Path-Integral Monte Carlo Scheme for Rigid Tops: Application to the Quantum Rotator Phase Transition in Solid Methane

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A new quantum propagator for asymmetric tops, exact for free tops, is applied to path-integral Monte Carlo simulations of quantum rotors. The algorithm does not suffer from the sign problem if the full density matrix is considered or if the identity representation for the density matrix is chosen. The method is applied to simulation of crystalline CH_4, where the influence of quantum fluctuations in the lowering of the transition temperature from a plastic phase to an orientational ordered state is investigated. The possibility of an inverse hysteresis occurring at that transition is predicted and related to spin-statistical exchange effects. [S0031-9007(96)01147-7]

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A quantum mechanical description of rotational degrees of freedom (RDF) becomes important at low temperatures where tunneling and ground state fluctuations play an important role in orientational phase transitions [1], e.g., solid methane CH_4 undergoes a phase transition from a plastic cubic phase to an orientationally ordered phase at the temperature $T_1(CH_4) = 20.4$ K while its deuterated counterpart CH_4 shows the same transition at $T_1(CH_4) = 27.4$ K [2]. Because of its larger rotational constant B_{rot}, the ground state of solid CH_4 has a certain fraction of tunneling nonoriented molecules while in the case of CD_4 all molecules are oriented at zero temperature [2–4]. The computational treatment of this and related low-temperature phenomena requires a path-integral scheme for simulating RDF's. The most general case is, of course, the treatment of asymmetric-top molecules, for which all three principle moments of inertia $0 < I_a < I_b < I_c$ differ from each other. Much attention has been given to the development of path-integral methods for treating quantum translations [5,6] but not much has been given to the treatment of RDF's.

Kuharski and Rossky introduced a method for simulating rigid asymmetric-top molecules based on the fixed-axis approximation [7], an approach which is only exact up to order $1/P^2$ with P the Trotter number. Furthermore, the action is calculated at constant angular velocity. Hence this approach omits the winding numbers [8] when applied to rotations in a plane, e.g., by taking the limits $I_a \to 0$, $I_b \to I_c$ and thus contains systematic errors. An approximation-free path-integral Monte Carlo (PIMC) method for simulating linear molecules has been proposed by Marx [9], which, however, suffers from the sign problem [10] even at high temperatures and even angular momenta l. This is due to the introduction of intermediate free-rotator eigenstates in order to represent the state of a molecule at each Trotter slice. For most cases it is possible to circumvate the sign problem in this approach by summing over all intermediate free-rotator eigenstates [11]. The sign problem then only persists at low temperatures and odd l, e.g., for *ortho*-H_2 (even total nuclear spin I) and *para*-H_2 (odd I). In these cases the free-rotator kernels are antisymmetric and thus contain negative contributions invoking intrinsically the sign problem at low temperatures [12].

It is the purpose of this Letter to derive an exact free-rotator kernel for simulating nonlinear rotators. Using group theory, it is shown how to include the spin-statistical exchange effects of identical particles. We also apply our method to the quantum rotator phase transition in solid methane.

First an accurate expression for the high-temperature density matrix $\rho(\omega, \omega'; \beta/P)$ is derived. Here, ω denotes the Euler angles (ϕ, θ, χ) specifying the orientation of the rigid body in the space fixed frame and $\beta = 1/k_B T$. P is the Trotter number. Once an accurate expression for the free-rotator kernel is known it is a simple matter to apply it to PIMC simulations of rotators in the presence of an external potential or in multirotator systems. For details of the path-integral method in general, see, e.g., Refs. [8,13,14], and for details of the PIMC method we refer to Refs. [5,6,15].

The density matrix or kernel for the free top can be expressed as

$$\rho\left(\omega, \omega'; \frac{\beta}{P}\right) = \langle \omega | \exp\left(-\frac{\beta}{P} \hat{T}_{\mathrm{rot}}\right) | \omega' \rangle , \qquad (1)$$

where $\hat{T}_{\mathrm{rot}}$ is the operator of the rotational kinetic energy.

If we now transform this equation into the molecule fixed frame of the bra and insert the resolution of the identity operator $\hat{\mathbf{1}}$, where the eigenstates [16] of the free asymmetric top with the eigenenergies $E_{\tilde{K}}^{(JM)}$ are used, we obtain

$$\rho(\omega, \omega'; \beta/P) = \sum_{JM\tilde{K}K} \exp\left(-\frac{\beta}{P} E_{\tilde{K}}^{(JM)}\right) |A_{\tilde{K}K}^{(JM)}|^2 \times \langle 0 | JMK \rangle \langle JMK | \tilde{\omega}' \rangle , \qquad (2)$$

where $\tilde{\omega}'$ are the Euler angles of the ket in the coordinate system of the bra. The eigenfunctions

$\Psi_{JMK}(\omega) = \langle \omega \,|\, JMK \rangle$ of the symmetric top (moment of inertia $I_a \neq I_b = I_c$) can be expressed in terms of the elements of the $(2J + 1)$-dimensional irreducible representation $\mathcal{D}^J_{MK}(\phi, \theta, \chi)$ of the rotation operator $\exp(-i\hat{J}_z \phi) \exp(-i\hat{J}_y \theta) \exp(-i\hat{J}_z \chi)$,

$$\Psi_{JMK}(\omega) = \left(\frac{2J + 1}{8\pi^2}\right)^{1/2} \mathcal{D}^{J^*}_{MK}(\phi, \theta, \chi), \qquad (3)$$

which themselves can be calculated using the Wigner functions $d^J_{MK}(\theta)$:

$$\mathcal{D}^{J^*}_{MK}(\phi, \theta, \chi) = \exp(iM\phi) d^J_{MK}(\theta) \exp(iK\chi). \qquad (4)$$

Furthermore, using $d^J_{MK}(0) = \delta_{MK}$, the final equation for the kernel of the asymmetric top is

$$\begin{aligned} \rho(\omega, \omega'; \beta/P) = \sum_{JM\tilde{K}} & \left(\frac{2J + 1}{8\pi^2}\right) d^J_{MM}(\tilde{\theta}') \\ & \times \cos[M(\tilde{\phi}' + \tilde{\chi}')] \, |A^{(JM)}_{\tilde{K}M}|^2 \\ & \times \exp\left(-\frac{\beta}{P} E^{(JM)}_{\tilde{K}}\right), \end{aligned} \qquad (5)$$

where the $d^J_{MM}(\theta)$ can be calculated with the help of Wigner's formula. In Eq. (5) the sum over M was implicitly symmetrized, resulting in a real valued function for the kernel. This symmetrization of the sum is possible because of $d^J_{MM}(\theta) = d^J_{-M-M}(\theta)$ and because of $|A^{(JM)}_{\tilde{K}M}| = |A^{(JM)}_{\tilde{K}-M}|$. Furthermore, the eigenenergy $E^{(JM)}_{\tilde{K}}$ does not depend on the quantum number M.

In order to obtain the coefficients $A^{(JM)}_{\tilde{K}M}$ and the eigenenergies $E^{(JM)}_{\tilde{K}}$, the following secular equation has to be solved [16]:

$$\hat{T}_{\mathrm{rot}} \sum_K A^{(JM)}_{\tilde{K}K} \Psi_{JMK} = E^{(JM)}_{\tilde{K}} \sum_K A^{(JM)}_{\tilde{K}K} \Psi_{JMK}. \qquad (6)$$

The necessary matrix elements $\langle JMK' | \hat{T}_{\mathrm{rot}} | JMK \rangle$ to solve Eq. (6) are given in Ref. [16].

Once the temperature and the Trotter number are chosen for the system under consideration, $\rho(\omega, \omega'; \beta/P)$ depends only on two quantities, namely, the Euler angle $\tilde{\theta}'$ and the sum of the Euler angles $\tilde{\phi}'$ and $\tilde{\chi}'$, where $\tilde{\omega}'$ are the Euler angles related to ω' in the frame of the molecule with orientation ω. Even though $\rho(\omega, \omega'; \beta/P)$ might not be accessible analytically, it can be computed numerically to very high precision and then be tabulated on a fine grid [17]. The sum over J is clearly convergent, and hence all systematic errors can be kept controllably small.

Notice that the elements of the high-temperature density matrix for the one-dimensional rotation (rotation of a molecule around only one axis) and for the two-dimensional rotation (rotation of a linear molecule in three dimensions) follow straightforwardly from the kernel for the three-dimensional rotation, Eq. (5).

Up to now, spin statistics have been neglected. However, the spin configuration constrains the symmetry of the rotational state even without direct coupling between nuclear spins and the angular momentum due to the exchange of indistinguishable particles. For given nuclear spins of the atoms composing the molecule, the symmetry of the rotational wave functions are predetermined [1,18]. States belonging to different symmetry classes or representations cannot be reached from one another for reasons of nuclear-spin conservation [1]. It is generally possible to generate symmetrized orientational states $|\omega_\mu\rangle = \hat{P}_\mu |\omega\rangle$, belonging to only one representation, say, representation μ, with the help of a projection operator $\hat{P}_\mu$ [18]

$$\hat{P}_\mu = \frac{d_\mu}{g} \sum_R \chi_R^{(\mu)*} \hat{D}(R), \qquad (7)$$

where we sum over all symmetry operations (rotations) R. In Eq. (7), $\hat{D}(R)$ generates the symmetry operation, $\chi_R^{(\mu)}$ denotes the character of R in the representation μ, g is the order of the group, and d_μ the dimension of the representation μ.

The symmetrized orientations $|\omega_\mu\rangle$ now replace the nonsymmetrized $|\omega\rangle$ states in Eq. (1) for the calculation of the kernel $\rho_\mu(\omega, \omega'; \beta/P)$ belonging to representation μ:

$$\rho_\mu(\omega, \omega'; \beta/P) = \langle \omega_\mu | \exp\left(-\frac{\beta}{P} \hat{T}_{\mathrm{rot}}\right) | \omega'_\mu \rangle. \qquad (8)$$

Using Eq. (5) and the projection-operator property of P_μ, $\rho_\mu(\omega, \omega'; \beta/P)$ can be reexpressed as

$$\rho_\mu\left(\omega, \omega'; \frac{\beta}{P}\right) = \frac{d_\mu}{g} \sum_R \chi_R^{(\mu)*} \rho\left(0, \tilde{\omega}'(R); \frac{\beta}{P}\right) \qquad (9)$$

with $|\tilde{\omega}'(R)\rangle = \hat{D}^+(\omega) \hat{D}(R) |\omega'\rangle$. Notice that the computation of $|\tilde{\omega}'(R)\rangle$ reduces to simple matrix multiplications if $|\omega'\rangle$ is represented by a matrix.

We will now discuss the consequences of symmetrization of the kernel for methane. This molecule has tetrahedral symmetry, and, consequently, the rotational wave function can be decomposed into states belonging to the identity representation A, the representation T, and the representation E, which can be further decomposed into the two complex conjugate representations E_1 and E_2 [18]. The nuclear spin I in the case of CH_4 is $I = 2$ for A-CH_4, $I = 1$ for T-CH_4, and $I = 0$ for E-CH_4 [19]. In Fig. 1 the kernel ρ_A belonging to representation A and the full kernel ρ, in which no exchange effects are considered, are shown for $PT = 64$ K. The maxima of ρ_A can be attributed to symmetry operations, namely, the peaks at $\theta = \pi$, $\phi + \chi = 0$, $\theta = 0$, $\phi + \chi = \pi$, and $\theta = \pi$, $\phi + \chi = \pi$ to rotations about the twofold symmetry axis, and the peaks at $\theta = \pi/4$, $\phi + \chi = \pi/2, 3\pi/2$ to rotations about the threefold symmetry axis of the CH_4 molecules. In the case of the T representation, negative minima are found for ρ_T at those points attributed to symmetry operations about the twofold symmetry axis, and,

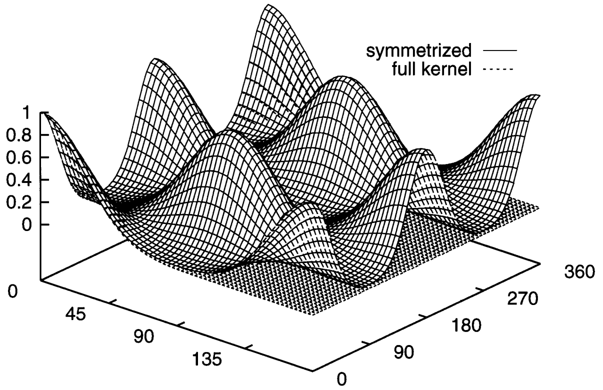

FIG. 1. $\rho(\theta, \phi + \chi; \beta/P)$ for CH_4 at $(\beta/P)^{-1} = 64 k_B T$. The full kernel shows only one maximum at $\theta = 0$, $\phi + \chi = 0$.

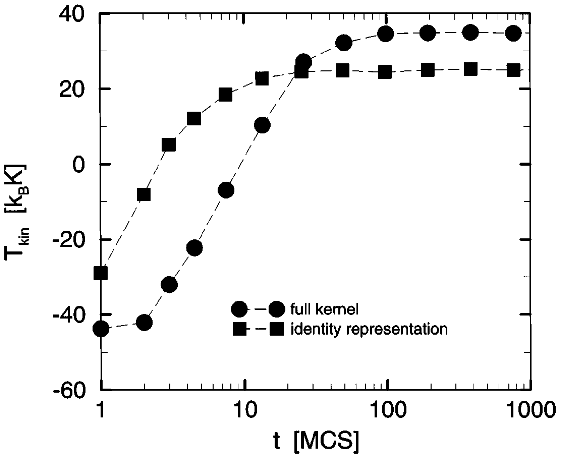

FIG. 2. Kinetic energy estimator T_{kin} as a function of time in Monte Carlo sweeps for solid CH_4 at $T = 16$ K with Trotter number $P = 4$.

for ρ_E, negative minima are found at the points attributed to symmetry operations around the threefold axis. For fully deuterated methane molecules CD_4, the features of the kernels are qualitatively the same as for CH_4, but the total nuclear spins are different; e.g., $I = 0$ invokes the identity representation. While there is a one-to-one relation of total nuclear spin with the symmetry of the rotational wave function for CH_4, this is no longer the case for CD_4 [19].

It is worth noting that, for all examples investigated, spherical, symmetric, and asymmetric tops, we always find positive valued density matrices for the identity representation and for the full density matrix. All other representations also have negative contributions, which intrinsically lead to the well known sign problem in a path-integral simulation [10,12]. The standard methods to treat the sign problem must then be applied [9–11].

Before presenting some details of the simulations, we want to point out two advantages of choosing the identity representation for the path-integral simulation: (i) Correlation times for many observables, e.g., kinetic energy T_{kin}, are smaller (see Fig. 2), and (ii) ground state properties can be accessed at relatively high temperatures because the energetically low lying excited states are projected out. Remember that the ground state is fully obtained in the identity representation.

In the application of Eqs. (5) and (9) to the quantum-rotator phase transition in cubic methane, we want to investigate the dependence of the transition temperature on the rotational constant B_{rot} and on the symmetry of the wave function. In the latter investigation we concentrate on the nonsymmetrized case and the identity representation.

It is well known that translation-rotation coupling V_{TR} is symmetry forbidden for the investigated transition in cubic CH_4 [20]. Consequently, the relative volume jump at the order-disorder transition is only about 1% due to higher order couplings such as V_{TTR}. The translational and orientational degrees of freedom can therefore be separated to a good approximation. In our simulation, the molecules are fixed to their lattice sites, and in the following we only concentrate on the rotational degrees of freedom. The lattice constant is chosen such that it corresponds to the experimentally observed lattice constant at the transition from a plastic to an orientationally ordered phase.

For the intermolecular model potential, which has been fitted to the *ab initio* data of the CH_4 dimer [21], we chose the exp-6 potential plus Coulomb-Coulomb interactions. At each temperature, runs with different Trotter numbers P were performed such that $64 \leq PT \leq 128$ K. The quantum limit is obtained by performing a Trotter scaling plot. The particle number N in the final runs was chosen to be $N = 864$. For a given Trotter number, the system is cooled down and reheated again. At every temperature, $2000P$ Monte Carlo sweeps were used for equilibration and $3000P$ Monte Carlo sweeps were used for observation. These experiments have been repeated four times with different initialization numbers for the random number generator.

For the classical system we observe a transition at $T_1 \approx 27$ K, which is shifted to $T_1 \approx 16$ K for the quantum-mechanical no-spin treatment (full kernel), see Fig. 3, where the potential energy V_{pot} is shown for both systems. If the identity representation is chosen, the transition temperature is furthermore lowered to $T_1 \approx 10$ K. In the case of no-spin CH_4 the transition temperature is close to the classical value, namely, $T_1 \approx 23$ K.

The strong dependence of the transition temperature on the symmetry of the rotational states may invoke an inverse hysteresis effect. If the methane solid is cooled down at a rate so that spins can equilibrate, we expect the transition to take place close to the no-spin case at $T_1 = 16$ K. At temperatures considerably lower than T_1,

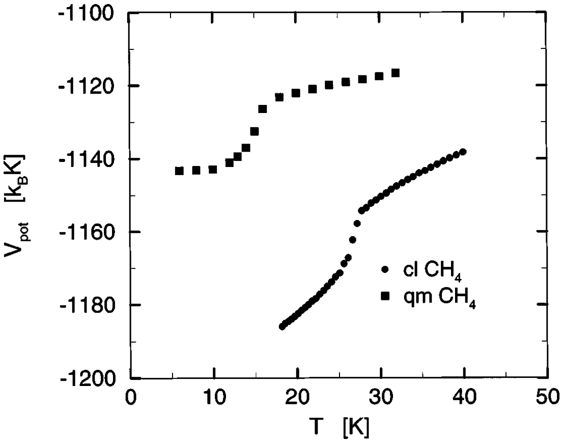

FIG. 3. Potential energy V_{pot} as a function of temperature for "classical" and "quantum" CH_4.

the ground state, which is fully contained in the identity representation, will dominate, thus the nuclear spin I of each molecule will be $I = 2$. If the system is reheated rapidly, the symmetry of the rotational states will remain in the identity representation due to long spin conversion times, and the transition will be found at $T_1 = 10$ K. The numerical results may change slightly if the translational degrees of freedom are taken into account as well. This, however, would have required a much larger numerical effort.

The computed transition temperatures compare well with experimental data, where $T_1(CH_4) = 20.4$ K and $T_1(CD_4) = 27.4$ K. To achieve this agreement, very accurate potentials were needed because the specific heat for CH_4 is already very small due to quantum effects, and thus the transition temperatures are extremely sensitive to small variations of the potential. This sensitiveness can be seen in the considerable dependence of the transition temperature on the symmetry of the thermal wave function. Remember that at high temperatures this dependence will vanish because exchange effects no longer play an important role.

The path-integral propagator introduced here provides an efficient method for simulating the low-temperature thermodynamics of rigid nonlinear molecules. For example, it makes possible the study of quantum-rotator phase transitions in solid methane, and will be useful in future studies of thermal properties arising from molecular librations and tunneling in clusters and solids.

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