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The calculation of excited states with quantum Monte Carlo. II. Vibrational excited states

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Using a new Monte Carlo method for computing properties of excited quantum states, correlation function quantum Monte Carlo, we calculate the lowest ten vibrational excited state energies of H_2O and H_2CO in the Born–Oppenheimer approximation. The statistical errors for H_2O are 0.1 cm^{-1} for the ground state and 15 cm^{-1} for the tenth excited state while for H_2CO they are 2 cm^{-1} for the ground state and 30 cm^{-1} for the eighth excited state. The algorithm presented here is easily extensible to larger systems.

I. INTRODUCTION

The calculation of the rotational–vibrational spectra of polyatomic molecules from an assumed potential energy surface is a great challenge. Comparison of an accurate calculated spectrum with the very precise experimentally measured spectrum can, in principle, be used to assess the accuracy of potential energy functions (or "force fields") and perhaps refine them. These force fields can then be used to calculate dynamical properties of molecules. The lack of accurate methods for determining force fields is probably the major impediment to the even more widespread use of computer simulation for molecular systems.

Reliable methods for calculating rotational–vibrational spectra are, to date, limited to diatomic and triatomic molecules.[1] Diatomic molecules can, of course, be solved by a variety of simple methods since they reduce to the solution of a one-dimensional Schrödinger equation. Triatomic molecules, once center of mass and rotational motion are taken into account, reduce to a three-dimensional wave equation. In the past, that equation has been solved by the variational method (VM). There, one expands the wave function in an appropriate basis set, performs the required integrals with numerical (deterministic) methods, and then solves the resulting eigenvalue problem in the subspace spanned by the basis set. This is quite satisfactory for triatomics since a basis with several thousand elements will span the space reasonably well. On today's supercomputers one could also use a direct basis of finite elements.

For larger molecules, however, the variational method becomes much too expensive. The Schrödinger equation for a molecule with four atoms has dimensionality 6. The basis set needed to span this space would have millions of elements so the required matrices would have the order of 10^{12} elements. In practice, one has been forced to resort to a normal mode analysis of the vibrational spectrum. One makes a quadratic approximation for the potential around its minimum, transforms to normal coordinates, and then solves the resulting eigenvalue problem. The approximation is not appropriate when the potential surface has significant anharmonic contributions as is the case when light atoms or weakly bound atoms are present or for highly excited states. One also cannot deal with the situation where multiple potential energy minima may be important as with large and "floppy" molecules. Semiclassical methods can also be applied to the calculation of vibrational energy levels. Although these methods can be quite accurate and quick it is difficult to systematically improve their accuracy. Also there is no *a priori* way of estimating the error of the method.

This paper contains a preliminary investigation into whether a recently developed Monte Carlo approach can calculate accurate excited-state properties of polyatomic molecules. The method, which we call correlation function quantum Monte Carlo (CFQMC) is described in a previous paper (referred to hereafter as I.[2] Here we will restrict consideration to calculation of the vibrational excited state energies, i.e., only the $J = 0$ state will be addressed. The calculation of the complete rotation–vibration spectrum leads only to more complex formulas, not conceptual difficulties.

As in the VM, the input for the Monte Carlo calculation is also a basis of functions. In both methods, the convergence is faster as the basis approaches the exact wave function basis. But in the CFQMC the basis is then vastly improved by projecting out high energy components with the operator e^{-tH}, where H is the Hamiltonian. Thus the number of basis functions is not critical; we have used around 50 in this study; in fact much larger basis sets than this could be handled. In addition, any kind of basis function can be used. The disadvantage is that CFQMC needs a large amount of computational time. Indeed, the statistical error decreases in the most favorable case as $\sqrt{p}$, where p is the number of sampled points for the estimation of matrix elements. In order to ob-

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tain one order of magnitude higher precision requires two orders of magnitude more computational time. Even slower convergence will be obtained for highly excited states.

In this paper, we show that going from three- to four-atom molecules, CFQMC does not lead to a large increase in either computational time or in the complexity of the method. We think that the proposed CFQMC technique will encounter no major difficulties in calculating properties of larger molecules. In fact, the main difficulties are in finding sufficiently accurate potential energy surfaces for polyatomic molecules and finding simple, yet accurate basis sets.

Let us recall some characteristics of the method proposed in I. The main advantages of the method are: zero variance, which means that as better and more complete basis sets are used, the statistical error per MC step decreases to zero; freedom in the choice of the basis set, as long as the basis and its first and second derivatives can be quickly computed and if the method converges the exact answer is obtained within known errors. If the method does not converge, that should be obvious from the results. Careful examination of the results should suggest ways of improving the basis.

There are, however, some problems introduced by applying QMC techniques to excited states: the error decreases very slowly with computer time for highly excited states. Further, there is nontrivial bias caused by the need to orthogonalize to lower states.

The paper is organized as follows. Section II summarizes the method presented in I. Section III describes the trial functions, the guiding function, and symmetries. Section IV presents the results for H_2O and H_2CO, and specific problems related to each molecule. Section V compares this method with other methods, and provides the conclusions.

II. CORRELATION FUNCTION QUANTUM MONTE CARLO

Here we briefly review the algorithm described in I. Let $H = T + V$ be a Hamiltonian composed of the kinetic energy T:

$$T = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 \qquad (1)$$

and the potential energy $V(R)$. Here R is the $3N$ vector of particle coordinates and N is the number of particles. Let the eigenvalues of H be E_i and the eigenvectors $\phi_i(R)$. Let $\{f_\alpha(R)\}_m$ be a basis set of m (known) functions. With these functions, define the $m \times m$ matrices:

$$N_{\alpha\beta}(t) = \int dR_1 \, dR_2 \, f_\alpha(R_2) e^{-tH} f_\beta(R_1), \qquad (2)$$

$$H_{\alpha\beta}(t) = \int dR_1 \, dR_2 \, Hf_\alpha(R_2) e^{-tH} f_\beta(R_1). \qquad (3)$$

Then, consider the generalized eigenvalue equation

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

where $d_k(t)$ is the k th eigenvector (an m component vector) and $\Lambda_k(t)$ is its eigenvalue. We have shown in I that

$$\lim_{t \to \infty} \Lambda_k(t) = E_k, \quad 1 \leqslant k \leqslant m \qquad (5)$$

as long as the basis set $\{f_\alpha(R)\}_m$ has some overlap with all the m eigenstates ϕ, and is linearly independent. We have also shown that $\Lambda_k(t)$ is monotonically decreasing and converges exponentially fast to E_k.

The matrix elements defined in Eqs. (2) and (3) are evaluated using a Monte Carlo method. There are three parts to the algorithm: (1) the generation of random walks; (2) the calculation, during the walks, of the basis functions f_α and the accumulation of the matrix elements $N_{\alpha\beta}(t)$ and $H_{\alpha\beta}(t)$; (3) the diagonalization whereby Eq. (4) is solved. Bias and error estimations are done at this stage.

It is the similarity between the matrices defined in Eqs. (2) and (3) to correlation functions in classical molecular dynamics that gives rise to the name CFQMC. Quantum Monte Carlo is used to generate the "dynamics" implied by the operator e^{-tH}. This is not true quantum dynamics (that would be given by the operator e^{-itH}), but is only a method of projecting out high energy components from the basis $\{f_\alpha(R)\}_m$.

A. The random walks

As explained in I, the Green's function of the imaginary-time Schrödinger equation with a guiding function ψ can be solved in the $\tau \to 0$ limit. The evaluation of $N_{\alpha\beta}(t)$ and $H_{\alpha\beta}(t)$ is done by performing a guided random walk in the configuration space of the molecule. The updating scheme (dynamics) of the coordinates for a time step τ is

$$R_{i+1} = R_i + \tau d \, \Psi^{-1} \nabla \Psi(R_i) + (2\tau d)^{1/2} \chi_i, \qquad (6)$$

where χ_i is a normally distributed random $3N$ vector with zero mean and unit variance with all elements independent of each other and $d = \hbar^2/2m$. Repeated application of Eq. (6) leads to a "trajectory" in phase space with a probability distribution proportional to $\psi^2(R)$. To determine matrix elements of e^{-tH} one must weigh each segment of the trajectory by

$$W_{n,n+k}$$
$$= \exp\left(-0.5\tau \sum_{j=n}^{n+k-1} [E_{L\psi}(R_j) + E_{L\psi}(R_{j+1})]\right), \qquad (7)$$

where the local energy function is defined in terms of the action of the Hamiltonian on the guiding function

$$E_{L_\psi}(R) = \psi^{-1}(R) H\psi(R). \qquad (8)$$

B. Evaluation of the matrix elements

Following the formulas of Eq. (16) of I, the matrix elements are calculated as

$$n_{\alpha\beta}(k\tau) = \frac{1}{p} \sum_{i=1}^{p} F_\alpha(R_i) W_{i,i+k} F_\beta(R_{i+k}), \qquad (9)$$

$$h_{\alpha\beta}(k\tau) = \frac{1}{p} \sum_{i=1}^{p} F_\alpha(R_i)$$
$$\times W_{i,i+k} F_\beta(R_{i+k}) E_{L_\beta}(R_{i+k}), \qquad (10)$$

where

$$F_\alpha(R) = f_\alpha(R)/\psi(R), \tag{11}$$

$$E_{L_\beta}(R) = f_\beta^{-1}(R)Hf_\beta(R), \tag{12}$$

where E_{L_β} is called the local energy of the basis function f_β and $[R_1,...,R_p]$ are the points of the trajectory generated by the random walk. As $p \to \infty$, $n_{\alpha\beta}(k\tau)$ and $h_{\alpha\beta}(k\tau)$ converge to $N_{\alpha\beta}(k\tau)$ and $H_{\alpha\beta}(k\tau)$.

The most time consuming part of the calculation is the evaluation of these matrix elements: the computer time will be proportional to pm^2. To minimize this computer time we compute f_β every L th time step rather than every time step. Then k in Eqs. (9) and (10) is taken as a multiple of L, where L is an integer generally between 2 and 20. The local energy of the guiding function is calculated at every step in order to obtain an accurate weight W [in Eq. (7)], but the trial functions and matrix elements are computed only for the points R_j in the trajectory when j is a multiple of L. Nearby points on the trajectory are strongly correlated and so it does not pay to compute properties every step.

Finally one can symmetrize $n_{\alpha\beta}$ and $h_{\alpha\beta}$ to reduce fluctuations:

$$n_{\alpha\beta}(k\tau) = \frac{1}{2p}\sum_{i=1}^{p} [F_\alpha(R_i)F_\beta(R_{i+k})$$
$$+ F_\alpha(R_{i+k})F_\beta(R_i)]W_{i,i+k}, \tag{13}$$

$$h_{\alpha\beta}(k\tau) = \frac{1}{4p}\sum_{i=1}^{p} [F_\alpha(R_i)F_\beta(R_{i+k})E_{L_\beta}(R_{i+k})$$
$$+ F_\alpha(R_{i+k})F_\beta(R_i)E_{L_\beta}(R_i)$$
$$+ E_{L_\alpha}(R_i)F_\alpha(R_i)F_\beta(R_{i+k})$$
$$+ E_{L_\alpha}(R_{i+k})F_\alpha(R_{i+k})F_\beta(R_i)]W_{i,i+k}. \tag{14}$$

The second equality follows from the Hermitian property of H.

C. Diagonalization

Ideally one could start from an arbitrary basis set and compute directly $n_{\alpha\beta}(t)$ and $h_{\alpha\beta}(t)$. This will not usually work because of exponentially growing round-off errors (see I). We propose the following procedure to reduce both the round-off errors and the number of basis functions. First, start from the *best* simple approximations to the excited-state eigenfunctions. Then a variational diagonalization, i.e., the solution of Eq. (4) for $t = 0$, is done. For this part a large time step τ is used: note that the weights W are always equal to 1 at $t = 0$. The new orthonormal basis set is denoted as $\{\tilde{f}_\alpha\}$. In order to obtain m eigenstates, it may be useful to start with $2m$ or $3m$ functions. After the variational diagonalization, we throw away the highest energy states and keep only the m states of lowest energy. It is important to keep states close in energy in the basis because otherwise slow convergence could result.

With the m new states, do another walk and compute the $n_{\alpha\beta}(t)$ and $h_{\alpha\beta}(t)$. Then a diagonalization gives the eigenvalues $\lambda_k(t)$, which are estimates of $\Lambda_k(t)$ in Eq. (4). If the basis set is good enough, we find that the eigenvalues decrease to a given value when the time t increases, then

reach a plateau and finally begin to fluctuate strongly. In I, it is shown that $\Lambda_k(t)$ is a monotonically decreasing function. The plateau corresponds to the *exact* eigenvalue of the Hamiltonian. The oscillations are due to the statistical noise which grows exponentially at large time. The existence of the plateau is necessary to ensure that the convergence is obtained. The absence of a plateau indicates that convergence has not been reached before statistical fluctuations have begun to grow rapidly. Longer runs will of course reduce statistical fluctuations somewhat. A better procedure is to improve the basis set. In any case the computed energies are upper bounds to the excited-state energies within the computed statistical errors.

It is sometime necessary to repeat the procedure of orthogonalizing the basis and winnowing out high energy states at a larger time $t_1 > 0$. This gives a basis closer to the exact eigenstates than the variational basis $\{\tilde{f}_\alpha\}$. This new basis is obtained from the solution of Eq. (4) at the time t_1 and the variational basis by

$$\hat{f}_\alpha(t_1) = \sum_{j=1}^{m} \tilde{f}_j d_{j\alpha}(t_1). \tag{15}$$

With this basis, new trajectories are carried out. The general idea to keep in mind is to use always the best basis set available in order to reduce the round-off error.

As pointed out in the Introduction, one of the great advantages of this method is the possibility of calculating the statistical error bar of each quantity, and thereby have an estimate of the precision of the calculation. This is explained in detail in I. The noise can be evaluated by comparing the results of different trajectories. We have generated $N_T = 64$ or 128, random walks in parallel since this allows efficient use of a parallel or vector computer. Because a large number of random numbers are used, to prevent correlation an intermediate table of random numbers is built in from which numbers are picked randomly and used ones are replaced.

From the N_T estimates of $n_{\alpha\beta}(t)$ and $h_{\alpha\beta}(t)$, the mean value and the variance of all eigenvalues $\lambda_\alpha(t)$ are calculated. Because the eigenvalues have a nonlinear dependency on the matrix elements $n_{\alpha\beta}(t)$ and $h_{\alpha\beta}(t)$, the value $\lambda_\alpha^T(t)$ obtained from the mean matrices

$$\frac{1}{N_T}\sum_{i=1}^{N_T} n_{\alpha\beta}^{(i)}(t)$$

and

$$\frac{1}{N_T}\sum_{i=1}^{N_T} h_{\alpha\beta}^{(i)}(t)$$

differs from the mean value of the $\lambda_\alpha^{(i)}(t)$ obtained for each trajectory:

$$\lambda_\alpha^T(t) \neq \bar{\lambda}_\alpha(t) = \frac{1}{N_T}\sum_{i=1}^{N_T} \lambda_\alpha^{(i)}(t). \tag{16}$$

This difference is the bias of the eigenvalue and it vanishes in the limit $p \to \infty$ as p^{-1} as is discussed in I. When the statistical noise is small enough, the results can be corrected for the effect of the bias.

III. TRIAL FUNCTIONS

In this section, we present a simple way to generate the trial functions f_α. This method is a local-mode approach because the basis functions are directly expressed in terms of interatomic distances, not angles or any more complicated coordinates. Thus, the trial functions are easily generalizable to any molecule. Although they might not be as accurate as other choices for any particular molecule they are expected to be always reasonable. For molecules with symmetries such as H_2CO some care is needed to ensure that the basis is complete. Here the basis set for only the rotational ground state, $J = 0$, is presented, although generalization to rotationally excited states is straightforward.

Let us begin with a molecule of N atoms $(N > 2)$. The potential surface is assumed to depend only on internal coordinates. Let $\mathbf{r}_i$ be the position of atom i. We define the local modes by

$$S_\nu = \|\mathbf{r}_i - \mathbf{r}_j\|, \quad 1 \leq i < j \leq N, \quad 1 \leq \nu \leq \frac{N(N-1)}{2}. \quad (17)$$

The number of independent internal coordinates is $3N - 6$, which coincidentally equals the number of local modes for three- and four-atom molecules. For larger molecules the number of local modes is greater than the number of internal coordinates so the set S_ν is overcomplete. For simplicity, let us suppose that the potential energy surface has only one pronounced minimum and define the values of the local modes there to be S_ν^0. If other minima are present, each should have its own basis.

First, we determine a trial function for the ground state ψ_0. We then define other trial functions in terms of ψ_0 and the local modes, and finally we choose the form of the guiding function.

A. The ground state

We present two different ways of defining the ground state. Both are based on the same analytical form:

$$\psi_0 = \exp\left(\sum_{\nu,\mu} \Delta S_\nu A_{\nu\mu} \Delta S_\mu\right), \quad (18)$$

where

$$\Delta S_\nu = S_\nu - S_\nu^0 \quad (19)$$

and the symmetric matrix A is a set of variational parameters. Symmetries reduce the number of independent parameters: for H_2O there are only 3 independent ones, while there are 13 for H_2CO.

In the first method the parameters are determined by minimizing the variational energy of this trial function. Because the energy is a nonlinear function of them, the Monte Carlo method is used to perform this minimization. A trajectory is generated using an initial guess for the parameters [corresponding to a trial function $\psi_{00}^2 = P_0(R)$] and several thousand points on the trajectory are stored. Then the reweighting method[3] is used to find the best set of parameters. An estimate for the variational energy with a different set of parameters is given by

$$E_\nu[\psi_0] = \sum_{i=1}^{P} E_L(R_i) w(R_i) \bigg/ \sum_{i=1}^{P} w(R_i), \quad (20)$$

where $w(R) \equiv \psi_0^2(R)/P_0(R)$. The above estimator is minimized using a steepest descent-like method with respect to the matrix A. Indeed the absolute value of this estimator may be inaccurate, but the change of the variational energy with respect to changes of $A_{\nu\mu}$ will be more precise than rerunning the code provided that the trial function does not change too much. This approach has the advantage of optimizing the local energy globally. Problems can occur for large molecules where the number of parameters is large. Instead of the local energy, it is preferable to minimize a linear combination of the local energy and its variance.[4,5]

In the second method we determine the parameters of A by relating them to a harmonic wave function. First, approximate the potential energy surface around its minimum as

$$V(R) = \frac{1}{2} \sum_{\nu,\mu} \Delta S_\nu F_{\nu\mu} \Delta S_\mu + \cdots, \quad (21)$$

where the $F_{\nu\mu}$ are elements of the force constant matrix. For a molecule of more than four atoms, one has to choose a subset of only $3N$–6 local modes. Then one obtains the normal modes $\{Q\}$ for a given equilibrium geometry R^0:

$$Q_k = \sum_i L_{ki}(R_i - R_i^0). \quad (22)$$

L is a $3N \times 3N$ matrix. Six of the modes, corresponding to rotation and translation, are irrelevant for the vibrational problem. Close to the equilibrium geometry we express the internal coordinates as

$$\Delta S_\nu = T_{\nu i}(R_i - R_i^0). \quad (23)$$

Note that both matrices L and T depend on R^0. To express Q_ν in term of S_ν, we have to invert the rectangular matrix T. Therefore, the equations corresponding to the conservation laws are added to Eq. (23), and the matrix T is inverted:

$$Q_\nu = L_{\nu\gamma} T_{\gamma\mu}^{-1} \Delta S_\mu = U_{\nu\mu} \Delta S_\mu. \quad (24)$$

The matrix A of Eq. (18) is then

$$A_{\nu\mu} = \sum_k E_{0_k} U_{k\nu} U_{k\mu}, \quad (25)$$

where E_{0_k} is the ground state energy of the mode k.

While this second method is simple and general, ψ_0 will be accurate only close to the equilibrium geometry and will break down if there are multiple minima of the potential energy, including those due to symmetry, if tunneling between those minima is important. It is of course possible to mix the two methods and use the second one as a starting point of the first one.

B. Excited state trial functions

We define the excited state basis set:

$$f_\alpha = \psi_0 \prod_{\nu=1}^{N_p} S_\nu^{n_\nu(\alpha)} \equiv (n_1, \ldots, n_{N_p}), \quad (26)$$

where N_p is the number of local modes included in the basis. As constructed, the $\{f_\alpha\}$ form a nonorthogonalized, nonnormalized basis which has large overlap with the ground state. This leads to very ill-conditioned matrices $n_{\alpha\beta}$ and $h_{\alpha\beta}$ and causes inaccuracies in the diagonalization procedure.

For this reason, we subtract a term f_α^0 from f_α:

$$f_\alpha^0 = \psi_0 \prod_{\nu=1}^{m} (S_\nu^0)^{n_\nu(\alpha)}. \tag{27}$$

An excited-state basis could also be built from normal modes but because the potential energy surface is in general highly anharmonic away from the equilibrium position and because the molecule makes larger excursions away from the minimum in an excited state, the use of normal modes for excited states is not recommended.

The functions $\{f_\alpha\}$ are determined by the set of exponents $\{n_\nu(\alpha)\}$. We keep all functions satisfying the conditions

$$\sum_{\nu=1}^{N_p} \omega_\nu n_\nu(\alpha) \leqslant \Gamma, \tag{28}$$

where ω_ν are local mode weights, which depend on the molecule. When all the ω_ν are equal to 1, the number of generated states is

$$N_{\text{state}} = \frac{(N_p + \Gamma)!}{N_p! \Gamma!}. \tag{29}$$

Let us show how to fix the parameters ω_ν and Γ, for the case of H_2O, where the normal mode representation is reasonable for the lowest excited states. There are three normal modes, and each excited state can be approximately labeled by the quantum numbers for each: (i, j, k). Good approximate wave functions are

$$f_{(i,j,k)} = \psi_0 Q_1^i Q_2^j Q_3^k. \tag{30}$$

The first 15 states of lowest energy involve functions where the powers i, j, or k are less than or equal to 2. In order to find a good variational representation of these states, we take all states where i, j, or k are less than or equal to 4. They are obtained if in Eq. (28) we take $\Gamma = 4$ and $\omega_\nu = 1$.

C. Calculation of the local energy

We must calculate the local energy of Eq. (12) which involves taking the Laplacian of each member of the basis set. This is conveniently done by writing the basis functions in the form

$$f_\alpha = \exp\left(G_0 + \sum_{\nu=1}^{m} n_\nu(\alpha) \ln S_\nu\right), \tag{31}$$

where $G_0 = \ln \psi_0$ is the ground-state contribution. Differentiating f_α with respect to the coordinate of each particle i, we find

$$f_\alpha^{-1} \nabla_i f_\alpha = \nabla_i G_0 + \sum_{\nu=1}^{m} n_\nu(\alpha) \frac{\nabla_i S_\nu}{S_\nu} \tag{32}$$

and

$$f_\alpha^{-1} \nabla_i^2 f_\alpha = [f_\alpha^{-1} \nabla_i f_\alpha]^2 + \nabla_i^2 G_0 + \sum_{\nu=1}^{m} n_\nu(\alpha) \nabla_i\left(\frac{\nabla_i S_\nu}{S_\nu}\right). \tag{33}$$

For example, with $S_1 = \|r_1 - r_2\|$:

$$\frac{1}{S_1} \nabla_1 S_1 = -\frac{1}{S_1} \nabla_2 S_1 (r_1 - r_2),$$

$$\nabla_i S_1 = 0 \quad \text{for } i \neq 1 \text{ or } 2 \tag{34}$$

and

$$\nabla_1\left(\frac{\nabla_1 S_1}{S_1}\right) = \nabla_2\left(\frac{\nabla_2 S_1}{S_1}\right) = \frac{1}{\|r_1 - r_2\|^2},$$

$$\nabla_i\left(\frac{\nabla_i S_1}{S_1}\right) = 0 \quad \text{for } i \neq 1 \text{ or } 2. \tag{35}$$

A loop over the local modes permits us to calculate all terms. It is very useful to verify the programming of all the derivatives by the use of finite differences.

If the molecule contains two identical atoms the wave functions are either symmetric or antisymmetric with respect to interchange of those atoms. It is highly desirable to work with basis functions which have this symmetry. This saves computational time since some matrix elements need not be computed and eliminates some of the statistical noise. We compute one matrix between symmetric trial functions and one matrix between antisymmetric trial functions. Consequently, the functions defined in Eq. (26) have to be symmetrized. The exchange of identical atoms i and j corresponds to exchanges of the internal coordinates. For H_2O, suppose that S_3 is the distance r_{HH}. Then the Hamiltonian is symmetric with respect to the exchange of S_1 and S_2. With the notation of Eq. (26), one can form symmetric and antisymmetric states as follows:

$$(n_1, n_2, n_3)_\pm = (n_1, n_2, n_3) \pm (n_2, n_1, n_3). \tag{36}$$

This operation is performed on both f_α and Hf_α as needed in Eqs. (9)–(12).

D. The guiding function

The effect of the guiding function is to drive the random walks to the region of the phase space where it is large. Because we want to sample all states at the same time, this function should be large wherever an excited trial function is large, and small only when all functions are small. In I, Eqs. (29) and (31), we discuss the optimal guiding function but for simplicity in this calculation we have used the simpler form

$$\Psi = (\Psi_0)^\rho, \tag{37}$$

where ρ is a parameter which depends on the number of excited states we want to sample. A simple formula is adopted: $\rho = \Gamma^{-1/2}$, where Γ is defined in Eq. (28). The advantage of this form is that the local energy of the guiding function E_{L_ψ} is simply related to the local energy of ψ_0 and thus quick to evaluate.

IV. RESULTS

CFQMC is tested on the water molecule H_2O, and then applied to the four-atom molecule H_2CO using a potential energy surface (PES) constructed from experimental information.

A. H_2O

The water molecule is nonlinear with two identical hydrogen atoms. It has two symmetric modes (bending and stretch) and one antisymmetric stretch mode. It is a much

studied system and we refer the interested reader to the article by Johnson and Reinhardt[6] for a review. More recent related studies have appeared by Bowman et al.[7] and Shipsey and Kohl.[8]

We have used a potential function derived from experimental data by Carney, Curtiss, and Langhoff.[9] It involves an expansion in Simons–Parr–Finlan coordinates about the equilibrium geometry and consists of 19 terms. The ground-state trial function defined by Eq. (18) depends on four parameters. Let us define $S_1 = r_{OH_1}$, $S_2 = r_{OH_2}$, and $S_3 = r_{H_1H_2}$. Then the matrix A has the following symmetries: $A_{ij} = A_{ji}$, $A_{11} = A_{22}$, and $A_{13} = A_{23}$. As optimized by the Monte Carlo reweighting method, the parameters we used have the values: $A_{11} = -19.61$, $A_{33} = -8.60$, $A_{12} = 12.20$, and $A_{13} = 8.63$ in units of Å^{-2}. The parameters used to determine the sequence of basis elements are $\Gamma = 4$, $\omega_v = 1$ which leads to 35 basis elements, 22 even functions and 13 odd functions. After the diagonalization of Eq. (4) at time 0 (variational QMC), the 10 (4) lowest states for the symmetric (antisymmetric) functions were kept. Four runs with $p = 320\,000$ steps and $N_T = 64$ trajectories in parallel with a time step $\tau = 2$ hartree^{-1} and $L = 8$ were performed.

For the water molecule, the variational basis is very accurate for the ground state; its energy only differs from the converged values by 2 cm^{-1}. The excited-state energy estimates are reported in Table I. The eigenvalues $\lambda_\alpha(t)$ converge at a time between 150 and 200 hartree^{-1}. No bias corrections have been carried out for this case.

Good precision (0.1 cm^{-1}), is found for the ground-state energy due to the accuracy of the corresponding trial function in the CFQMC calculation. The precision of the results is a few cm^{-1} for the first few excited states and about 10 cm^{-1} for the others. The fourth bending excited state is not converged; a minimum but no plateau is observed. This state is poorly described by the trial functions.

The Monte Carlo results are in good agreement with variational calculation that used an expansion in Hermite polynomials (220 terms) and a numerical deterministic integration method.[9] Our first symmetric excited state has a significantly lower energy than that obtained with the VM.

B. H_2CO

There has been considerable work on deriving a Born–Oppenheimer potential surface for the formaldehyde molecule from experimental data and ab initio calculations.[10,11] It is the only four-atom molecule for which all the harmonic couplings have been experimentally measured. As mentioned earlier there are no accurate variational calculations with which to test the surface.

The formaldehyde molecule presents some difficulty with our choice of the ground-state and trial functions not because of the number of atoms, but only due to its planar equilibrium geometry (the geometry at the absolute minimum of the PES). It is not possible to describe all normal modes with only the internal coordinates defined in Eq. (17). As a consequence, the matrix T_{R_0} of Eq. (23) is not invertible. A planar geometry of four atoms is completely fixed with only five distances (or three distances and two angles). The missing degree of freedom is the motion out of the equilibrium plane. To describe this mode, we need an angle Ω of one vector r_{12} with respect to the plane of the atoms (2,3,4). An angle and its first and second derivatives are time consuming to calculate and can be singular, so it is preferable to use the determinant of a 3×3 matrix:

$$S_7 = |r_{12}, r_{23}, r_{34}|. \qquad (38)$$

Note that close to equilibrium, this internal mode S_7 is proportional to the angle Ω and its absolute value equals the volume of the molecule. An interesting feature of S_7 is that it is linear with respect to all coordinates r_i, therefore one finds

$$\nabla_i^2 S_7 = 0 \quad \text{for all } i. \qquad (39)$$

TABLE I. Excited-state vibrational energies of H_2O in units of cm^{-1}. The first ten states are symmetric, and the last four states are antisymmetric. The numbers in ( ) are the estimated statistical error (one standard deviation). The * denotes unconverged energies (no plateau observed), so only an upper bound is obtained. VM refers to the variational calculation of Ref. 9 and the experimental entries are from Ref. 14.

i state	E_i	$E_i - E_0$	$E_i - E_0$ VM	Expt.	
1	4 639.1 (0.1)				
2	6 234.0 (0.3)	1594.9	1596	1594.6	2_1
3	7 789 (4)	3150	3156	3151.5	2_2
4	8 294 (2)	3655	3659	3657.1	1_1
5	9 316 (15)	4677	4679	4667	2_2
6	9 870 (10)	5231	5237	5235	$1_1 2_1$
7	10 870* (20)	6230*	6169	6136	2_4
8	11 418 (15)	6799	6777	6775	$1_1 2_2$
9	11 860 (15)	7221	7211	7201	1_2
10	12 090 (15)	7451	7453	7445	3_2
1	8 395 (1)	3756	3758	3756.0	3_1
2	9 960 (10)	5321	5335	5331	$2_1 3_1$
3	11 525 (15)	6886	6877	6872	$2_2 3_1$
4	11 895 (15)	7256	7261	7250	$1_1 3_1$

This can be seen by using the bilinearity property of determinants:

$$S_7 = |r_{12}, r_{23}, r_{34}| = |r_{12}, r_{13}, r_{34}| = |r_{12}, r_{24}, r_{34}|. \quad (40)$$

These equalities are used to obtain expressions of the gradients of S_7:

$$\nabla_1 S_7 = |\epsilon, r_{23}, r_{34}|, \quad (41)$$

where

$$\epsilon = (1,1,1). \quad (42)$$

Similar expressions are obtained for the other gradients. We chose the following determinant:

$$S_7 = |r_{OC}, r_{CH_1}, r_{CH_2}|, \quad (43)$$

which is then completely antisymmetric under exchange of the two hydrogen atoms. We have ordered the local modes as

$$S_1 = r_{OC}, \quad S_4 = r_{CH_1},$$
$$S_2 = r_{OH_1}, \quad S_5 = r_{CH_2}, \quad (44)$$
$$S_3 = r_{OH_2}, \quad S_6 = r_{H_1H_2}.$$

The ground-state trial function has been obtained as described in Sec. III A. First, we found values of A using only the harmonic part of the $V(R)$ and the set of internal coordinates $(S_1, S_2, S_3, S_4, S_5, S_7)$. The matrix A [Eq. (18)] has the properties $A_{22} = A_{33}$, $A_{44} = A_{55}$, $A_{12} = A_{13}$, $A_{14} = A_{15}$, $A_{24} = A_{35}$, $A_{25} = A_{34}$, and in addition, $A_{i7} = 0$ for $i = 1,5$ because S_7 is of different symmetry from $(S_1, ..., S_6)$ (see Table II). Then the coefficients are optimized for the complete surface in order to minimize the quantity $E + \text{error}(E)$ of production runs, where E is the energy of the ground-state trial function, and $\text{error}(E) = \sqrt{\text{variance}(E)/p}$. For the optimization procedure[4,5] we use blocks of 10 paths of 400 steps, whereas production runs have 64 paths of 20 000 steps. Then, the quantity $E + \sqrt{\text{variance}(E)/(64*20\,000)}$ is minimized in the optimization procedure. We also add $S_6 = r_{H_1H_2}$ to the list of internal coordinates. The optimized

coefficients are listed in Table II. The variational energy is then 6235 cm^{-1}.

The trial functions are given by Eq. (26) (see Sec. III B) using all the internal coordinates $(S_1, ..., S_7)$. For simplicity these states are denoted $(n_1, ..., n_7)$. These trial functions have been linearly combined to give the correct symmetry. The H_2CO molecule belongs to the symmetry C_{2v} which has four symmetry groups: A_1, A_2, B_1, and B_2. The internal coordinates belong to the following symmetry groups:

$$\begin{aligned}
A_1, \quad &\tilde{S}_1 = r_{OC}, \\
A_1, \quad &\tilde{S}_2 = r_{CH_1} + r_{CH_2}, \\
A_1, \quad &\tilde{S}_3 = r_{OH_1} + r_{OH_2}, \\
B_2, \quad &\tilde{S}_4 = \det(r_{OC}, r_{OH_1}, r_{OH_2}), \quad (45)\\
B_1, \quad &\tilde{S}_5 = r_{CH_1} - r_{CH_2}, \\
B_1, \quad &\tilde{S}_6 = r_{OH_1} - r_{OH_2}, \\
A_1, \quad &\tilde{S}_7 = r_{H_1H_2}.
\end{aligned}$$

States of symmetry A_2 are obtained by multiplying states of symmetry B_1 by states of symmetry B_2. With this notation, the vibrational modes v_i are mapped roughly onto the coordinate $\tilde{S}_i$.

The local mode $\tilde{S}_4$ is involved in most of the first excited states. To have a good description of this bending mode, the following weights defined in Eq. (28) are used:

$$\omega_i = 2 \quad \text{for } i \neq 4, \quad \omega_4 = 1. \quad (46)$$

Different values of Γ lead to different numbers of states for each symmetry (see Table III).

Table IV gives the variational energies for the two basis sets used. The only improvement is for the B_1 and A_2 states, where the basis set size has been increased. Notice that the ground-state energy has decreased by 170 cm^{-1} from the ground-state trial function energy, which indicates that the Gaussian form is not a very good representation.

TABLE II. Matrix elements of A for the ground state of H_2CO [Eq. (18)]. Upper panel: harmonic part of the potential [Eq. (25)]. Lower panel: matrix elements optimized for the energy + error for the complete potential surface. S_7 is the determinant of three vectors, defined in Eq. (43). Units are a_0^{-2}, where a_0 is the Bohr radius.

	r_{OC}	r_{OH_1}	r_{OH_2}	r_{CH_1}	r_{CH_2}	$r_{H_1H_2}$	S_7
r_{OC}	−73.27	19.57	19.57	−18.22	−18.22		0
r_{OH_1}	19.57	−21.95	−6.34	19.92	6.11		0
r_{OH_2}	19.57	−6.34	−21.95	6.11	19.92		0
r_{CH_1}	−18.26	19.92	6.11	−29.91	−4.95		0
r_{CH_2}	−18.22	6.11	19.92	−4.95	−29.91		0
S_7	0	0	0	0	0		−0.105
r_{OC}	−65.43	16.79	16.79	−9.16	−9.16	0.72	0
r_{OH_1}	16.79	−23.48	−7.84	19.21	5.80	−3.04	0
r_{OH_2}	16.79	−7.84	−23.48	5.80	19.21	−3.04	0
r_{CH_1}	−9.16	19.21	5.80	−25.12	−0.08	2.95	0
r_{CH_2}	−9.16	5.80	19.21	−0.08	−25.12	2.95	0
$r_{H_1H_2}$	0.72	−3.04	−3.04	2.95	2.95	−5.88	0
S_7	0	0	0	0	0	0	−0.100

TABLE III. Number of H_2CO trial functions for each symmetry vs basis set. Weights are defined by Eq. (46).

Γ	Total size	Variational level				Correlation function level			
		A_1	B_1	B_2	A_2	A_1	B_1	B_2	A_2
4	44	24	6	12	2	6	4	6	2
5	72	24	24	12	12	8	8	6	4

Table V reports the excited-state energies obtained for different runs with various time steps τ and basis set sizes ($m = 44$ and $m = 72$). All runs are with $N_T = 64$ and $p = 20\,000$. The parameter L (defined in Sec. II B) depends on τ in such a way that $\tau L = 30$ hartree^{-1}. In all cases the basis is diagonalized in two steps: first variationally ($t = 0$) and then at a time $t_1 = 120$ hartree^{-1}. The statistical errors are calculated from the variance of the $N_T = 64$ trajectories. The reported values include bias corrections, but generally the uncorrected values are within the statistical errors. All runs are made with a projection time of 180 hartree^{-1}. No obvious time-step error can be deduced for our results: it is probably less than the statistical errors. With the present algorithm and basis set, a time step of 5 hartree^{-1} is sufficiently small. Using a larger basis set leads to eigenvalues which converge faster with respect to the time t. However, we do not believe that our basis set is very accurate.

Table VI presents the differences between the excited-state energies and the ground state. The errors are calculated directly from the variance of these differences. The errors are not reported because they are essentially the same as the errors of the eigenvalues: the differences are less than 2 cm^{-1} which is the error of the ground state, as they should be.

As already noticed,[12] the states E_2 and E_3 are difficult to separate for B_2 and A_2 symmetries. Direct evaluation of the energy difference leads to a value of 34 (40) cm^{-1} for the B_2 case.

The main conclusions for H_2CO are (i) the time-step error is within the statistical errors of the energy (see Table V); (estimates of the time-step error using a guiding function different from the trial function for the ground state show a much smaller time-step error than when these two functions are identical). (ii) Good improvement is found in the accuracy of energies of the B_1 and A_2 states by increasing the basis set. This is not unexpected because the initial basis set was chosen for its simplicity. The general idea here is that the CFQMC method can improve upon the variational QMC energies by ~90% to 95%, but generally not more. So

if a variational energy is in error by 100 cm^{-1}, the final accuracy obtained with CFQMC will be ~5 to 10 cm^{-1}. For variational energies in error by 500 cm^{-1}, the final accuracy is ~50 cm^{-1} (see Tables IV and V). (iii) A path of $p = 20\,000$ steps does not provide sufficient statistical accuracy to evaluate the energies for each independent path for times larger than 180 hartree^{-1}. One consequence of the poor statistics is that the N matrix may become negative due to noise in the off-diagonal elements. When this happens, the results of the independent trajectories are added together until the N matrix is positive. In some runs all paths have had to be added together for the A_2 symmetry, which is an indication of the poor efficiency of the paths generated for this symmetry. (iv) The guiding function should be chosen with care. In preliminary runs, the stretch mode v_1 (CO) was not well represented in the ground-state trial function nor in the guiding function. This led to large values of the CO distance. Test calculations provided reasonable energy estimates, however, simulations always led to unreasonable energies. An improved description of the v_1 mode in the guiding function eliminated this problem.

V. DISCUSSION AND CONCLUDING REMARKS

Let us compare two techniques of obtaining excited-state energies, the usual variational method (VM), where the integrals are performed deterministically and the present CFQMC method. For the water molecule, both methods are in good agreement within the error bars for the same Hamiltonian (see Table I). For most cases, the CFQMC energies are smaller than the VM ones, as they should be.[2] The standard variational approach is found to take less computational time than the Monte Carlo approach for triatomics to achieve comparable accuracy, as is to be expected. But Monte Carlo method is the best way to perform general multidimensional integrals for dimensionalities greater than 3.

In Table VI we give relative energies for formaldehyde for both methods. Only the fundamental frequencies have been evaluated with the VM.[10,11] The comparison of the first antisymmetric state of B_1 and B_2 and the second symmetric state shows good agreement. But a significant discrepancy appears for the first symmetric excited state. The CFQMC energy is about 80 cm^{-1} above that of the VM, which is outside of the statistical error of both methods. In the VM the full Hamiltonian was not used, only the zeroth-order approximation to the Watson Hamiltonian.[11,13] Thus the VM results are not reliable. In a later paper we will present results with the zeroth-order Watson Hamiltonian which are in better agreement with the VM results. For the other

TABLE IV. H_2CO variational energies (cm^{-1}) vs basis set size.

m	Symmetry	E_1	E_2	E_3	E_4	E_5	E_6
24	A_1	6063	7 682	7898	8425	8886	9 060
6	B_1	7286	9 036	9188	9663		
24	B_1	7205	8 873	9098	9536		
12	B_2	7429	9 254	9286	9422	9631	10 813
2	A_2	8706	10 849				
12	A_2	8581	10 361				

TABLE V. CFQMC H_2CO vibrational energies (cm^{-1}) vs time step (τ) and number of basis functions. τ is the time step in hartree^{-1}. The numbers in ( ) are statistical errors calculated from the variance of the results of the $N_T = 64$ trajectories of each run. The projection time for all numbers is 180 hartree.

Symmetry		$\tau = 10$ $n = 44$	$\tau = 2.5$ $n = 44$	$\tau = 10$ $n = 72$	$\tau = 5$ $n = 72$	$\tau = 2.5$ $n = 72$
A_1	1	5 966 (2)	5 968 (2)	5 964 (2)	5 967 (2)	5 970 (2)
	2	7 456 (13)	7 474 (10)	7 480 (10)	7 480 (10)	7 490 (10)
	3	7 712 (9)	7 714 (9)	7 723 (7)	7 727 (6)	7 726 (6)
	4	8 829 (9)	8 216 (14)	8 215 (9)	8 220 (11)	8 223 (8)
	5	8 425 (18)	8 415 (34)	8 440 (30)	8 447 (15)	8 427 (26)
	6	8 720 (25)	8 738 (25)	8 740 (40)	8 725 (50)	8 760 (23)
	7			9 110 (30)	9 075 (60)	9 080 (60)
	8			9 280 (30)	9 260 (50)	9 286 (60)
B_1	1	7 121 (5)	7 117 (5)	7 110 (4)	7 120 (4)	7 116 (3)
	2	8 635 (43)	8 694 (15)	8 667 (14)	8 642 (15)	8 672 (9)
	3	8 866 (25)	8 890 (18)	8 850 (20)	8 894 (10)	8 858 (25)
	4	9 362 (30)	9 344 (13)	9 290 (25)	9 307 (18)	9 280 (30)
	5			9 602 (17)	9 630 (24)	9 580 (50)
	6			9 920 (40)	9 960 (45)	9 970 (30)
	7			10 240 (60)	10 125 (125)	10 282 (40)
	8			10 470 (40)	10 440 (110)	10 504 (40)
B_2	1	7 184 (11)	7 203 (6)	7 182 (11)	7 202 (8)	7 198 (8)
	2	8 730 (40)	8 700 (40)	8 740 (30)	8 720 (40)	8 766 (30)
	3	8 735 (40)	8 810 (30)	8 755 (40)	8 760 (40)	8 800 (30)
	4	9 038 (30)	9 020 (40)	9 013 (35)	9 030 (24)	9 015 (30)
	5	9 473 (20)	9 440 (30)	9 500 (15)	9 450 (30)	9 460 (30)
	6	10 096 (60)	10 100 (100)	10 100 (100)	10 100 (100)	10 150 (50)
A_2	1	9 347 (20)	8 340 (140)	8 344 (13)	8 336 (15)	8 329 (10)
	2	9 850 (135)	9 920 (110)	9 880 (40)	9 935 (50)	9 880 (40)
	3			9 930 (40)	9 980 (40)	9 920 (40)
	4			10 170 (40)	10 150 (50)	10 175 (30)

TABLE VI. H_2CO excited-state vibrational energies (cm^{-1}) relative to the ground state vs τ and the number of basis functions. The projection time is 180 hartree. τ is the time step in hartree^{-1}. The VM entries are from Ref. 10, using a partial Hamiltonian (see Sec. V). The experimental results are from Ref. 15 and state refers to their normal mode notation.

Symmetry		$\tau = 2.5$ $n = 72$	VM	Expt.	Expt. notation
A_1	2	1520	1464	1500.2	3_1
	3	1756	1792	1746	2_1
	4	2253		2327	4_2
	5	2457			
	6	2790	2690	2782.5	1_1
	7	3110		2999.5	3_2
	8	3316		3238.5	$2_1 3_1$
B_1	1	1146	1164	1167.3	4_1
	2	2702		2655.5	$3_1 4_1$
	3	2888		2905	$2_1 4_1$
	4	3310			
	5	3610			
	6	4000			
	7	4312			
	8	4534			
B_2	1	1228	1239	1249.1	6_1
	2	2796		2719.2	$3_1 6_1$
	3	2830	2836	2843.3	5_1
	4	3045		3000.1	$2_1 6_1$
	5	3490			
	6	4180			
A_2	1	2359			
	2	3910			
	3	3950			
	4	4205			

states there are also discrepancies. We found that even the fundamental frequencies of each mode are mixed with other modes, so that one cannot analyze them in terms of normal modes. Indeed, several intermediate energy levels are found with CFQMC to lie between those of VM. Increasing the basis set size of VM will certainly lead to a much improved estimation of these excited state energies.

Romanowski et al.[12] have also studied the vibrational problem for H_2CO. These authors obtain frequencies close to the experiment by adjusting force constants to agree with experimental data. It is worth noting that the present frequencies are in better accord with experiment than those obtained by Romanowski et al. on their unmodified potential energy surface (PES). In common with the Romanowski et al. paper, we also found very large mixing of the modes for excited states.

Computer time for the CFQMC method increased by a factor of 3 in going from H_2O to H_2CO. The CFQMC method can certainly be improved using better trial functions and optimized guiding functions.

There is a fundamental limitation for all methods. It is the availability of accurate potential energy surfaces. The CFQMC results cannot be unambiguously compared to experiment because of the inaccuracies of the PES used in these calculations. The PES is typically constructed to be accurate near its equilibrium position. In the VM, the integration can be restricted to a domain around the equilibrium position. In CFQMC, the same can be achieved by making the guiding function small in unphysical regions. However, if the ground-state wave function is large in an unphysical region

because of an unphysical minimum, there is a small probability that a random walk will tunnel into that region and lead to unphysical results. A better approach is to change the PES to eliminate such minima. The best solution is, of course, to find globally accurate potential energy functions. We hope that the new capabilities provided by CFQMC will help in their construction. Finally, the CFQMC provides an alternate and fundamentally different way of calculating molecular excitations.

In the next paper in this series, we shall present a CFQMC approach that solves the zeroth-order approximation to the Watson Hamiltonian. In this alternative approach, all trial functions are first tabulated using reduced one-dimensional Hamiltonians. The guiding function can be any combination of these trial functions and is also tabulated. Because of these tabulations, the approach is much faster, but the Hamiltonian is approximate.

ACKNOWLEDGMENTS

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