

# Converged vibrational energy levels and quantum mechanical vibrational partition function of ethane

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The vibrational partition function of ethane is calculated in the temperature range of 200–600 K using well-converged energy levels that were calculated by vibrational configuration interaction, and the results are compared to the harmonic oscillator partition function. This provides the first test of the harmonic oscillator approximation for a molecule with more than five atoms. The absolute free energies computed by the harmonic oscillator approximation are in error by 0.59–0.62 kcal/mol over the 200–600 K temperature range. © 2006 American Institute of Physics.

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## I. INTRODUCTION

The canonical partition function describes the statistical and thermodynamic properties of a system in thermal equilibrium.<sup>1–3</sup> All thermodynamic variables of a system, for example, internal energy, free energy, and entropy, can be expressed in terms of the partition function and its derivatives. Partition functions are also required for calculations of thermal reaction rate constants.<sup>1–4</sup>

The internal partition function of a polyatomic system is often computed by making a series of approximations. First, the Born-Oppenheimer approximation is invoked to treat the motion of the nuclei separately from that of the electrons. Second, rotation and vibration are assumed separable. Third, the rotational partition function is calculated by the rigid rotator approximation. Fourth, the harmonic oscillator approximation is used to calculate the vibrational partition function. These are very convenient approximations because they allow us to write the partition function in an analytical form that depends only on the temperature, equilibrium geometry, and the normal mode frequencies of vibration. The most serious approximation in this sequence is usually the harmonic oscillator (HO) approximation. An alternative to the harmonic oscillator approximation is to include the anharmonic effects in the partition function calculation,<sup>5–12</sup> which is the objective of the present work. Converged vibrational eigenvalue calculations have been successfully carried out for small systems such as H<sub>2</sub>O and CH<sub>4</sub>; however, it is very difficult to obtain enough accurate eigenvalues to calculate the partition function for more complex systems.<sup>13–25</sup>

In this article, we report converged vibrational levels and converged quantum mechanical vibrational partition function of ethane in the temperature range of 200–600 K. The Born-Oppenheimer approximation is used, and the calculations are carried out on the ground-state electronically adiabatic potential energy surface using a combined valence-bond molecular mechanics (CVBMM) potential energy surface.<sup>26</sup> The calculations are carried out for zero total angular momentum

( $J=0$ ), for which all rotation-vibrational coupling terms in the Hamiltonian are neglected. The vibrational energy levels are computed using the vibrational configuration interaction (VCI) scheme<sup>27,28</sup> that has been successfully used on other smaller polyatomic systems.<sup>8,10</sup> The VCI scheme is a variational method in which the matrix elements of the vibrational Hamiltonian are evaluated in a suitable basis set, and the resulting matrix is diagonalized to obtain the eigenvalues. After the vibrational energy levels of ethane are calculated, the partition function is obtained by summing over the Boltzmann factors associated with the energy levels at a given temperature.

There are two main challenges associated with the application of the VCI method to polyatomic systems. The first is the integration over the vibrational coordinates to evaluate the matrix elements of the Hamiltonian operator, and the second is the convergence of the eigenvalues with respect to the size of the basis set. In this article, we have addressed these issues by using the  $n$ -mode hierarchical expansion scheme developed by Carter *et al.*<sup>29</sup> for calculating the matrix elements and by demonstrating convergence with respect to the number of basis functions. The vibrational partition functions are calculated over a range of temperature, and the results are compared with the harmonic oscillator partition functions.

Section II summarizes the theoretical formulation used in the present work. The details of the calculations are provided in Sec. III. In Sec. IV we present the results and discussion. The conclusions drawn from the present study are summarized in Sec. V.

## II. QUANTUM MECHANICAL THEORY

The form of the vibrational Hamiltonian operator in mass-scaled normal mode coordinates  $\{Q_i\}$  is<sup>27–30</sup>

$$H = \frac{-\hbar^2}{2\mu} \sum_{i=1}^F \frac{\partial^2}{\partial Q_i^2} + V(Q_1, \dots, Q_F), \quad (1)$$

where  $F$  is the number of vibrational degrees of freedom, and  $\mu$  is the scaling mass. One method of obtaining the eigen-

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values of the Hamiltonian is to calculate its matrix elements in some suitable basis and then diagonalize the resulting matrix.

An important computational bottleneck in obtaining the eigenvalues and eigenfunctions of the vibrational Hamiltonian is the dimensionality of the system. As the number of vibrational degrees of freedom of the system increases, the evaluation of the matrix elements of the Hamiltonian operator becomes computationally demanding. To make the computation tractable, the potential energy operator is expanded in a hierarchical fashion,<sup>29</sup>

$$V(Q_1, \dots, Q_F) = \sum_{i=1}^F V_i^{(1)}(Q_i) + \sum_{i>j}^F V_{ij}^{(2)}(Q_i, Q_j) + \sum_{i>j>k}^F V_{ijk}^{(3)}(Q_i, Q_j, Q_k) + \dots \quad (2)$$

By approximating the potential as a sum of one-mode, two-mode, three-mode, and four-mode terms, we have to evaluate only four-dimensional integrals. The  $n$ -mode expansion of the potential energy operator has been successfully used in a number of bound-state calculations on polyatomic systems.<sup>8,10,22,27–29</sup> To get accurate results one has to converge the calculation with respect to the number of terms in the potential energy expansion. The eigenfunctions of the vibrational Hamiltonian are obtained by solving the eigenvalue equation

$$H\Psi_L = E_L\Psi_L, \quad (3)$$

where  $E_L$  and  $\Psi_L$  are the eigenvalues and eigenfunctions, respectively. The VCI method involves representing the eigenvector  $\Psi_L$  as a linear combination of configuration state functions (CSFs),

$$\Psi_L = \sum_{K=1}^N C_{KL}\Phi_K, \quad (4)$$

where  $\{\Phi_K\}$  is the set of CSFs,  $\{C_{KL}\}$  is the set of expansion coefficients that are determined variationally, and  $N$  is the basis size. The resulting eigenvalue equation can be written in matrix notation as

$$\mathbf{H}\mathbf{C}_L = E_L\mathbf{S}\mathbf{C}_L, \quad (5)$$

where  $\mathbf{S}$  is the overlap matrix.

The vibrational partition function  $Q(T)$  at temperature  $T$  is calculated from the eigenvalues using

$$Q(T) = \sum_{L=1}^N e^{-E_L/k_B T}, \quad (6)$$

where  $k_B$  is the Boltzmann constant. In the above expression, the zero of energy for  $Q(T)$  is defined at the minimum of the potential energy surface. The zero of energy can also be defined at the ground vibrational state energy  $E_G$  and in such cases; the partition function is called  $\tilde{Q}(T)$ . The relation between the two partition functions is given as

TABLE I. Values used for the  $\tilde{E}_{\max}^{\text{HO}}$  parameter (in  $\text{cm}^{-1}$ ) and the corresponding numbers of basis functions.

$\tilde{E}_{\max}^{\text{HO}}$	Basis size <sup>a</sup>
3000	244
3500	481
4000	974
4500	1 875
5000	3 333
5500	5 997
5700	7 470
5900	9 440
6000	10 491
6300	14 352

<sup>a</sup>The basis size is  $N$ .

$$Q(T) = e^{-E_G/k_B T} \tilde{Q}(T). \quad (7)$$

One of the important differences between the two partition functions is their low temperature limit. As temperature approaches 0 K, the value of  $Q(T)$  approaches zero while the value of  $\tilde{Q}(T)$  approaches unity.

### III. CALCULATIONS

The construction of basis functions is an important step in the VCI calculation. It is desirable to have a small set of basis functions to keep the computational cost of the calculation tractable. In the present calculations, the basis functions are constructed by taking a direct product of harmonic oscillator functions,

$$\Phi_K(Q_1, \dots, Q_{18}) = \varphi_{n_{1K}}(Q_1) \varphi_{n_{2K}}(Q_2) \cdots \varphi_{n_{18K}}(Q_{18}), \quad (8)$$

where  $\varphi_{n_{iK}}(Q_i)$  is the one-dimensional harmonic oscillator function with quantum number  $n_{iK}$  associated with mode  $Q_i$ , which has a normal mode frequency of  $\omega_i$ . The 18-dimensional basis functions are completely specified by a set of 18 quantum numbers  $(n_{1K}, \dots, n_{18K})$ , and we will use this compact notation in the following discussions. These quantum numbers are also used to define the harmonic oscillator energy  $\tilde{E}_K^{\text{HO}}$  associated with each basis function  $\Phi_K$  using the expression

$$\tilde{E}_K^{\text{HO}} = n_{1K}\hbar\omega_1 + \cdots + n_{18K}\hbar\omega_{18}. \quad (9)$$

In Eq. (9), as in Sec. II, the tilde denotes a quantity with the zero of energy at the zero point level. For the VCI calculation, a parameter  $\tilde{E}_{\max}^{\text{HO}}$  with units of energy is defined, and all basis functions with energies  $\tilde{E}_K^{\text{HO}} \leq \tilde{E}_{\max}^{\text{HO}}$  are selected for calculations. Table I lists the values of  $\tilde{E}_{\max}^{\text{HO}}$  that are used in the present calculations and the corresponding numbers of basis

TABLE II. Number of Gauss-Hermite quadrature points used for each mode.

Mode index	Quadrature points
1-12	5
13-17	7
18	23

TABLE III. Comparison of the zero point energy (in  $\text{cm}^{-1}$ ) for the three mode and four-mode expansions for different basis sets.

Basis size	Three mode	Four mode
244	15 891	15 889
481	15 877	15 875
974	15 864	15 862
1 875	15 851	15 850
3 333	15 835	15 835
5 997	15 825	15 827
7 470	15 821	15 824
9 440	15 817	15 820
10 491	15 815	15 818
14 352	15 813	15 816
$\infty$	15 812	15 815

functions. The matrix elements of the Hamiltonian operator are evaluated by integrating over the basis functions, and the eigenvalues are obtained by diagonalizing the resulting Hamiltonian matrix. In the present calculation, numerical integration over the basis function is carried out using the Gauss-Hermite quadrature scheme, and the number of quadrature points for each mode is listed in Table II. To make the computation of the integrals faster, the potential energy at the quadrature nodes is precomputed and is stored on disk at the beginning of the calculation.

All the above calculations were carried out with a new computer program developed from scratch.<sup>31</sup>

We have estimated completely converged values of  $E_G$ ,  $\tilde{Q}$ , and  $Q$  by extrapolating them to an infinite basis set using the following equations:

$$E_G = E_{G,\infty} + \frac{A_1}{N} + \frac{A_2}{N^2}, \quad (10)$$

$$\tilde{Q} = \tilde{Q}_\infty + \frac{A_3}{N} + \frac{A_4}{N^2}, \quad (11)$$

$$Q = Q_\infty + \frac{A_5}{N} + \frac{A_6}{N^2}, \quad (12)$$

where the variables on the right-hand side of the equations are fitting coefficients. Note that as  $N \rightarrow \infty$ , the values of  $E_G$ ,  $\tilde{Q}$ , and  $Q$  approach  $E_{G,\infty}$ ,  $\tilde{Q}_\infty$ , and  $Q_\infty$ , respectively. The fitting coefficients are obtained by minimizing the root mean square (rms) deviation of Eq. (10) and (11), or (12) from the results of the VCI calculations using the four largest basis sets. The extrapolation of  $\tilde{Q}$  and  $Q$  is done at all temperatures under study.

The calculated energy levels and the partition function are converged with respect to three different quantities: (1) the order of the  $n$ -mode hierarchical expansion, (2) the number  $N$  of basis functions used in the VCI expansion, and (3) the order of Gauss-Hermite quadrature points. The convergence with respect to these parameters is discussed in the following section.

## IV. RESULTS AND DISCUSSION

### IV.A. Convergence

The zero point energy  $E_G$  calculated using various basis sets is listed in Table III. The second and third columns list the energies obtained using the three-mode and four-mode expansions, respectively. The largest difference in the zero point energy (ZPE) between the three- and four-mode calculations is  $3 \text{ cm}^{-1}$  over the entire range of basis functions used in the present work. Comparing the ZPE obtained from the calculations with the two largest basis sets as listed in rows nine and ten of Table III, we find that the addition of the final 3861 basis functions decreases the ZPE by only 0.01% for both the three-mode and four-mode calculations. Table III shows that that computed ZPE is converged with respect to number of basis functions and the number of terms in the  $n$ -mode expansion of the potential energy operator. The extrapolated ZPE for both the three-mode and four-mode calculations are within  $1 \text{ cm}^{-1}$  of the values obtained using the largest basis set.

TABLE IV. Computed  $\tilde{Q}(T)$  values for the three-mode and four-mode expansions using various numbers of basis functions.

$T$ (K)	244	481	974	1875	3333	5997	7470	9440	10 491 <sup>a</sup>	14 352 <sup>b</sup>	$\infty$
Three-mode expansion											
200	1.11	1.11	1.13	1.15	1.15	1.16	1.16	1.17	1.17	1.17	1.19
300	1.31	1.31	1.35	1.38	1.38	1.41	1.41	1.42	1.42	1.43	1.48
400	1.65	1.66	1.72	1.75	1.77	1.81	1.81	1.83	1.83	1.85	1.92
500	2.21	2.24	2.32	2.38	2.41	2.47	2.48	2.50	2.51	2.54	2.68
600	3.06	3.14	3.28	3.38	3.44	3.54	3.57	3.60	3.62	3.68	3.92
Four-mode expansion											
200	1.11	1.11	1.14	1.15	1.15	1.17	1.17	1.17	1.17	1.17	1.20
300	1.31	1.31	1.35	1.38	1.39	1.42	1.42	1.42	1.42	1.43	1.48
400	1.65	1.66	1.72	1.76	1.78	1.82	1.83	1.83	1.84	1.85	1.93
500	2.22	2.24	2.33	2.38	2.42	2.49	2.50	2.52	2.53	2.55	2.69
600	3.07	3.15	3.29	3.39	3.45	3.57	3.60	3.63	3.64	3.70	3.94

<sup>a</sup>Basis A.

<sup>b</sup>Basis B.

TABLE V. Computed  $Q(T)$  values for the three-mode and four-mode expansions using various numbers of basis functions.

$T$ (K)	244	481	974	1875	3333	5997	7470	9440	10 491 <sup>a</sup>	14 352 <sup>b</sup>	$\infty$
Three-mode expansion											
200	2.50E-50	2.76E-50	3.11E-50	3.46E-50	3.85E-50	4.19E-50	4.34E-50	4.47E-50	4.52E-50	4.64E-50	4.91E-50
300	1.04E-33	1.12E-33	1.23E-33	1.33E-33	1.44E-33	1.54E-33	1.57E-33	1.61E-33	1.62E-33	1.66E-33	1.75E-33
400	2.48E-25	2.61E-25	2.84E-25	3.04E-25	3.24E-25	3.43E-25	3.50E-25	3.57E-25	3.60E-25	3.67E-25	3.90E-25
500	3.06E-20	3.22E-20	3.47E-20	3.70E-20	3.91E-20	4.12E-20	4.20E-20	4.28E-20	4.32E-20	4.41E-20	4.72E-20
600	8.64E-17	9.17E-17	9.89E-17	1.05E-16	1.11E-16	1.17E-16	1.19E-16	1.21E-16	1.23E-16	1.25E-16	1.36E-16
Four-mode expansion											
200	2.53E-50	2.81E-50	3.15E-50	3.48E-50	3.87E-50	4.15E-50	4.25E-50	4.37E-50	4.41E-50	4.52E-50	4.81E-50
300	1.05E-33	1.13E-33	1.24E-33	1.34E-33	1.44E-33	1.53E-33	1.56E-33	1.59E-33	1.60E-33	1.63E-33	1.73E-33
400	2.50E-25	2.64E-25	2.87E-25	3.06E-25	3.26E-25	3.43E-25	3.49E-25	3.55E-25	3.57E-25	3.64E-25	3.87E-25
500	3.09E-20	3.25E-20	3.50E-20	3.71E-20	3.93E-20	4.13E-20	4.20E-20	4.27E-20	4.30E-20	4.38E-20	4.68E-20
600	8.70E-17	9.24E-17	9.95E-17	1.06E-16	1.12E-16	1.17E-16	1.19E-16	1.21E-16	1.22E-16	1.25E-16	1.35E-16

<sup>a</sup>Basis A.<sup>b</sup>Basis B.

The convergence of the energy levels with respect to the number of basis functions and the  $n$ -mode expansion of the potential are demonstrated in the supporting information.<sup>32</sup> The material presented there shows that the first 100 modes are converged on average with respect to increasing the expansion from three modes to four modes to (on average) 3.6 cm<sup>-1</sup>, which corresponds to 0.02% of their average value. Furthermore, increasing  $N$  from 10 491 (which is called basis A) to 14 352 (which is called basis B) lowers the first 100 eigenvalues by an average of over 13.7–13.9 cm<sup>-1</sup>, which corresponds to 0.07% of their average value.

The supporting information also discusses the convergence with respect to quadrature grids, which is excellent.

The calculated values of  $\tilde{Q}(T)$  for the three-mode and four-mode expansions using different basis functions are shown in Table IV. Comparing the results for bases A and B shows that, for either the three-mode or the four-mode expansion, increasing the basis size by 27% changes  $\tilde{Q}(T)$  by less than 1.0% at 200 K and by 1.6% at 600 K. Comparing the results for the basis B column for the two expansion sizes shows that the computed  $\tilde{Q}(T)$  differ by less than 1.0% for the three-mode and four-mode calculations over the whole temperature range of 200–600 K. The extrapolated  $\tilde{Q}(T)$  at 200 and 600 K differs from the largest basis set results by 1.7% and 6.1%, respectively, for the three-mode calculations and by 2.5% and 6.1%, respectively, for the four-mode calculations.

Whereas  $\tilde{Q}(T)$  is independent of the zero point energy,  $Q(T)$  depends strongly on it. The calculated values of  $Q(T)$

TABLE VI. Number of eigenvalues required for 1% and 3% convergence of the partition function.

$T(K)$	1%	3%
200	3	2
300	14	6
400	53	24
500	225	90
600	873	318

for the three-mode and four-mode expansions using different numbers of basis functions are shown in Table V. For the three-mode calculations, the computed  $Q(T)$  changes by 2.6% at 200 K and by 1.6% at 600 K as the basis size is increased from 10 491 to 14 352. Since the  $\tilde{Q}(T)$  is well converged at 200 K, the 2.6% change in  $Q(T)$  is dominated by the 2 cm<sup>-1</sup> difference in the ZPE as shown in Table III. Similar analysis shows that the comparable changes for the four-mode calculations are 2.4% and 1.6%, respectively, and the converged (extrapolated) results differ from the largest basis by only 6%–8%. Comparing the three-mode and four-mode results for the largest basis set used in the present work, the computed  $Q(T)$  differs by 2.7% at 200 K and by less than 1.0% at 600 K.

Although we sum all the Boltzmann factors in Eq. (6), it

TABLE VII. Normal mode frequencies (in cm<sup>-1</sup>) for the CVBMM potential energy surface for ethane compared to accurate values of the fundamentals.

Mode index	Frequencies <sup>a</sup>	Fundamentals <sup>b</sup>	Deviation	[%]
1	3029	3004	-26	0.9
2	3029	3004	-26	0.9
3	3005	3014	9	0.3
4	2963	2883	-80	2.8
5	2963	2884	-80	2.8
6	2873	2774	-99	3.6
7	1491	1467	-24	1.6
8	1491	1468	-23	1.6
9	1466	1461	-6	0.4
10	1463	1425	-38	2.7
11	1463	1425	-38	2.7
12	1405	1405	-1	0.1
13	1106	1112	6	0.5
14	1106	1112	5	0.5
15	972	964	-8	0.9
16	948	959	10	1.1
17	948	959	10	1.1
18	291	265	-26	9.9

<sup>a</sup>Frequency =  $\omega_r/2\pi c$ , where  $c$  is the speed of light.<sup>b</sup>The fundamental is  $\Delta E/hc$ , where  $\Delta E$  is the energy difference between an excited state with one quantum of excitation and the ground state, and  $h$  is the Planck constant.

TABLE VIII. Comparison of the harmonic oscillator partition function with the VCI partition function calculated using extrapolated basis functions and the four-mode expansion.

$T$ (K)	$e^{-\beta E_G}/e^{-\beta E_{G,HO}}$	$\tilde{Q}/\tilde{Q}_{HO}$	$Q/Q_{HO}$
200	4.114	1.073	4.414
300	2.601	1.065	2.769
400	2.056	1.060	2.181
500	1.776	1.051	1.866
600	1.618	1.031	1.669

is interesting to ask how many eigenvalues are significant. Therefore, we truncated Eq. (6) with successively smaller numbers of terms until the error is 1%. Then we truncated it further until the error is 3%. (These tests were performed with basis B, four-mode eigenvalues.) Table VI shows the number of eigenvalues required for 1% and 3% convergence as a function of temperature; note that these results are the same for either  $Q(T)$  or  $\tilde{Q}(T)$ . A minimum of 3 and 873 eigenvalues are required to converge the partition function at 1% for 200 and 600 K, respectively.

#### IV.B. Test of harmonic oscillator approximation

The harmonic oscillator ZPE is  $16\,010.7\text{ cm}^{-1}$ , and the computed ZPE using the four-mode expansion with 14 352 basis functions is  $15\,816.3\text{ cm}^{-1}$ , which is lower than the harmonic oscillator ZPE by  $194.4\text{ cm}^{-1}$ , a deviation of 1.2%. The fact that the anharmonic result is lower than the harmonic one is easily understood by the Morse model<sup>30,33</sup> for the high-frequency stretches, which dominate the ZPE.

The zero point energy cannot be separated into contributions from individual modes. To understand the mode dependences of the anharmonicity, we consider the fundamental frequencies. Table VII lists the 18 harmonic frequencies and compares them to the frequencies obtained in the basis B calculation with the four-mode expansion (our best converged calculation). We find that the largest deviation of 10% for the torsional mode and the deviations in the remaining modes are all less than 4%.

A comparison between the converged and harmonic oscillator partition functions is presented in Table VIII. In the table  $E_{G,HO}$  refers to the harmonic oscillator ZPE, and  $\beta$  is  $1/k_B T$ . The converged partition function is larger than the harmonic oscillator partition function by factors of 4.4 and 1.7 at 200 and 600 K, respectively. However, with the zero of energy at the ground state the error in the harmonic approximation is only 3%–7% over the whole 200–600 K range.

Although statistical mechanics textbooks<sup>1–3,34</sup> invariably focus on  $\tilde{Q}(T)$ , the calculation of thermodynamic functions from electronic structure calculations of potential energy surfaces, a subject of increasing importance for the modern application of theoretical chemistry,<sup>35–38</sup> requires the calculation of  $Q(T)$ . The errors in the calculation of  $Q(T)$  that are shown in Table VIII correspond to an error of 0.59–0.62 kcal/mol in the absolute free energy and a very similar amount for the absolute enthalpy. This may be com-

pared to a total mean absolute deviation of 0.56 kcal/mol for predictions of hydrocarbon enthalpies of formation at 298 K by the G3X semi-*ab-initio* model.<sup>39</sup> Clearly the errors in such electronic structure calculations, which employ harmonic frequencies to estimate vibrational contributions, have significant components from the vibrational contributions along with the more intensively studied electronic contributions, although these are no doubt somewhat ameliorated by scaling<sup>40</sup> the harmonic frequencies.

#### V. CONCLUDING REMARKS

Fully converged vibrational partition functions of ethane have been computed by summing over the vibrational levels for the temperature range of 200–600 K. The zero point energy is converged to about  $1\text{ cm}^{-1}$  and the partition function with respect to the zero point level is converged to about 3% at 200 K and 6% at 600 K. The difference in vibrational partition function for the three-mode and four-mode expansions of the potential was found to be negligible for the present work. The accurate results were compared with partition functions obtained using the harmonic oscillator approximation, and we found deviations in the absolute free energy of 0.6 kcal/mol. Ethane has 18 vibrational modes, and this is the first time that the harmonic oscillator approximation has been tested against a converged vibrational partition function for a realistic potential energy function for a molecule with more than nine vibrational modes.

The only previous molecule with a torsion for which converged vibrational or rovibrational partition functions have been obtained is  $\text{H}_2\text{O}_2$  (and several of its isotopomers),<sup>11,12</sup> with four atoms as compared to eight atoms here. The only previous molecule of any type with more than four atoms for which converged vibrational and rotational partition function have been calculated is  $\text{CH}_4$ ,<sup>10</sup> with five atoms, again considerably smaller than the present eight-atom case. Thus the present article shows that accurate vibrational contributions to the thermochemical properties can be computed for much larger molecules than has been previously possible. This advance is made possible primarily by the use of the hierarchical representation of the potential, as originally suggested by Carter *et al.*<sup>29</sup>

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