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Methods for calculating partition functions of molecules involving large amplitude and/or anharmonic motions

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Abstract

We present a method for calculating partition functions taking into account anharmonic contributions for systems involving both small-amplitude vibrations and hindered rotations. The Wang-Landau scheme is used in the first case, while two alternative schemes are used for hindered rotation based on imaginary time propagation and fitting of the exact energy levels as a function of quantum number. These two schemes are shown to be complementary in their ranges of applicability (in terms of the torsional rotational constant and the relevant potential). Partition functions for four different molecules are calculated and compared to simpler ones obtained using a harmonic model.

Introduction

Molecular partition functions are ubiquitous in physical chemistry as they contain the full thermodynamical information on systems in the canonical ensemble. Their use ranges from kinetics to thermodynamics of systems of any size. In the kinetics case, transition state theory (TST), in any of its many variations,^{1,2} is the method of choice for the calculation of both unimolecular and bimolecular rate constants where exact dynamical calculations are unfeasible (as is the case for most reactive systems of interest). The study of systems of astrochemical interest, as well as systems of relevance in combustion and atmospheric chemistry requires accurate values of rate constants and TST has proven to be a reliable tool for their calculation. The TST expression for the rate constant requires partition functions for both the reactants and the transition state and it leads to a clear understanding of various kinetic aspects such as the isotope effect. The same is true for thermodynamical problems, where partition functions can be used to calculate enthalpy and entropy variations, as well as equilibrium constants of chemical reactions and thus assess their spontaneity under given conditions.

The partition functions for the simple cases of the rigid rotor and the harmonic oscillator are well known from elementary statistical thermodynamics and are extensively used in the treatment of semi-rigid systems. On the other hand, degrees of freedom involving one or

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more large amplitude motions (LAM) are more difficult to handle. Examples of such motions include hindered rotations.

Obviously, the only way to obtain exact partition functions for hindered rotations is through the calculation of the energy spectrum of the Hamiltonian, i.e. through the diagonalization of an appropriate matrix. This approach is straightforward for monodimensional internal rotations and it has also been applied with Fast Fourier Transform to a series of coupled, bidimensional hindered rotors.¹² The main problem is the unfavorable scaling of the CPU time with the dimensionality of the coupled internal rotations.

On the other hand, no general formula exists for the partition function referring to these motions and, as a result, several models have been devised to deal with them.^{3–11} As simplifying assumptions, towards the limit of free rotation, the classical value of the hindered rotor partition function⁶ can be used. Moreover, at low temperatures, the harmonic expression can be used for oscillators as the effects of anharmonicity are not expected to be appreciable.

Here we present a unified scheme for the calculation of partition functions of molecular systems which include one or both of these complications, in the possible presence of a number of harmonic oscillators.

For the vibrations, a quadratic formula for the energy is assumed as a function of the quantum number (cross terms account for the coupling between oscillators) and we calculate the density of states (DOS) of the entire set of vibrational modes numerically via a phase space random walk approach, known as Wang-Landau method.¹³ In this way, the overall DOS is obtained through a clever state-counting algorithm. A subsequent Laplace transform yields the partition function as a function of the temperature. Thermodynamic properties can afterwards be extracted from it using well-known formulae from statistical mechanics.

Currently, the standard scheme for treating vibrations from a thermodynamical statistical point of view is to adopt the harmonic model, whereby the energy is expressed as a linear function of the relevant quantum number and no coupling between oscillators is assumed. Schemes such as the Beyer-Swinehart procedure can be used to convolute the density of states of a harmonic oscillator with that of other degrees of freedom.¹⁴ In the method presented here, we use the Wang-Landau scheme to treat extensive, semi-rigid systems (with small amplitude motions) beyond the harmonic model, assuming a quadratic expression for the energy with respect to the quantum number and including coupling between different vibrational modes. In this work, the largest molecule treated is biphenyl, including 60 vibrational modes.

Finally, in our work we demonstrate the inclusion of large amplitude motions (LAM) in the form of hindered rotations. Even though only one hindered rotation is included in our models, any number of them can be treated (assuming complete decoupling from the rest of the vibrational motions). For hindered rotations, we employ two alternative schemes to calculate the relevant partition function. In one case, we estimate the partition function through propagation in imaginary time of a statistically representative sample of initial wavepackets. A Chebyshev expansion is used to apply the propagator to the initial

wavepacket. This approach is already well established in the theory of time-dependent wavepacket propagation.^{15–19} The main differences from the use of the Chebyshev expansion in time-dependent propagation are:

1. The use of *imaginary* as opposed to *real* time.
2. Our interest lies only in the *trace* of the operator rather than its detailed effect.

Alternatively, we obtain a (reasonably small) subset of hindered rotor eigenvalues using a variational scheme and we subsequently fit all eigenvalues from a minimum quantum number onwards to a polynomial formula, while keeping the ones below minimum to their exact values. Afterwards, the Wang-Landau scheme is used to calculate the density of states and the partition function.

We illustrate our strategy by calculating partition functions for realistic systems which combine anharmonicity (treated perturbatively) and hindered rotation. In all cases, the partition function is assumed to be defined as the trace of the Boltzmann operator $e^{-\frac{H}{k_B T}}$ (see below) and thus all partition functions include a zero-point contribution, being calculated with respect to the potential minimum. In terms of thermodynamic quantities, this implies that quantities such as internal energy, enthalpy, free energy etc. are displaced by the zero-point energy whereas quantities such as entropy, heat capacity etc. remain unchanged.

The partition functions obtained are compared with the ones where hindered rotation has been treated variationally, as well as the ones where all vibration has been treated as harmonic. In section 2 the relevant theory is presented, whereas section 3 is devoted to the presentation of results for specific molecules. Section 4 concludes.

Theory

The Wang-Landau scheme

The Wang-Landau scheme is a highly successful method for calculating densities of states for anharmonic oscillators. As it has been amply discussed in the literature^{13,20,21} we will only give a brief overview here.

In the Wang-Landau scheme, as it is most commonly used, it is assumed that a set of N anharmonic oscillators described by a corresponding N -uplet of quantum numbers has an energy level manifold described by the quadratic form

$$E(v_1, \dots, v_n) = E_0 + \sum_{i=1}^N \omega_i v_i + \sum_{i,j=1}^N \chi_{ij} v_i v_j \quad (1)$$

where ω_i denotes the frequency of the i -th oscillator and χ_{ij} is the anharmonic coupling constant between oscillators i and j . In order to build up its density of states, an initial N -uplet of vibrational quantum numbers is chosen randomly and, subsequently, the vibrational quantum numbers are varied in a random fashion until the whole manifold has been adequately explored. In all cases, the derivative of the energy with the quantum number is

also obtained in order to ensure that the dissociation limit is not exceeded (where the turning point of the quadratic polynomial is reached). Dividing the energy range into small intervals, the number of levels within each gives the density of states $\rho(E)$. Subsequently, a Laplace transform yields the partition functions

$$Z(\beta) = \int_0^\infty \rho(E) e^{-\beta E} dE \quad (2)$$

where $\beta = 1/(k_B T)$, k_B being the Boltzmann constant and T the absolute temperature. It is to be noted that the Wang-Landau scheme can be used with any sequence assigning an energy value to a running integer which represents a quantum number. As will be shown later, the Wang-Landau scheme can also be used to calculate the density of states for a hindered rotor along with the anharmonic oscillators (thus avoiding the need of computing convolution functions for the overall density function).

Treatment of hindered rotors by Chebyshev expansion

The partition function is written as the trace of the Boltzmann operator $e^{-\beta H}$

$$Z(T) \equiv \sum_n e^{-\beta E_n} = \text{Tr} \left(e^{-\beta H} \right) \quad (3)$$

where H is the Hamiltonian of the system. Following a similar expression for the time propagator e^{-iHt} ,²² we write the operator $e^{-\beta H}$ in terms of a Chebyshev expansion as

$$e^{-\beta H} = e^{-\beta E_0} \sum_{n=0}^{\infty} (2 - \delta_{n0}) \left[e^{-\beta \Delta E} I_n(-\beta \Delta E) \right] T_n(H_s) \quad (4)$$

(E_0 and E are defined below). In this expression δ_{n0} is a Kronecker delta and I_n denotes a modified (hyperbolic) Bessel function of the first kind (as opposed to the ordinary J_n Bessel function used in the case of the time propagator), while T_n is a Chebyshev polynomial of the first kind with the property

$$T_n(\cos\theta) = \cos(n\theta) \quad (5)$$

The argument of the Chebyshev polynomial is a scaled Hamiltonian operator

$$H_s \equiv \frac{H - E_0}{\Delta E} \quad (6)$$

where the parameters E_0 and E are chosen so that the spectrum of H_s lies in the interval $[-1, 1]$. These parameters are determined from approximate values of the extrema of the kinetic and potential energies. In the case of a one-dimensional hindered rotor, described by

a discrete variable representation (DVR) basis set of $2N + 1$ points (corresponding to angular values θ_k , $1 \leq k \leq N$), we determine the spectrum using

$$E_{min} = \min_k V(\theta_k) \quad (7)$$

(the minimum value of the potential) and

$$E_{max} = AN^2 + \max_k V(\theta_k) \quad (8)$$

(the sum of the maximum value of the potential and the maximum representable kinetic energy on the grid), where A is the torsional rotational constant, assuming the standard angular coordinate is used (see later for the generalized coordinate). From these two values, we calculate

$$E_0 = \frac{E_{max} + E_{min}}{2} \quad (9)$$

and

$$\Delta E = \frac{E_{max} - E_{min}}{2} \quad (10)$$

The Chebyshev polynomials of the scaled Hamiltonian are calculated according to the recurrence relation

$$T_0(H_s) = 1, T_1(H_s) = H_s \quad (11)$$

$$T_{n+1}(H_s) = 2H_s T_n(H_s) - T_{n-1}(H_s) \quad (12)$$

As is well known,²² the sequence of Bessel functions converges exponentially as $n \rightarrow \infty$ and the convergence is faster the smaller βE is. As a result, we expect the expansion to converge with relatively few terms in the case of high temperatures and low-width spectra of the Hamiltonian (low torsional rotational constants and potential variations), i.e. the closer one finds oneself to the free-rotor limit. Moreover, omitting the exponential factor $e^{-\beta E_0}$ from the expansion and using the exponentially scaled modified Bessel functions $e^{-x} I_n(x)$ instead of simply $I_n(x)$ amounts to automatically shifting the potential minimum to 0 and this is what we choose to do, exploiting the boundedness of the exponentially scaled functions which simplifies the numerical aspect of the calculations.

We approximate the partition function by randomly choosing initial wavefunctions ψ_j and subsequently calculating (through the Chebyshev expansion) the expectation values $\langle \psi_j | e^{-\beta H} | \psi_j \rangle$. If one were to calculate the trace of the Boltzmann operator exactly, one would have to evaluate the expectation values for $2N + 1$ linearly independent functions. Alternatively, one would have to diagonalize the Hamiltonian operator (an operation which, in terms of CPU time, scales as N^3 where N is the basis size). However, if one uses wavefunctions that adequately (in a statistical sense) sample the phase space, an excellent approximation to the true partition function can be reached with only a fraction of initial wavepackets. Here, following the recipe of Manthe and coworkers,²³ we propagate initial real wavefunctions, whose overlap with the corresponding DVR function at each point around the 1-D rotor configuration space is either 1 or -1 (chosen randomly). This way, the wavepacket norm is equal to N and the trace can be approximated by the formula

$$\text{Tr} \left(e^{-\beta H} \right) = \frac{1}{n} \sum_{i=1}^n \langle \psi_i | e^{-\beta H} | \psi_i \rangle \quad (13)$$

where a number of n initial wavepackets is assumed. Such an approach also lends itself naturally to parallelization, whereby multicore processors can handle propagations of different wavepackets independently. The sample sizes used in all cases are shown in Table 1.

Generalized coordinate approach

Hindered rotations as a rule cannot be adequately treated by a local expansion of the potential energy surface (PES) such as a Taylor series approach, because of the slow convergence of such an expansion. As a first approximation, one can fit the hindered rotor potential to a specific model function (such as a trigonometric function, transforming the Schrödinger equation to a Mathieu-like one⁷). However, in general, this mode will be coupled to other intramolecular motions, rendering the behavior of the PES complicated. This is especially true when the molecule shows low symmetry along the path of internal rotation.

Our priority is to employ a single approach that can handle internal rotational modes for molecules of more than 10 atoms. Therefore, we have chosen to perform a fully relaxed *ab initio* scan of the rotational PES along the internal rotation, whereby the dihedral angle of the rotating units spans the interval $[0, 2\pi]$. This, essentially, entails an adiabatic separation of this particular DOF with respect to the others.

A well known problem regarding the identification and separation of different DOFs of a molecule is their coupling due to kinetic energy terms in the Hamiltonian, which leads to kinetic energy terms with variable effective mass.²⁴ This can introduce theoretical and numerical problems. A vast literature is focused on this argument due to its applications to a wide variety of different fields (see, as example,^{25,26} and references therein).

A promising approach is based on the work of Fukui^{27,28} on the definition of the Intrinsic Reaction Coordinate (IRC). The same formalism can be used to generate a *closed* curve that,

instead of connecting different points of the configuration space passing through a saddle point, represent the minimum energy path (MEP) in the mass-weighted Cartesian space \mathbf{X} of the motion along the internal rotation.^{29,30} In the space \mathbf{X} , the coordinates of a point \mathbf{x} are the elements of the set $\{x_i\}$, where $i = [1, 2 \dots 3N]$.

The closed curve $\mathbf{x}(s)$ with respect to s , the parameter corresponding to our generalized coordinate, is defined by the differential equation

$$\frac{d\mathbf{x}(s)}{ds} = \frac{\mathbf{g}}{\sqrt{\mathbf{g}^\dagger \cdot \mathbf{g}}} \quad (14)$$

where \mathbf{g} is the energy gradient in mass-weighted Cartesian coordinates³¹ and whose elements, labeled as g_i , are defined as

$$g_i = \frac{\partial E}{\partial x_i} \quad (15)$$

Equation 14 becomes indeterminate at any extremum point along the closed curve s , but it can be shown³¹ that even at these points the solution can be deduced from the knowledge of the second and third coefficients of the Taylor expansion of the PES, that we can perform automatically in the frame of VPT2.³²

Now, we need a practical way to evaluate the map $\mathbf{a}(s)$ that associates for each values of s a point \mathbf{x} in \mathbf{X} : we first note that Eq. 14 has six solutions that are identically zero, related to translations and external rotations, plus another one related to the curve itself, because we expect that the energy along the internal rotation varies slowly (otherwise, it should be treated as a vibration).

These considerations, implicit in the Reaction Path Hamiltonian (RPH) approach of Miller and co-workers,³³ lead to the following equation for the components $\mathbf{a}_i(s)$ of the map $\mathbf{a}(s)$ (Eq. 4.13 in³³)

$$x_i = \mathbf{a}_i(s) + \sum_{k=1}^{3N-7} \mathbf{L}_{i,k}(s) Q_k \quad (16)$$

where $\mathbf{L}_k(s)$ are the eigenvectors of the non-zero eigenvalues of the Hamiltonian (i.e. the vibrations) and Q_k are the normal modes.

Imposing the Eckart conditions to two consecutive optimized geometries and then superimposing their Eckart frames, we are able to minimize the rototranslational displacement between them. If the two geometries, actually two points \mathbf{x} in the configurational space \mathbf{X} , are close enough, the vibrational displacement (i.e. the second part of the RHS in Eq. 16, see³³ for the notation) is negligible and we can calculate pointwise $\mathbf{a}(s)$ as the distance in mass-weighted coordinate between the two points \mathbf{x}

$$|ds|^2 = |\mathbf{a}_{i+1}(s) - \mathbf{a}_i(s)|^2 = |\mathbf{x}_{i+1} - \mathbf{x}_i|^2 \quad (17)$$

In this scheme, the reduced mass is equal to unity and any information about kinematic coupling is stored in the discrepancy between the closed curve s , parametrized pointwise by the map $\mathbf{a}(s)$, and its geometrical counterpart, i.e. the dihedral angle that defines the internal rotation.

These previous equations represent a numerical solution for the problem of a monodimensional Hamiltonian with a variable effective mass, based, as shown before, on the approximation in Eq. 16.

Least squares fitting of eigenvalues

Another approach we are using in this work is to fit the discrete energies for the hindered rotor as a function of the quantum number (interpreted as a running integer spanning the Hamiltonian eigenvalues). For a free rotor, as well as a Morse oscillator, the energy is a quadratic function of the quantum number. Thus, if the fitting starts from a given quantum number n_0 onwards, it is expected to follow a convex quadratic function with increasing n_0 (as the levels tend to resemble those of a free rotor). However, for low energies, a polynomial performs rather poorly in reproducing the energies as a result of the (quasi)-degeneracies arising from tunnelling across the torsional potential maxima. Thus, for all systems, we define two limits:

1. The minimum quantum number n_0 , below which all energies are taken to have their exact (variational) values.
2. A limiting quantum number n_r , above which the free rotor limit is assumed to have been reached and the energies are assumed to follow a quadratic expression.

The intermediate region (between n_0 and n_r) is fit to a quartic polynomial expression and is chosen so that n_r is minimal. As the quantum number n_0 corresponds semiclassically to a certain value of the action around the torsional loop, it is chosen to be proportional to the curvilinear semiclassical integral

$$n_0 \propto \oint \sqrt{(V_{\max} - V(s))} ds \quad (18)$$

where V_{\max} is the maximum value of the potential. The integral is taken around the closed path in configuration space corresponding to a complete torsional loop. Thus, the quantum number n_0 will be higher for more massive systems (where the generalized parameter s spans a higher range) and systems with higher torsional variation of the potential. However, whenever the semiclassical integral should give a value less than 10 we have chosen to assume $n_0 = 10$ in order to avoid numerical difficulties associated with a large state spacing. In Table 1 is shown the minimum quantum number used for the specific molecules we have dealt with. In all cases, we have found that a good value for the limiting quantum number n_r is $3n_0$. Thus, between n_0 and $3n_0$ the eigenvalues were fitted using a quartic polynomial and

above $3n_0$ the free rotor limit is assumed to have been reached and a quadratic polynomial (obtained through fitting of the last three doubly-degenerate state pairs below $3n_0$).

In all cases, we compare our results to results based on a variationally obtained set of energy levels. In particular, we calculate variationally the spectrum of the Hamiltonian by diagonalization on a DVR basis set.³⁵ In order to be sure that the eigenvalues thus obtained are converged, we have performed stability tests with an increasing number of DVR basis functions. We subsequently calculate the average deviation $\langle \delta_\epsilon \rangle$ of two sets of eigenvalues δ_{IJU}^n , δ_{IJU}^{2n} obtained using two sets with n and $2n$ DVR functions respectively, using the equation

$$\langle \delta_{\text{IJU}} \rangle = \frac{1}{n} \sum_{i=1}^n \frac{\delta_{\text{IJU}}^n - \delta_{\text{IJU}}^{2n}}{\delta_{\text{IJU}}^n} \quad (19)$$

obtaining always a $\langle \delta_\epsilon \rangle \approx 10^{-4}$ or less. It is interesting that, when a DVR diagonalization is performed with enough basis functions to reach the free rotor limit, even the maximum eigenvalues are found to be converged, while the maximum deviation is found at the lowest energy levels. This effect can, in our opinion, be traced to the sensitivity of the bottom levels to the number of DVR functions found in high-potential, classically forbidden regions whereas at high energies no such dependence is expected.

Outline of method

As already mentioned, our objective is to calculate densities of states and partition functions for molecules involving anharmonic vibrations and/or hindered rotations. The main features of the calculation strategy presented here are:

- Vibrational densities of states are calculated by the Wang-Landau scheme. The scheme can include both harmonic and anharmonic vibrational motion. As an option, some of the vibrational modes of the molecule can be designated as harmonic. In this case, their density of states can be easily convoluted with the rest through a Beyer-Swinehart scheme.
- Hindered rotor densities of states are calculated using the imaginary time propagation scheme described above, with subsequent convolution with the rest of the degrees of freedom. Alternatively, the energy levels (as obtained variationally) are fitted to a function of the quantum number n and subsequently included in the overall Wang-Landau scheme.
- Free rotor densities of states are calculated using well-established classical formulas.

In all cases, the numerical results are shown together with exact ones (as obtained through variational methods) and a comparison is made between the two. Moreover, the partition function resulting from treating all vibrational modes as harmonic is also shown in order to assess the effect of anharmonicity as well as to serve as a "baseline" for the different methods.

Specific Molecules

Our objective is to examine a few test cases that illustrate a representative subset of various combinations of torsional rotational constants and hindering potentials. The molecules chosen for this purpose are biphenyl, 1,2-dichloroethane, methanol and fluoromethanol as they illustrate the four relevant combinations. Thus, biphenyl and 1,2-dichloroethane have a low torsional rotational constant (due to the large size of the molecule and/or the masses of the atoms involved) while methanol and fluoromethanol where, for the most part, it is hydrogen atoms that move torsionally, exhibit a high rotational constant. On the other hand, looking at the torsional potential, 1,2-dichloromethane and fluoromethanol exhibit a high torsional potential variation while biphenyl and methanol have a much lower one. Thus, these four cases span the entire spectrum of relevant conditions. In all cases, when plotting the torsional potentials, an angle of 0° is chosen to represent the global minimum of the potential and its features are subsequently explained.

In Table 1 we present the minimum quantum number needed for the fitting, the size of the Monte Carlo (MC) sample in the Chebyshev propagation and the minimum number of eigenvalues that we have to use to obtain a fully convergent partition function, truncating the spectrum when the Boltzmann factor $e/\epsilon/k_B T > 10$. For 2000K, this occurs around 20000 cm^{-1}

All the electronic calculations have been performed at the DFT level, using the B3LYP functional and the SNSD basis set;³² in the case of biphenyl, dispersion contributions have been evaluated using the empirical correction proposed by Grimme.³⁶ The anharmonic corrections have been obtained using VPT2 as implemented in the quantum chemistry package GAUSSIAN09.³⁷ Each point along the internal rotation coordinate has been adiabatically relaxed.

In all cases, the partition function has been calculated using four different schemes:

1. Wang-Landau full anharmonic treatment of vibrations and hindered rotations, with fitting of the hindered rotation quantum numbers
2. Wang-Landau full anharmonic treatment of vibrations with imaginary time propagation of hindered rotation
3. Wang-Landau full anharmonic treatment of vibrations with exact (variational) treatment of hindered rotation
4. Harmonic treatment of all vibrations

Biphenyl

In Fig. 1 is shown the torsional potential for the biphenyl molecule. Despite the twofold torsional symmetry, the potential surface of biphenyl has four peaks: the interaction of hydrogen atoms in the coplanar configuration causes the first and the third ones, while the second and the fourth peaks (corresponding to a perpendicular configuration of the phenyl rings) are related to the repulsion of π molecular orbitals.

Due to the combination of a low torsional rotational constant ($\approx 1.7 \times 10^{-6}$ hartree) and a difference between maximum and minimum value of hindering potential of ≈ 0.0037 hartree (i.e. $\approx 800 \text{ cm}^{-1}$), the biphenyl molecule is a quantum system very close to the classical hindered rotor limit.

In Fig. 2 is shown the partition function of biphenyl, calculated in the four different modes shown previously. As expected, the harmonic treatment underestimates the total partition function (due to the higher spacing of the vibrational manifold). On the other hand, both line where the the time-propagation and the fitting schemes do an excellent job of approximating the variational results, although they slightly appear to overestimate and underestimate the partition function respectively. The underestimation by the fitting scheme can conceivably be traced to an overestimation of the quadratic "free rotor" torsional rotational constant by the fitting, a residue of the influence of the torsional potential. It is more difficult to assess the precise effect of the time-propagation convergence because of its fundamentally stochastic nature. Nevertheless, all methods appear to perform excellently at all temperatures considered.

The minimum fitting quantum number for biphenyl was found to be 37. Its relatively high value can be traced to the high torsional rotational constant, which confines a large number of states in the torsional potential. On the other hand, the torsional free rotor limit was assumed to be reached after around 110 states.

1,2-dichloroethane

The potential energy profile in Fig. 3 shows a global minimum for the *anti* conformation of the two Cl atoms and two symmetric local minima for the two *gauche* rotamers. The presence of the two vicinal chlorine atoms in the *syn* configuration produces a single peak in the torsional profile of about 3200 cm^{-1} or 0.0145 hartree, that corresponds to an equivalent temperature of about 4000 K.

However, the other two peaks have a height of 0.007 hartree. This kind of torsion can be viewed as a large amplitude motion with a single barrier due to eclipsing repulsion of the two chlorine atoms.

Figure 4 shows the canonical partition functions. The agreement with exact results is seen to be excellent again. The only appreciable deviation at high temperatures is due to the time-propagation treatment of the hindered rotation (which still, nevertheless, is essentially coincident with the exact results). As the deviation at low temperatures is essentially zero, the slight high-T deviation is probably due to incomplete Monte Carlo sampling of the configuration space.

Interestingly, at low temperatures the harmonic partition function appears to be slightly higher than the other ones. Presumably this is due to a negative anharmonicity coefficient and/or coupling between modes which serves to increase the anharmonic spacing of some low-lying states.

The minimum fitting quantum number in this case is 56, with the free rotor limit reached around 160. Even though the torsional rotational constant of 1,2-dichloroethane is higher,

the torsional potential is so much higher than in the case of biphenyl that more states need to be taken into account variationally. We remind that this is all indicated by the semiclassical integral shown previously.

Methanol

The methanol molecule has been extensively studied^{38,39} and, moreover, represents a prototype of hindered rotation. The small potential barrier, of about 360 cm^{-1} (or 0.0015 hartree), corresponding to the eclipsed H atom configuration, suggests that the free rotor limit is reachable even for medium temperatures, as shown in Fig. 5.

On the other hand, at lower temperatures (50-100 K) quantum effects become strong and the classical and harmonic partition functions underestimate the exact one: the ground state is a quasi-degenerate triplet because of the threefold symmetry of the torsional potential. The high torsional rotational constant of methanol means that, at moderate temperatures, even though the phase space is adequately sampled with only a few wavefunctions, these have a relatively high spatial "wavelength". The case of methanol, therefore, is among the ones least amenable to a Monte Carlo approach (where the phase of the sample wavefunctions is randomly distributed) and more to an exact one.

At high temperatures, both hindered rotation schemes approximate the variational partition function rather well, if slightly overestimating it. On the other hand, at low temperatures, the time propagation approach seriously underestimates the partition function. As mentioned before, this can be traced to the highly "quantum", delocalized nature of methanol low torsional levels. On the other hand, the fitting scheme does excellently at low temperatures (as expected, since low levels are taken with their variational values).

The minimum fitting quantum number for methanol was found to be 3 by the semiclassical integral and, as mentioned before, we have taken it to be 10 in order to avoid numerical problems. This is both an effect of the low torsional potential and the high torsional rotational constant.

Fluoromethanol

In order to assess the effect of a high torsional barrier (1750 cm^{-1} , ≈ 0.0076 hartree) on a hindered rotor with a high torsional rotational constant, we have also studied fluoromethanol.

Even though the molecular structure suggests the presence of three asymmetrical minima (Fig. 5 and Fig. 7), the potential energy surface shows only two minima associated with the two *gauche* rotamers. The *anti* conformation (where the F-C-C-H angle is 180°) is actually the highest maximum (the second peak in Fig. 7) and the *syn* conformation (where the F-C-C-H angle is 0°) is the lower maximum, i.e. the first peak.

This behavior is presumably associated to an interplay between eclipsing interactions between the O-H and the C-H and C-F bonds and an intramolecular O-H...F hydrogen bond.

The fluoromethanol partition function converges relatively slowly with the number of initial wavepackets. An explanation for this fact lies in the higher torsion potential profile: the resulting eigenfunctions have a relatively localized structure and are therefore less easily represented with sample eigenfunctions whose amplitude is uniform throughout the configuration space. This is also reflected in the fact (as in the case of methanol) that, at low temperatures, the time-propagation partition function seriously underestimates the variational one. On the other hand, the fitting partition function does well at all temperatures.

From the interplay of a medium torsional rotational constant and a relatively high torsional potential, a minimum fitting quantum number of 8 is calculated (therefore, again, the value of 10 is adopted).

The computational cost of our method can be assessed from Table 2. It can be seen that the cost of the variational method is essentially negligible to the Monte Carlo cost. In the case of the variational approach, the cost is higher for the bulkier molecules (owing to their high density of rotational levels and hence the higher number of levels to fit). The trend is essentially reversed in the Monte Carlo case where, methanol aside (which requires twice the number of sampling wavefunctions), the propagation time is higher where the torsional potential is higher (leading to a higher spectral width of the Hamiltonian).

Conclusions

We have presented numerical partition functions for a series of molecules. Both the harmonic and the Wang-Landau anharmonic scheme have been used for the vibrations, whereas, for the hindered rotations, two alternative schemes have been used: a scheme based on Monte Carlo sampling followed by propagation in imaginary time and a scheme based on polynomial fitting of high torsional levels ("high" being defined through the calculation of a classical action integral).

It can be seen that the harmonic model can be very inadequate and, for accurate results, anharmonicity as well as coupling between normal vibrational modes is indispensable. Moreover, the two hindered rotor schemes turn out to be complementary in their range of applicability. The time propagation scheme performs nicely in the case of large, classical-like molecules where, on the one hand, the quantum phase space is efficiently sampled by a Monte Carlo scheme and, on the other hand, the calculation (and subsequent fitting) of a large number of discrete levels would be cumbersome. The main drawback of this approach, as is common with all Monte Carlo approaches, where random sampling of a large population is involved, is the absence of a unique way to determine the error when the exact solution is not available. However, we expect that its advantages far outweigh the disadvantages in the treatment of the thermodynamics of large systems. Instead, the fitting scheme does well for smaller, quantum-like molecules where only a small number of discrete levels needs to be taken into account and Monte Carlo sampling tends to perform poorly, especially at low temperatures.

In this work we have presented some test cases of specific molecules. In all cases, anharmonicity was fully taken into account within the VPT2 scheme and only one hindered

rotation dimension was involved. However, the approach is expected to work equally well in multidimensional hindered rotation cases, at least when the coupling between the hindered rotors is negligible. We draw attention to various possibilities of a massive parallelization of the code, where propagation of the Monte Carlo wavepackets and/or different hindered rotors are treated separately by different cores. The latter feature is very useful in multi-dimensional cases when thousands of wavefunctions may need to be propagated. Moreover, this method is expected to have a considerable advantage over a traditional diagonalization technique in cases of systems with low torsional rotational constants, a steep torsion potential profile and high temperatures, where many eigenfunctions would be needed for an accurate calculation. The final aim is to fully incorporate this scheme into the Gaussian suite of programs in order to obtain a reliable and functional tool for the calculation of statistical thermodynamics information from electronic data.

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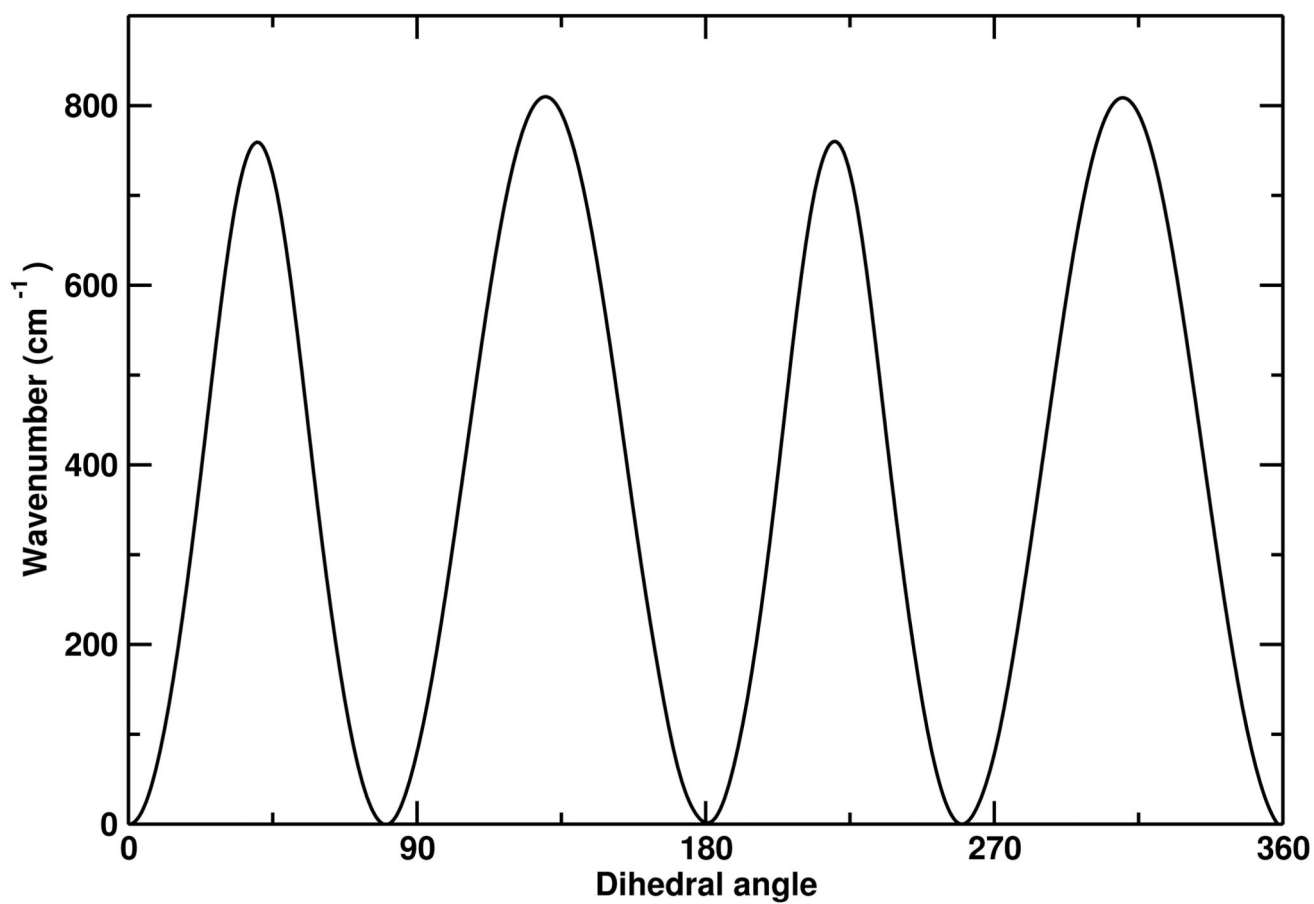


Figure 1. Biphényl potential: the first and the third peak are around 780 cm^{-1} (0.0034 hartree) while the second and the fourth about 810 cm^{-1} (0.0037 hartree).

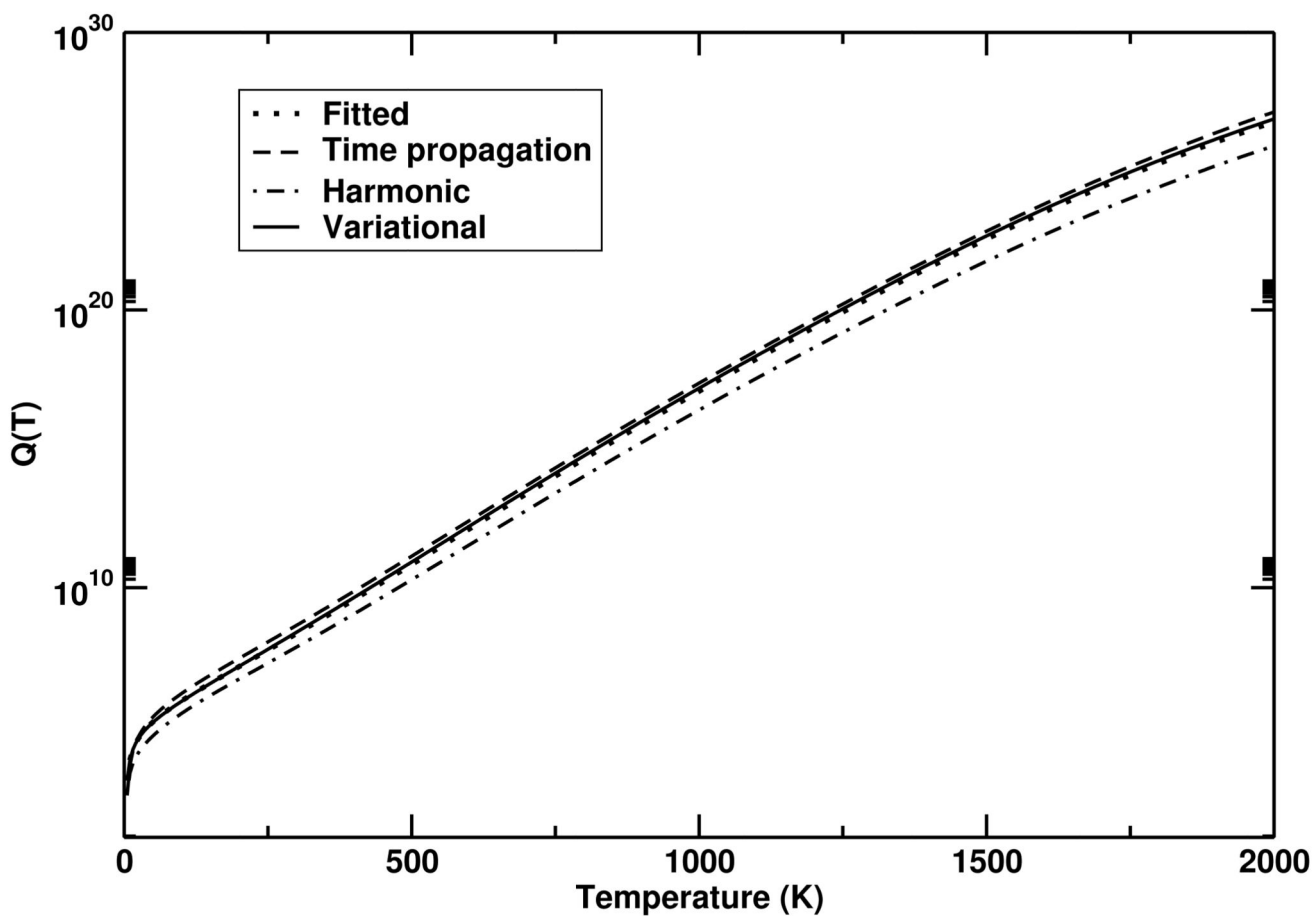


Figure 2. Biphenyl partition functions. The continuous line refers to the variational results, the dashed line where hindered rotation has been treated through imaginary time propagation, the dotted line where hindered rotation eigenvalues have been fitted and the dot-dashed line where the harmonic vibrational scheme has been used.

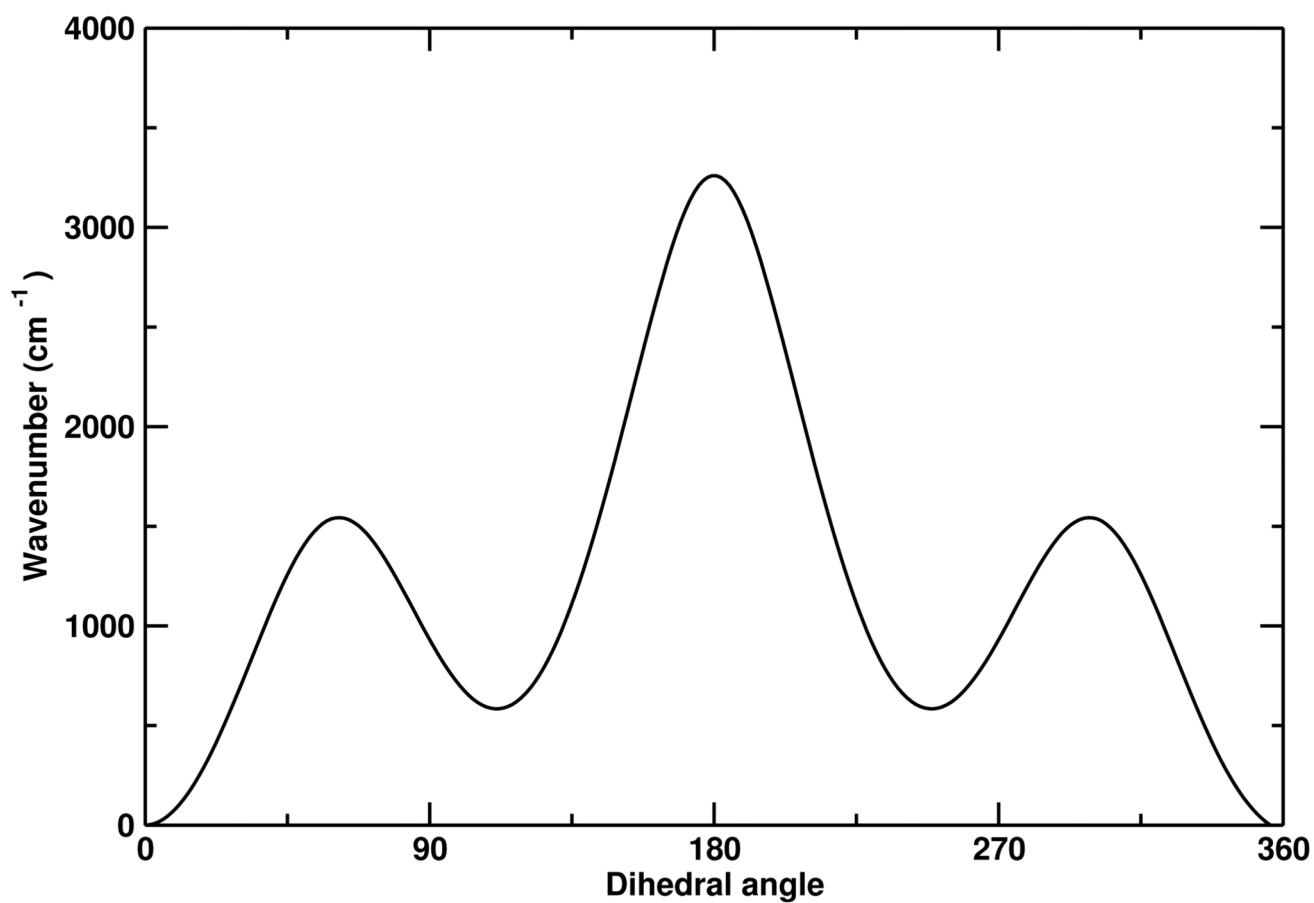


Figure 3.
1,2-dichloroethane potential: the first and the third peaks lie at 1600 cm^{-1} while the second one lies at 3200 cm^{-1}

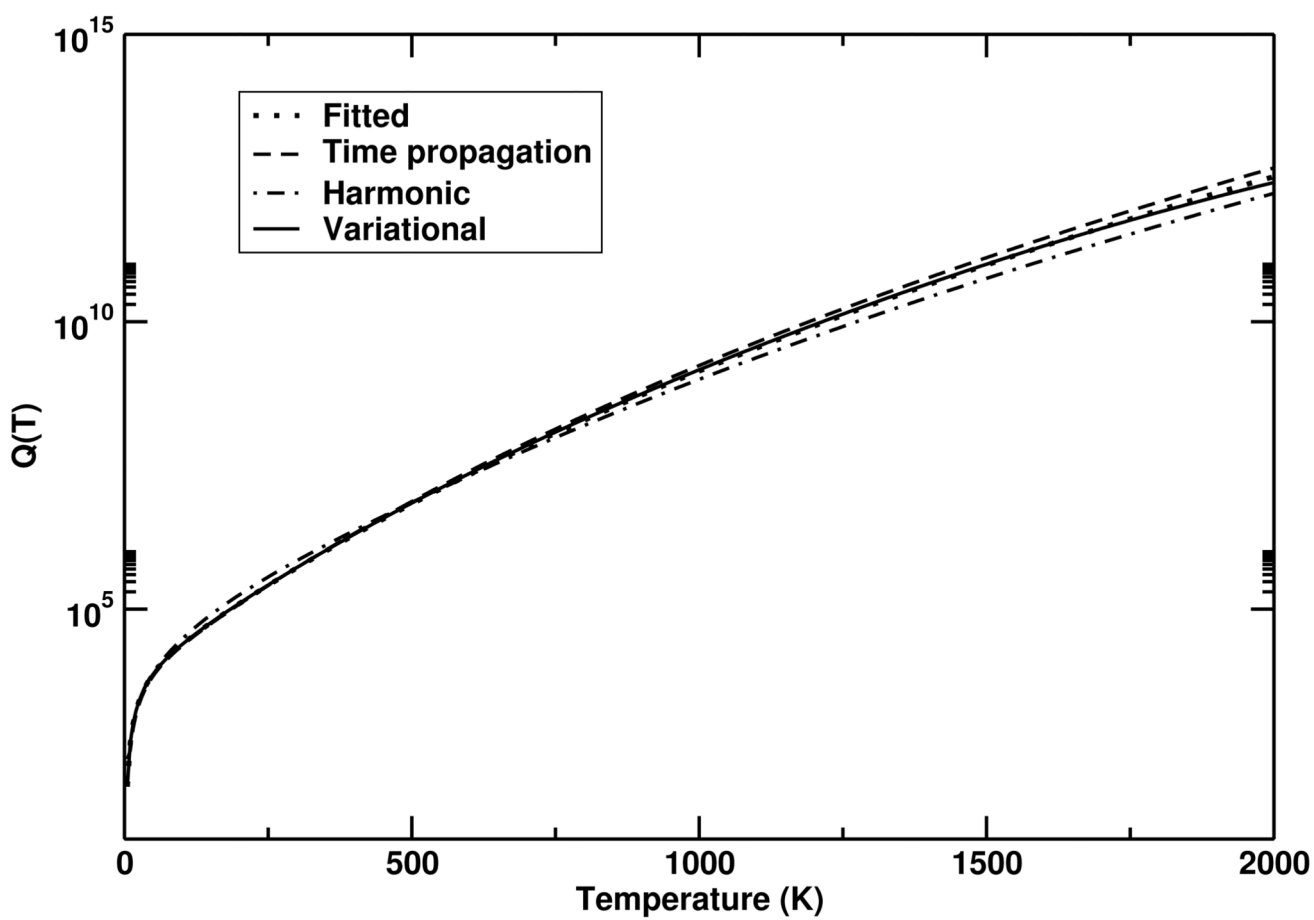


Figure 4.
As in Fig. 2 for 1,2-dichloroethane.

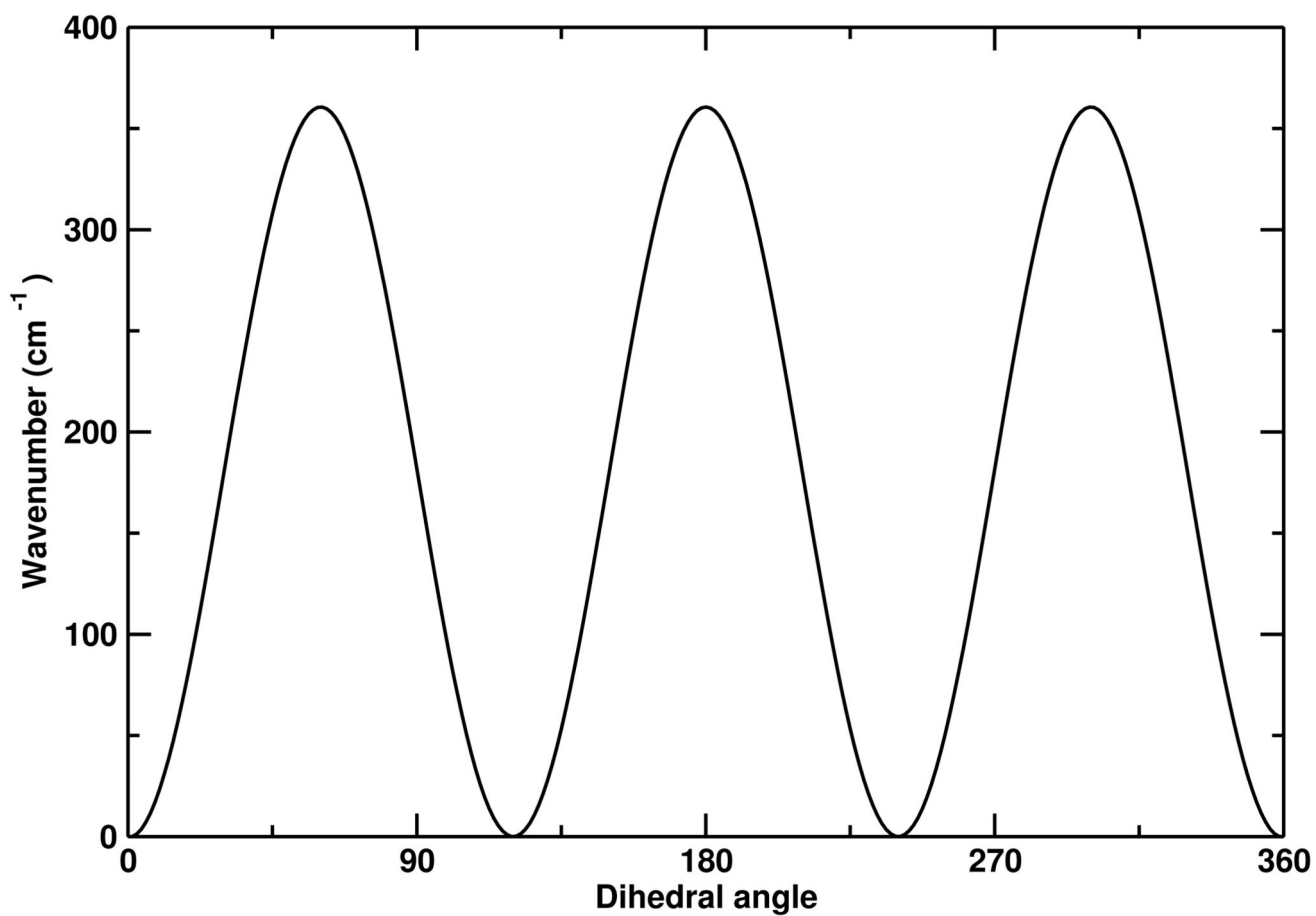


Figure 5. Methanol potential: the three degenerate maxima have a value of 360 cm^{-1} .

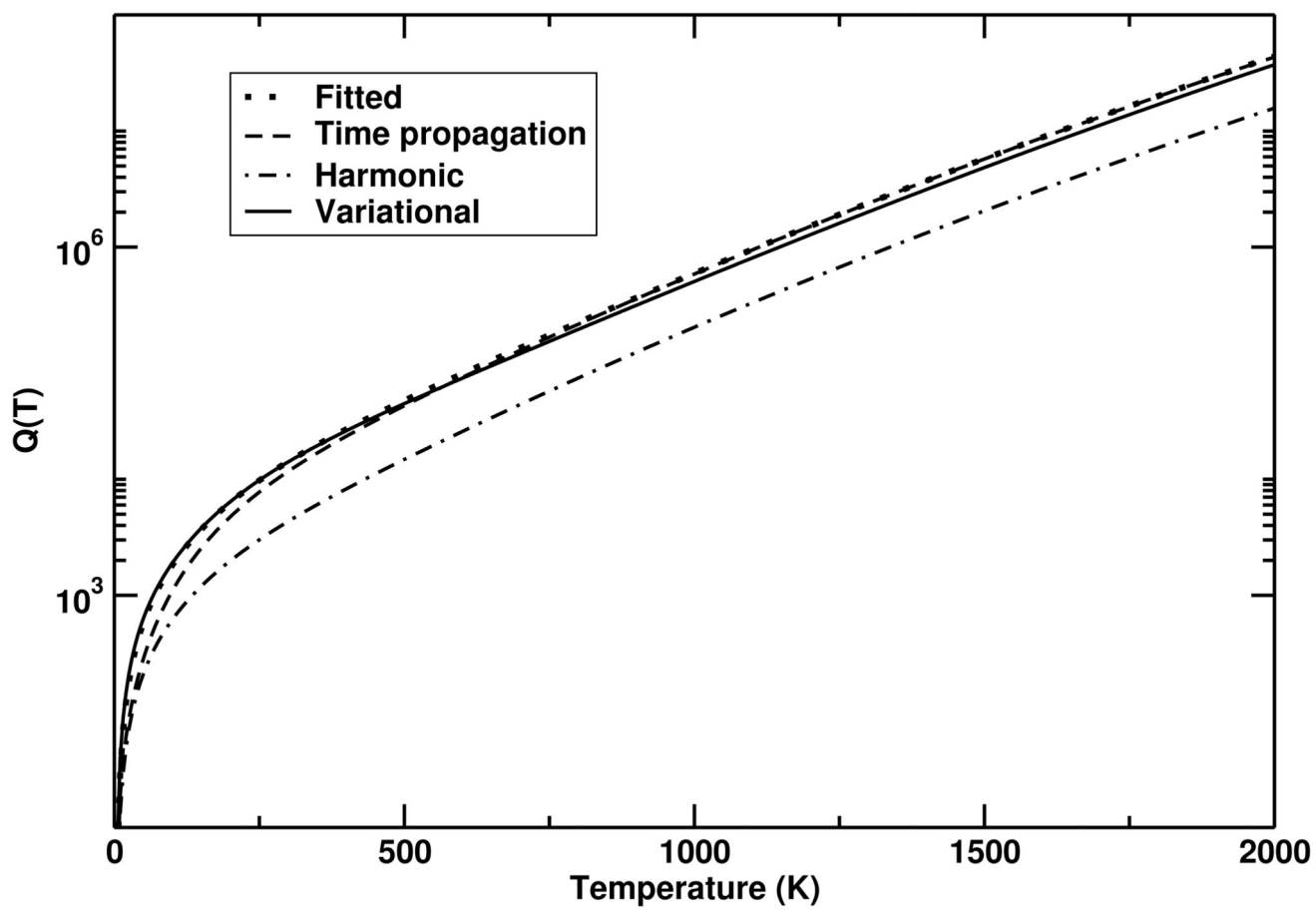


Figure 6.
As in Fig. 2 for methanol.

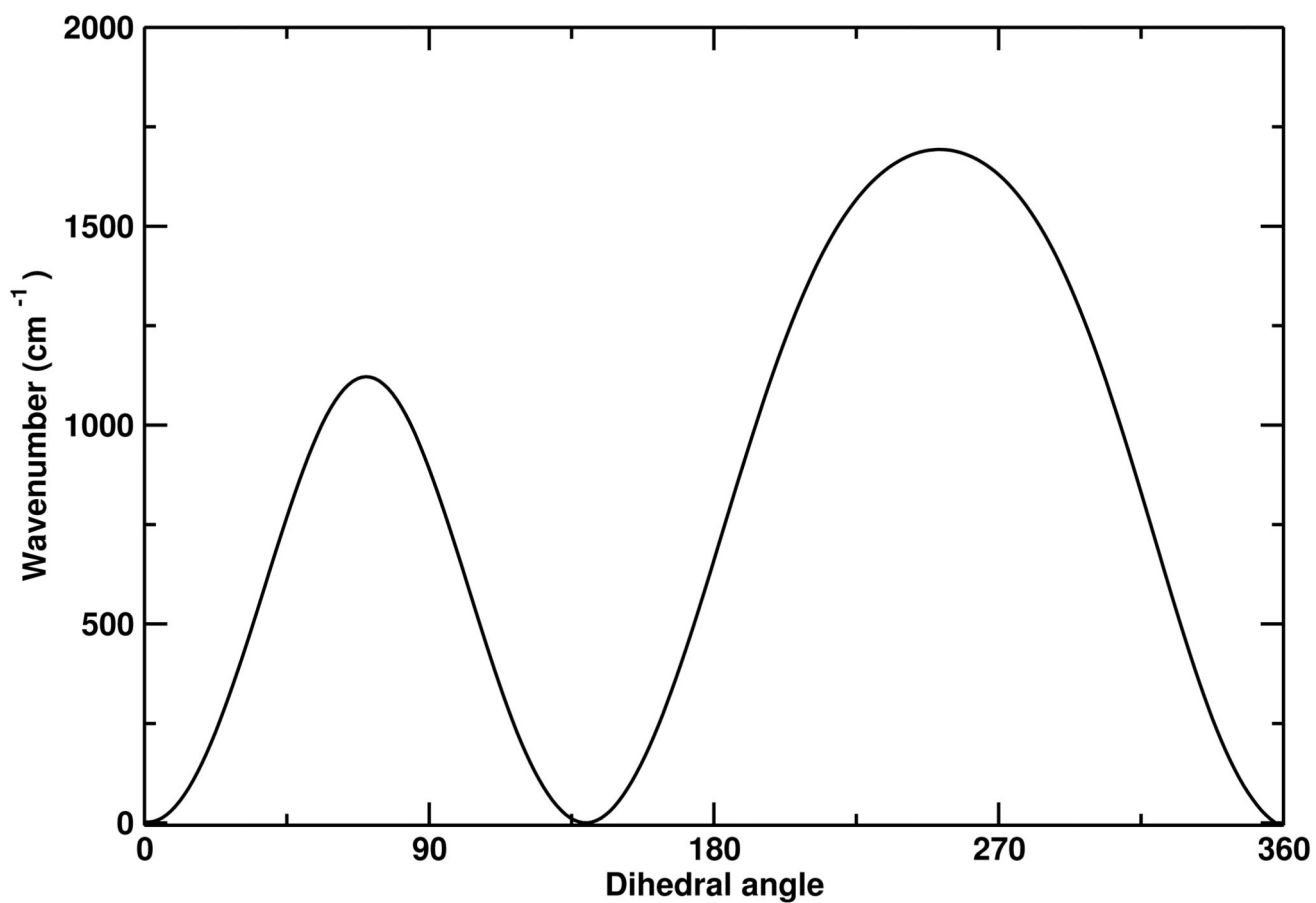


Figure 7.
Fluoromethanol potential: the two maxima correspond to 1000 cm⁻¹ and 1750 cm⁻¹.

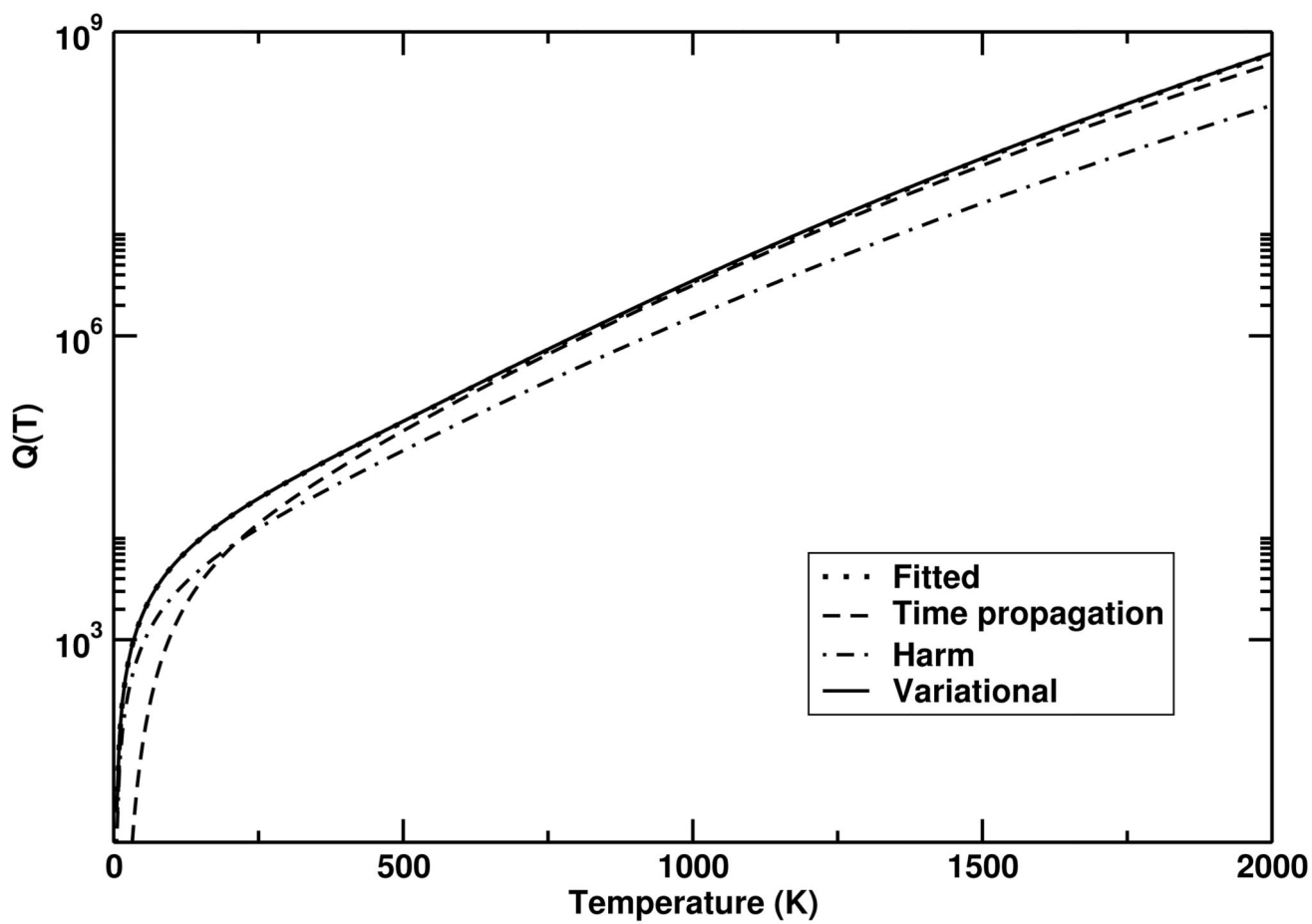


Figure 8.
As in Fig. 2 for fluoromethanol

Table 1

Minimum rotational quantum number, Monte Carlo sample size and number of DVR basis functions for each molecule

Molecule	Min. quant. num.	MC sample	Min. DVR basis set
Methanol	3	160	56
Fluoromethanol	8	80	59
Biphenyl	37	80	456
1,2-Dichloroethane	56	80	252

Table 2

CPU time cost (in seconds) of the Variational and Monte Carlo approach (in parenthesis the number of sampling wavefunctions used)

Molecule	Variational	Monte Carlo
Methanol	0.052	3418.95 (160)
Fluoromethanol	0.060	2927.79 (80)
1,2-Dichloroethane	0.24	537.76 (80)
Biphenyl	2.75	228.39 (80)