Quantum free-energy calculations: A three-dimensional test case

Robert Q. Topper, a) Gregory J. Tawa, and Donald G. Truhlar
Department of Chemistry, Supercomputer Institute, and Army High Performance Computing Research Center, University of Minnesota, Minneapolis, Minnesota 55455-0431

(Received 3 April 1992; accepted 29 May 1992)

An optimized integration scheme for calculating vibrational–rotational partition functions by the Fourier path-integral method, as presented in the previous paper [R. Q. Topper and D. G. Truhlar, J. Chem. Phys. 97, 3647 (1992)] is applied to a three-dimensional test case involving the coupled vibrational and rotational motions of a diatomic HCl molecule in Cartesian coordinates. Converged partition functions are calculated by the new Fourier path-integral Monte Carlo scheme and by standard variational methods, and the two sets of results are compared. We obtain good agreement (~2%) between the two methods over a range of a factor of 20 in temperature.

I. INTRODUCTION

In the preceding paper we presented a new Monte Carlo integration scheme for the calculation of quantum-mechanical vibrational–rotational partition functions2 and demonstrated its convergence properties for a problem involving two coupled modes. The scheme is based on the Fourier path-integral representation of the density operator, 3 Box–Muller importance sampling4 of Fourier coefficient space, and adaptively optimized stratified sampling in coordinate space. In the present paper we present calculations on a three-dimensional test case.

A general motivation for the present study is the calculation of free energies (and hence equilibrium constants and transition-state theory rate constants) for small polyatomic molecules exhibiting strong anharmonicity or vibration–rotation coupling, wide-amplitude motions, multiple minima, or other features that make conventional approximations based on separable modes inaccurate or conventional quantum-mechanical calculational approaches based on harmonic-oscillator–spherical-harmonic basis functions hard to converge. In many such cases the essential complications of physical interest involve only two or three strongly coupled modes, and the demonstration here that the scheme converges for three-dimensional problems is directly relevant. In other cases the full vibrational–rotational space (six degrees of freedom for a triatomic, nine for a tetra-atomic, etc.) may be strongly coupled, and the present example may be considered a small-dimensional demonstration of convergence and a first step toward the application of such schemes to more demanding problems. In this regard we note that the scheme is well suited for implementation on parallel computers.

Section II presents the test problem. Section III presents a conventional calculation of the vibrational–rotational partition function for the test problem. Section IV presents the application of the new integration scheme. Section V presents the results of the two methods, and these results are compared and discussed in Sec. VI. Section VII is a summary with concluding remarks.

II. THE TEST PROBLEM

The test problem considered here is the diatomic HCl molecule, modeled in Cartesian coordinates. After removal of the center-of-mass coordinates and making the Born–Oppenheimer approximation, the vibrational–rotational Hamiltonian for a diatomic molecule is

\[
\hat{H} = \frac{\hbar^2}{2\mu} \sum_{j=1}^{3} \frac{\partial^2}{\partial x_j^2} + V[(x_1^2 + x_2^2 + x_3^2)^{1/2}],
\]

where \(\mu\) is the reduced mass of the diatom, and \(V(r)\) is the potential energy as a function of the internuclear distance \(r\). The advantages of choosing this problem as the test case are (i) the exact partition functions are easily computed by standard methods by separating the problem in spherical polar coordinates, and (ii) it illustrates a general scheme which may also be applied to polyatomics, where vibration–rotation separation is not trivial (in the generalization of the present scheme to polyatomics we envision replacing \(r\) by the hyperradius). 5

The internuclear potential we have chosen is the empirical form due to Hubert and Hirschfelder. 6 Thus \(V(r)\) is approximated by

\[
V(r) = D_e \left[ (1 - e^{-\gamma r})^2 + c \gamma e^{-2\gamma r} (1 + b r) \right],
\]

where \(\gamma\) is a reduced internuclear distance defined by

\[
y(r) = \frac{\omega}{2(B e D_e)^{1/2}} \left( \frac{r - r_e}{r_e} \right),
\]

and the parameters \(b\) and \(c\) are given in terms of other constants:

\[
b = 2 - \frac{1}{c} \left( \frac{7 - D_e A_2}{12A_0} \right),
\]

\[
c = 1 + A_1 \sqrt{D_e A_2},
\]

with \(A_0\), \(A_1\), and \(A_2\) given by

\[
A_0 = \omega / 4 B e
\]

a) Present address: Department of Chemistry, University of Rhode Island, Kingston, RI 02881.
De to evaluate Eq. (11), we solve the equation. 

\[ \text{TABLE I. Experimentally measured properties of HCl.} \]

<table>
<thead>
<tr>
<th>Property</th>
<th>Reported value(^a)</th>
<th>Value in atomic units(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_0 )</td>
<td>35 759.1</td>
<td>1.712 242.9 × 10^{-1}</td>
</tr>
<tr>
<td>( \omega )</td>
<td>2 990.946.3</td>
<td>1.362 785.9 × 10^{-2}</td>
</tr>
<tr>
<td>( \omega_x )</td>
<td>52.818.6</td>
<td>2.406 611.0 × 10^{-4}</td>
</tr>
<tr>
<td>( \omega_z )</td>
<td>0.224 37</td>
<td>1.022 312.8 × 10^{-6}</td>
</tr>
<tr>
<td>( \omega_\varepsilon )</td>
<td>-0.012 18</td>
<td>-5.549 66 × 10^{-8}</td>
</tr>
<tr>
<td>( B_e )</td>
<td>10.593 416</td>
<td>4.811 227.0 × 10^{-5}</td>
</tr>
<tr>
<td>( \alpha_e )</td>
<td>0.307 161</td>
<td>1.399 630.4 × 10^{-6}</td>
</tr>
<tr>
<td>( r_e )</td>
<td>1.274 552</td>
<td>2.380 935.5</td>
</tr>
<tr>
<td>( \mu )</td>
<td>0.979 592.72</td>
<td>1.785 686.6 × 10(^3)</td>
</tr>
</tbody>
</table>

\(^a\)From Ref. 7. Energies in cm\(^{-1}\), lengths in Å, masses in amu.

\(^b\)Energies in hartrees, lengths in \( a_0 \), masses in atomic units. 1 hartree = 4.356 37 × 10^{-18} cm\(^{-1}\), 1 \( a_0 \) = 0.529 177 Å, and 1 amu = 1822.89 atomic units of mass [A. Szabo and N. S. Ostlund, Modern Quantum Chemistry (McGraw-Hill, New York, 1989); E. R. Cohen and B. N. Taylor, Phys. Today 44 (No. 8), 9 (1991)].

\[ A_1 = -1 - \alpha_e \omega_z / 6 B_e, \quad (7) \]

\[ A_2 = \frac{1}{3} A_1 - 2 \omega_x / 3 B_e. \quad (8) \]

Here \( r_e \) is the equilibrium distance, and \( D_e \) is the equilibrium dissociation energy, which is obtained by applying the expression

\[ D_e = D_0 + \omega_e - \omega_x \omega_z / 3 B_e, \quad (9) \]

with \( D_0 \) the ground-state dissociation energy, \( B_e \) the rota­tional constant, \( \alpha_e \) the vibration–rotation coupling constant, and \( \omega_e, \omega_x, \omega_z \) the anharmonicity constants in a Dunham series expansion of the vibrational–rotational energies:

\[ E_{\omega} / \hbar c = \omega \left( v + \frac{1}{2} \right) - \omega_x \left( v + \frac{1}{2} \right)^2 + \omega_z \left( v + \frac{1}{2} \right)^3 - \alpha_e \left( v + \frac{1}{2} \right) J(J+1) + \cdots. \quad (10) \]

The integers \( v \) and \( J \) are, respectively, the vibrational and rotational quantum numbers for the diatom.

The experimental parameters\(^7\) used as input for the potential function are given in Table I, and the resulting potential curve is shown in Fig. 1. The dissociation energy \( D_e \) is 0.169 69 hartrees.

**III. APPLICATION OF STANDARD VARIATIONAL METHODS**

The vibrational–rotational partition function is conventionally obtained by applying variational methods to obtain the bound vibrational–rotational energy levels \( \epsilon_{\omega J} \) and summing their Boltzmann factors, weighting each Boltzmann factor with the appropriate degeneracy factor:

\[ Q(T) = \sum_{\omega J} (2J+1) \exp(-\beta \epsilon_{\omega J}), \quad (11) \]

where the sum over states includes only states which are energetically bound, and \( \beta = 1/k_B T \), where \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. In order to evaluate Eq. (11), we solve the equation\(^8,9\)

**FIG. 1. Potential energy as a function of internuclear distance for HCl computations.**

\[ \left[ -\frac{\hbar^2}{2 \mu r^2} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2 \mu r} \right] \chi_{\omega}(r) = 0, \quad (12) \]

where \( \chi_{\omega}(r) \) is the vibrational wave function. The vibrational wave functions and associated eigenenergies are obtained by the Rayleigh–Ritz variational principle.\(^10\) We use a basis of 1500 harmonic-oscillator eigenfunctions. The Hamiltonian matrix elements are calculated using 1600-point Gauss–Hermite quadrature.\(^11\) Since the harmonic-oscillator wave functions are defined on the region \((-\infty, \infty)\) and thus do not have the desired \( r=0 \) boundary conditions, their use requires some special handling.\(^12\) First, we reset all quadrature nodes for which \( r < \delta \) to \( r = \delta \), where \( \delta \) is set equal to \( 10^{-2} a_0 \) with \( a_0 \) the Bohr radius. Second, the elements proportional to \( 1/r^2 \) are made nonsingular by replacing \( r^2 \) in the denominator by \( r^2 + r_0^2 \), where we take \( r_0 \) to be \( 2 \times 10^{-3} a_0 \). For this potential, we have found that the calculation is quite insensitive to the exact values of \( \delta \) and \( r_0 \); thus, no practical problems are encountered by handling the \( r=0 \) boundary condition in this fashion.

**IV. APPLICATION OF THE NEW FOURIER PATH-INTEGRAL METHOD**

As discussed in the previous paper,\(^1\) the partition function is obtained by representing it as the trace of the density matrix in configuration space. The density matrix is represented as a path integral in complex time,\(^13\) and the paths are expanded in a Fourier series\(^3\) about a free-particle “reference path.”

We could solve the present problem as a one-dimensional problem by using spherical coordinates, but instead we solve it in Cartesian coordinates as a prototype example of a three-dimensional nonseparable problem to test the convergence properties of our algorithm in three dimensions.

In order to represent the partition function in a computationally convenient form, the ratio of the partition function for the fully coupled system is divided by the partition function for a particle in a sphere centered about
the molecular center of mass. The domain in configuration space is truncated to the sphere, and the infinite Fourier series is truncated to include a finite number \((K)\) of terms per degree of freedom. We then obtain a Riemann integral over a \([3+(3\times K)]\)-dimensional domain:

\[
Q^{(K)}(T) = Q_{ps}(T) \int_D dx \int^\infty_{-\infty} da \exp[-S(x,a)]g(a),
\]

where \(Q_{ps}(T)\) is the partition function for a particle in a sphere, equal to

\[
Q_{ps}(T) = \mathcal{V} \prod_{j=1}^3 \left( \frac{\mu}{2\pi \beta h^2} \right)^{1/2}
\]

with \(\mathcal{V}\) the volume of the spherical domain \(D\). Here, as in Eq. (1), the vector \(x\) is a three-dimensional set of Cartesian coordinates specifying the positions of the nuclei in a coordinate system with origin at the molecular center of mass, \(a\) is a \((3\times K)\)-dimensional array of Fourier coefficients, and \(S(x,a)\) is an "action" integral of the potential energy along all paths which begin and end at the same value of \(x\) in a complex time interval \(\beta \hbar\):

\[
S(x,a) = \int_0^{\beta \hbar} ds \mathcal{V}[\bar{x}(s)],
\]

with the components of \(\bar{x}(s)\) given by

\[
\bar{x}_j(s) = x_j + \sum_{l=1}^K a_{j,l} \sin \left( \frac{\pi s}{\beta \hbar} \right).
\]

The function \(g(a)\) is a normalized probability density function in Fourier coefficient space, given by

\[
g(a) = \frac{G(a)}{\int^\infty_{-\infty} da \; G(a)},
\]

where \(G(a)\) is a multidimensional Gaussian about the origin

\[
G(a) = \exp \left( -\sum_{j=1}^3 \sum_{l=1}^K \frac{a_{j,l}^2}{2\sigma_{j,l}^2} \right)
\]

with temperature-dependent widths given by

\[
\sigma_{j,l}^2 = 2\beta^2 / m \gamma^2 P.
\]

The integral in Eq. (13) is evaluated by the Monte Carlo method described in the preceding paper.\(^1\) In particular, the Fourier coefficient degrees of freedom are sampled according to \(g(a)\) by using the Box–Muller algorithm,\(^4\) which generates an uncorrelated sample in the Fourier coefficient space, and the nuclear coordinates are sampled using the method of adaptively optimized stratified sampling. We have previously referred to this combination of techniques as the AOSS–U (adaptively optimized stratified sampling, where \(U\) denotes the samples are fully uncorrelated) method.\(^1\)

In the present implementation of the AOSS–U method, three concentric spherical boundaries enclosing the center of mass define the strata to be sampled optimally. The boundaries of the strata are determined adaptively during the course of the integration, using the function evaluations taken during the optimization stages as part of the final sample used for purposes of integration.\(^1\) At each sample, all coordinates and Fourier coefficients are varied simultaneously. The one-dimensional integral in Eq. (15) is evaluated via 50-point Gauss–Legendre quadrature.\(^1\) The Monte Carlo estimate of the integral is then given by

\[
\langle Q(T) \rangle = \sum_{k=1}^3 \left[ \frac{Q_{ps}(T)}{n_k} \right] \sum_{i=1}^{n_k} \exp[-S(x_{i,k})],
\]

where \(n_k\) is the number of samples within each stratum, \(n\) is the total number of samples, and \(Q_{ps}(T)\) is given by Eq. (14), but with the volume of the \(k\)th stratum \((\mathcal{V}_k)\) substituted for \(\mathcal{V}\). In all calculations we have used \(n = 100,000\) samples.

Note that the accuracy achieved by this procedure depends on careful attention to several convergence issues: (i) the number of Fourier coefficients used per degree of freedom, (ii) the order of Gauss–Legendre quadrature used to evaluate the action integral, (iii) the size of the configuration space domain \(D\), and (iv) the statistical error of the Monte Carlo procedure. We addressed these issues as discussed in detail in the preceding paper.

V. RESULTS

In this section we present vibrational–rotational partition functions computed by the variational and Fourier path-integral AOSS–U methods. In the variational partition function calculations, we have used 920 vibrational–rotational states to evaluate Eq. (11), which corresponds to including all bound states up to \(J_{\text{max}} = 64\). The variational calculation is well converged with respect to the number of states included (the partition function is converged to three significant figures at 6000 K). The numerical parameters used to carry out the Fourier path-integral calculations via Eq. (20) are given in Sec. IV. Unless otherwise specified, we have used 128 Fourier coefficients per degree of freedom, i.e., \(K = 128\). The domain of integration in calculations with this value of \(K\) is therefore 387-dimensional.

Table II gives the variational results obtained by Eq. (11) and the path-integral results obtained by Eq. (20). The error bars given for the latter calculation represent 95% confidence limits. For both these calculations we take the zero of energy at a consistent location, namely the minimum of the potential-energy curve, where \(V(r)\) defined by Eq. (2) equals zero. For interpretive purposes Table II also gives the variational results for the partition function with the zero of energy at the ground state, i.e.,

\[
\tilde{Q}(T) = \sum_n (2J+1) \exp[-\beta (e_n - e_0)].
\]

As is well known from textbook discussions, \(\tilde{Q}(T)\) represents the effective number of occupied states.

Table II shows that the two methods for evaluating the partition function agree within the Monte Carlo error bars over the range of temperatures \(T > 500\) K. However, the Fourier path-integral AOSS–U calculations at \(T = 300\) and
VI. DISCUSSION

In order to further assess the success of the Fourier path-integral method, we compare our results to results obtained through various commonly used approximate expressions. In particular, we consider the approximate separation of vibrational and rotational motions. In this approximation, the partition function is treated as a product of vibrational and rotational contributions:

\[ Q(T) = Q_{\text{vib}}(T) Q_{\text{rot}}(T). \]  

(22)

If we treat the rotational part as a quantum rigid rotor (QRR) and the vibrational part of the problem as a quantum harmonic oscillator (QHO), the factors in Eq. (22) are\(^\text{5}\)

\[ Q_{\text{rot}}^{\text{QRR}}(T) = \sum_{J} (2J+1) \exp \left( -\frac{\beta J(J+1)}{2 \mu_{r}^{2}} \right), \]  

(23)

\[ Q_{\text{vib}}^{\text{QHO}}(T) = \exp \left( -\frac{\beta \hbar \omega}{2} \right) \left[ 1 - \exp \left( -\beta \hbar \omega \right) \right]. \]  

(24)

If the rigid-rotor–harmonic-oscillator (RRHO) is treated by classical (C) mechanics instead of quantum mechanics, the product contributions are\(^\text{2}\)

\[ Q_{\text{rot}}^{\text{RRHO}}(T) = 8\pi^{2} \mu_{r} \beta \hbar, \]  

(25)

\[ Q_{\text{vib}}^{\text{C}}(T) = \frac{1}{\beta \hbar \omega}. \]  

(26)

However, with the vibrational–rotational eigenvalues in hand one can obtain a “best separable” approximation by summing over all rotational states with \(v=0\) to obtain the vibrating-rotator partition function,

\[ Q_{\text{rot}}^{\text{VR}}(T) = \sum_{J} (2J+1) \exp \left[ -\beta (\epsilon_{J} - \epsilon_{0}) \right], \]  

(27)

and summing over all vibrational states with \(J=0\) to obtain a quantum anharmonic-oscillator partition function:

\[ Q_{\text{vib}}^{\text{AO}}(T) = \sum_{v} \exp \left( -\beta \epsilon_{v} \right). \]  

(28)

Equations (22)–(28) can be applied to calculate partition functions for the HCl molecule, and the results obtained with these approximations can be compared with the other treatments in order to assess the importance of quantum effects, anharmonicity effects, and vibration–rotation coupling. Note, however, that converged quantum calculations are necessary to evaluate Eqs. (27) and (28).

In Table IV we present the separable approximations to the partition function, obtained through the classical and quantal versions of the RRHO model, as well as through the quantal vibrating-rotor–anharmonic-oscillator (labeled BS, for “best separable”) approximation of Eqs. (27) and (28). We compare partition functions obtained in this fashion to those obtained through the variational method described in Sec. III and through the Fourier path-integral (FPI) AOSS-U method described in Sec. IV.

We first notice that the classical and quantal versions of the RRHO approximation are quite different from one another over the entire temperature range, although the
disagreement is not so extreme at the high end of the temperature range. This establishes the strongly quantum-mechanical nature of this molecule and shows that the present test case is not a "nearly classical" one. Next, we note that at temperatures between 600 and 4000 K, the quantum RRHO and variational partition functions only agree to one significant figure. At the higher temperatures the agreement is only qualitative, with errors up to 15% in the harmonic results. Thus the high-temperature results are not "nearly harmonic" either. The quantum "best separable" partition functions are quite accurate at low temperatures where mainly the \( v=0 \) states are populated, but the errors increase to 4% at 6000 K and of course the system is not even approximately separable in the Cartesian coordinates in which we solved it by the path-integral approach, which is why this is a good test case. This establishes the importance of quantum anharmonicity, nonrigidity, and nonseparability in this test case, at least in the high-temperature regime.

The present study is instructive because it dramatically emphasizes the importance of including enough Fourier coefficients in the calculation and how this Fourier expansion converges more slowly at low temperature. In addition, we have demonstrated that the AOSS-U algorithm is robust enough to achieve a fully converged result while sampling a 3075-dimensional space. Moreover, in this system and in the system studied in the previous paper\(^3\) we have observed that the fractional statistical error for a given number of samples actually decreases as a function of the number of Fourier coefficients included in the calculation. These observations imply that smooth convergence of the megadimensional integrals over the Fourier space are attainable with the present uncorrelated-samples Monte Carlo method.

Another point worth emphasizing is the complementary nature of the variational and the FPI AOSS-U calculations. For diatomic HCl the variational method is accurate and relatively inexpensive to apply, and it requires fewer basis functions to converge a low-temperature partition function than one at high temperature. This is important, because the numerical effort necessary to carry out the variational calculation grows rapidly as a function of the number of basis functions used to represent the system, due to the scaling properties of matrix diagonalization computations. However, the FPI AOSS-U method requires many Fourier coefficients at low temperatures and fewer at high temperatures, and the fractional statistical error for a fixed number of Fourier coefficients decreases as a function of the temperature. Therefore, if only high temperatures were of interest, the FPI AOSS-U method would be much less expensive than the variational method. However, the path-integral method does not become useful only in the "near classical" limit. For example, we note that even with \( K \) as low as 128, the path-integral calculation agrees with the quantum calculation within its 2% statistical uncertainty at 600 K, whereas the classical separable approximation is still in error by a factor of 4.8 at this temperature.

However complementary the variational and FPI AOSS-U methods are for a diatomic system, we expect the situation to change dramatically when one considers partition functions for polyatomic molecules. Variational calculations for vibrational–rotational states of triatomic molecules with \( J > 0 \) are currently considered to be state of the art,\(^4\) and only a few large-\( J \) calculations currently exist in the literature. In order to calculate the high-temperature partition functions for HCl, at least 60 rotational states are needed to obtain convergence to three significant figures. This situation is typical for hydrides, and much higher \( J \) would be required for nonhydrides, and for this reason fully converged high-temperature partition functions for triatomic molecules have not yet been reported in the literature. However, the FPI AOSS-U method does not suffer from this difficulty, as rotations are included in the Cartesian domain. Moreover, the FPI AOSS-U method is Monte Carlo.

### TABLE IV. Comparison of approximate vibrational–rotational partition functions with exact calculations.

<table>
<thead>
<tr>
<th>( T (K) )</th>
<th>( Q(CRRO)^{a} )</th>
<th>( Q(QRRO)^{b} )</th>
<th>( Q(BS)^{c} )</th>
<th>( \langle Q(T) \rangle^{d} )</th>
<th>( Q(var)^{f} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.372</td>
<td>0.0154</td>
<td>0.016 51</td>
<td>0.016 ± 0.000 8</td>
<td>0.016 51</td>
</tr>
<tr>
<td>400</td>
<td>2.439</td>
<td>0.123</td>
<td>0.130 0</td>
<td>0.139 ± 0.005 0</td>
<td>0.130 0</td>
</tr>
<tr>
<td>500</td>
<td>3.812</td>
<td>0.448</td>
<td>0.471 8</td>
<td>0.49 ± 0.02</td>
<td>0.471 8</td>
</tr>
<tr>
<td>600</td>
<td>5.489</td>
<td>1.101</td>
<td>1.153</td>
<td>1.17 ± 0.02</td>
<td>1.153</td>
</tr>
<tr>
<td>700</td>
<td>12.35</td>
<td>5.483</td>
<td>5.711</td>
<td>5.76 ± 0.07</td>
<td>5.713</td>
</tr>
<tr>
<td>1200</td>
<td>21.95</td>
<td>13.54</td>
<td>14.10</td>
<td>14.2 ± 0.2</td>
<td>14.11</td>
</tr>
<tr>
<td>2000</td>
<td>60.99</td>
<td>50.77</td>
<td>53.31</td>
<td>53.6 ± 0.5</td>
<td>53.55</td>
</tr>
<tr>
<td>4000</td>
<td>243.9</td>
<td>232.9</td>
<td>252.5</td>
<td>257 ± 2</td>
<td>257.3</td>
</tr>
<tr>
<td>5000</td>
<td>381.2</td>
<td>370.0</td>
<td>408.7</td>
<td>420 ± 3</td>
<td>421.0</td>
</tr>
<tr>
<td>6000</td>
<td>548.9</td>
<td>537.7</td>
<td>606.7</td>
<td>636 ± 5</td>
<td>630.5</td>
</tr>
</tbody>
</table>

\(^a\)Classical rigid-rotor–harmonic-oscillator partition function.  
\(^b\)Quantal rigid-rotor–harmonic-oscillator partition function.  
\(^c\)Quantal nonrigid-rotor–anharmonic-oscillator partition function.  
\(^d\)Fully coupled partition function evaluated via Fourier path integrals (see Table II). Unless otherwise noted, all calculations use \( K = 128 \) Fourier coefficients.  
\(^e\)Same as footnote \( d \), except \( K = 1024 \).  
\(^f\)Fully coupled partition function evaluated via standard variational methods (see Table II).
Carlo based, and therefore scales well as a function of the dimensionality of the space to be sampled. We are currently carrying out calculations on H$_2$O in order to address whether the scheme will perform as well for a six-dimensional triatomic.

VII. SUMMARY

We have carried out Fourier path-integral Monte Carlo calculations of vibrational–rotational partition functions, and hence quantum free energies, for the diatomic HCl molecule, using adaptively optimized stratified sampling in the nuclear configuration space and uncorrelated sampling in the Fourier coefficient space. The new method is in quantitative agreement with calculations carried out via standard variational methods over a wide temperature range (300<T<6000 K). In particular, we obtained 1% or better agreement at 900–6000 K, ~2% at 300 and 600 K, and 4%–7% agreement at 400 and 500 K. Furthermore, it is clear from the convergence studies at 300 K that good agreement could be obtained at 400–500 K as well by increasing the number of Fourier coefficients. Comparison of these calculations with various approximate methods, which separate the partition functions into vibrational and rotational contributions, show that vibrational–rotational coupling, anharmonicity, nonrigidity, and quantum effects are important dynamical factors within this temperature range, and that the Fourier path-integral method accurately includes these effects. As the Fourier path-integral calculations are carried out in three-dimensional Cartesian coordinates, this work constitutes a fairly stringent test of the accuracy and generality of the method. Since the method is Monte Carlo based, there is good reason to expect that the method will scale favorably with respect to the number of degrees of freedom and be successfully applied to similar calculations on small polyatomic molecules.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation. Partial support for this work has also come from the Army research office contract number DAALO3-89-C-0038 with the Army High Performance Computing Research Center at the University of Minnesota.

10 L. Pauling and E. B. Wilson, Jr., Introduction to Quantum Mechanics With Applications to Chemistry (Dover, New York, 1963), pp. 188–190, and references therein.
16 R. Q. Topper and D. G. Truhlar (unpublished).