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Ab Initio Vibrational State Calculations with a Quartic Force Field: Applications to H₂CO, C₂H₄, CH₃OH, CH₃CCH, and C₆H₆

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Abstract

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***Ab initio* vibrational state calculations with a quartic force field: Applications to H₂CO, C₂H₄, CH₃OH, CH₃CCH, and C₆H₆**

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I. INTRODUCTION

Vibrational energy levels comprise one of the most important properties of polyatomic molecules, so prediction of these energy levels from first principles has been an important goal in theoretical chemistry.¹ Recent advances in theoretical methods and computational technologies have made it feasible to calculate harmonic frequencies for polyatomic molecules using quantum chemistry program packages, and there have been a wide variety of applications. When studying highly excited vibrational states or large amplitude vibrations of floppy modes, however, it is important to consider anharmonic effects in the determination of vibrational energy levels. Anharmonic effects have also been of great interest in dynamics calculations, such as vibrational energy relaxation and intramolecular vibrational energy transfer in polyatomic molecules.^{2,3} The development of general theoretical methods beyond the harmonic approximation has therefore been a challenge for theoretical chemistry.

One of the difficulties in vibrational state calculations arises from the fact that the adiabatic potential energy term does not have a general analytic form. Many theoretical studies for triatomic and tetra-atomic molecules have employed curvilinear internal coordinates where the adiabatic potential energy term can be expressed in a rather compact form, although the kinetic energy term has a very complicated form.¹ The Watson Hamiltonian⁴ is written in terms of normal coordinates, in which the kinetic energy term is expressed in a simple general form, while higher-order terms need to be taken into account to represent the adiabatic potential energy

surface (PES) accurately. Note that the harmonic frequencies are obtained by assuming primitive harmonic potentials for each normal mode. Thus, the crux of the problem in vibrational state calculations is how the adiabatic potential energy term is evaluated.

Direct dynamics methodology is one of the solutions to this problem, since the adiabatic potential energy required in dynamics calculations is computed directly through *ab initio* electronic structure calculations. In principle, this approach can be applied to dynamics calculations in general, and practical implementations have made a marked impact in the field of reaction dynamics.^{5–12} Recently, the direct dynamics scheme has been extended to the determination of vibrational energy levels, by employing the discrete variable representation approach¹³ and the vibrational self-consistent field (VSCF) theory.^{14–17} Chaban, Jung, and Gerber¹⁴ have implemented the VSCF (Refs. 18–20) and correlation corrected VSCF (cc-VSCF) (Refs. 21–23) methods within the GAMESS program package²⁴ (referred to as direct VSCF and direct cc-VSCF methods, respectively, in this paper). Following their work, direct VSCF and vibrational configuration interaction (VCI) (Ref. 25) calculations have been carried out by our group¹⁵ and by Irlle and Bowman.¹⁶ Matsunaga, Chaban and Gerber¹⁷ have recently proposed a degenerate perturbation theory for adding correlation corrections to the VSCF results, which is now the default cc-VSCF method in GAMESS. In spite of the large computational cost in direct approaches, successful applications are increasing in number.^{26–34} A recent comparison³⁴ of the effect of improving the electronic structure treatment has shown that for both

H₂O and the highly anharmonic F⁻(H₂O) that improving the atomic basis set from TZP to aug-cc-pVTZ is worth 30–40 cm⁻¹, and improving the electronic structure from MP2 to CCSD(T) has a 20–30 cm⁻¹ effect on the results. These methods have made it possible to carry out quantitative calculations of the vibrational energy levels for polyatomic systems.

The direct dynamics approach entails extensive computational costs for large molecules, so it is important to develop more efficient theoretical methods to evaluate the adiabatic potential energy term. There have been several attempts to determine highly accurate potential energy functions (PEF) for vibrational state calculations.^{15,35–41} Xie and Bowman³⁷ have proposed a new least-squares procedure to fit the potential, gradient, and Hessian data of the function, and applied this method to vibrational state calculations for H₂O. Global fitting procedures in terms of normal coordinates have been developed by Carter and co-workers,^{38,39} and extensively tested for vibrational state calculations of H₂CS. Maeda and Ohno⁴⁰ have proposed a new method to construct a full-dimensional PEF using a polar coordinate interpolation technique. This approach successfully generated highly accurate PEFs for H₂O and H₂CO. Ruden, Taylor, and Helgaker⁴¹ have recently presented an automatic scheme to generate a quartic force field (QFF) by numerical differentiations of the adiabatic potential energy. The method has been applied to AlH₃ to generate a highly accurate QFF based on the CCSD(T) level of theory.

Previously,^{15,35,36} we employed a reduced QFF for vibrational state calculations. This QFF includes terms that contain up to three coordinate couplings in a fourth-order Taylor expansion PEF in terms of normal coordinates. Third- and fourth-order derivatives were evaluated by finite differentiations of elements of the Hessian matrices. The accuracy of this 3MR-QFF method has been carefully examined through comparisons of the VCI/3MR-QFF results and the corresponding direct VCI results. It was shown that VCI/3MR-QFF calculations reproduced fundamental frequencies, overtones, and combination bands of H₂CO with an absolute error of ~8 cm⁻¹.³⁶ This feature of 3MR-QFF is very promising since it has a general functional form and can be constructed with less computational effort than the direct VSCF (and VCI) calculations. This 3MR-QFF approach has been employed successfully in VCI calculations for methane by Burcl, Carter, and Handy.⁴² Very recently, Barone has calculated fundamental frequencies, zero-point energy, and thermodynamic functions based on the 3MR-QFF approach for a number of molecules of small and medium size using the density functional theory.^{43,44}

In this paper, *n*-mode coupling representations which include the terms up to *n* coordinate couplings in the QFF of the quartic force field (*n*MR-QFF) are presented. The computational scheme to evaluate third- and fourth-order derivatives by finite differentiations of the energy, instead of the Hessian matrices, is fully described. This approach has been implemented into GAMESS, and cc-VSCF 2MR-QFF calculations have been carried out for several molecules as demonstrations. The results are compared with the corresponding direct cc-VSCF results.

II. N-MODE COUPLING REPRESENTATION OF QUARTIC FORCE FIELD

The vibrational Hamiltonian of nonlinear *N*-atom molecules can be written in terms of normal coordinates as,

$$H = -\frac{1}{2} \sum_{i=1}^f \frac{\partial^2}{\partial Q_i^2} + V(\mathbf{Q}), \quad (1)$$

where \mathbf{Q} and V denote $f (= 3N - 6)$ normal coordinates and the adiabatic potential energy term, respectively, and vibration-rotation coupling terms are neglected. Recently, Carter, Culik, and Bowman⁴⁵ have proposed an efficient way to expand the adiabatic potential energy term based on the number of couplings of normal coordinates. The approximate PES including up to *n* coordinate couplings is referred to as $V^{(n)}$ (*n*-mode coupling representation: *n*MR); in this context, the exact PES can be denoted as $V^{(f)}$. $V^{(n)}$ for $n = 1, 2, 3$, and 4 are shown below:

$$V^{(1)} = \sum_{i=1}^f V_i(Q_i), \quad (2)$$

$$V^{(2)} = \sum_{i>j}^f V_{ij}(Q_i, Q_j) - (f-2)V^{(1)}, \quad (3)$$

$$V^{(3)} = \sum_{i>j>k} V_{ijk}(Q_i, Q_j, Q_k) - (f-3)V^{(2)} - \frac{(f-3)(f-2)}{2} V^{(1)}, \quad (4)$$

$$V^{(4)} = \sum_{i>j>k>l}^f V_{ijkl}(Q_i, Q_j, Q_k, Q_l) - (f-4)V^{(3)} - \frac{(f-4)(f-3)}{2} V^{(2)} - \frac{(f-4)(f-3)(f-2)}{6} V^{(1)}, \quad (5)$$

where V_i , V_{ij} , V_{ijk} , and V_{ijkl} denote a one-, two-, three-, and four-dimensional PES in the subspace of the related normal coordinates, respectively. The *n*MR-PES has been introduced in recent VSCF and post-VSCF calculations.^{14–16,38,39,45}

In the direct VSCF method based on an *n*MR-PES, the energies at quadrature points are calculated directly from electronic structure calculations for each subspace of *n* normal coordinates. The number of quadrature points is $\sim (f!/n!(f-n)!) \times M^n$, where M is the number of grid points along each normal coordinate. For example, the number of quadrature points for VSCF calculations with a 2MR-PES is written as,

$$N_{\text{grid}}^{(2)} = 1 + fM + \frac{f(f-1)}{2} M^2. \quad (6)$$

The major drawback of the direct VSCF method is its unfavorable scaling of the computational task, which increases very rapidly as the number of atoms increases or as higher-order coupling terms are included.

In the n MR-PES scheme, a QFF can be reduced according to the number of couplings of the normal coordinates. The QFF is written as

$$V^{\text{QFF}}(\mathbf{Q}) = V_0 + \frac{1}{2} \sum_{i=1}^f h_i Q_i^2 + \frac{1}{6} \sum_{i,j,k}^f t_{ijk} Q_i Q_j Q_k + \frac{1}{24} \sum_{i,j,k,l}^f u_{ijkl} Q_i Q_j Q_k Q_l, \quad (7)$$

where V_0 , h_i , t_{ijk} , and u_{ijkl} denote the potential energy and its second-, third-, and fourth-order derivatives with respect to the normal coordinates, respectively, at the equilibrium geometry. In the n -mode coupling representation, $V^{\text{QFF}}(\mathbf{Q})$ is partitioned as,

$$V_{\text{QFF}}^{(1)} = V_0 + \sum_{i=1}^f \left[\frac{1}{2} h_i Q_i^2 + \frac{1}{6} t_{iii} Q_i^3 + \frac{1}{24} u_{iiii} Q_i^4 \right], \quad (8)$$

$$V_{\text{QFF}}^{(2)} = V_{\text{QFF}}^{(1)} + \sum_{i \neq j}^f \left[\frac{1}{2} t_{ijj} Q_i Q_j^2 + \frac{1}{6} u_{ijjj} Q_i Q_j^3 \right] + \frac{1}{4} \sum_{i < j}^f u_{iijj} Q_i^2 Q_j^2, \quad (9)$$

$$V_{\text{QFF}}^{(3)} = V_{\text{QFF}}^{(2)} + \sum_{i < j < k}^f t_{ijk} Q_i Q_j Q_k + \frac{1}{2} \sum_{i \neq j < k}^f u_{iijk} Q_i^2 Q_j Q_k, \quad (10)$$

$$V_{\text{QFF}}^{(4)} = V_{\text{QFF}}^{(3)} + \sum_{i < j < k < l}^f u_{ijkl} Q_i Q_j Q_k Q_l, \quad (11)$$

where $V_{\text{QFF}}^{(n)}$ denotes a reduced QFF including up to n coordinate couplings [referred to as an n -mode coupling representation quartic force field (n MR-QFF)]. Note that 4MR-QFF is equivalent to the full QFF in Eq. (7), since the coupling of the normal coordinates is at most four in the QFF.

The third- and fourth-order derivatives of the energy in Eqs. (8)–(11) can be obtained through numerical differentiations. In our previous study, we presented an algorithm to evaluate these coefficients by numerical differentiations of elements of the Hessian matrices.¹⁵ In the present study, these coefficients are evaluated by numerical differentiations of the energy, because analytical Hessian matrices are not always available in electronic structure calculations, especially at higher levels of theory. The coefficients in the 1MR-QFF, t_{iii} and u_{iiii} , are calculated by,

$$t_{iii} = \frac{1}{8 \delta_i^3} [V(+3 \delta_i) - 3V(+\delta_i) + 3V(-\delta_i) - V(-3 \delta_i)], \quad (12)$$

$$u_{iiii} = \frac{1}{\delta_i^4} [V(+2 \delta_i) - 4V(+\delta_i) + 6V_0 + 4V(-\delta_i) - V(-2 \delta_i)], \quad (13)$$

TABLE I. The number of grid points in the direct VSCF method based on 2MR-PES ($M=12$) and the number of points required to determine 2MR-QFF and 4MR-QFF for N atom molecules.

Molecule	N	f	$N_{\text{(grid)}}^{(2)}$	$N_{\text{QFF}}^{(2)}$	$N_{\text{QFF}}^{(4)}$
H ₂ CO	4	6	2233	217	617
C ₂ H ₄ , CH ₃ OH	6	12	9649	865	10 545
CH ₃ CCH	7	15	15 301	1351	26 831
C ₆ H ₆	12	30	63 001	5401	476 361

where δ_i denotes the differential step for the i th normal coordinate, and $V(n \delta_i)$ denotes the energy at $Q_i = n \delta_i$, with other coordinates fixed to zero. The coefficients in the 2MR-QFF, t_{iij} , u_{iijj} , and u_{iijj} , are calculated by

$$t_{iij} = \frac{1}{2 \delta_i^2 \delta_j} \{ [V(+\delta_i, +\delta_j) + V(-\delta_i, +\delta_j) - 2V(+\delta_j)] - [V(+\delta_i, -\delta_j) + V(-\delta_i, -\delta_j) - 2V(-\delta_j)] \}, \quad (14)$$

$$u_{iijj} = \frac{1}{16 \delta_i^3 \delta_j} \{ [V(+3 \delta_i, +\delta_j) - 3V(+\delta_i, +\delta_j) + 3V(-\delta_i, +\delta_j) - V(-3 \delta_i, +\delta_j)] - [V(+3 \delta_i, -\delta_j) - 3V(+\delta_i, -\delta_j) + 3V(-\delta_i, -\delta_j) - V(-3 \delta_i, -\delta_j)] \}, \quad (15)$$

$$u_{iijj} = \frac{1}{\delta_i^4} \{ [V(+\delta_i, +\delta_j) + V(-\delta_i, +\delta_j) + V(+\delta_i, -\delta_j) + V(-\delta_i, -\delta_j)] - 2[V(+\delta_i) + V(-\delta_i) + V(+\delta_j) + V(-\delta_j)] + 4V_0 \}, \quad (16)$$

where $V(n_i \delta_i, n_j \delta_j)$ denotes the energy at $(Q_i, Q_j) = (n_i \delta_i, n_j \delta_j)$, with other coordinates fixed to zero. The formulas for the remaining coefficients are given in the Appendix. The number of points required to determine all the coefficients in the 2MR-QFF and 4MR-QFF, respectively, are

$$N_{\text{QFF}}^{(2)} = 1 + 6f + 12 \times \frac{f(f-1)}{2}, \quad (17)$$

$$N_{\text{QFF}}^{(4)} = 1 + 6f + 12 \times \frac{f(f-1)}{2} + 8 \times \frac{f(f-1)(f-2)}{6} + 16 \times \frac{f(f-1)(f-2)(f-3)}{24}. \quad (18)$$

Since each of these single point calculations can be done independently of the others, this approach can take advantage of the coarse-grained parallelism in the generalized distributed data interface recently implemented in GAMESS.⁴⁶ Table I gives a comparison of the number of required electronic structure calculations in the direct VSCF method and in determinations of 2MR-QFF and 4MR-QFF for several molecules. These numbers indicate that 2MR-QFF can be constructed with about ten times less computational effort than the direct VSCF calculations. Previously, Ruden, Taylor, and Helgaker,⁴¹ presented a method to generate a full QFF

TABLE II. The fundamental frequencies (in cm^{-1}) of formaldehyde obtained from cc-VSCF/2MR-QFF calculations with different stepsizes δy at the level of MP2/aug-cc-pVTZ.

	$\delta y=0.9$	$\delta y=0.7$	$\delta y=0.5$	$\delta y=0.3$	$\delta y=0.2$
$\nu_1 (a_1)$	2818.3	2827.2	2833.3	2835.8	2829.0
$\nu_2 (a_1)$	1720.4	1721.2	1721.0	1713.9	1685.9
$\nu_3 (a_1)$	1504.9	1505.3	1505.5	1503.9	1496.2
$\nu_4 (b_1)$	1160.3	1160.7	1160.9	1159.5	1237.0
$\nu_5 (b_2)$	2863.6	2870.0	2874.5	2875.3	2865.9
$\nu_6 (b_2)$	1241.6	1242.0	1242.2	1241.7	1158.0

(i.e., 4MR-QFF) by numerical differentiations, so the number of points required to generate 4MR-QFF is nearly the same as their number. The number of points can be greatly reduced by neglecting the three- and four-mode coupling terms in the QFF, as shown in Table I.

Finally we give a technical note on the determination of the stepsize for numerical differentiations. The stepsizes for the respective normal coordinates are determined by a dimensionless reduced coordinate defined by,

$$y_i = \sqrt{\frac{\omega_i}{\hbar}} Q_i, \quad (19)$$

where ω_i and \hbar are the angular frequency for the i th normal mode and Planck's constant divided by 2π , respectively. The same stepsize δy is assigned to all the reduced coordinates, which generates different stepsizes δQ_i for each mode according to Eq. (19). Stability in the numerical differentiations is achieved in this way by taking larger and smaller stepsizes for lower and higher frequency modes, respectively.

III. APPLICATIONS

The code to generate the n MR-QFF has been implemented into GAMESS, and interfaced with the VSCF and cc-VSCF codes. The existing VSCF code can treat two-mode couplings, and thus, cc-VSCF/2MR-QFF calculations were carried out in the present applications. The method was applied to formaldehyde (C_{2v}), ethylene (D_{2h}), methanol (C_s), propyne (C_{3v}), and benzene (D_{6h}). The number of *ab initio* energy calculations required for the generation of 2MR-QFF surfaces are given in Table I. For comparison, direct cc-VSCF calculations were also performed for the above molecules except for benzene. The number of quadrature points along the respective normal coordinates was taken as $M=12$. *Ab initio* electronic structure calculations were carried out at the level of second-order Møller-Plesset perturbation theory (MP2) (Ref. 47) with the aug-cc-pVTZ (Refs. 48 and 49) and cc-pVDZ (Ref. 48) basis sets for formaldehyde and benzene, respectively, and cc-pVTZ (Ref. 49) for the others.

Table II gives the fundamental frequencies of formaldehyde obtained from cc-VSCF/2MR-QFF calculations with different stepsizes δy for numerical differentiations [see Eq. (19)]. It is seen that the dependence of the vibrational energy level on the stepsize is modest, although a very small value

TABLE III. Fundamental frequencies (in cm^{-1}) of formaldehyde obtained from the harmonic approximation, cc-VSCF/2MR-QFF, and the direct cc-VSCF (2MR) calculations at the level of MP2/aug-cc-pVTZ. In parentheses the errors from the experimental values are given in percentage [see Eq. (20)], and the mean errors are given in the last row.

	Harmonic	cc-VSCF/2MR-QFF	Direct cc-VSCF	Expt. ^a
$\nu_1 (a_1)$	2973.7 (6.9)	2833.3 (1.8)	2819.6 (1.4)	2782
$\nu_2 (a_1)$	1752.9 (0.4)	1721.0 (1.4)	1721.5 (1.4)	1746
$\nu_3 (a_1)$	1540.1 (2.7)	1505.5 (0.4)	1504.8 (0.3)	1500
$\nu_4 (b_1)$	1196.9 (2.6)	1160.9 (0.5)	1163.4 (0.3)	1167
$\nu_5 (b_2)$	3047.6 (7.2)	2874.5 (1.1)	2837.4 (0.2)	2843
$\nu_6 (b_2)$	1266.8 (1.3)	1242.2 (0.6)	1241.8 (0.7)	1250
ME ^b	3.5	1.0	0.7	

^aReference 50.

^bMean errors in percentage.

of $\delta y=0.2$ shows divergences. Taking into account these results, a stepsize of $\delta y=0.5$ was employed for numerical differentiations in the following calculations.

Tables III–VII give the fundamental frequencies of formaldehyde, ethylene, methanol, propyne, and benzene, respectively, obtained from the cc-VSCF/2MR-QFF calculations and the direct cc-VSCF calculations (except for benzene), together with the harmonic frequencies and experimental values. Although we focus on the fundamental energy levels in this study, note that the 2MR-QFF potential surfaces can be readily used for the calculations of other vibrational states, such as overtones or combination bands. The errors from the experimental values are given as percentages by

$$\Delta_{\text{error}} = \frac{|\nu - \nu_{\text{expt}}|}{\nu_{\text{expt}}} \times 100. \quad (20)$$

The mean errors are given in the last row. The harmonic frequencies give relatively large mean errors of 2.6%–4.2%. In particular, frequencies for CH and OH stretching vibrations give large errors ranging from 4.6% to 7.4%, indicating large anharmonic effects in these modes. In cc-VSCF/2MR-

TABLE IV. Fundamental frequencies (in cm^{-1}) of ethylene obtained from the harmonic approximation, cc-VSCF/2MR-QFF, and the direct cc-VSCF (2MR) calculations, at the level of MP2/cc-pVTZ. In parentheses the errors from the experimental values are given in percentage [see Eq. (20)], and the mean errors are given in the last row.

	Harmonic	cc-VSCF/2MR-QFF	Direct cc-VSCF	Expt. ^a
$\nu_1 (a_g)$	3197.3(5.7)	3057.5(1.0)	3051.0(0.8)	3026
$\nu_2 (a_g)$	1684.1(3.8)	1644.7(1.3)	1643.9(1.3)	1623
$\nu_3 (a_g)$	1384.1(3.1)	1359.4(1.3)	1358.4(1.2)	1342
$\nu_4 (a_u)$	1076.0(5.2)	1060.5(3.7)	1057.7(3.4)	1023
$\nu_5 (b_{1g})$	3267.8(5.3)	3134.8(1.0)	3126.3(0.8)	3103
$\nu_6 (b_{1g})$	1246.7(0.9)	1234.6(0.1)	1231.9(0.3)	1236
$\nu_7 (b_{2g})$	959.5(1.8)	952.6(1.0)	948.9(0.6)	943
$\nu_8 (b_{1u})$	3179.3(6.4)	3060.5(2.4)	3054.0(2.2)	2989
$\nu_9 (b_{2u})$	3294.6(6.0)	3162.6(1.8)	3154.2(1.5)	3106
$\nu_{10} (b_{2u})$	827.9(0.2)	837.6(1.4)	834.0(1.0)	826
$\nu_{11} (b_{3u})$	1484.7(2.8)	1456.5(0.9)	1455.1(0.8)	1444
$\nu_{12} (b_{3u})$	982.9(3.6)	973.1(2.5)	971.0(2.3)	949
ME ^b	3.7	1.5	1.4	

^aReference 51.

^bMean errors in percentage.

TABLE V. Fundamental frequencies (in cm^{-1}) of methanol obtained from the harmonic approximation, cc-VSCF/2MR-QFF, and the direct cc-VSCF (2MR) calculations, at the level of MP2/cc-pVTZ. In parentheses the errors from the experimental values are given in percentage [see Eq. (20)], and the mean errors are given in the last row.

	Harmonic	cc-VSCF/2MR-QFF	Direct cc-VSCF	Expt. ^a
$\nu_1 (a')$	3880.0(5.4)	3570.0(3.0)	3649.6(0.9)	3681
$\nu_2 (a')$	3183.7(6.1)	3018.9(0.6)	3022.8(0.8)	3000
$\nu_3 (a')$	3053.9(7.4)	2978.9(4.7)	3017.5(6.1)	2844
$\nu_4 (a')$	1536.2(4.0)	1489.8(0.9)	1489.5(0.9)	1477
$\nu_5 (a')$	1495.5(2.8)	1465.8(0.7)	1463.7(0.6)	1455
$\nu_6 (a')$	1387.6(3.2)	1336.3(0.7)	1317.3(2.1)	1345
$\nu_7 (a')$	1102.6(4.0)	1128.2(6.4)	1104.8(4.2)	1060
$\nu_8 (a')$	1067.6(3.4)	1014.0(1.8)	999.6(3.2)	1033
$\nu_9 (a'')$	3122.8(5.5)	2944.2(0.5)	2903.2(1.9)	2960
$\nu_{10} (a'')$	1521.5(3.0)	1485.1(0.6)	1480.7(0.3)	1477
$\nu_{11} (a'')$	1187.5(1.9)	1164.2(0.1)	1163.1(0.2)	1165
$\nu_{12} (a'')$	312.4	NC ^b ...	NC...	200–295
ME ^c	4.2	1.8	1.9	

^aReference 51.

^bNot converged.

^cMean errors in percentage (not including an error in ν_{12}).

QFF calculations, the results are greatly improved with mean errors of 1.0%–1.9%. The errors in the direct cc-VSCF results indicate the accuracy of the cc-VSCF/2MR-PES method at the MP2 level, which are estimated as 0.7%–1.9% mean error. More sophisticated *ab initio* methods than MP2 are likely to improve the coincidence with experiments.³⁴ The close agreement of the cc-VSCF/2MR-QFF to the direct cc-VSCF results indicates the accuracy of the 2MR-QFF. The present results lead to the conclusion that the 2MR-QFF is a highly accurate potential energy function for vibrational state calculations of fundamental frequencies. In the following, we give brief discussions for each molecule.

For formaldehyde we reported previously the detailed analyses of VSCF and VCI calculations for fundamentals, overtones, and combination bands.³⁶ In this molecule CH symmetric and antisymmetric stretching modes, ν_1 and ν_5 , show a large deviation between harmonic frequencies and

TABLE VI. Fundamental frequencies (in cm^{-1}) of propyne obtained from the harmonic approximation, cc-VSCF/2MR-QFF, and the direct cc-VSCF (2MR) calculations, at the level of MP2/cc-pVTZ. In parentheses the errors from the experimental values are given in percentage [see Eq. (20)], and the mean errors are given in the last row.

	Harmonic	cc-VSCF/2MR-QFF	Direct cc-VSCF	Expt. ^a
$\nu_1 (a_1)$	3502.9(5.1)	3359.6(0.8)	3360.8(0.8)	3334
$\nu_2 (a_1)$	3084.4(5.7)	2959.3(1.4)	2950.2(1.1)	2918
$\nu_3 (a_1)$	2151.2(0.4)	2103.8(1.8)	2101.4(1.9)	2142
$\nu_4 (a_1)$	1419.2(2.7)	1397.4(1.1)	1394.2(0.9)	1382
$\nu_5 (a_1)$	949.9(2.0)	941.6(1.1)	940.8(1.0)	931
$\nu_6 (e)$	3169.7(5.4)	2980.4(0.9)	2952.6(1.8)	3008
$\nu_7 (e)$	1499.3(3.3)	1456.1(0.3)	1454.9(0.2)	1452
$\nu_8 (e)$	1063.7(1.0)	1047.2(0.6)	1045.3(0.7)	1053
$\nu_9 (e)$	624.3(1.4)	511.7(19.2)	561.3(11.3)	633
$\nu_{10} (e)$	326.5(0.5)	339.5(3.5)	334.5(2.0)	328
ME ^b	2.6	1.2 ^c	1.1 ^c	

^aReference 51.

^bMean errors in percentage.

^cNot including an error in ν_9 .

TABLE VII. Fundamental frequencies (in cm^{-1}) of benzene obtained from the harmonic approximation and cc-VSCF/2MR-QFF calculations at the level of MP2/cc-pVDZ. In parentheses the errors from the experimental values are given in percentage [see Eq. (20)], and the mean errors are given in the last row.

	Harmonic	cc-VSCF/2MR-QFF	Expt. ^a
$\nu_1 (a_{1g})$	3247.1(6.1)	3096.3(1.1)	3062
$\nu_2 (a_{1g})$	1017.0(2.5)	1003.0(1.1)	992
$\nu_3 (a_{2g})$	1358.8(2.5)	1346.1(1.5)	1326
$\nu_4 (a_{2u})$	685.8(1.9)	728.2(8.2)	673
$\nu_5 (b_{1u})$	3209.7(4.6)	3082.6(0.5)	3068
$\nu_6 (b_{1u})$	1007.0(0.3)	1002.0(0.8)	1010
$\nu_7 (b_{2g})$	961.8(3.3)	1013.0(1.8)	995
$\nu_8 (b_{2g})$	633.9(9.8)	696.8(0.9)	703
$\nu_9 (b_{2u})$	1472.4(12.4)	1444.9(10.3)	1310
$\nu_{10} (b_{2u})$	1163.0(1.1)	1161.4(1.0)	1150
$\nu_{11} (e_{1g})$	858.8(1.2)	878.4(3.5)	849
$\nu_{12} (e_{1u})$	3237.2(5.7)	3090.2(0.9)	3063
$\nu_{13} (e_{1u})$	1504.9(1.3)	1484.8(0.1)	1486
$\nu_{14} (e_{1u})$	1061.3(2.2)	1053.8(1.5)	1038
$\nu_{15} (e_{2g})$	3220.8(5.7)	3075.1(0.9)	3047
$\nu_{16} (e_{2g})$	1649.6(3.4)	1620.0(1.5)	1596
$\nu_{17} (e_{2g})$	1190.6(1.1)	1182.7(0.4)	1178
$\nu_{18} (e_{2g})$	605.6(0.1)	602.9(0.5)	606
$\nu_{19} (e_{2u})$	953.6(2.2)	981.5(0.7)	975
$\nu_{20} (e_{2u})$	400.9(2.2)	408.1(0.5)	410
ME ^b	3.5	1.9	

^aReference 51.

^bMean errors in percentage.

experimental fundamentals. The agreement is improved significantly in the cc-VSCF results shown in Table III. For ν_5 there is a relatively large deviation between cc-VSCF/2MR-QFF and direct cc-VSCF results, i.e., 37.1 cm^{-1} . In our previous study,³⁶ we carried out VCI/3MR-QFF calculations for formaldehyde in which the corresponding deviation was only 6 cm^{-1} . This difference is related to the fact that there is a strong Fermi resonance among ν_5 , $\nu_3 + \nu_6$, and $\nu_2 + \nu_6$, which are coupled through the three-mode coupling terms.

The results for the fundamentals of ethylene are given in Table IV. This application is the most successful one, and the agreement between cc-VSCF/2MR-QFF and direct cc-VSCF results is so good that the largest deviation is at most 8.5 cm^{-1} in ν_5 . Although some modes still show 2%–3% errors compared to the experimental values, better agreement should be obtained by using a higher level of *ab initio* electronic structure method. This can be efficiently attained with the use of the 2MR-QFF.

There are several points to be addressed regarding the results for methanol, presented in Table V. First, VSCF calculations for the first excited state of the 12th mode did not converge. This mode corresponds to the torsional motion of the OH fragment which is expected to be very floppy, and so large amplitude motion should be taken into account to reproduce the fundamental of ν_{12} accurately.⁵² Second, the calculated ν_3 gives a large error of 6.1% in the direct cc-VSCF method, which suggests that perhaps a higher level of electronic structure theory should be used or perhaps high levels of correlation in the vibrational state calculations. Finally, ν_1 calculated by the cc-VSCF/2MR-QFF method gives a large deviation from the corresponding direct cc-VSCF result of

79.6 cm^{-1} , which indicates that QFF is not capable of representing the strong anharmonicity of the OH stretching mode. This defect, however, may be removed by the interpolation of the QFFs defined at several points in the configuration space, as demonstrated for H_2O and H_2CO in our previous study.^{35,36}

The results for propyne are given in Table VI. ν_9 is calculated to be 561.3 cm^{-1} in the direct cc-VSCF calculations with a large error of 11.3% relative to the experimental value of 633 cm^{-1} . The fundamental frequency of ν_9 was evaluated to be 631.7 cm^{-1} at the VSCF level of theory. These results reflect a divergence in the perturbation theoretical treatment, where the first- and second-order corrections are 7.4 and 70.1 cm^{-1} , respectively. The calculated VSCF/2MR-QFF ν_9 is 635.9 cm^{-1} , which agrees well with the direct VSCF result as well as with the experimental value, while the cc-VSCF result is in a poor agreement with both of them. The degenerate space for the cc-VSCF calculation in GAMESS is taken so as to include excitation of a single mode to first excited level for all degrees of freedom.¹⁷ In the present case, the first excited level of Q_9 and the second excited level of Q_{10} are likely to be degenerate, so the degenerate perturbation theory will work correctly if the degenerate space is extended to include these vibrational states. Nevertheless, the overall agreement is good between the calculated and experimental frequencies with mean errors of 1.2 and 1.1% for the 2MR-QFF and direct cc-VSCF calculations, respectively. Note that the error in ν_9 has not been included in these mean errors.

Table VII gives the results for benzene obtained by cc-VSCF/2MR-QFF calculations with MP2/cc-pVDZ level of theory. This is the largest molecule in the present applications, which includes 12 atoms and 30 internal degrees of freedom. For such a large system, it is not realistic to perform direct VSCF calculations. The cc-VSCF/2MR-QFF calculations took 7184.0 min of total CPU time on a LINUX PC 2.5 GHz Pentium 4, divided into 6670.7 and 513.3 min for the construction of the 2MR-QFF and the cc-VSCF calculation, respectively. Note that the CPU time to construct the 2MR-QFF can be greatly reduced by making use of symmetry, which was not employed at all in the present calculation. The calculated ν_9 has a large error of 10.3% relative to the experimental value. This is a known problem caused by the MP2 method.^{53,54} The harmonic frequency for this mode has been estimated by Martin, Taylor and Lee⁵⁴ to be 1326 cm^{-1} using CCSD(T) with atomic natural orbital basis sets of $[4s3p2d1f/4s2p]$ quality. This is very close to the experimental value, 1310 cm^{-1} . The same authors have also found that harmonic frequencies of ν_7 and ν_8 are underestimated by $\sim 70\text{ cm}^{-1}$ with the cc-pVDZ basis set. In the present study, the anharmonic corrections increase the frequencies of ν_7 and ν_8 by 51.2 and 62.9 cm^{-1} , respectively, in the cc-VSCF method, which leads to accidental agreement with the experimental values. In VSCF calculations, ν_7 and ν_8 are predicted to be 1015.3 and 698.4 cm^{-1} , respectively, so that the divergence of the perturbation expansion is not observed here. Note also that the frequencies of low-lying modes in the region less than 1000 cm^{-1} are increased by the cc-VSCF calculations except for ν_{18} . Therefore, this error should be

considered a defect in the present VSCF scheme and higher-order coupling terms need to be incorporated in the potential to overcome this problem. Although such a prescription is highly prohibitive in the direct VSCF calculations, it will be possible using the n MR-QFF approach.

IV. CONCLUSIONS

In the present study, n -mode coupling representations of the quartic force field (n MR-QFF) are presented, which include the terms up to n coordinate couplings in the QFF. The computational scheme to evaluate third- and fourth-order derivatives by finite differentiations of the energy is fully described. It is verified that the n MR-QFF can be constructed with much less computational effort than the direct VSCF calculations based on the n MR-PES. The code to generate n MR-QFF has been implemented into GAMESS and interfaced with the VSCF and cc-VSCF codes.

As a demonstration, cc-VSCF/2MR-QFF calculations have been carried out for formaldehyde, ethylene, methanol, propyne, and benzene. Direct cc-VSCF calculations have also been carried out for the above molecules except for benzene. The fundamental frequencies have been obtained with errors of 1.0%–1.9% from the experimental value by the cc-VSCF/2MR-QFF method, which is the same quality as the direct cc-VSCF results. These results lead to the conclusion that 2MR-QFF is a very accurate potential energy function for evaluation of the vibrational energy levels of polyatomic system.

As is demonstrated in the present study, 2MR-QFF can be generated automatically for medium-sized molecule such as benzene (12 atomic molecule) with reasonable computational costs using GAMESS. Further developments to reduce the computational cost are under progress by taking into account the point-group symmetry of the molecule, and by incorporating the parallel computational techniques. This potential energy function itself may be also useful to calculate other excited levels, such as overtones or combination bands, and to study the vibrational energy flow dynamics of the molecule. The performance of the present potential energy function for such cases will be shown in the future study.

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APPENDIX: EVALUATION OF THE 3 AND 4MR COEFFICIENTS

The third- and fourth-order derivatives of the energy are evaluated by numerical differentiations of the energy determined by *ab initio* electronic structure calculations. Here, the algorithm to evaluate the 3MR and 4MR terms is presented. The coefficients t_{ijk} and u_{ijk} are calculated by,

$$t_{ijk} = \frac{1}{8\delta_i\delta_j\delta_k} [V(+\delta_i, +\delta_j, +\delta_k) - V(-\delta_i, +\delta_j, +\delta_k) - V(+\delta_i, -\delta_j, +\delta_k) - V(+\delta_i, +\delta_j, -\delta_k) + V(+\delta_i, -\delta_j, -\delta_k) + V(-\delta_i, -\delta_j, +\delta_k) + V(-\delta_i, +\delta_j, -\delta_k) - V(-\delta_i, -\delta_j, -\delta_k)], \quad (\text{A1})$$

$$u_{ijk} = \frac{1}{4\delta_i^2\delta_j\delta_k} \{V(+\delta_i, +\delta_j, +\delta_k) - V(+\delta_i, -\delta_j, +\delta_k) - V(+\delta_i, +\delta_j, -\delta_k) + V(+\delta_i, -\delta_j, -\delta_k) + V(-\delta_i, +\delta_j, +\delta_k) - V(-\delta_i, -\delta_j, +\delta_k) - V(-\delta_i, +\delta_j, -\delta_k) + V(-\delta_i, -\delta_j, -\delta_k) - 2[V(+\delta_j, +\delta_k) - V(-\delta_j, +\delta_k) - V(+\delta_j, -\delta_k) + V(-\delta_j, -\delta_k)]\}, \quad (\text{A2})$$

where $V(n_i\delta_i, n_j\delta_j, n_k\delta_k)$ denotes the energy in terms of normal coordinates at $Q_i=n_i\delta_i$, $Q_j=n_j\delta_j$, and $Q_k=n_k\delta_k$ (other coordinates are fixed to zero). The coefficient u_{ijkl} is calculated by

$$u_{ijkl} = \frac{1}{16\delta_i\delta_j\delta_k\delta_l} [V(+\delta_i, +\delta_j, +\delta_k, +\delta_l) - V(-\delta_i, +\delta_j, +\delta_k, +\delta_l) - V(+\delta_i, -\delta_j, +\delta_k, +\delta_l) - V(+\delta_i, +\delta_j, -\delta_k, +\delta_l) - V(+\delta_i, +\delta_j, +\delta_k, -\delta_l) + V(-\delta_i, -\delta_j, +\delta_k, \delta_l) + V(-\delta_i, +\delta_j, -\delta_k, +\delta_l) + V(-\delta_i, +\delta_j, +\delta_k, -\delta_l) + V(+\delta_i, -\delta_j, -\delta_k, +\delta_l) + V(+\delta_i, -\delta_j, +\delta_k, -\delta_l) + V(+\delta_i, +\delta_j, -\delta_k, -\delta_l) - V(-\delta_i, -\delta_j, -\delta_k, +\delta_l) - V(-\delta_i, -\delta_j, +\delta_k, -\delta_l) - V(-\delta_i, +\delta_j, -\delta_k, -\delta_l) - V(+\delta_i, -\delta_j, -\delta_k, -\delta_l) + V(-\delta_i, -\delta_j, -\delta_k, -\delta_l)], \quad (\text{A3})$$

where $V(n_i\delta_i, n_j\delta_j, n_k\delta_k, n_l\delta_l)$ denotes the energy in terms of normal coordinates at $Q_i=n_i\delta_i$, $Q_j=n_j\delta_j$, $Q_k=n_k\delta_k$, and $Q_l=n_l\delta_l$ (other coordinates are fixed to zero).

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