{\text{TOSH}} &= \langle \phi_1 | \hat{H} | \phi_1 \rangle - \langle \phi_0 | \hat{H} | \phi_0 \rangle \\ &= \omega + \frac{\eta_{1111}}{8\omega^2} + \frac{\eta_{1111}\sigma}{2\omega} + \frac{\eta_{1111}\sigma^2}{4\omega} \end{aligned} \quad (17)$$

and this may be compared to the energy of the unshifted wavefunction obtained from first- and second order perturbation theories:

$$\Delta E^{\text{VPT1}} = \omega + \frac{\eta_{1111}}{8\omega^2} \quad (18)$$

$$\Delta E^{\text{VPT2}} = \omega + \frac{\eta_{1111}}{8\omega^2} - \frac{5\eta_{111}^2}{24\omega^4} - \frac{\eta_{11111}^2}{32\omega^4} \quad (19)$$

If we assume  $\sigma$  is small, we can ignore the  $\sigma^2$  term and by comparing the coefficients of  $\eta_{111}$  in the expressions (17) and (19) we can obtain a value for the shift

$$\sigma = -\frac{5}{12} \frac{\eta_{111}}{\omega^3} \quad (20)$$

that is optimal for the  $0 \rightarrow 1$  transition. For this reason, we call (15) and (16) TOSH functions. Using this value for  $\sigma$  for diatomic systems allows us to obtain an approximation to the second-order energy from a first-order expression. Note that we are unable to match the  $\eta_{1111}^2$  part of the VPT2 energy expression, however, this term is often neglected and is also absent from (12).

For polyatomic molecules, the  $0 \rightarrow 1$  transition energy for the  $i$ th mode obtained from using the TOSH wavefunction in Eq. (9)

$$\Delta E_i^{\text{TOSH}} = \omega_i + \frac{1}{8\omega_i} \sum_j \frac{\eta_{iij}}{\omega_j} + \frac{1}{2\omega_i} \sum_j \eta_{iij}\sigma_{ij} + \frac{1}{4\omega_i} \sum_{j,k} \eta_{iijk}\sigma_{ij}\sigma_{ik} \quad (21)$$

where we have allowed for a different shift in each function, for each vibrational frequency. The corresponding energy difference from Eqs. (12) and (13) is

$$\Delta E_i^{\text{VPT2}} = \omega_i + \frac{1}{8\omega_i} \sum_j \frac{\eta_{iij}}{\omega_j} - \frac{1}{8\omega_i} \sum_{j=1}^m \sum_{k=1}^m \frac{\eta_{iik}\eta_{jjk}}{\omega_j\omega_k^2} + \frac{1}{4\omega_i} \times \sum_{j=1}^m \sum_{k=1}^m \frac{(\omega_i^2 + \omega_j^2 - \omega_k^2) \eta_{ijk}^2}{\omega_j [(\omega_i - \omega_j)^2 - \omega_k^2] [(\omega_i + \omega_j)^2 - \omega_k^2]} \quad (22)$$

If, as before, we neglect the terms that are quadratic in the shifts, then from Eq. (21) we see that  $\sigma_{ij}/2\omega_i$  is the coefficient of the  $\eta_{iij}$  derivatives. Looking for the coefficient of these derivatives in Eq. (22) and comparing this to  $\sigma_{ij}/2\omega_i$  we obtain

$$\frac{\sigma_{ij}}{2\omega_i} = \frac{-1}{8\omega_i\omega_j^2} \sum_{k=1}^m \frac{\eta_{kkj}}{\omega_k} - \frac{(2\omega_i^2 - \omega_j^2) \eta_{iij}}{4\omega_i^2\omega_j^2(4\omega_i^2 - \omega_j^2)} + \frac{\omega_j\eta_{iij}}{4\omega_i[(\omega_i - \omega_j)^2 - \omega_i^2][(\omega_i + \omega_j)^2 - \omega_i^2]} \quad (23)$$

which can be simplified to

$$\sigma_{ij} = \frac{(\delta_{ij} - 2)(\omega_i + \omega_j)\eta_{iij}}{4\omega_i\omega_j^2(2\omega_i + \omega_j)} - \sum_k \frac{\eta_{kkj}}{4\omega_k\omega_j^2} \quad (24)$$

The energy obtained using this approach is only an approximation to the VPT2 energy as several terms have been neglected, in particular the coefficients of the  $\eta_{ijk}$  terms cannot, and have not, been matched. However, the TOSH expression has the advantage that it does not break down for degenerate systems and it requires only one- and two-mode derivatives. We present the results of using our TOSH approach in Sect. 5.

Rather than shifting the origin of the vibrational wavefunctions, other groups have suggested shifting the nuclei from their equilibrium positions to either the vibrational averaged or experimental structure, and calculating the derivatives at this new geometry [32]. This approach is distinct from ours as we still calculate the derivatives at the equilibrium geometry. Studies show [33,34] that the shifted PES with carefully chosen coordinates can yield a good force field, however, large-amplitude vibrational motions are likely to be poorly treated because the higher derivatives can be anomalously

large when evaluated at the non-equilibrium reference geometries.

### 3 Numerical Derivatives

In order to compute anharmonic vibrational frequencies, third- and higher-order derivatives of the energy must be calculated. These derivatives are both difficult and expensive to compute analytically and, therefore, finite-difference methods are usually used. The optimal strategy for calculating these numerical derivatives depends on what information (energies, gradients, etc.) is available, the relative costs of computing these data, and also the effects of truncation and round-off errors. Before developing such a strategy, it is worth pausing to consider the relative importance of the types of higher-order derivative that arise in calculating anharmonic corrections.

Traditionally the expansion of the PES, Eq. (1), is truncated after quartic terms. Higher derivatives can be important in highly anharmonic systems such as water [35], but the high cost of computing these derivatives diminishes their value and the use of a QFF is often considered a useful compromise. However, the derivatives in the QFF are not all equally important. This is demonstrated in Table 1 which shows the mean absolute deviations in the vibrational frequencies of the molecules in the D1 data set (see Table 2) applying full VPT2 (including all terms involving the fourth-order derivatives) to the B3LYP/6-31G(d) PES. The differences are between the frequencies calculated using the full QFF (4MR) and those obtained using various subsets of the derivatives. In this table we introduce the notations used to describe the various approximations to the full QFF. The model force fields are characterised by the different types of derivative used, where a derivative type is determined by the order of derivative and how many different indices there are. For example,  $\eta_{iii}$  characterises one type, which is distinct from  $\eta_{iij}$  and  $\eta_{iiii}$ , (the restriction  $i \neq j$  is implicit within our notation).

Table 1 shows that couplings between three and four modes contribute little to the total anharmonic correction. Furthermore, neglecting the  $\eta_{iiii}$  derivatives in our model potential increases the error only marginally ( $1 \text{ cm}^{-1}$ ) and so these too can be safely ignored. However, any attempt to remove further two-mode coupling derivatives (as shown by the unnamed models in Table 1) increases the error by approximately  $20 \text{ cm}^{-1}$ . From this we conclude that the TOSH force field (TFF), so named because it includes only those derivatives required by our TOSH method, is the smallest subset of the QFF which gives acceptable (less than  $10 \text{ cm}^{-1}$ ) errors. The observation that only one- and two-mode coupling derivatives are required to obtain accurate anharmonic frequencies has been made previously [2]. This model of the QFF is simpler than those found elsewhere in the

**Table 1** Notations and derivatives used for various approximations of the QFF: HFF (harmonic force field), TFF (TOSH force field), PFF (derivatives in the truncated VPT2 force field), CFF (cubic force field), *n*MR (*n* mode-coupling representation)

Model	Derivatives used									Error/cm <sup>-1</sup>	Number of geometries required	
	$\eta_{ii}$	$\eta_{iii}$	$\eta_{iiii}$	$\eta_{ijj}$	$\eta_{iij}$	$\eta_{iii}$	$\eta_{ijk}$	$\eta_{iij}$	$\eta_{ijkl}$		Energy-only scheme	EGH scheme
HFF	✓									52	1	1
1MR	✓	✓	✓							36	1 + 4 <i>m</i>	1 + 2 <i>m</i>
	✓	✓	✓	✓						26	1 + 4 <i>m</i> + 4 $\binom{m}{2}$	1 + 2 <i>m</i>
	✓	✓	✓		✓					29	1 + 4 <i>m</i> + 4 $\binom{m}{2}$	1 + 2 <i>m</i> + 2 $\binom{m}{2}$ <sup>a</sup>
TFF	✓	✓	✓	✓	✓					8	1 + 4 <i>m</i> + 4 $\binom{m}{2}$	1 + 2 <i>m</i> + 2 $\binom{m}{2}$ <sup>a</sup>
2MR	✓	✓	✓	✓	✓	✓				7	1 + 4 <i>m</i> + 12 $\binom{m}{2}$	1 + 2 <i>m</i> + 2 $\binom{m}{2}$ <sup>a</sup>
PFF	✓	✓	✓	✓	✓		✓			3	1 + 4 <i>m</i> + 4 $\binom{m}{2}$ + 8 $\binom{m}{3}$	1 + 2 <i>m</i> + 2 $\binom{m}{2}$ <sup>b</sup>
CFF	✓	✓		✓			✓			29	1 + 4 <i>m</i> + 12 $\binom{m}{2}$ + 8 $\binom{m}{3}$	1 + 2 <i>m</i> + 2 $\binom{m}{2}$ <sup>b</sup>
3MR	✓	✓	✓	✓	✓	✓	✓	✓		0	1 + 4 <i>m</i> + 12 $\binom{m}{2}$ + 8 $\binom{m}{3}$	1 + 2 <i>m</i> + 2 $\binom{m}{2}$ <sup>b</sup>
4MR	✓	✓	✓	✓	✓	✓	✓	✓	✓	0	1 + 4 <i>m</i> + 12 $\binom{m}{2}$ + 8 $\binom{m}{3}$ + 16 $\binom{m}{4}$	1 + 2 <i>m</i> + 2 $\binom{m}{2}$ + 2 $\binom{m}{3}$

<sup>a</sup> only 1 + 2*m* gradients required<sup>b</sup> gradients required at all points

The errors are the mean differences (in cm<sup>-1</sup>) between the anharmonic frequencies computed using the indicated model and those computed using the 4MR (≡ full QFF) for molecules in the D1 set of molecules (see Table 2). Also shown is the number of grid points required if the energy-only and EGH schemes are used to compute the numerical derivatives, where *m* is the number of modes

**Table 2** Lists of the molecules in each of the sets used in this Paper

Data set	Molecules
D1	H <sub>2</sub> CO, CH <sub>2</sub> Cl <sub>2</sub> , HCOOH, CH <sub>2</sub> CH <sub>2</sub> , CH <sub>2</sub> CCl <sub>2</sub> , CH <sub>3</sub> OH, <i>cis</i> -CHClCHCl, <i>cis</i> -CHFCHF, ClF <sub>3</sub> , ClNO <sub>2</sub> , COCl <sub>2</sub> , COClF, COF <sub>2</sub> , CSCl <sub>2</sub> , CSF <sub>2</sub> , F <sub>2</sub> NH, F <sub>2</sub> SO, HN <sub>3</sub> , HNCO, HNO <sub>3</sub> , N <sub>2</sub> F <sub>2</sub> , NCl <sub>2</sub> F, NClF <sub>2</sub> , OCHCHO, S <sub>2</sub> F <sub>2</sub> , SiH <sub>2</sub> Cl <sub>2</sub> , SOCl <sub>2</sub> , <i>trans</i> -CHClCHCl, <i>trans</i> -CHFCHF
D2	B <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> Cl <sub>2</sub> , C <sub>2</sub> N <sub>2</sub> , <i>cyclo</i> -C <sub>2</sub> H <sub>4</sub> NH, <i>cyclo</i> -C <sub>2</sub> H <sub>4</sub> O, <i>cyclo</i> -C <sub>3</sub> H <sub>6</sub> , CH <sub>2</sub> CCH <sub>2</sub> , CH <sub>2</sub> CCHCl, CH <sub>2</sub> CCl <sub>2</sub> , CH <sub>2</sub> CH <sub>2</sub> , CH <sub>2</sub> CHCHCH <sub>2</sub> , CH <sub>2</sub> CHCHO, CH <sub>2</sub> Cl <sub>2</sub> , <sup>1</sup> CH <sub>2</sub> , <sup>3</sup> CH <sub>2</sub> , CH <sub>3</sub> CH <sub>2</sub> Cl, CH <sub>3</sub> CH <sub>2</sub> CN, CH <sub>3</sub> CH <sub>2</sub> F, CH <sub>3</sub> CHO, CH <sub>3</sub> COCH <sub>3</sub> , CH <sub>3</sub> COF, CH <sub>3</sub> COOH, CH <sub>3</sub> NH <sub>2</sub> , CH <sub>3</sub> NNCH <sub>3</sub> , CH <sub>3</sub> OCH <sub>3</sub> , CH <sub>3</sub> OH, CH <sub>3</sub> SiH <sub>3</sub> , CH, <i>cis</i> -CHClCHCl, <i>cis</i> -CHFCHF, Cl <sub>2</sub> O, ClCN, ClF <sub>3</sub> , ClNO <sub>2</sub> , ClNO, ClSN, CO <sub>2</sub> , COCl <sub>2</sub> , COClF, COF <sub>2</sub> , COS, CS <sub>2</sub> , CSCl <sub>2</sub> , CSF <sub>2</sub> , F <sub>2</sub> , F <sub>2</sub> NH, F <sub>2</sub> O, F <sub>2</sub> SO, FCN, FH, CH <sub>2</sub> ClCH <sub>2</sub> Cl, H <sub>2</sub> CO, H <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub> S <sub>2</sub> , H <sub>2</sub> S, HCCCCH, HCCCH <sub>2</sub> Cl, HCCCH <sub>2</sub> F, HCCCl, HCCF, HCCH, HCN, HCO, HCOOCH <sub>3</sub> , HCOOH, HN <sub>3</sub> , HNCO, HNO <sub>3</sub> , HOCl, HOF, LiF, N <sub>2</sub> , N <sub>2</sub> F <sub>2</sub> , N <sub>2</sub> O, NCl <sub>2</sub> F, NClF <sub>2</sub> , NH, NO <sub>2</sub> , NSF, O <sub>2</sub> , O <sub>3</sub> , OCHCHO, OH, ONF, PH, S <sub>2</sub> F <sub>2</sub> , SCl <sub>2</sub> , SH, SiH <sub>2</sub> Cl <sub>2</sub> , SiH, SO <sub>2</sub> , SOCl <sub>2</sub> , <i>trans</i> -CH <sub>2</sub> ClCH <sub>2</sub> Cl, <i>trans</i> -CHClCHCl, <i>trans</i> -CHFCHF

literature, where the perturbation force field (PFF) has been used with VPT2 [19, 26–29, 36] and two-mode coupling representation (2MR) has been frequently used for vibrational self-consistent field theory (VSCF) [30, 37–42].

Computing the 4MR derivatives using energy-only evaluations requires evaluating the energy at a number of geometries that scales with the fourth power of the number of modes:

$$N_{\text{grid}}^{4\text{MR}} = 1 + 4m + 12\binom{m}{2} + 8\binom{m}{3} + 16\binom{m}{4} \quad (25)$$

where  $\binom{m}{n}$  is a binomial coefficient. The high cost of computing the 4MR surface, and the small contribution from three- and four-mode coupling derivatives, makes restricting the force field to one- and two-mode coupling derivatives an attractive proposition. The necessary derivatives for this two-mode representation can be computed via the following

finite-difference scheme:

$$\eta_{iii} = \frac{1}{2h^3} (-E_{-2,0} + 2E_{-1,0} - 2E_{1,0} + E_{2,0}) + \frac{h^2}{4}\eta^{(5,0)} + \dots \quad (26)$$

$$\eta_{ijj} = \frac{1}{2h^3} (2E_{0,-1} - 2E_{0,1} - E_{-1,-1} + E_{-1,1} - E_{1,-1} + E_{1,1}) + \frac{h^2}{12} (2\eta^{(2,3)} + \eta^{(4,1)}) + \dots \quad (27)$$

$$\eta_{iii} = \frac{1}{h^4} (6E_{0,0} + E_{-2,0} - 4E_{-1,0} - 4E_{1,0} + E_{2,0}) + \frac{h^2}{6}\eta^{(6,0)} + \dots \quad (28)$$

$$\eta_{iij} = \frac{1}{4h^4} (E_{-2,-1} - E_{-2,1} - 2E_{-1,-1} + 2E_{-1,1}$$

$$\begin{aligned}
 &+2E_{1,-1} - 2E_{1,1} - E_{2,-1} + E_{2,1}) \\
 &+ \frac{h^2}{12} \left( 2\eta^{(3,3)} + 3\eta^{(5,1)} \right) + \dots \quad (29)
 \end{aligned}$$

$$\begin{aligned}
 \eta_{ijij} = & \frac{1}{h^4} \left( 4E_{0,0} - 2E_{0,-1} - 2E_{0,1} - 2E_{-1,0} + E_{-1,-1} \right. \\
 & \left. - E_{-1,1} - 2E_{1,0} + E_{1,-1} + E_{1,1} \right) \\
 & + \frac{h^2}{12} \left( \eta^{(2,4)} + \eta^{(4,2)} \right) + \dots \quad (30)
 \end{aligned}$$

where  $\eta^{(a,b)}$  is the mixed derivative of order  $a$  and  $b$  in the  $i$ th and  $j$ th normal mode, respectively, and  $E_{c,d}$  is the energy calculated at the point  $\mathbf{x}_0 + c h \mathbf{q}_i + d h \mathbf{q}_j$ . The number of energy evaluations required for this reduced representation scales quadratically with  $m$ :

$$N_{\text{energy}}^{2\text{MR}} = 1 + 4m + 12 \binom{m}{2} \quad (31)$$

Around two thirds of these points are required only for the  $\eta_{ijij}$  derivatives and, if these derivatives are also neglected, a further reduction in the number of grid points is possible. To reduce the number of grid points still further, we must introduce additional information at some of the geometries. If we compute the gradient of the energy at the displacements  $(\pm h, 0)$  and  $(0, \pm h)$  and compute both the gradient and Hessian (which are available from the harmonic frequency calculation) at the stationary point,  $(0, 0)$ , then the following scheme, truncated before the  $\mathcal{O}(h^2)$  terms, can be used to compute all the two-mode derivatives:

$$\eta_{iii} = \frac{1}{h^2} \left( E_{-1,0}^{(1,0)} - 2E_{0,0}^{(1,0)} + E_{1,0}^{(1,0)} \right) + \frac{h^2}{12} \eta^{(5,0)} + \dots \quad (32)$$

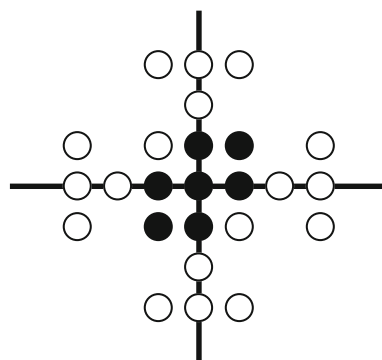
$$\eta_{ijj} = \frac{1}{h^2} \left( E_{-1,0}^{(0,1)} - 2E_{0,0}^{(0,1)} + E_{1,0}^{(0,1)} \right) + \frac{h^2}{12} \eta^{(4,1)} + \dots \quad (33)$$

$$\eta_{iiii} = \frac{3}{h^3} \left( E_{1,0}^{(1,0)} - 2hE_{0,0}^{(2,0)} - E_{-1,0}^{(1,0)} \right) + \frac{h^2}{20} \eta^{(6,0)} + \dots \quad (34)$$

$$\eta_{iiij} = \frac{3}{h^3} \left( E_{1,0}^{(0,1)} - E_{-1,0}^{(0,1)} \right) + \frac{h^2}{20} \eta^{(5,1)} + \dots \quad (35)$$

$$\begin{aligned}
 \eta_{ijij} = & \frac{-1}{2h^4} \left( 8E_{0,0} - 4E_{-1,-1} - 4E_{1,1} - hE_{0,-1}^{(0,1)} \right. \\
 & + hE_{0,1}^{(0,1)} - 4hE_{-1,0}^{(0,1)} + 4hE_{1,0}^{(0,1)} + 2h^2E_{0,0}^{(0,2)} \\
 & - 4hE_{0,-1}^{(1,0)} + 4hE_{0,1}^{(1,0)} - hE_{-1,0}^{(1,0)} + hE_{1,0}^{(1,0)} \\
 & + 2h^2E_{0,0}^{(2,0)} \left. \right) + \frac{h^2}{360} \left( \eta^{(0,6)} + 30\eta^{(2,4)} + 40\eta^{(3,3)} \right. \\
 & \left. + 30\eta^{(4,2)} + \eta^{(6,0)} \right) + \dots \quad (36)
 \end{aligned}$$

Note that Eqs. (35) and (36) make use of the fact that the  $\eta_{ij}$  derivatives are identically zero, which is a consequence of the



**Fig. 1** Grid points used for constructing the TFF. *Solid black points* are those used in the EGH method, *circled points* indicate the additional points required by Yagi's method [2]

orthogonality of the normal modes. Note also that Eqs. (32) and (33) involve the gradient of the energy at the stationary point. Although these gradients should be zero, they can have small values bounded by the convergence threshold of the geometry optimisation procedure, and these residual values should be taken into account to minimise error in the finite-difference scheme. Because this new scheme combines energy, gradient, and Hessian information, we call it the EGH method. Using these new formulae, (32)–(36), the two-mode derivatives can be obtained from the following number of geometries:

$$N_{\text{EGH}}^{2\text{MR}} = 1 + 2m + 2 \binom{m}{2} \quad (37)$$

which is approximately one sixth of the number required by the energy-only approach. In addition to the energy evaluations, gradient calculations are also required at  $1 + 2m$  of these points, but these typically take less time than the self-consistent field calculation required to compute the energy at the same geometry. The EGH philosophy can also be applied to the three- and four-mode coupling derivatives to reduce the number of geometries that need to be considered for the 4MR force field. We defer the formulae for these derivatives to the Appendix.

The EGH scheme can be compared to that of Yagi et al. [2] who use finite-difference formulae similar to (26)–(30) except that the  $\eta_{iii}$  and  $\eta_{iiij}$  derivatives are calculated by stepping out three, rather than two, units. Their approach requires only an additional  $2m$  points over and above those required for the scheme embodied in Eqs. (26)–(30). Figure 1 illustrates which points are needed for constructing the two-mode derivatives using these two finite-difference schemes. The EGH method uses only the solid black points whereas Yagi's method requires these and the additional circled points.

The efficiency of the EGH method can be compared to other approaches that use only one type of derivative infor-

mation. In Table 3 the timings per point and number of points required for energy-only, gradient-only, Hessian-only and EGH finite-difference schemes are shown for the  $C_1 - C_7$  linear alkanes. For the TFF our EGH scheme is the most efficient for systems smaller than heptane. EGH becomes more expensive than the Hessian approach for larger systems as the number of points required scales quadratically with the number of modes, whereas the number of points required using the Hessian approach scales only linearly with the number of modes. For the 4MR the EGH scheme is always the cheapest option for these alkanes, but for larger systems the Hessian approach will eventually win as for the 4MR surface it requires only a quadratic number of geometries versus the cubic number required by EGH. These conclusions are only valid for the relatively modest 6-31G(d) basis set. For larger bases, particularly those with higher angular momentum functions, the cost of computing the second derivatives required for the Hessians rises rapidly and the EGH scheme will be competitive for larger systems.

One aspect of the EGH approach that we have not fully investigated is the possibility of introducing cutoffs when calculating the TFF. Because a maximum of two modes are coupled in this force field, the derivatives would not have to be calculated if, for example, the two modes were well separated spatially. These cutoffs could be used to reduce the number of geometries required to compute the TFF using EGH. No such cutoffs can be used with the Hessian-only approach as each displacement is in the direction of only a single normal mode in this force field.

#### 4 Step size selection

The accuracy of finite-difference formulae depends on both the step size and the highest-order derivative information used. Various step sizes have been suggested in the literature which are either fixed or chosen adaptively based on local information about the PES. For example, if internal coordinates are used and analytical third derivatives are available, Császár [32] suggests using  $0.01 a_0$  to determine the fourth derivatives numerically. For analytical second derivatives, Császár [32] propose using  $0.02 a_0$  to determine the fourth derivatives whilst Åstrand [43] recommends  $0.001 a_0$  for computing the third derivatives. If analytical first derivatives are available, Császár [32] suggests  $0.02 a_0$  for fourth derivatives. Meanwhile, Åstrand [43] advocates  $0.0075 a_0$  for calculating the cubic force field from analytical first derivatives. If only single-point energy calculations are feasible, Császár [32] suggests using  $0.04 a_0$  for calculating numerical fourth derivatives.

Adaptive step sizes have also been considered, and these are usually based on information about the curvature of the PES at the equilibrium geometry. For example, Barone

proposed the following expression [19]:

$$\Delta q_i = \frac{\sqrt{\Delta E^{(2)}}}{2\pi c \omega_i} \quad (38)$$

where  $\Delta E^{(2)}$  is the change in the quadratic approximation of the energy. This expression typically yields step sizes in the range  $0.006-0.02 a_0$ . Burcl [18] suggested the step size should be chosen to ensure a increase in the potential energy of  $1 \text{ mE}_h$ , assuming the convergence threshold of the electronic structure calculation is  $10^{-8} \text{ E}_h$ , whilst Yagi [2] assumed the step size is proportional to the square-root of the harmonic frequencies, and proposed the dimensionless step size

$$\delta y_i = \sqrt{\frac{w_i}{\hbar}} q_i \quad (39)$$

where  $w_i$  is the angular frequency. Later, in the same paper, the authors observe that the use of this equation is not always possible because of numerical problems, and adopt a uniform value of  $\delta y = 0.5$  for all modes. This corresponds to a step size of approximately  $0.12 a_0$  for the bending mode in water. Boese et al. [44] considered several strategies, similar to those above, for determining the step size for DFT calculations. They compared the calculated frequencies using both fixed and variable step sizes with values obtained using Richardson extrapolation and favoured the use of a variable step size that depends on both the reduced mass,  $\mu_i$ , and harmonic frequency:

$$\delta y_i \propto \sqrt{\frac{\mu_i}{\omega_i}} \quad (40)$$

The plentitude of suggested step sizes is because the numerical derivatives must be computed using finite-precision values, a factor which is curiously absent in the above recommendations. The total error associated with numerical finite-difference methods consists of truncation error, which arises from ignoring higher derivatives in the Taylor series expansion, and round-off error, which depends on the accuracy threshold of the computed molecular property (energy, gradient, etc.). However, because the finite-difference schemes involve differences of these quantities, the effects of cancellation must also be taken into account.

The EGH formula for the  $\eta_{iii}$  derivatives can be rewritten:

$$\eta_{iii} = \frac{1}{h^2} \left( E_{-1,0}^{(1,0)} - E_{0,0}^{(1,0)} \right) + \frac{1}{h^2} \left( E_{1,0}^{(1,0)} - E_{0,0}^{(1,0)} \right) + \frac{h^2}{12} \eta^{(5,0)} + \dots \quad (41)$$

The truncation error is dominated by the leading order term which, if we assume the fifth-order derivatives are  $\mathcal{O}(1)$ , is  $h^2/12$ . The round-off error associated with each of the terms

**Table 3** Timings for calculations required to generate the TFF and the 4MR derivatives at the B3LYP/6-31G(d) level of theory using energy-only gradient-only, Hessian-only and the EGH scheme

Molecule	Methane	Ethane	Propane	Butane	Pentane	Hexane	Heptane
Atoms	5	8	11	14	17	20	23
Modes	9	18	27	36	45	54	63
Time for single point calculation (s) using the B3LYP/6-31G(d) <sup>a</sup>							
Energy	0.89	2.41	6.80	13.31	28.70	44.44	62.60
Gradient	0.32	0.88	2.95	6.36	12.16	19.25	28.49
Hessian	10.75	51.58	167.34	382.25	733.43	1229.04	1852.94
Number of grid points needed for the TFF							
Energy	181	685	1513	2665	4141	5941	8065
Gradient	181	685	1513	2665	4141	5941	8065
Hessian	19	37	55	73	91	109	127
EGH	91	343	757	1333	2071	2971	4033
Total time required for the TFF (days)							
Energy	0.002	0.019	0.119	0.411	1.376	3.056	5.843
Gradient	0.003	0.026	0.171	0.607	1.958	4.379	8.503
Hessian	0.003	0.023	0.111	0.334	0.803	1.607	2.816
EGH	0.001	0.011	0.063	0.215	0.709	1.567	2.986
Number of grid points needed for 4MR							
Energy	3157	57397	308521	1007305	2509501	5275837	9872017
Gradient	853	7213	24913	59785	117661	204373	325753
Hessian	91	343	757	1333	2071	2971	4033
EGH	259	1975	6607	15613	30451	52579	83455
Total time required for the 4MR (days)							
Energy	0.033	1.601	24.282	155.176	833.596	2713.640	7152.641
Gradient	0.012	0.275	2.811	13.611	55.644	150.654	343.436
Hessian	0.012	0.214	1.525	6.103	18.268	43.791	89.414
EGH	0.004	0.076	0.748	3.559	14.409	38.773	88.007

<sup>a</sup> These calculations were run on a 1.6 Ghz Itanium2 machine

in parentheses is  $2\varepsilon_G$  where  $\varepsilon_G$  is the precision of the gradient information. The cancellation error can be estimated by considering a one-sided finite-difference expression for the second derivative

$$\eta_{ii} = \frac{1}{h} \left( E_{0,0}^{(1,0)} - E_{-1,0}^{(1,0)} \right) + \frac{h}{2} \eta^{(3,0)} + \dots \quad (42)$$

If we assume the  $\eta_{ii}$  terms are  $\mathcal{O}(1)$ , then it follows that each of the terms in parentheses in (41) is  $\mathcal{O}(h)$  and therefore  $|\log(h)|$  digits of precision are lost through cancellation. This gives an effective error of  $\varepsilon_G/h$  for the terms in parentheses and results in the following expression for the total error that must be minimised with respect to the step size  $h$

$$\delta_{iii} = \frac{4\varepsilon_G}{h^3} + \frac{h^2}{12} \quad (43)$$

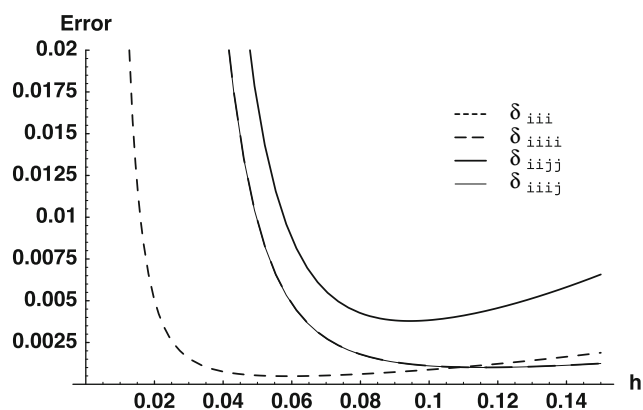
Of course, each of the EGH formulae has different round-off and truncation errors, and will therefore have different

optimal step sizes. In practice it is not possible to use more than one step size to compute the derivatives and a compromise must be made. Figure 2 shows the behaviour of the total error in each of the EGH formulae as a function of the step size,  $h$ . From this plot it is clear that the largest error is incurred by the  $\eta_{ijj}$  derivatives. If we wish to minimise the maximum error in our derivatives, then we must choose  $h$  to minimise the error in Eq. (36), which is given by

$$\delta_{ijj} = \frac{8\varepsilon_E}{h^4} + \frac{10\varepsilon_G}{h^4} + \frac{2\varepsilon_H}{h^2} + \frac{17h^2}{60} \quad (44)$$

where  $\varepsilon_E$  and  $\varepsilon_H$  are the precisions of the the energy and Hessian information, respectively, and where we have assumed the sixth-order derivatives are all  $\mathcal{O}(1)$ . Solving this equation with the estimates  $\varepsilon_E = 10^{-11}$  and  $\varepsilon_G = \varepsilon_H = 10^{-8}$  yields an optimal step size of  $0.1a_0$  for the EGH scheme. If we assume  $\varepsilon_E \ll \varepsilon_G$ , then an approximate step size can be obtained from the simplified expression  $2\sqrt[6]{\varepsilon_G}$ . Although some of the adaptive step sizes are as large as our value, most





**Fig. 2** Total error estimates for computing the various derivatives via the EGH scheme as a function of the step size ( $\varepsilon_E = 10^{-11}$ ,  $\varepsilon_G = \varepsilon_H = 10^{-8}$ ). Note that the error function for the  $\eta_{ij}$  derivatives is the same as that for  $\eta_{iii}$ , and the error functions for  $\eta_{iiii}$  and  $\eta_{iiij}$  only differ by  $6\varepsilon_H h^{-2}$  and appear indistinguishable on this plot

recommendations are smaller. The reason our value, which has been optimised for the EGH scheme, is larger is because of the use of gradient information in the formulae. Because the gradients are calculated close to a stationary point, they are very small and we therefore have to step out further to reduce the cancellation error.

## 5 Results

The TOSH method, (21), and the EGH formulae, (32)–(36), for computing third- and fourth-order derivatives have been implemented within the Q-CHEM 3.0 package [45], which was used to generate the TOSH, VPT2 and VCI results in this Section. All derivatives were calculated using the EGH expressions with the recommended step size of  $0.1a_0$ . The VSCF results were obtained from the GAMESS [46] package using the default step size, which is based on the harmonic frequency [see Eq. (40)].

In order to compare the TOSH approach with other molecular vibrational theories (MVT), we used high-level VCI rather than experimental values as our ‘exact’ results. This isolates the errors due to the MVT from those due to the level of electronic structure theory, size of the basis set, accuracy of derivatives, and, in the case of DFT calculations, quality of the quadrature grid. VCI( $n$ ) calculations ( $n = 1, \dots, 7$ ) were performed on all the tri- and tetra-atomic systems in the set considered by Scott et al. [47] using the HF/STO-3G PESs. Higher levels of VCI theory were not considered due to their prohibitive memory requirements for the tetra-atomic systems. In the case of HCN, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S<sub>2</sub>, HCCCl, HCCF, HCCH, HNCO and SO<sub>3</sub> the contribution from seven-quanta configurations was greater than  $5\text{ cm}^{-1}$  and the VCI calculations were deemed not to have converged and the systems

removed from our set. The HCO and NO<sub>2</sub> radicals were also deleted as we encountered SCF convergence problems when trying to compute the VSCF results. The remaining systems are listed in Table 4, which shows the mean absolute deviations between the anharmonic shifts computed using VCI(7) and various levels of vibrational theory. The results have been averaged over all the modes in each molecule.

The performances of the TOSH, VPT2 and VSCF methods are strikingly similar both from an overall perspective, where they all agree to within  $10\text{ cm}^{-1}$  of the VCI(7) results, and on an individual molecule basis, where their successes and failures tend to mirror one another. The molecules for which the performance of these methods is the poorest, H<sub>2</sub>CO, H<sub>2</sub>O, NH<sub>3</sub> and PH<sub>3</sub>, all have large anharmonic corrections which, on closer inspection of the individual modes, arise from the X–H stretches in these systems. TOSH is based on VPT2 theory and, therefore, it is unsurprising to see similar results for these methods. Notable exceptions include COCl<sub>2</sub> and COF<sub>2</sub> whose VPT2 results are adversely affected by the Fermi resonances which occur at this level of theory. For COCl<sub>2</sub>, the C–O stretch ( $2,130\text{ cm}^{-1}$ ) is approximately twice the asymmetric stretching mode ( $1,061\text{ cm}^{-1}$ ) and for COF<sub>2</sub>, the C–O stretch ( $2,168\text{ cm}^{-1}$ ) is approximately twice the symmetric stretching mode ( $1,075\text{ cm}^{-1}$ ). TOSH is unaffected by these resonances and out-performs VPT2 for these two systems with average errors of 22 and  $12\text{ cm}^{-1}$ , respectively. The error for the TOSH results is never more than  $10\text{ cm}^{-1}$  larger than the VPT2 results, with the worst relative performance occurring for NH<sub>3</sub>. We note that this system has the largest anharmonic corrections and also has one of the most slowly converging VCI series in the table.

The total cost of computing the anharmonic corrections is dominated by the cost of computing the force field which, in turn, depends on the efficiency of the finite-difference scheme and how efficiently the program can compute the energies and/or gradients and second derivatives. Using the EGH expressions for the derivatives, the PFF is approximately twice as expensive to compute as the TFF, making TOSH a cost-effective alternative to VPT2 theory. The 4MR force field is a factor of  $m$  more expensive than the PFF, where  $m$  is the number of modes in the molecule.

The VCI results highlight the importance of avoiding odd low-levels of theory. VCI(1) allows mixing and lowering of the energy for the first excited state, but not the ground state, an unbalanced situation that results in an error that is worse than even the harmonic approximation. VCI(3) is similarly unbalanced and has an error larger than VCI(2), but beyond this the effects of parity are less significant. As mentioned, the VCI( $n$ ) series for several molecules did not converge by  $n = 7$  and it is worth stressing that the convergence of the VCI series is not guaranteed on a QFF. In fact many molecular quartic potentials are unbounded and therefore only exhibit pseudo-solutions whose existence is

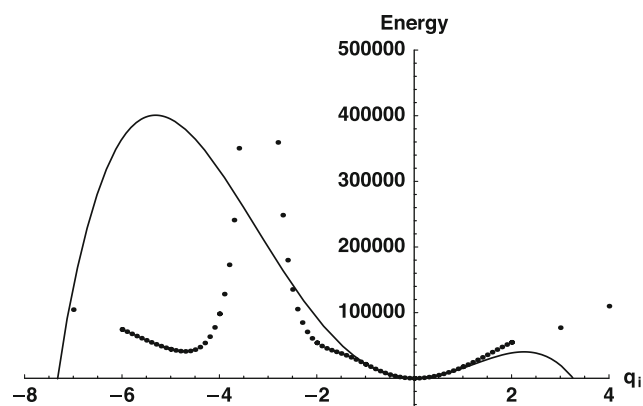
**Table 4** Mean absolute deviations ( $\text{cm}^{-1}$ ) from VCI(7) in the vibrational modes using different levels of molecular vibrational theory

Force Field	HFF	TFF	PFF	4MR				VCI(1)	VCI(2)	VCI(3)	VCI(4)	VCI(5)	VCI(6)
	Harmonic	TOSH	VPT2	VSCF	PT2-VSCF	CI-VSCF							
AlCl <sub>3</sub>	3	1	1	2	1	1	3	1	1	0	0	0	
BF <sub>3</sub>	10	1	0	2	1	3	23	3	5	0	0	0	
C <sub>2</sub> Cl <sub>2</sub>	9	2	1	3	1	8	7	4	11	1	0	0	
C <sub>2</sub> N <sub>2</sub>	15	10	3	11	9	22	29	17	33	5	1	1	
<sup>1</sup> CH <sub>2</sub>	63	13	10	10	12	11	152	15	21	3	0	0	
<sup>3</sup> CH <sub>2</sub>	73	12	12	8	13	15	154	21	30	4	1	0	
CO <sub>2</sub>	6	3	1	5	0	7	19	6	10	1	0	0	
COCl <sub>2</sub>	16	7	29	7	22	14	9	10	7	1	0	0	
COCIF	8	3	0	3	2	3	17	4	6	1	0	0	
COF <sub>2</sub>	19	4	16	4	4	5	20	4	7	5	0	0	
COS	9	8	6	8	1	7	21	6	10	1	0	0	
CS <sub>2</sub>	4	3	1	4	0	3	12	2	3	0	0	0	
CSCl <sub>2</sub>	20	1	0	1	0	1	11	1	3	0	0	0	
CSF <sub>2</sub>	6	1	0	2	0	3	17	2	4	0	0	0	
Cl <sub>2</sub> O	10	1	0	1	0	1	12	1	2	0	0	0	
CICN	9	7	3	10	2	12	22	10	17	3	1	0	
ClF <sub>3</sub>	19	1	0	1	0	2	18	2	3	0	0	0	
CINO	13	2	0	2	1	1	21	3	5	0	0	0	
CINO <sub>2</sub>	6	3	0	4	1	6	32	5	8	1	0	0	
CISN	8	1	0	1	1	1	14	1	3	0	0	0	
F <sub>2</sub> NH	43	23	19	22	11	23	49	18	26	5	1	0	
F <sub>2</sub> O	10	2	0	2	0	2	23	2	3	0	0	0	
F <sub>2</sub> SO	8	2	2	1	1	2	27	3	4	1	0	0	
FCN	12	5	1	6	1	7	10	6	11	1	0	0	
H <sub>2</sub> CO	46	16	7	16	15	18	79	17	29	4	0	0	
H <sub>2</sub> O	97	17	14	14	18	16	221	23	30	5	0	0	
H <sub>2</sub> S	53	8	4	6	7	8	133	15	18	3	0	0	
HN <sub>3</sub>	63	9	15	11	13	23	91	34	45	13	5	3	
HOCl	51	14	4	15	5	8	84	17	25	4	0	0	
HOF	51	13	4	13	4	6	94	15	23	3	0	0	
N <sub>2</sub> F <sub>2</sub>	10	2	0	2	1	3	21	2	5	0	0	0	
N <sub>2</sub> O	32	4	4	5	1	9	48	17	18	4	1	0	
NCl <sub>2</sub> F	5	2	2	2	2	3	11	2	3	0	0	0	
NCIF <sub>2</sub>	6	1	0	2	0	2	14	2	3	0	0	0	
NF <sub>3</sub>	7	1	0	2	1	3	18	2	4	0	0	0	
NH <sub>3</sub>	111	27	17	30	13	38	188	37	49	12	3	2	
NSF	5	0	0	0	0	0	15	1	2	0	0	0	
O <sub>3</sub>	35	8	2	9	0	6	57	9	12	2	0	0	
ONF	12	1	0	1	1	1	30	3	4	0	0	0	
PCl <sub>3</sub>	2	1	0	1	0	1	6	1	1	0	0	0	
PF <sub>3</sub>	4	1	1	1	1	2	10	1	2	0	0	0	
PH <sub>3</sub>	81	16	15	40	28	43	108	20	23	4	1	0	
S <sub>2</sub> F <sub>2</sub>	4	1	0	2	1	3	6	2	5	0	0	0	
SCL <sub>2</sub>	3	1	0	1	0	1	7	1	1	0	0	0	
SO <sub>2</sub>	18	3	1	4	0	3	28	4	5	1	0	0	

**Table 4** continued

Force Field	HFF	TFF	PFF	4MR								
	Harmonic	TOSH	VPT2	VSCF	PT2-VSCF	CI-VSCF	VCI(1)	VCI(2)	VCI(3)	VCI(4)	VCI(5)	VCI(6)
SOCl <sub>2</sub>	12	2	2	2	1	2	21	4	7	1	0	0
Average	22.5	5.6	4.6	6.7	4.5	8.3	39.4	8.0	12.0	2.1	0.4	0.22

All results are derived from a HF/STO-3G PES



**Fig. 3** Cross section of the STO-3G PES for the H<sub>2</sub>O along the bending normal coordinate. The energy is given in wavenumbers and the displacement is in atomic units. The dots indicate the exact PES and the solid line is the 4MR approximation

due to the incompleteness of the basis used to expand the nuclear wavefunction. This is made clearer by Fig. 3 which shows a cross section of the HF/STO-3G PES for the water molecule taken along the bending mode. The singularity in the exact PES occurs when the hydrogen atoms coalesce. The lack of symmetry about this point is because the cross section is taken along the normal coordinate and not the curvilinear coordinate associated with the exact motion of the nuclei. The plot shows that the PES is being accurately modelled around the equilibrium geometry ( $\delta q = 0$ ) and will therefore yield accurate low-lying vibrational states. However, the height of the artifactual barrier seen around  $\delta q \approx 2.3$  is only  $40,000 \text{ cm}^{-1}$  and is thus only able to bind approximately 20 vibrational levels. For this system, the VCI( $n$ ) series appears to converge by  $n = 7$  as the unphysical parts of the PES are not sampled. Nevertheless, it is clear that the VCI series cannot converge for this potential as more quanta are included. For the deleted systems the picture is similar because in all these systems there exist directions along which the potential is only pseudo-bound. For example, although we did not perform a comprehensive search, were able to find barrier heights on the QFF of around  $14,000 \text{ cm}^{-1}$  for the HCN molecule. With frequencies as high as  $3,900 \text{ cm}^{-1}$  in this system, it is clear that lower orders of VCI will exhibit problems.

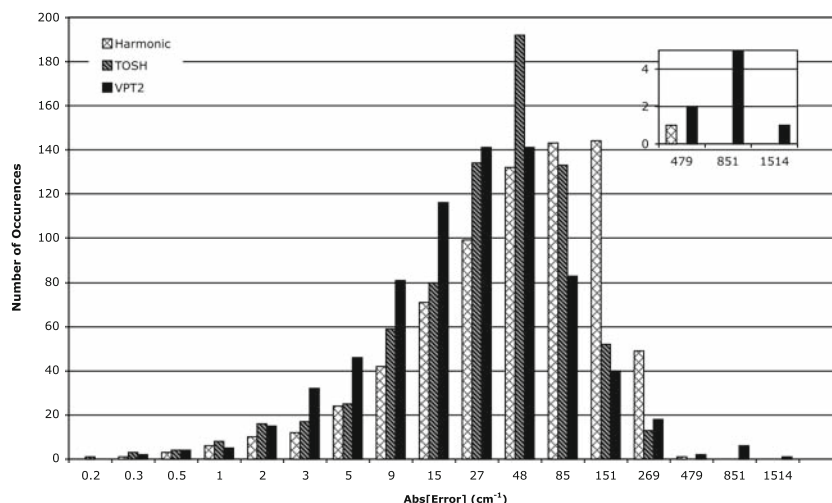
To gauge the ability of TOSH to predict experimental frequencies, we considered the 97 molecules in the D2 set

listed in Table 2. This set is based on that of Scott [47], but does not include systems with a C<sub>3</sub> rotation axis. These systems were excluded because the octahedral symmetry of the DFT quadrature grids yields optimised structures that have the incorrect point group symmetry [48]. Harmonic, TOSH and VPT2 frequencies were computed using PESs obtained using B3LYP/6-31G(d) and the SG-1[48] quadrature grid, and comparisons made with the experimental values. Figure 4 shows the distribution of errors for each of the three methods. Note that we use a logarithmic scale for the error values and include an enlargement of the 398–1,585  $\text{cm}^{-1}$  region to show the few systems with very large errors. The mean error for the harmonic approximation is  $58 \text{ cm}^{-1}$  and both TOSH and VPT2 are able to improve on this value significantly with mean errors of 38 and  $39 \text{ cm}^{-1}$ , respectively. What can not be seen from the plot is that all three methods have a tendency to overestimate the true frequencies. Although the mean errors for TOSH and VPT2 are similar, Fig. 4 clearly shows they have different distributions with most of the VPT2 errors less than those of TOSH, but with a few outlying errors where the method has failed catastrophically. These catastrophic errors arise because of Fermi resonances and give the VPT2 distribution a long upper tail. The VPT2 errors are as large as  $1,452 \text{ cm}^{-1}$ , which occurs for the CH<sub>2</sub> twisting mode in CH<sub>3</sub>CH<sub>2</sub>F. This mode has a harmonic frequency of  $1,311.72 \text{ cm}^{-1}$  and it resonates with the CCF deformation ( $\omega = 406.41 \text{ cm}^{-1}$ ) and CF stretch ( $\omega = 905.18 \text{ cm}^{-1}$ ) modes. The sum of these last two modes is  $1,311.59 \text{ cm}^{-1}$  and combines with the CH<sub>2</sub> twisting mode to give a small denominator in the last term in Eq. (22). TOSH does not suffer the same problems with resonant frequencies and all the errors are less than  $270 \text{ cm}^{-1}$ .

## 6 Conclusion

We have presented a computationally efficient approach for computing anharmonic corrections to vibrational frequencies. By shifting the centre of the basis functions used to expand the nuclear wavefunction, it is possible to incorporate anharmonic effects directly into the zeroth-order wavefunction without having to resort to expensive configuration interaction expansions. For PESs generated at the B3LYP/6-31G(d) level of theory, the performance of TOSH is only slightly inferior to VPT2, but it is at least a factor of two cheaper,

**Fig. 4** Simplified distributions of errors between experimental and calculated frequencies for molecules in the D2 set (see Table 2) using the B3LYP/6-31G(d) PES



depending on the finite-difference scheme used to compute the higher-order derivatives. Furthermore, because the TOSH energy expression is based on first-order perturbation theory, it does not suffer from the problems associated with Fermi resonances, which plague the VPT2 approach. We have coupled the TOSH method with an optimised finite-difference scheme, EGH, which computes only the most important third- and fourth-order derivatives. By judicious use of energy, gradient and Hessian information, the number of different geometries that need to be considered when computing the QFF can be significantly reduced, thus lowering the cost of the most expensive aspect of computing anharmonic vibrational frequencies.

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## Appendix

The three-mode coupling derivatives,  $\eta_{ijk}$  and  $\eta_{ijkl}$  can be obtained using the same number of geometries as the two-mode EGH method, except that the gradient of the energy must be computed at all the non-axial points. Thus, a total of

$$N_{\text{EGH}}^{3\text{MR}} = 1 + 2m + 2 \binom{m}{2} \quad (45)$$

energy and gradient calculations are required, in addition to the single Hessian calculation. The following scheme can be used to compute these three-mode derivatives:

$$\begin{aligned} \eta_{ijk} = & \frac{1}{2h^2} \left( 2E_{0,0,0}^{(1,0,0)} - E_{0,0,-1}^{(1,0,0)} - E_{0,0,1}^{(1,0,0)} - E_{0,-1,0}^{(1,0,0)} \right. \\ & \left. + E_{0,-1,-1}^{(1,0,0)} - E_{0,1,0}^{(1,0,0)} + E_{0,1,1}^{(1,0,0)} \right) \\ & + \frac{h^2}{12} \left( 2\eta^{(1,1,3)} + 3\eta^{(1,2,2)} + 2\eta^{(1,3,1)} \right) + \dots \quad (46) \end{aligned}$$

$$\begin{aligned} \eta_{iijk} = & \frac{1}{2h^3} \left( E_{-1,-1,0}^{(0,0,1)} - E_{-1,0,0}^{(0,0,1)} - E_{0,-1,0}^{(0,0,1)} + E_{0,1,0}^{(0,0,1)} \right. \\ & + E_{1,0,0}^{(0,0,1)} - E_{1,1,0}^{(0,0,1)} + E_{-1,0,-1}^{(0,1,0)} - E_{-1,0,0}^{(0,1,0)} \\ & - E_{0,0,-1}^{(0,1,0)} + E_{0,0,1}^{(0,1,0)} + E_{1,0,0}^{(0,1,0)} - E_{1,0,1}^{(0,1,0)} - E_{0,-1,-1}^{(1,0,0)} \\ & \left. + E_{0,-1,0}^{(1,0,0)} + E_{0,0,-1}^{(1,0,0)} - E_{0,0,1}^{(1,0,0)} - E_{0,1,0}^{(1,0,0)} + E_{0,1,1}^{(1,0,0)} \right) \\ & + \frac{h^2}{12} \left( \eta^{(1,2,3)} + \eta^{(1,3,2)} + \eta^{(2,1,3)} + \eta^{(2,3,1)} \right. \\ & \left. + \eta^{(3,1,2)} + \eta^{(3,2,1)} + \eta^{(4,1,1)} \right) + \dots \quad (47) \end{aligned}$$

The four-mode coupling derivatives requires gradients at a number of points that scales as  $m^3$ :

$$N_{\text{EGH}}^{4\text{MR}} = 1 + 2m + 2 \binom{m}{2} + 2 \binom{m}{3} \quad (48)$$

and these can be computed using the following scheme:

$$\begin{aligned} \eta_{ijkl} = & \frac{1}{2h^3} \left( -E_{-1,-1,-1,0}^{(0,0,0,1)} + E_{-1,-1,0,0}^{(0,0,0,1)} + E_{-1,0,-1,0}^{(0,0,0,1)} \right. \\ & - E_{-1,0,0,0}^{(0,0,0,1)} + E_{0,-1,-1,0}^{(0,0,0,1)} - E_{0,-1,0,0}^{(0,0,0,1)} - E_{0,0,-1,0}^{(0,0,0,1)} \\ & + E_{0,0,1,0}^{(0,0,0,1)} + E_{0,1,0,0}^{(0,0,0,1)} - E_{0,1,1,0}^{(0,0,0,1)} + E_{1,0,0,0}^{(0,0,0,1)} \\ & \left. - E_{1,0,1,0}^{(0,0,0,1)} - E_{1,1,0,0}^{(0,0,0,1)} + E_{1,1,1,0}^{(0,0,0,1)} \right) \\ & + \frac{h^2}{12} \left( 2\eta^{(1,1,3,1)} + 3\eta^{(1,2,2,1)} + 2\eta^{(1,3,1,1)} \right. \\ & \left. + 3\eta^{(2,1,2,1)} + 3\eta^{(2,2,1,1)} + 2\eta^{(3,1,1,1)} \right) + \dots \quad (49) \end{aligned}$$

Note that the formulae for  $\eta_{ijk}$  and  $\eta_{ijkl}$  are not symmetric with respect to the coordinates and, therefore, several alternative formulae exist.

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