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# The ground state tunneling splitting and the zero point energy of malonaldehyde: A quantum Monte Carlo determination

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Quantum dynamics calculations of the ground state tunneling splitting and of the zero point energy of malonaldehyde on the full dimensional potential energy surface proposed by Yagi *et al.* [J. Chem. Phys. **115**, 10647 (2001)] are reported. The exact diffusion Monte Carlo and the projection operator imaginary time spectral evolution methods are used to compute accurate benchmark results for this 21-dimensional *ab initio* potential energy surface. A tunneling splitting of  $25.7 \pm 0.3 \text{ cm}^{-1}$  is obtained, and the vibrational ground state energy is found to be  $15\,122 \pm 4 \text{ cm}^{-1}$ . Isotopic substitution of the tunneling hydrogen modifies the tunneling splitting down to  $3.21 \pm 0.09 \text{ cm}^{-1}$  and the vibrational ground state energy to  $14\,385 \pm 2 \text{ cm}^{-1}$ . The computed tunneling splittings are slightly higher than the experimental values as expected from the potential energy surface which slightly underestimates the barrier height, and they are slightly lower than the results from the instanton theory obtained using the same potential energy surface. © 2007 American Institute of Physics. [DOI: 10.1063/1.2406074]

## I. INTRODUCTION

Tunneling of a light atom such as hydrogen is a textbook example of a quantum phenomenon. Ubiquitous to chemistry, physics, and biology, intramolecular proton transfer reactions have the potential to exhibit strong tunneling effects. The malonaldehyde molecule is a benchmark system for studying quantum effects on intramolecular hydrogen bonding that has been extensively studied both experimentally and theoretically. The two possible configurations in the hydrogen bond O–H–O give rise to a double well potential. The barrier for the intramolecular hydrogen transfer is relatively small resulting in a large ground state tunneling splitting of about  $22 \text{ cm}^{-1}$ . This large tunneling splitting, the amenable size, and the beta-diketone character are some of the reasons why malonaldehyde has been extensively studied.

The first experimental measurements of the ground state tunneling splitting in malonaldehyde<sup>1–5</sup> were soon followed by theoretical investigations. Carrington and Miller<sup>6,7</sup> showed that the proton tunneling in malonaldehyde cannot be reduced to a one-dimensional problem, in other words, the large amplitude motion is not restricted to a single reaction coordinate. An attempt was made to determine the essential degrees of freedom relevant to the proton tunneling with

reasonable success. Many theoretical studies on the malonaldehyde system followed which used methods ranging from reduced dimensional quantum models<sup>8–11</sup> via semiclassical treatments<sup>12–22</sup> to full dimensional vibrational configuration interaction calculations based on a reaction path Hamiltonian.<sup>23–25</sup> It has been shown that the quantum mechanical tunneling is not restricted to the motion of the hydrogen atom alone but is coupled to the motion of the heavy backbone atoms.<sup>21,26,27</sup> Thus, the proton transfer in malonaldehyde is a truly multidimensional tunneling process. Experimentally, the ground state tunneling splitting has been determined very accurately<sup>5,28</sup> to be  $21.583\,138\,29 \pm (63) \text{ cm}^{-1}$ . In contrast, the measurement of accurate tunneling splittings of excited vibrational states still posts a significant challenge and only results for a small number of excited states are available.<sup>29–31</sup>

Three of the different aspects of the theoretical description of the proton transfer in malonaldehyde can be discussed separately: the electronic structure calculations, the potential energy surface (PES) construction, and the quantum dynamics calculations. The best presently available electronic structure calculations yield barrier heights ranging from 3.8 kcal/mol [CCSD(T)/(aug-cc-pvtz)] (Ref. 22) to 4.3 kcal/mol (G2).<sup>32</sup> However, *ab initio* results at this level of theory have been restricted to a rather limited number of geometries and no complete potential energy surfaces

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have been obtained. The lower level MP2/6-31G ( $d,p$ )-calculations of Yagi *et al.*<sup>18</sup> yielded a barrier height of 3.6 kcal/mol which is only slightly lower than the results from the accurate *ab initio* calculations. Using this level of electronic structure calculations, Yagi *et al.* constructed a complete full dimensional PES (Ref. 18) employing the Shepard interpolation scheme developed by Collins and co-workers.<sup>33–39</sup> This PES is the starting point for the quantum dynamical calculations presented in this work.

Rigorous quantum dynamics calculations of vibrational states of a molecule having nine atoms (21 internal coordinates) pose a significant challenge. In a previous letter,<sup>40</sup> we presented the first results of quantum dynamics calculations for the tunneling splitting employing two completely different methods: the multiconfigurational time-dependent Hartree (MCTDH) (Refs. 41 and 42) and the Monte Carlo based projection operator imaginary time spectral evolution (POITSE) (Ref. 43) technique. The aim of this article is to provide a more complete description of the Monte Carlo calculations and to additionally present new results for the H/D isotopically substituted malonaldehyde. Emphasis is also placed on showing extensive convergence studies for the quantities computed, namely, the tunneling splittings and the zero point vibrational energies.

While vibrational energies of isolated molecules are usually calculated employing variational methods based on the expansion of the vibrational wave function in basis sets or on grids, quantum Monte Carlo (QMC) methods can be an interesting alternative for special cases such as ground state tunneling splittings. QMC methods avoid the use of basis sets and thus avoid the exponential scaling of the numerical effort with the systems dimensionality. The main idea behind these stochastic techniques is to evaluate multidimensional integrals with the help of random walks. Usually, three zero temperature and one finite temperature variants are included in the generic term “quantum Monte Carlo methods”, namely, (i) the variational Monte Carlo (VMC) method, (ii) the Green’s function Monte Carlo method (GFMC), (iii) its most common variant, the diffusion Monte Carlo method (DMC), and (iv) the path integral Monte Carlo method (PIMC). Since their first application to study energetics and structures of pure helium clusters more than 20 years ago,<sup>44</sup> QMC methods have been the methods of choice for studying quantum droplets (pure and doped helium and hydrogen clusters) which are characterized by quantum effects and floppiness.<sup>45–52</sup> Applications of QMC methods to more “chemical” species are more scarce and have been restricted to model systems of proteins<sup>53</sup> and to van der Waals type complexes.<sup>54,55</sup> In this work, we use DMC to compute the ground state energy of the malonaldehyde molecule, taking advantage of the availability of the full dimensional global potential energy surface.<sup>18</sup> Contrary to the study of ground state properties using QMC, the computation of excited states using stochastic methods is more challenging. The main difficulty arises from the fact that in DMC the wave function is interpreted as a (positive value) density, whereas excited state wave functions necessarily present at least one change of sign. Different strategies have been proposed to overcome the difficulty of this “sign problem”. The fixed-

node (FN) method is a widespread approximation which consists in using a guiding function (see below) with a node, thus enforcing a nodal surface for the distribution. This approximation becomes exact when the nodal structure is unambiguously known (by symmetry argument). However, for a general vibrational problem, the nodal structure is generally not known. Despite the efforts made in the direction of correcting the position of the nodal surfaces,<sup>56,57</sup> the FN method and the related released node approaches do not seem to be good candidates for the computation of excited states of a general vibrational problem. An alternative approach, the POITSE (Ref. 43) methodology which focuses on the computation of excitation energies only rather than the computation of both energies and wave functions, was proposed nearly ten years ago. In this method, a Laplace transform is used to extract the excitation energies from an imaginary time correlation function computed with the DMC algorithm.

For the specific case of intramolecular proton transfer, the two lowest vibrational states are the two tunneling split “ground states”. Typically an energy gap significantly larger than the tunneling splitting separates these two states from the higher excited ones. Thus, the problem of calculating the ground state tunneling splitting is a rather well suited case for the application of the POITSE technique. The present work demonstrates the prospects offered by this quantum Monte Carlo approach to study tunneling of a realistic benchmark system, and discusses the relevant technical aspects in detail.

The article is organized as follows: Sec. II discusses the details of the malonaldehyde system and defines the Hamiltonian used in the QMC calculations. The relevant QMC theory is reviewed in Sec. III. Detailed results are presented and discussed in Sec. IV and Sec. V.

## II. THE MALONALDEHYDE SYSTEM

For the description of the malonaldehyde molecule, we made use of the full dimensional PES proposed by Yagi *et al.*<sup>18</sup> The construction of this 21-dimensional *ab initio* PES relied on the use of the modified Shepard interpolation scheme introduced by Collins and co-workers<sup>33–39</sup> to interpolate *ab initio* energies. Due to the numerical effort for the construction of such an interpolated surface (computation of the energies and of the first and second derivatives), the *ab initio* description has been restricted to the second-order Møller-Plesset perturbation theory. The interpolation scheme has been done in Cartesian coordinates corrected from the noninvariance with respect to overall translation and rotation by the introduction of a molecular frame. The surface describes both the symmetrically equivalent  $C_s$  global minima as well as the  $C_{2v}$  proton transfer saddle point. The barrier height for the hydrogen transfer of 3.6 kcal/mol for this surface<sup>18</sup> is slightly lower than the results obtained with more elaborate levels of *ab initio* methods.<sup>22,32</sup>

Normal modes analyses have been performed for the global minimum ( $C_s$  symmetry) and for the  $C_{2v}$  saddle point geometry when the hydrogen atom is at equal distance from the two oxygen atoms. The frequencies obtained at the

minima lead to an harmonic approximation of the zero point energy of  $15\,203.73\text{ cm}^{-1}$ . Out of the 27 normal modes, computed at the  $C_{2v}$  saddle point geometry, the six normal modes which are associated with a quasinull frequency and correspond at first order to the overall translation and rotation are discarded, while the remaining 21 normal modes  $\mathbf{Q}=\{Q_1, \dots, Q_{21}\}$  have been chosen as coordinates for the dynamical study. A single normal mode  $Q_{21}$  is associated with an imaginary frequency and corresponds to the hydrogen transfer mode.

The  $J=0$  Hamiltonian has been approximated by

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{i=1}^{21} \frac{\partial^2}{\partial Q_i^2} + V(\mathbf{Q}), \quad (1)$$

in which the mixed derivatives in the kinetic energy operator resulting from vibrational angular momenta are neglected. Results from other studies of hydrogen transfer processes<sup>58–61</sup> indicate that the effect of the neglected terms is insignificant. An investigation trying to precisely quantify the effect of these terms is currently in progress.<sup>62</sup> Within the Monte Carlo scheme, the inclusion of such terms is not possible when using the 21 normal modes (cross derivative terms in the Hamiltonian). It is possible to include them when using the 27 Cartesian coordinates of the nine atoms. The use of the 21 normal modes together with the approximated Hamiltonian [Eq. (1)] is motivated by the possibility to compare with the results obtained with the MCTDH method<sup>40</sup> for which the use of the Cartesian coordinates is not possible. In Eq. (1),  $V(\mathbf{Q})$  is the PES of Yagi *et al.*,<sup>18</sup> and  $\mathbf{Q}$  are the 21 Cartesian normal modes determined at the  $C_{2v}$  saddle point.

### III. MONTE CARLO STUDIES

Stochastic techniques, which have a polynomial scaling with the dimensionality of the system, are the methods of choice for the quantum determination of bosonic ground states of large systems. The DMC method<sup>45,63–65</sup> has been used here to compute the ground state energy of the malonaldehyde molecule including all 21 internal degrees of freedom. The POITSE (Refs. 43 and 66) methodology has been employed to determine the ground state tunneling splitting which is the first excitation energy of the system. The basic principles of both techniques (DMC and POITSE) have been extensively described in the literature. Herein they will be briefly reviewed and the specific details of their application to the present problem will be discussed.

#### A. Diffusion Monte Carlo (DMC) and importance sampled DMC (IS-DMC)

The DMC method is based on the similarity of the Schrödinger equation to a diffusion process in the presence of a source term. The transformation of the time-dependent Schrödinger equation to imaginary time  $\tau=it/\hbar$  leads to the working equation of DMC for an  $\mathcal{N}$ -dimensional system,

$$\frac{\partial \Psi(\mathcal{X})}{\partial \tau} = \sum_{j=1}^{\mathcal{N}} D_j \frac{\partial^2}{\partial \mathcal{X}_j^2} \Psi(\mathcal{X}) - [V(\mathcal{X}) - E_{\text{ref}}] \Psi(\mathcal{X}), \quad (2)$$

where  $\mathcal{X}$  is a vector in the  $\mathcal{N}$ -dimensional space,  $D_j$  is  $\hbar^2/2m_j$  for each degree of freedom  $j$  associated with the mass  $m_j$ ,  $E_{\text{ref}}$  is an arbitrary energy shift,  $V(\mathcal{X})$  is the potential energy surface, and  $\Psi(\mathcal{X})$  is the solution of the equation. Note that in Eq. (2), the Hamiltonian is assumed to be expressed as a function of the Cartesian coordinates of the particles constituting the system. This choice ensures a simple kinetic term without cross derivative terms and it is the most popular one when studying quantum clusters. The absence of cross terms in the kinetic term when using the instantaneous principal axis frame to represent the rotation of rigid bodies<sup>67</sup> has also enabled the study of molecules embedded in helium clusters.<sup>68</sup> In principle, the study of malonaldehyde could have been conducted using the 27 Cartesian coordinates of the nine atoms. However, the Hamiltonian given in Eq. (1) for the malonaldehyde molecule represented using the 21 Cartesian mass weighted normal modes  $\mathbf{Q}$  has the same form as the Hamiltonian expressed in Cartesian coordinates. The use of the Cartesian mass weighted normal modes therefore leads to a DMC working equation analogous to Eq. (2) (without cross derivative terms), thus the DMC study can also make use of these 21 coordinates. This choice of coordinate system is actually favorable since quantities like the trial function required in importance sampling DMC or the projector required in POITSE can be much simpler in normal mode coordinates. It also allows direct comparison with the results obtained by the MCTDH approach.<sup>40</sup>

A very important procedure to greatly improve the efficiency of DMC is called IS-DMC. The corresponding working equation is obtained by multiplying Eq. (2) by a trial (or guiding) function  $\Psi_T(\mathcal{X})$  and by introducing the product function  $f(\mathcal{X})=\Psi(\mathcal{X})\Psi_T(\mathcal{X})$ ,

$$\frac{\partial f(\mathcal{X})}{\partial \tau} = \sum_{j=1}^{\mathcal{N}} \left\{ D_j \frac{\partial^2}{\partial \mathcal{X}_j^2} f(\mathcal{X}) - D_j \frac{\partial}{\partial \mathcal{X}_j} [f(\mathcal{X}) F_j(\mathcal{X})] \right\} - [E_l(\mathcal{X}) - E_{\text{ref}}] f(\mathcal{X}). \quad (3)$$

The guiding function  $\Psi_T(\mathcal{X})$  approximates the solution  $\Psi(\mathcal{X})$  of the equation and contains physical insights regarding the particular system under study. In the above equation,  $E_l(\mathcal{X})=\Psi_T(\mathcal{X})^{-1}\hat{H}\Psi_T(\mathcal{X})$  is the local energy and  $F_j(\mathcal{X})=(\partial/\partial \mathcal{X}_j) \ln|\Psi_T(\mathcal{X})|^2$  is the quantum force. The use of a guiding function, also known as “biased DMC”, improves the sampling of relevant parts of the configuration space where the trial function is large. When no guiding function is used ( $\Psi_T(\mathcal{X})=1$ ), Eq. (3) reduces to Eq. (2), and one refers to unbiased DMC.

A random walk technique is used to determine the steady state of Eq. (2) or (3). A walker (or configuration) is defined as a vector  $\mathcal{X}$  in the  $\mathcal{N}$ -dimensional space and represents the position of all the particles of the system under study. An ensemble of walkers is propagated from some arbitrary initial distribution using the short time approximation of the Green’s function appropriate to Eq. (2) or (3). Namely, each element of the vector  $\mathcal{X}$  is updated according to



$$\mathcal{X}_j(\tau + \Delta\tau) = \mathcal{X}_j(\tau) + \text{RAND} + D_j\Delta\tau F_j(\mathcal{X}(\tau)), \quad (4)$$

where the imaginary time has been discretized using the time step  $\Delta\tau$ . In the above equation,  $\text{RAND}$  is a random number sampled from a Gaussian of width  $\sqrt{2D_j\Delta\tau}$  which represents the diffusion process, and  $D_j\Delta\tau F_j(\mathcal{X}(\tau))$  is the drift force induced by the guiding function. After this move, the effect of the source term  $[V(\mathcal{X}) - E_{\text{ref}}]$  or  $[E_f(\mathcal{X}) - E_{\text{ref}}]$  is evaluated. There are different recipes to implement the source term. The original implementation assigns continuous weights to each walker  $j$ ,  $w_j$  which are updated at each time step according to

$$w_j(\tau + \Delta\tau) = w_j(\tau)e^{-(V(\mathcal{X}_j) - E_{\text{ref}})\Delta\tau}, \quad (5)$$

in the case of unbiased DMC, or

$$w_j(\tau + \Delta\tau) = w_j(\tau)e^{-(E_f(\mathcal{X}_j) - E_{\text{ref}})\Delta\tau}, \quad (6)$$

when a guiding function is used. This implementation is known to be unstable since at long propagation time, a very small number of walkers carry large weights, while the weights of the others vanish, leading to a poor statistics when averaging over the ensemble. An alternative implementation is to assign identical fixed weight to all walkers and to introduce branching at each time step. The simplest branching scheme is to replicate or kill walkers according to the integer  $n_j = \text{int}[e^{-(V(\mathcal{X}_j) - E_{\text{ref}})\Delta\tau + \xi}]$  (or  $n_j = \text{int}[e^{-(E_f(\mathcal{X}_j) - E_{\text{ref}})\Delta\tau + \xi}]$ ), where  $\xi$  is a uniformly distributed random number on  $[0, 1)$ . A walker  $j$  is destroyed for  $n_j = 0$ , otherwise  $n_j$  copies of this walker are propagated independently in the next DMC move. While the implementation with continuous weights ensures a constant number of walkers, the branching algorithm presented above does not. The implementation used in this work relies on a combination of weights and branching, resulting in a fixed ensemble size<sup>69</sup> similar to the implementation used in Ref. 70. Namely, a variable weight  $w_i(\tau)$  is assigned to each walker. Each time the relative weight  $w_i^{\text{rel}}(\tau) = w_i(\tau)/\sum_j w_j(\tau)$  of a walker falls below a predefined value, an elimination step is performed. Depending on the value of a uniformly distributed random number, the walker  $i$  is eliminated randomly with the probability  $1 - w_i^{\text{rel}}(\tau)$ , and simultaneously the walker  $j$  of the ensemble with the largest relative weight  $w_j^{\text{rel}}(\tau)$  is split into two walkers each with half of the weight  $w_j(\tau)$ . If the walker  $i$  is not eliminated, its weight is increased to the average weight of the ensemble. This mechanism allows the elimination of walkers with both small and large weights while keeping a constant number of walkers. In case of nonconstant trial function  $\Psi_T$ , a Metropolis step is added at each time step which forces an increased sampling in the regions where  $\Psi_T$  is large.

Using the formal solution of Eq. (2) and introducing a complete set of eigenfunctions of the Hamiltonian  $\hat{H}$ ,  $\{|\Psi_n\rangle\}$  on which the initial wave function is expanded, one obtains the imaginary time evolution of  $\Psi$

$$|\Psi(\tau)\rangle = e^{-\hat{H}\tau}|\Psi(0)\rangle = \sum_n C_n e^{-E_n\tau}|\Psi_n\rangle. \quad (7)$$

This equation ensures, assuming an energy scale such that  $E_0 = 0$ , that the ground state solution is achieved asymptotically. When no trial function or a nodeless trial wave function is employed, the ground state energy of the system is

obtained by averaging the potential energy or local energy over the walkers and the random walk, in the limit of large number of walkers and of infinitively small imaginary time step used during the walk. The variation of the total weight of the ensemble,  $W = \sum_j w_j$ , after  $n$  time steps, provides another estimation of the ground state energy,

$$E_{\text{growth}} = E_{\text{ref}} + \frac{1}{n\Delta\tau} \ln \frac{W(\tau)}{W(\tau + n\Delta\tau)}. \quad (8)$$

In order to estimate the error bars on the final energy, the blocking technique is used. In this technique, the propagation time is separated into blocks of  $n_{\text{time}}$  time steps, with  $n_{\text{time}}$  larger than the correlation length. The average over the ensemble is taken once per block from which the standard deviation is computed.

## B. POITSE

The determination of excited states using stochastic methods is more complex because the solution of Eq. (3) relies on the interpretation of  $f(\mathcal{X}) = \Psi(\mathcal{X})\Psi_T(\mathcal{X})$  or  $\Psi(\mathcal{X})$  in the unbiased DMC case, as a positive and finite probability. Excited states can be computed in an approximate manner (or exactly if the nodal structure is known by symmetry considerations) using a guiding function  $\Psi_T(\mathcal{X})$  with a node. Note that in the particular case of the computation of the malonaldehyde ground state tunneling splitting, the exact nodal structure is given by symmetry considerations, thus the fixed-node approximation would lead to an exact computation of the first excited energy level. However, in general and because of the inherent statistical noise on the results, the ‘‘fixed node’’ approximation is unsuitable when the difference in energy between the levels is much smaller than their absolute value. A tunneling splitting in a large molecule, such as malonaldehyde, corresponds to such an unfavorable case. In the POITSE methodology,<sup>43,66</sup> which does not assume predefined nodal surfaces, one directly extracts excitation energies from the two-sided inverse Laplace transform of an imaginary time correlation function  $\tilde{\kappa}(\tau)$ . This correlation decay is computed using a combination of a main VMC integration walk and DMC sidewalks (see the schematic view presented in Fig. 1 of Ref. 43). One of the main differences between DMC and POITSE is that in DMC one performs a long random walk to make sure that the ground state distribution has been projected out before evaluating properties [see Eq. (7)], whereas in POITSE one uses the information at short imaginary time propagation well before the complete decay of the walker distribution into the ground state. The decay of the correlation,

$$\tilde{\kappa}(\tau) \propto \langle \Psi_T | A \exp[-(\hat{H} - E_0)\tau] A^\dagger | \Psi_T \rangle, \quad (9)$$

contains information about energy differences  $E_f - E_0$ , where  $E_0$  is the ground state energy and  $E_f$  an excited state energy level. In this equation,  $A$  is a local operator chosen to project from the trial function  $|\Psi_T\rangle$  onto some excited state  $|\Psi_f\rangle$ . An inverse Laplace transform of  $\tilde{\kappa}(\tau)$  yields the desired spectral information  $\kappa(\omega)$ ,

$$\kappa(\omega) = \sum_f |\langle \Psi_T | A | \Psi_f \rangle|^2 \delta(E_0 - E_f + \omega). \quad (10)$$

The renormalized POITSE correlation function can be written<sup>43</sup> in a convenient form for Monte Carlo evaluation,

$$\tilde{\kappa}(\tau) = \frac{\langle \Psi_T | A \exp[-(\hat{H} - E_{\text{ref}})\tau] A^\dagger | \Psi_T \rangle \langle \Psi_T | \Psi_T \rangle}{\langle \Psi_T | \exp[-(\hat{H} - E_{\text{ref}})\tau] | \Psi_T \rangle \langle \Psi_T | \Psi_T \rangle}, \quad (11)$$

where  $E_{\text{ref}}$  is a reference energy which is usually given by an estimate of the ground state energy  $E_0$ . The correlation decay  $\tilde{\kappa}(\tau)$  and the Laplace transform spectral weight function  $\kappa(\omega)$  can be seen as the imaginary time analogs of the autocorrelation function and Fourier transform spectrum in real time. The main difference comes from the ill-posed numerical problem of the inverse Laplace transform of multiple exponential and noisy decays. The POITSE approach relies on the use of an operator  $A$  which reduces the number of exponential decays in the sum of Eq. (7). The inverse Laplace transform of the resulting decay  $\tilde{\kappa}(\tau)$  is still an ill-posed problem but can be solved by a maximum entropy analysis.<sup>71–73</sup> The operator  $A$  must be chosen based on physical insight in order to select the excitation energy of interest. The perfect operator  $A$  would be the one for which  $|\langle \Psi_T | A | \Psi_f \rangle|^2$  is zero except for one excited state  $f$ . A “bad” operator  $A$  (i.e., an operator such as  $|\langle \Psi_T | A | \Psi_f \rangle|^2$  which is non-negligible for a large number of states  $f$ ) leads to a correlation decay which is hard (in the best case) or impossible to invert numerically. In all cases, the excitation energies obtained are the exact ones and do not depend on  $A$  or on any nodal structure information contained in  $A$ .

In order to compute the tunneling splitting in malonaldehyde, the implementation of POITSE using the combination of weights and branching as detailed above has been chosen. It has been shown<sup>66,74</sup> that the original implementation of POITSE based only on weights is not suited for the computation of very long correlation decays needed for the extraction of small energy differences.

## IV. RESULTS

### A. Convergence test and construction of the trial function: Unbiased DMC

Since no previous Monte Carlo computations on this particular system have been done, extensive tests that vary the imaginary time step  $\Delta\tau$  and the number of walkers in the ensemble have been conducted. Figure 1 presents a summary of the computations performed. In this figure, the ground state energy, estimated from the growth energy estimator [Eq. (8)], is presented for time steps varying from 2 to 20 a.u. and for four different ensemble sizes, namely, 500, 1000, 2000, and 3000 walkers. For each calculation, the average includes 2000 blocks of 100 time steps which have been performed after the equilibration steps. A time step dependence of the energy as a function of the time step  $\Delta\tau$  is observed. Additionally, there is a much larger dependence of the estimated energy on the number of walkers in the ensemble. Explorative computations for several values of  $\Delta\tau$  using up to 6000 walkers show that even with such a large ensemble size, a bias due to the finite ensemble is still non-

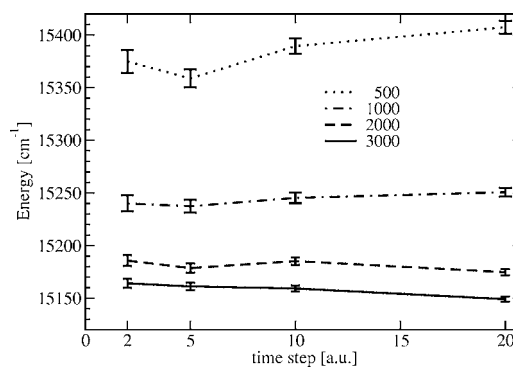


FIG. 1. Ground state energy in  $\text{cm}^{-1}$  as a function of the time step  $\Delta\tau$  and the number of walkers used in the unbiased Monte Carlo walk.

negligible. This ensemble size bias is known<sup>64</sup> but it is hardly ever studied. Its relation to the fluctuation of the average energy over the ensemble of walkers leads to a scaling of this bias as the inverse of the ensemble size.<sup>64,75</sup> A way to reduce the fluctuations of the energy is to introduce a trial function for which one expects that the local energy  $E_L(\mathcal{X}) = \Psi_T(\mathcal{X})^{-1} \hat{H} \Psi_T(\mathcal{X})$  will be a much smoother function than the potential term  $V(\mathcal{X})$ .

The construction of a reasonable trial function in many dimensions is not trivial. In an unbiased DMC computation, the walkers of the ensemble are distributed according to the exact ground state eigenfunction. Therefore, in principle, an ideal trial function could be obtained from an unbiased DMC calculation. However, the dimensionality of the problem (21 for malonaldehyde) usually prohibits practical access to this function. One needs to find a simpler trial function which approximates the exact ground state. One of the simplest trial functions possible is a product of single coordinate functions. Unbiased DMC computations provide a way to evaluate the wave function projected along each of the variables by doing histogram of the distribution of walkers during the walk. More involved trial functions, including, for example, two coordinate correlations, are possible. However, a balance between the complexity of a more exact trial function, which increases the computer time per Monte Carlo step, and simplicity, which increases the number of Monte Carlo steps required, must be found.

TABLE I. Parameters (in a.u.) of the trial wave function defined in Eq. (13).

$i$	$a_i$	$b_i(\times 10^2)$	$i$	$a_i$	$b_i(\times 10^2)$
1	0.381 63	0.072 072	2	0	0.065 949
3	0	0.111 85	4	-40.663	0.056 569
5	0.061 505	0.177 19	6	-12.971	0.185 78
7	0.011 475	0.220 78	8	0	0.236 23
9	0.026 560	0.234 60	10	0	0.258 50
11	0.145 18	0.194 06	12	0	0.307 80
13	-0.813 90	0.299 37	14	0	0.337 41
15	2.6084	0.367 36	16	0	0.357 49
17	8.4278	0.333 52	18	0	0.697 95
19	-0.544 84	0.701 45	20	-0.633 86	0.730 39
		$a_{21}=32.739$			$b_{21}=0.001\ 697\ 3$
					$c_{21}=0.017\ 390$

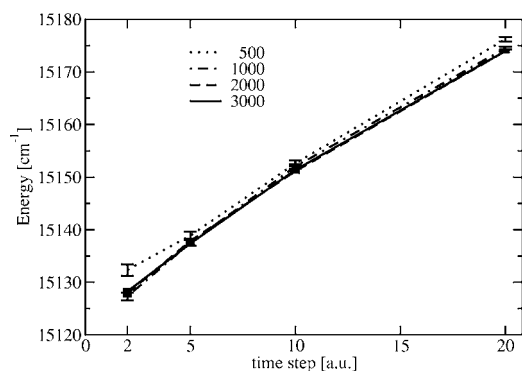


FIG. 2. Ground state energy in  $\text{cm}^{-1}$  as a function of the time step  $\Delta\tau$  and the number of walkers used in the importance sampled Monte Carlo walk.

For the study of malonaldehyde a simple product of one-dimensional functions of the 21 normal modes,

$$\Psi_T^{(21d)}(\mathbf{Q}) = \prod_{i=1}^{21} \Phi_i(Q_i), \quad (12)$$

has been chosen. For all except the tunneling coordinate, the one coordinate functions  $\Phi_i(Q_i)$  are taken as Gaussian functions, while a more involved expression is used for  $\Phi_{21}(Q_{21})$ ,

$$\Phi_i(Q_i) = e^{-b_i(Q_i - a_i)^2}, \quad i = 1, \dots, 20,$$

$$\Phi_{21}(Q_{21}) = [e^{-b_{21}(Q_{21} - a_{21})^2} + e^{-b_{21}(Q_{21} + a_{21})^2}]e^{-c_{21}Q_{21}^4}. \quad (13)$$

The 43 parameters of Eq. (13) have been determined by fits to the projections of the wave function along the 21 coordinates obtained via unbiased DMC calculations and are presented in Table I. Note that for the asymmetric modes, the above Gaussians are unable to correctly represent the dissymmetry of the histograms obtained. However, this imprecision of the trial wave function has no effect on the DMC energy itself but only on the error bars.

## B. Ground state energy

A similar series of convergence tests with respect to the time step and the ensemble size has been performed within the IS-DMC scheme using the trial function of Eq. (12). Figure 2 presents the energies obtained. Except for the smallest ensemble size (500 walkers) the energies are converged with respect to the ensemble size. This shows that the simple trial function used greatly reduces the fluctuations of the average of the energy over the walkers. The time step depen-

dence is linear, as expected for a guided walk. Extrapolation to zero time step leads to a ground state energy of  $15121 \pm 5 \text{ cm}^{-1}$ , only  $82 \text{ cm}^{-1}$  lower than the harmonic approximation value. We infer that this small difference with the harmonic value is fortuitous and might be due to compensation effects. Indeed, inspection of the potential energy surface clearly indicates that the out-of-plane modes are strongly anharmonic.

## C. Tunneling splitting

The POITSE methodology requires no exact knowledge of the nodal surface of the excited states but only a “good” estimate of it. In the case of double well, it was previously shown<sup>76</sup> that the projector  $\hat{A} = Q_{21}$  enables the computation of the excitation energy to the first antisymmetric state thus giving the tunneling splitting. This choice of projector is evident since  $Q_{21}$  is the symmetry breaking coordinate for the proton transfer. The decays have been computed using the trial function defined in Eq. (12) up to  $\tau_{\text{final}} \approx 15000 \text{ a.u.}$  The left panel of Fig. 3 presents an average over 6500 decays. Because of the quality of the trial function used, the short time part of the decays is polluted by higher excitation energies. This multiple exponential part of the decay, for very short imaginary time propagation, has been discarded<sup>47</sup> before performing the inverse Laplace transform of the truncated decay with the MaxEnt method (see Ref. 46 for details). An example of the resulting spectrum is presented on the right panel of Fig. 3. This spectrum contains a single peak, thus showing that the truncated decay is dominated by a single exponential. The width of the obtained spectrum is not physically relevant. However, an estimation of the error bars, resulting from the statistical noise of the exponential decays, has been estimated as explained in Ref. 46. This estimation is shown in Fig. 3 as vertical lines. Sensitivity and convergence with respect to the usual Monte Carlo parameters (time step, number of walkers) as well as the POITSE parameters (imaginary propagation time, number of decays) have been carefully studied. For example, Fig. 4 compares the tunneling splitting values as a function of the time step employed, when using 2000 (full line) and 1000 (dotted line) walkers. For each  $\Delta\tau$  and each of the two ensemble sizes tested, the inverse Laplace transform of the correlation decay  $\tilde{\kappa}(\tau)$  averaged over 6500 decays leads to a single peak. We have checked that with this number of decays the position of the peak of the associated spectrum is converged. The position of the peaks with the associated estimation of the error

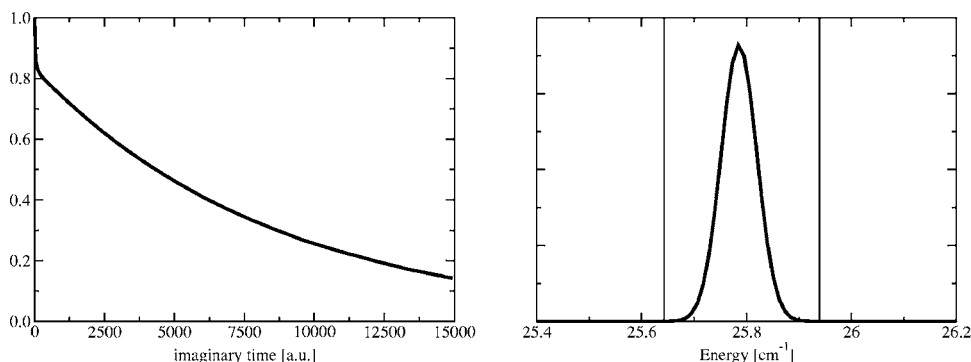


FIG. 3. Example of correlation decay  $\tilde{\kappa}(\tau)$  as a function of imaginary time  $\tau$  (left panel) and the associated spectrum (right panel) where the error bar has been shown as vertical lines.

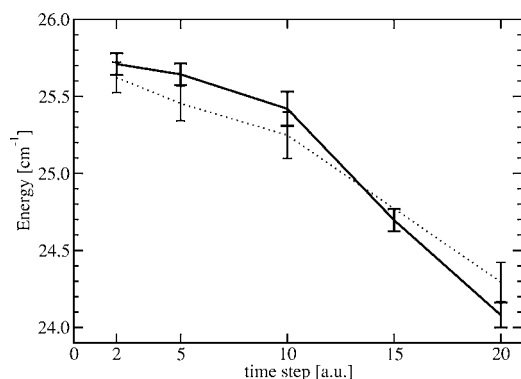


FIG. 4. Tunneling splitting values and associated error bar estimates obtained from the inversion of 6500 decays as a function of  $\Delta\tau$  using an ensemble size of 2000 (full line) and 1000 (dotted line) walkers.

bars, reported on the figure, converges as  $\Delta\tau$  decreases. Since the values obtained for 1000 and for 2000 walkers are in agreement within the error bars, we assume that 2000 walkers are enough to reach convergence. The ensemble size necessary to have convergence is in agreement with the one obtained for the ground state study (see Sec. IV B), which seems reasonable given that POITSE is based on importance sampling DMC walks. We have checked that the tunneling splitting value is stable with respect to the propagation time  $\tau_{\text{final}}$ .

On Fig. 5 we have reproduced the peak position for the 2000 walkers case as a function of time step (full line) together with the results obtained using an alternative implementation of POITSE based on branching only (dashed line).<sup>66,74</sup> This implementation<sup>66,74</sup> of the DMC walk does not impose a constant number of walkers since the replication of walkers is made independently of the creation. As a consequence a relatively small time step must be used within this implementation in order to keep a reasonable ensemble size. A time step that is too large induces large energy fluctuations over the walkers which then causes consequent branching leading quickly to an increase or decrease of the ensemble size. At the limit of small time steps, the two implementations lead to the same tunneling splitting value.

For this 21-dimensional quantum calculation, the converged value for the tunneling splitting is found to be  $25.7 \pm 0.3 \text{ cm}^{-1}$ , keeping in mind that the error bar estimate is

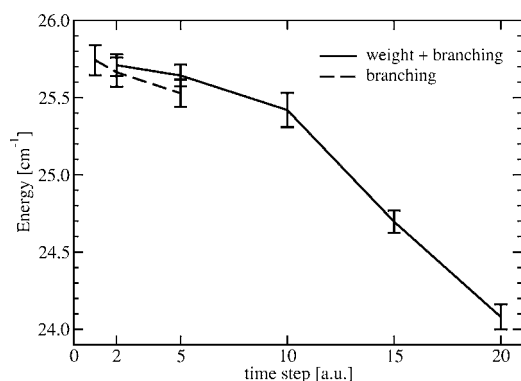


FIG. 5. Tunneling splitting values and associated error bar estimates obtained from the inversion of 6500 decays as a function of the time step  $\Delta\tau$  (in a.u.) using the branching+weight and the branching implementation.

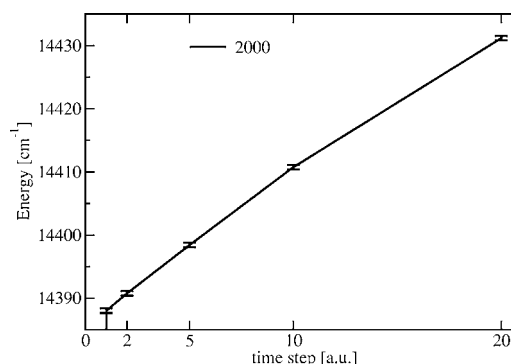


FIG. 6. Ground state energy of the isotope in  $\text{cm}^{-1}$  as a function of the time step  $\Delta\tau$  using 2000 walkers in the guided Monte Carlo walk.

only an indication of the order of magnitude of the error itself.<sup>46</sup> This value perfectly agrees with the one independently obtained using MCTDH,<sup>40</sup> namely,  $25 \text{ cm}^{-1}$  converged to about 10%. This agreement validates the two quantum methods, the convergence of the presented results, as well as the particular choice of the guiding function and projection operator employed here.

Our theoretical value is found to be 20% higher than the experimental value of  $21.6 \text{ cm}^{-1}$ .<sup>28</sup> Given the known underestimation by about 0.6 kcal/mol of the barrier height of the Yagi *et al.*<sup>18</sup> potential, some difference was expected. Still this difference is quite small.

The present converged quantum calculation provides a benchmark value to be used for comparison with results from approximate dynamical methods. To the best of our knowledge, the present work provides for the first time the possibility of comparison for a realistic 21-dimensional potential energy surface that describes intramolecular proton tunneling. Within this viewpoint, it is interesting to note that the POITSE value is 20% lower than the  $30.7 \text{ cm}^{-1}$  obtained by Mil'nikov *et al.*<sup>22</sup> using the instanton approach<sup>77</sup> on the same surface. Taking into account the relative simplicity of the instanton approach compared to rigorous quantum dynamics, such an agreement can be considered as rather good.

## V. ISOTOPE RESULTS

We have repeated similar studies for the deuterium isotope. Figure 6 presents the time step dependence of the growth energy obtained with the importance sampling scheme. The guiding function used is identical to the one given in Eq. (7) with the parameters summarized in Table II. Note that given the fast convergence of the results with respect to the number of walkers in the hydrogen case, we have not performed a systematic study in the deuterium case, assuming that 2000 walkers are enough here too. Extrapolation to the zero time step limit leads to a ground state energy of  $14\,385 \pm 2 \text{ cm}^{-1}$ .

For the POITSE determination of the tunneling splitting, decays up to  $\tau_{\text{final}} \approx 30\,000 \text{ a.u.}$  have been computed. Due to the smaller tunneling splitting in the deuterium case, a doubling of  $\tau_{\text{final}}$  with respect to the hydrogen case has been necessary in order for the exponential decays to decrease sufficiently. Figure 7 presents the time step convergence study of the tunneling splitting values obtained. For each



TABLE II. Parameters (in a.u.) of the trial wave function defined in Eq. (13) for the isotope case.

$i$	$a_i$	$b_i(\times 10^2)$	$i$	$a_i$	$b_i(\times 10^2)$
1	-0.473 17	0.064 007	2	0	0.065 552
3	0	0.104 68	4	45.964	0.064 010
5	0.171 12	0.176 36	6	0.023 061	0.161 97
7	-16.986	0.182 31	8	-0.039 615	0.189 13
9	0	0.237 61	10	0.747 86	0.235 77
11	0	0.258 18	12	-11.522	0.243 09
13	0	0.307 59	14	-4.2592	0.304 34
15	0	0.336 88	16	0	0.367 31
17	0.131 65	0.369 39	18	0	0.695 69
19	-0.611 39	0.703 57	20	-0.609 28	0.732 02
		$a_{21}=46.539$			$b_{21}=0.001\ 954\ 2$
					$c_{21}=0.017\ 218$

time step, an average over 5000–6000 decays has been performed to compute the correlation decay  $\tilde{\kappa}(\tau)$  which has been then inverted. Similarly to the ground state computation, an ensemble size of 2000 walkers has been used. Extrapolation to the zero time step limit leads to a final value of  $3.21 \pm 0.09 \text{ cm}^{-1}$ . As for the hydrogen case, our theoretical value is found to be higher than the experimental value<sup>4</sup> of  $2.915 \text{ cm}^{-1}$  but only by 10% (20% for H). Again this is coherent with the fact that the barrier height of the surface is known to be too small. The instanton approach on the same surface<sup>22</sup> gives  $4.58 \text{ cm}^{-1}$  thus being about 40% higher than our POITSE result.

## VI. CONCLUSION

In this work, the ground state energy and the ground state tunneling splitting of the malonaldehyde molecule and its isotopically substituted analog have been quantum mechanically determined in 21 dimensions. Details on the quantum Monte Carlo techniques employed, namely, importance sampling diffusion Monte Carlo for the ground state and POITSE for the excitation energy, as well as convergence studies have been presented. The use of these statistical quantum methods, together with a very simple trial function, makes these 21-dimension quantum calculations possible. The zero point energy value is found to be very close to the harmonic estimation which is probably due to compensation effects between the anharmonic modes. The tunneling splitting value of  $25.7 \pm 0.3 \text{ cm}^{-1}$  is identical to the one independently obtained with MCTDH. This theoretical result is 20% above the experimental value. Assuming a negligible effect of the use of linearized normal modes as internal degrees of freedom, the discrepancy is a measure of the accuracy of the potential energy surface since the dynamical method is exact. The provided tunneling splitting establishes a benchmark value for the unbiased evaluation of the accuracy of approximated dynamical methods. For example, the instanton approach<sup>22,77</sup> is found to be 20% accurate for this system.

For the isotopically substituted malonaldehyde, where the transferring hydrogen is replaced by a deuterium, a tunneling splitting of  $3.21 \pm 0.09 \text{ cm}^{-1}$  is calculated. This result is only 10% above the experimental value. Here the instanton approach overestimates the tunneling splitting by 40%.

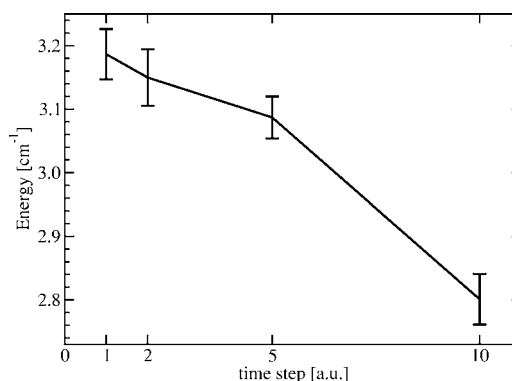


FIG. 7. Tunneling splitting values for the isotope and associated error bar estimates obtained from the inversion of 5000–6000 decays as a function of  $\Delta\tau$  using an ensemble size of 2000 walkers.

The computation of the tunneling splitting for vibrationally excited states is, in principle, possible within the POITSE method, but it is expected to be challenging because of the increasing complexity in the projection operator and the difficulties in inverting multiple exponential decays. The main feature of POITSE is to extract directly the excitation energies with respect to the ground state. Unfortunately, in the case of excited tunneling splittings, this feature cannot be directly exploited like in the case of the ground state tunneling splitting computation. A method relying on basis set expansion like the one in Ref. 40 is surely more suitable.

The POITSE method, initially tested on a model harmonic and double well potential,<sup>43,76</sup> is popular in the quantum clusters community where it has been used, for example, to determine rotational excitations of molecules in helium clusters<sup>74,78,79</sup> as well as the tunneling splitting in water trimer.<sup>80</sup> However, to our knowledge, this study is one of the first examples of the use of POITSE to study an excitation within a single molecule using a realistic potential. The agreement obtained with an alternative rigorous quantum approach<sup>40</sup> and the small error bar of the POITSE result stresses the power of this quantum Monte Carlo technique.

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