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Quantum-Monte Carlo study of rovibrational states of molecular systems

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Abstract

A novel procedure to calculate the excited rovibrational energy levels of quantum-molecular systems based on the correlation-function quantum-Monte Carlo (CFQMC) method is proposed. The procedure utilizes rotating wavefunctions as the trial basis in the CFQMC method. We test the present methodology in two low-dimensional systems: a rotating harmonic oscillator and rotating Morse potential. Comparisons are made with numerical ‘exact’ results and they are shown to be accurate. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The study of the rovibrational motions of molecules and clusters from given potential energy surfaces is a topic of great importance in molecular physics. Usually, the calculation of excited rovibrational energy levels are performed using variational methods. Variational methods expand the wavefunction in an appropriate basis set, evaluate the required integrals using quadrature or pointwise methods, and solve the resulting eigenvalue problem in a subspace spanned by the basis set. However, the number of basis functions grows exponentially with the number of particles. Calculations of rovibrational energy levels of tetratomic molecules have been reported [1–4], but the extension to larger molecules is still doubtful.

An alternative approach is the use of quantum-Monte Carlo (MC) techniques to compute the multi-

dimensional integrals that appear in the time-independent problems [5]. These techniques have been employed with great success in the calculation of properties of ground-state and finite-temperature quantum systems. However, there are few studies of excited states. The use of the correlation-function quantum-Monte Carlo (CFQMC) method, developed by Bernu and co-workers [6,7], to calculate the excited vibrational states of triatomic [7–9] and tetratomic [7,8] molecules, the study of multidimensional tunneling motion in complexes using the rigid-body diffusion Monte Carlo (RBDMC) method [10,11] and the use of the projection-operator imaginary-time spectral evolution (POITSE) [12] to calculate the rovibrational states of molecular systems [13] are some examples of the study of excited states.

The aim of this Letter is to develop a novel procedure to calculate the excited rovibrational energy levels based on the CFQMC method. For this, we propose to utilize rotating functions as the trial basis functions in the CFQMC method. We apply the

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present procedure in the study of two low-dimensional systems to verify its accuracy: a rotating harmonic oscillator and rotating Morse potential. In Section 2, we summarize the CFQMC method, and the procedure to calculate rovibrational states is shown in Section 3. In Section 4 we present the results and Section 5 is dedicated to concluding remarks.

2. Correlation-function quantum Monte Carlo

To obtain the rovibrational energy levels is necessary to solve the following eigenvalue problem:

$$H\Phi_i(\mathbf{R}) = E_i\Phi_i(\mathbf{R}), \quad (1)$$

where the Hamiltonian associated with the relative motion of particles (excluding the kinetic energy of the center of mass) [14] is given as

$$H = - \sum_{i=1}^{N-1} \frac{\hbar^2}{2\mu_i} \nabla_i^2 + V(\mathbf{R}), \quad (2)$$

μ_i is the reduced mass, \mathbf{R} is the vector of $3(N-1)$ coordinates, $V(\mathbf{R})$ is the potential energy, and E_i and Φ_i are the eigenvalues and eigenvectors of H .

In this section, we summarize the CFQMC method used to solve Eq. (1). Let $\{f_\alpha(\mathbf{R})\}$ be a trial basis set of m known functions, we can define the overlap and Hamiltonian matrix elements as

$$N_{\alpha\beta}(t) = \int d\mathbf{R}_1 d\mathbf{R}_2 f_\alpha(\mathbf{R}_2) e^{-tH} f_\beta(\mathbf{R}_1),$$

$$H_{\alpha\beta}(t) = \int d\mathbf{R}_1 d\mathbf{R}_2 H f_\alpha(\mathbf{R}_2) e^{-tH} f_\beta(\mathbf{R}_1), \quad (3)$$

respectively. Associated with these matrices, the generalized eigenvalue problem is defined as

$$\sum_{\beta=1}^m [H_{\alpha\beta}(t) - \Lambda_k(t) N_{\alpha\beta}(t)] d_{k\beta}(t) = 0, \quad (4)$$

with $d_k(t)$ being the k th eigenvector and $\Lambda_k(t)$ its associated eigenvalue. It has been shown [6,7] that

$$\lim_{t \rightarrow \infty} \Lambda_k(t) = E_k \quad 1 \leq k \leq m, \quad (5)$$

as long as the basis set $\{f_\alpha(\mathbf{R})\}$ has some overlap with the eigenstates $\{\Phi_i\}$, and is linearly independent.

The matrix elements defined in Eq. (3) are evaluated using Monte Carlo methods. For this, we gener-

ate random walks according to the diffusion equation in imaginary time [15] using the following updating scheme of the coordinates at a time step τ :

$$\mathbf{R}_{i+1} = \mathbf{R}_i + \tau d \Psi^{-1}(\mathbf{R}_i) \nabla \Psi(\mathbf{R}_i) + (2\tau d)^{1/2} \chi_i \quad (6)$$

where $d = \hbar^2/2\mu$, Ψ is a guiding wavefunction and χ_i is a normally distributed random variable vector with zero mean and unit variance. After successive applications of Eq. (6) we obtain a ‘trajectory’ in phase space with probability $|\Psi(\mathbf{R})|^2$. To determine the matrix elements, each fragment of the trajectory must be weighted by

$$W_{n,n+k} = \exp \left[-0.5\tau \sum_{j=n}^{n+k-1} [E_{L_\Psi}(\mathbf{R}_j) + E_{L_\Psi}(\mathbf{R}_{j+1})] \right], \quad (7)$$

where $E_{L_\Psi} = \Psi^{-1} H \Psi$ is the local energy function. The matrix elements, after symmetrization, are evaluated as

$$n_{\alpha\beta}(k\tau) = \frac{1}{2p} \sum_{i=1}^p [F_\alpha(\mathbf{R}_i) F_\beta(\mathbf{R}_{i+k}) + F_\alpha(\mathbf{R}_{i+k}) F_\beta(\mathbf{R}_i)] W_{i,i+k}$$

$$h_{\alpha\beta}(k\tau) = \frac{1}{4p} \sum_{i=1}^p [F_\alpha(\mathbf{R}_i) F_\beta(\mathbf{R}_{i+k}) E_{L_\beta}(\mathbf{R}_{i+k}) + F_\alpha(\mathbf{R}_{i+k}) F_\beta(\mathbf{R}_i) E_{L_\beta}(\mathbf{R}_i) + E_{L_\alpha}(\mathbf{R}_i) F_\alpha(\mathbf{R}_i) F_\beta(\mathbf{R}_{i+k}) + E_{L_\alpha}(\mathbf{R}_{i+k}) F_\alpha(\mathbf{R}_{i+k}) F_\beta(\mathbf{R}_i)] W_{i,i+k}, \quad (8)$$

where

$$F_\alpha(\mathbf{R}) = f_\alpha(\mathbf{R}) / \Psi(\mathbf{R}), \quad (9)$$

$$E_{L_\beta}(\mathbf{R}) = f_\beta^{-1}(\mathbf{R}) H f_\beta(\mathbf{R}). \quad (10)$$

As $p \rightarrow \infty$, $n_{\alpha\beta}(k\tau)$ and $h_{\alpha\beta}(k\tau)$ converge to $N_{\alpha\beta}(k\tau)$ and $H_{\alpha\beta}(k\tau)$. After the system has reached the stationary state, the generalized eigenvalue problem is solved and the rovibrational spectrum is obtained.

The variational Monte Carlo (VMC) consists of considering $t = 0$ in Eq. (3). Thus, the trajectory

weight W is always equal to 1 and in the matrix elements Eq. (8), the constant k is equal to 0. The variational eigenvalues and eigenfunctions are obtained solving the generalized eigenvalue problem Eq. (4) at $t = 0$. The vibrational eigenfunction will be used to define the $\{f_\alpha(\mathbf{R})\}$ trial basis in Section 3.

3. Rotating trial functions

In Ref. [7], Bernu et al. presented a simple way to generate the trial functions $\{f_\alpha\}$ that are used to calculate the vibrational energy levels. In the method, the basis functions were directly expressed in terms of interatomic distances. Acioli and Soares Neto [8] proposed a similar method, with a few differences in the excited state trial functions. In this Letter, we propose the following procedure to generate rotating trial basis functions. First, start from a simple approximation to the excited vibrational state eigenfunctions $\{\tilde{f}_j\}$ (for example, the Acioli et al. trial basis). Second, using the VMC method, calculate a new orthonormal vibrational basis $\{f_j\}$. Then, the rotating trial basis set $\{f_\alpha\}$ is obtained as a combination of a $\{f_j\}$ function and the eigenfunctions of $\hat{\mathbf{J}}^2$ operator (e.g., spherical harmonics for spherical symmetrical potential and Wigner functions for general systems [16]). The $\{f_\alpha\}$ basis functions are the trial basis set used in the CFQMC method. Here, we show the present procedure for diatomic and triatomic molecules.

The Hamiltonian of the relative motion of a diatom is:

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r), \quad (11)$$

where $\mu = m_1 m_2 / (m_1 + m_2)$, ∇^2 is the Laplacian in 3D Cartesian coordinates and r is the interatomic distance. The initial basis functions are given by:

$$\tilde{f}_j(r) = \frac{1}{r} (r - r_e)^j e^{-\alpha(r - r_e)^2} \quad j = 0, \dots, N. \quad (12)$$

Utilizing the VMC method, the new orthonormal vibrational basis set is:

$$f_i(r) = \sum_{j=0}^N c_{ij} \tilde{f}_j(r) \quad i = 0, \dots, n_{\text{vib}} - 1. \quad (13)$$

The rotating trial basis functions for diatomic molecules are given by

$$f_\alpha(x, y, z) \equiv f_i(r) Y_{lm}(\theta, \phi), \quad (14)$$

where

$$r = (x^2 + y^2 + z^2)^{1/2},$$

$$\theta = \arccos \frac{z}{(x^2 + y^2 + z^2)^{1/2}},$$

$$\phi = \arctan \frac{y}{x}, \quad (15)$$

are the spherical polar coordinates. As the rotational energy levels are degenerate with respect to the quantum number m , we simplify our calculation considering $m = 0$ in the rotating trial basis. The number of rotating basis functions is equal to $n_{\text{vib}} n_{\text{rot}}$, where n_{rot} is the number of desired rotational states. Our choice of guiding function Ψ to generate the random walks is

$$\Psi(\mathbf{r}) = [f_0(x, y, z)]^{1/n} = [f_0(r) Y_{00}(\theta, \phi)]^{1/n}. \quad (16)$$

where n is chosen in order to assure a good integration of all the states included in our calculation. Note that with the present procedure, we obtain several rotational states in one calculation.

This procedure can be easily extended to triatomic or larger molecules. For triatomic molecules, the Hamiltonian in the mass scaled Jacobi coordinate system, after removal of the motion of the center of the mass, is [17]

$$H = -\frac{\hbar^2}{2\mu} (\nabla_{\mathbf{R}}^2 + \nabla_{\mathbf{r}}^2) + V(r_{\text{AB}}, r_{\text{BC}}, r_{\text{CA}}), \quad (17)$$

where $\mu = [(m_{\text{A}} m_{\text{B}} m_{\text{C}}) / (m_{\text{A}} + m_{\text{B}} + m_{\text{C}})]^{1/2}$, $\nabla_{\mathbf{R}}^2$ and $\nabla_{\mathbf{r}}^2$ are Laplacians in 3D Cartesian coordinates and r_{AB} , r_{BC} and r_{CA} are the interatomic distances between atoms A and B, B and C, and C and A, respectively. The initial basis functions are given by [9]

$$\tilde{f}_{n_1, n_2, n_3} = \exp \left(\sum_{\nu, \eta} \Delta S_\nu A_{\nu, \eta} \Delta S_\eta \right) \prod_{\nu=1}^3 (\Delta S_\nu)^{n_\nu}, \quad (18)$$

where $\Delta S_1 = r_{\text{AB}} - r_{\text{AB}}^0$, $\Delta S_2 = r_{\text{BC}} - r_{\text{BC}}^0$ and $\Delta S_3 = r_{\text{CA}} - r_{\text{CA}}^0$, r_{AB}^0 , r_{BC}^0 and r_{CA}^0 are the equilibrium

distances between atoms A and B, B and C, and C and A, respectively. The variational parameters $\{A_{\nu\eta}\}$ are optimized in order to minimize the variational energy of ground state ($n_\nu = 0$ in Eq. (18)) or its variance. Utilizing the VMC method, the new orthonormal vibrational basis set is

$$f_i(r_{AB}, r_{BC}, r_{CA}) = \sum_{n_1} \sum_{n_2} \sum_{n_3} c_i^{n_1 n_2 n_3} \tilde{f}_{n_1 n_2 n_3}(r_{AB}, r_{BC}, r_{CA}). \quad (19)$$

The rotating trial basis functions for triatomic molecules are given by

$$f_\chi(R_x, R_y, R_z, r_x, r_y, r_z) \equiv f_i(r_{AB}, r_{BC}, r_{CA}) D_{MN}^J(\alpha, \beta, \gamma), \quad (20)$$

where D_{MN}^J is the Wigner function and α , β and γ are the Euler angles. Note that there is no problem with the coriolis terms because our Hamiltonian is written in 6D Cartesian coordinates. Even working in other coordinate systems, the coupling between states would not be a problem as they are numerically integrated using Monte Carlo techniques.

4. Results

In this section, we present applications of the CFQMC method using the rotating trial basis set to the computation of rovibrational states in two diatomic model systems. The exact energy levels for excited rotational levels ($l > 0$) can be obtained by numerical solution of the 1-dimensional Schrödinger equation [18] containing the centrifugal potential, which is obtained after separating off the rotational motion. We compare CFQMC results with the results obtained using a very efficient variational procedure: the p-version of the finite element method (FEM) with optimized mesh [19].

4.1. Rotating harmonic oscillator

The harmonic oscillator potential is given by

$$V(r) = \frac{k}{2}(r - r_e)^2. \quad (21)$$

We consider $\mu = 1$, $\alpha = 0.5$, $k = 1$ and $r_e = 5.0$. In this calculation, we only employ the VMC method

because the initial basis functions Eq. (12) (or a linear combination of them) are the exact vibrational eigenfunctions of the harmonic oscillator. Initially, we used 10 basis functions Eq. (12) to calculate the orthonormal vibrational basis Eq. (13). And used $n_{\text{vib}} = n_{\text{rot}} = 5$, totalling 25 rotating trial basis functions Eq. (14). Employing the VMC method, we calculated the rovibrational excited energy levels. In Table 1, we display the results for the first 15 rovibrational states in comparison with the 'exact' results that were obtained using the FEM. The VMC results are in agreement with the FEM results.

4.2. Rotating Morse potential

The Morse potential is given by

$$V(r) = D(1 - e^{-\omega(r - r_e)})^2, \quad (22)$$

where $D = 0.1744$, $\omega = 1.02764$ and $r_e = 1.40201$ are the parameters which shape the H_2 molecule. We consider $\mu = 918.49108886719$ and $\alpha = 9.5292219$. First, we utilized 34 basis functions (12) to calculate the orthonormal basis set (13). And we used $n_{\text{vib}} = 11$ and $n_{\text{rot}} = 7$, totalling 77 rotating trial basis functions (14). Employing the CFQMC method, we calculated the rovibrational excited energy levels and we display the first 42 levels in Table 2. The

Table 1
Rovibrational energy levels for the harmonic oscillator potential. Comparison between VMC and FEM methods. Energies are in hartree

States Rotational		Vibrational		
		0	1	2
0	FEM	0.500000	1.500000	2.500000
	VMC	0.500000	1.499999	2.500000
1	FEM	0.542507	1.548400	2.555777
	VMC	0.542502	1.548400	2.555781
2	FEM	0.626513	1.643451	2.664272
	VMC	0.626509	1.643451	2.664285
3	FEM	0.750185	1.782134	2.820588
	VMC	0.750183	1.782134	2.820594
4	FEM	0.911143	1.960807	3.019338
	VMC	0.911141	1.960807	3.019339

Table 2

Rovibrational energy levels for the H₂ molecule. Comparison between CFQMC and FEM methods. Energies are in hartree

States		Vibrational					
Rotational		0	1	2	3	4	5
0	FEM	0.009869	0.028745	0.046472	0.063048	0.078475	0.092752
	DMC	0.009869	0.028744	0.046470	0.063047	0.078474	0.092752
1	FEM	0.010412	0.029267	0.046970	0.063523	0.078925	0.093176
	DMC	0.010411	0.029266	0.046969	0.063522	0.078924	0.093175
2	FEM	0.011493	0.030304	0.047962	0.064467	0.079818	0.094017
	DMC	0.011492	0.030303	0.047961	0.064466	0.079817	0.094016
3	FEM	0.013101	0.031847	0.049437	0.065869	0.081145	0.095264
	DMC	0.013100	0.031846	0.049435	0.065868	0.081144	0.095263
4	FEM	0.015222	0.033881	0.051378	0.067714	0.082888	0.096902
	DMC	0.015221	0.033880	0.051376	0.067713	0.082887	0.096901
5	FEM	0.017838	0.036386	0.053766	0.069981	0.085028	0.098910
	DMC	0.017837	0.036385	0.053765	0.069981	0.085027	0.098908
6	FEM	0.020925	0.039339	0.056579	0.072646	0.087541	0.101264
	DMC	0.020924	0.039338	0.056578	0.072645	0.087540	0.101264

CFQMC results are in agreement with the results obtained employing the FEM developed in Ref. [19].

5. Conclusion

In this Letter, we reported the use of the CFQMC method to obtain the rovibrational energy levels of molecular systems. For this, we proposed a general procedure to generate rotating trial basis functions and showed the analytic forms of the rotating trial wavefunctions to diatomic and triatomic molecules. Note that the analytic forms are simple and easy to apply. We employed the present method to calculate the rovibrational energy levels of the two models of diatomic molecule. The procedure can be generalized to study rovibrational states of larger molecules following the basic steps shown in this Letter.

The results displayed in Tables 1 and 2 have an accuracy comparable to the traditional variational methods. We conclude that the use of rotating trial basis sets to obtain the rovibrational excited energies employing the CFQMC method is very efficient. The great advantage of the quantum Monte Carlo methods is that they do not grow exponentially with the

number of degrees of freedom. Currently, we are calculating the rovibrational energy levels for triatomic molecules and are extending the present methodology to calculate the rovibrational energy levels for tetratomic molecules.

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