

A study of the fixed-node error in quantum Monte Carlo calculations of electronic transitions: The case of the singlet $n \rightarrow \pi^*$ (CO) transition of the acrolein

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(Received 1 October 2008; accepted 29 January 2009; published online 20 March 2009)

We report fixed-node diffusion Monte Carlo (FN-DMC) calculations of the singlet $n \rightarrow \pi^*$ (CO) vertical transition of acrolein. The impact of the fixed-node approximation on the excitation energy is investigated. To do that, trial wave functions corresponding to various nodal patterns are used. They are constructed by using either a minimal complete-active-space self-consistent field (CASSCF) calculation involving an oxygen lone pair n and the π^* (CO) molecular orbitals or a more complete set involving all the molecular orbitals expected to play a significant role in the excitation process. Calculations of both states have been performed with molecular orbitals optimized separately for each state via standard “state specific” CASSCF calculations or by using a *common* set of optimized orbitals [“state averaged” CASSCF calculations] whose effect is to introduce some important correlation between the nodal patterns of the two electronic states. To investigate the role of the basis set three different basis of increasing size have been employed. The comparative study based on the use of all possible combinations of basis sets, active spaces, and type of optimized molecular orbitals shows that the nodal error on the difference of energies is small when chemically relevant active space and state-averaged-type CASSCF wave functions are used, although the fixed-node error on the individual total energies involved can vary substantially. This remarkable result obtained for the acrolein suggests that FN-DMC calculations based on a simple strategy (use of standard *ab initio* wave functions and no Monte Carlo optimization of molecular orbital parameters) could be a working computational tool for computing electronic transition energies for more general systems. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3086023]

I. INTRODUCTION

Quantum Monte Carlo (QMC) methods are known to be the most powerful approaches for computing total ground-state energies of many-electron systems (see, e.g., Ref. 1). In short, QMC is based on two key ingredients: (i) The use of an approximate trial wave function Ψ_T and (ii) the introduction of stochastic rules to sample the $3N$ -dimensional electronic configuration space according to some target probability density [proportional to Ψ_T^2 in variational Monte Carlo (VMC) and $\Psi_T\Phi_0$ in diffusion Monte Carlo (DMC), Φ_0 being the exact ground state].

The approximate trial wave function is chosen to be the best compromise available between compactness and accuracy. A common choice for ψ_T consists of a product of two terms. The first term has a standard determinantal form describing the one-particle shell structure of molecules. It is obtained from a preliminary Hartree–Fock (HF), complete-active-space self-consistent-field (CASSCF), configuration interaction (CI), or density functional theory (DFT) calculation and is expressed as one (or a combination of a few) determinant(s) of single-particle orbitals. The second term is more original and is introduced to impose the electron-electron cusp condition (in the Kato’s sense, Ref. 2) of the

exact wave function and also to incorporate some explicit coupling between electron-nucleus and electron-electron coordinates (see Ref. 3).

Regarding the choice of the stochastic rules, many variants have been proposed. This diversity is at the origin of the great variety of acronyms found in the QMC literature: VMC, DMC, PDMC, GFMC, projector MC, reptation MC, etc. However, from a theoretical point of view, all these methods actually differ very little. In practice, the most widely used approach is the so-called fixed-node diffusion Monte Carlo (FN-DMC) method and this will be the variant used in what follows. The stochastic rules of FN-DMC can be summarized as follows.

- (i) A stochastic diffusion step corresponding to a free Brownian motion for the electrons.
- (ii) A deterministic move done along the drift vector given as

$$\mathbf{b} = \nabla \Psi_T / \Psi_T. \quad (1)$$

- (iii) A branching step simulated by the death or the duplication (birth) of the electronic configurations according to the magnitude of the local energy defined as

$$E_L \equiv H \Psi_T / \Psi_T. \quad (2)$$

The QMC simulation is performed by applying these

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rules a large number of times over a large enough population of electronic configurations (or walkers). At equilibrium, the exact ground-state energy is obtained by simply averaging the local energy over the walkers.

In a FN-DMC calculation there exist essentially two types of error. The first one is the usual statistical error resulting from a finite simulation time. This error, present in any Monte Carlo scheme (either classical or quantum), behaves as $1/\sqrt{K}$ where K is the number of Monte Carlo steps. In principle, by using a *brute force* approach (more and more central processing unit time, i.e., $K \rightarrow \infty$), it is always possible to decrease the statistical down to the accuracy desired. The origin of the second type of error which will be the focus of the present study is less obvious and is related to the nodal properties of the trial wave function. To understand its origin, let us remark that at the nodes of Ψ_T (nodes are defined as configurations verifying $\Psi_T=0$) the drift vector, Eq. (1), diverges and the nodal surfaces act as infinitely repulsive barriers for the walkers. Consequently, each diffusing walker is trapped for ever within the nodal hyperdomain where it starts and the Schrödinger equation is solved stochastically *separately* within each nodal domain. Now, because the $(3N-1)$ -dimensional nodes of an antisymmetric trial wave function are in general different from the exact ones, the FN-DMC simulation introduces a finite error related to the wrong location of these nodes. This error is referred to as the “fixed-node error” and it can be shown that the fixed-node energy is an upper bound of the exact energy (variational property).⁴

Now, the central issue is the importance of the fixed-node error. In other words, can the FN-DMC algorithm be used with success for realistic chemical problems or, stated differently, can QMC compete with the most accurate methods of quantum chemistry, e.g., coupled cluster with single and double and perturbative triple excitations [CCSD(T)] or multireference CI methods? To answer this question it is necessary to distinguish between calculations of total energies and calculations of *differences* of energies. In the first case, it is true that QMC methods are presently the most powerful approaches for computing ground-state energies [and, more generally, ground-state energies in each symmetry sector (space and spin)]. For the various molecular systems treated up to now, it has been found that about 90%–100% of the correlation energy can be recovered, the magnitude of the “small” residual fixed-node error depending on the type of systems treated and on the nodal pattern of the trial wave function employed. For small systems, such an accuracy corresponds typically to a CCSD(T) calculation with a large basis set (see Ref. 5). For larger systems such high-quality *ab initio* calculation are no longer possible [the formal scaling of CCSD(T) with number of electrons N is N^7] but FN-DMC simulations are still possible (to date, the largest calculation has involved about 1000 electrons⁶) and there is no reason not to believe that a large fraction of the total correlation energy for these large systems is recovered. On the other hand, it is also clear that total ground-state energies by themselves are not of great interest for chemistry. Indeed, roughly speaking, it can be said that all chemistry is about differences of energies. Chemists are interested in comparing the ener-

gies of different structures (reactants, products, etc.), potential energy profiles, height of barriers, electronic transitions, electron affinities, etc. Even the properties other than the energy can be reformulated as *infinitesimal* differences of energies using the Hellmann–Feynman theorem.⁷

At this point, a most important point consists in remarking that these differences of energies so important in chemistry are typically of the same order of magnitude as the fixed-node error itself on each component of the energy difference. Accordingly, we are in a tricky situation where some important and controlled compensation of errors must absolutely be at work if we want the FN-DMC method to be useful. However, it is most important to emphasize that this situation is not specific to QMC methods. In any electronic structure calculations (either DFT or *ab initio* wave function based) we are faced with the very same problem. In a DFT calculation, each energy component of a small difference of energies must absolutely be computed with the same method (local density approximation, B3LYP, generalized gradient approximation, etc.) and the same basis set. In *ab initio* approaches, the same method and basis sets must also be used and there is a long history about devising clever schemes for avoiding calculating large and expensive contributions which are supposed to cancel out when differences are computed (e.g., perturbational approaches such as symmetry-adapted-perturbation theories⁸).

In this work we address this problem by reporting a detailed analysis of the role of the fixed-node approximation for a prototypical electronic transition occurring in an organic molecule. We have chosen the well-studied singlet $n \rightarrow \pi^*$ vertical transition on the carbonyl part of the acrolein (or propenal) molecule, C_3H_4O . In this transition a lone pair electron of the oxygen atom is promoted to the empty π^* antibonding orbital of the CO bond. The two total energies computed using FN-DMC correspond to two ground-state energies in their respective symmetry space (even/odd parity with respect to the molecular plane). For each state, various nodal patterns associated with various trial wave functions have been employed. Despite the fact that, as expected, the fixed-node errors on each total energy may vary a lot (of the order of the transition energy) we have found that it is possible to propose a simple strategy for getting accurate and controlled transition energies.

Note that the use of FN-DMC for computing transition energies in organic molecules is not new. We can cite, for example, the work of Grossman *et al.*⁹ about excitation energies for the silane and methane molecules, the work of Aspuru-Guzik *et al.*¹⁰ on electronic transitions in free-base porphyrin, the work of Drummond *et al.*¹¹ on excitation energies and ionization energies of diamondoids, and very recently the study of Tiago *et al.*¹² on the low-energy excitations of several carbon fullerenes. In all these works, comparisons between QMC results and previous high-quality *ab initio* or DFT calculations and also experimental results, when available, have illustrated the excellent performances of QMC. However, no *systematic* study of the impact of the nodal structure on the results is in general done even if, in some cases, some particular aspects are investigated: dependence on the type of orbitals (HF, Kohn–Sham, natural), sen-

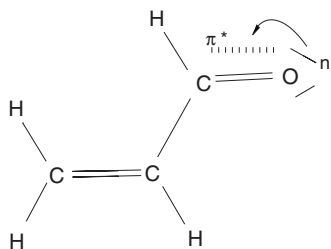


FIG. 1. Pictorial representation of the excitation process corresponding to the promotion of a lone pair electron of the oxygen atom (orbital n) to the empty π^* antibonding orbital of the CO group. The geometry considered is the experimental geometry proposed by Blom *et al.* (Ref. 20).

sitivity to the number of determinants used, etc. Now, for the reasons discussed above we would like to emphasize that, despite the good results obtained in these works, the problem of obtaining systematic good FN-DMC results for the small energy differences of chemistry is not at all solved. To give a precise example, in a recent work on the O_4 molecule, Cafarel *et al.*¹³ found that the height of the dissociation barrier (an energy difference of about 12 kcal/mol) is extremely dependent on the nature of the nodes.

In a number of recent works,^{14–17} interesting contributions toward defining a more systematic strategy to obtain controlled energy differences have been made. In these works, a full optimization of the trial wave functions at the VMC level is performed. The optimization involves not only the complete set of the parameters of the Jastrow part but also the parameters of all molecular orbitals involved and the coefficients of the determinantal expansion. By doing this, the hope is to improve nodes (although it is not certain¹⁸) and to get better differences of energy (not certain also). Here, we shall follow a quite different route. As we shall see, no optimization will be done and we shall strongly rely on the use of the *fixed* nodal patterns associated with simple and standard trial wave functions of quantum chemistry. Our general and long-term objective is to devise a simple (use of standard *ab initio* wave functions) and robust (no system-dependent optimization) strategy for computing electronic transitions, which is feasible not only for the small molecules but also for the large systems for which full optimizations appear difficult to perform. In this work, we have found that such a strategy leads to very good results in the case of the acrolein molecule.

The organization of this paper is as follows. In Sec. II the acrolein molecule and the electronic transition considered are presented. In Sec. III the computational details (methods, trial wave functions, and basis sets) are given. In Sec. IV the FN-DMC results are presented and some comparisons with *ab initio* CI calculations are made. Finally, we present some summary and perspectives in Sec. V.

II. THE ACROLEIN MOLECULE AND THE $n \rightarrow \pi^*$ TRANSITION

In this work we are concerned with the $n \rightarrow \pi^*$ vertical electronic transition of the acrolein (or propenal) molecule, $CH_2=CH-CHO$, between the two lower-lying singlet states (ground state and first singlet excited state). As represented pictorially in Fig. 1 this excitation process is associated with

the promotion of a lone pair electron of the oxygen atom (occupying the orbital n) to the empty π^* antibonding orbital of the CO group. In this work we have considered two different geometries for the molecule. The first one corresponds to a model geometry which has been used in previous works¹⁹ and which allows to perform easily systematic studies for series of polyenals of increasing sizes, the acrolein molecule being the smallest one. The geometry considered corresponds to a *s-cis* configuration and the internuclear distances are given by $d_{C-O}=1.22$ Å, $d_{C-C}=1.45$ Å, $d_{C=C}=1.35$ Å, $d_{C-H}=1.1$ Å, and $\widehat{XCY}=120^\circ$ (for all combinations $X, Y=C, H, O$). To make contact with experiments we also consider the experimental geometry as obtained by Blom *et al.*²⁰ using microwave spectroscopy. The geometry, given in Ref. 20 and represented in Fig. 1, is that of the *s-trans* isomer which, at room temperature, represents the great majority of the molecules.²¹ Note that in both cases the geometry corresponds to a planar structure and the molecule has a C_s symmetry group. Molecular orbitals are classified according to the two irreducible representations A' (symmetric with respect to the plane) and A'' (antisymmetric). The closed-shell ground state is of symmetry A' while the open-shell excited state belongs to A'' .

III. COMPUTATIONAL DETAILS

A. Methods

The computational method at the heart of this study is the FN-DMC. In Sec. I, the key ideas of the method necessary to the understanding of the present work have already been presented. For details of FN-DMC the reader is referred, e.g., to Ref. 22 or Ref. 1. For comparisons, we also present results obtained with the CI method using single and double excitations on a mono-SCF or multi-CASSCF configurational references. CI being a standard and well-documented approach, we refer the reader interested by the details to the relevant literature.

B. Trial wave functions

The fundamental quantity governing the efficiency of our Monte Carlo simulations is the trial wave function. It enters the simulation via the drift vector, Eq. (1), and the local energy, Eq. (2). The key point is that “good” trial wave functions are associated with small fixed-node biases (errors due to approximate nodes) and small statistical errors on the energy estimator. In the limit of an exact trial wave function, both errors entirely vanish. This property is known as the zero-variance zero-bias property.⁷ Here, we have chosen to employ a form consisting of the product of a Jastrow part and a Slater-type part consisting of a linear combination of a small number of determinants,

$$\psi_T(\vec{R}) = \exp\left[\sum_{\alpha} \sum_{\langle i,j \rangle} U(r_{i\alpha}, r_{j\alpha}, r_{ij})\right] \sum_k c_k D_k^\uparrow(\vec{R}) D_k^\downarrow(\vec{R}), \quad (3)$$

where the sum over α denotes a sum over the nuclei, $\sum_{\langle i,j \rangle}$ is a sum over the pair of electrons, c_k are the coefficients of the multiconfigurational expansion, and D_k^σ ($\sigma = \uparrow$ or \downarrow) are determinants made of one-particle space orbitals. The exponen-

tial Jastrow term which depends explicitly on interelectronic distances is introduced to reproduce the small electron-electron distance behavior of the exact wave function (cusp condition) and also to incorporate explicit couplings between electron-nucleus and electron-electron coordinates. Here, we have chosen to use the form introduced in Ref. 7. Regarding the determinantal part, we have used either a monoconfigurational form obtained via a SCF calculation or a multiconfigurational form obtained via a CASSCF calculation. The CASSCF form is introduced to incorporate the main part of the multiconfigurational character of the exact wave function issued from the interference between the various low-energy components ("nondynamic" correlation effects). This multiconfigurational character is known to play an important role for excited states. The choice of the active space is crucial to get a chemically relevant CASSCF wave function. Here, two choices have been considered. The first choice is the minimal one. It consists in considering only the two molecular orbitals associated with the oxygen lone pair n and the π^* orbital of the CO bond. The resulting active space built with two electrons within two orbitals is denoted as CAS(2,2). Because of the C_s symmetry it is of dimension 2 both for the ground and excited states. The second choice is based on the fact that the CO π bond is expected to interact with the π system of the C=C double bond. Letting aside the much more inert σ -bond system we propose to consider the active space built by distributing six electrons within the five molecular orbitals n , π_{CO} , π_{CO}^* , π_{CC} , π_{CC}^* [denoted as the CAS(6,5) active space]. Using symmetry considerations this active space consists of 52 and 48 determinants for the ground and excited states, respectively.

To build the Slater-type multiconfigurational wave functions two types of approach have been considered. First, we have made standard CASSCF calculations for both states. In such calculations the molecular orbitals (both occupied and active) as well as the coefficients of the determinantal expansion are fully optimized (in the deterministic *ab initio* sense) in an *independent* way for the two states. Such calculations are referred here to as state specific (SS) (SS-CASSCF). In the second approach, the CASSCF wave functions are optimized in a *correlated* way using a common set of molecular orbitals, the linear coefficients of the expansion being still taken as independent. In practice, this is realized by making stationary with respect to the various parameters a weighted average of the energies of the states under consideration (the standard choice consisting in taking equal weights is adopted here). This approach is known as a state-averaged (SA) method.²³

Regarding optimization of the Jastrow part of the trial wave function very little has been done here: Only a few parameters of the Jastrow factor have been optimized in order to reduce the statistical fluctuations. It has been done separately for both states using standard techniques (see Ref. 24). Let us emphasize that by optimizing only the Jastrow part as done here the nodal patterns of the various *ab initio* trial wave functions introduced in this work are kept unchanged.

Finally, let us give some practical details. The present FN-DMC calculations are all-electron calculations done with

a very small time step, $\tau=0.00025$, to ensure a proper treatment of the nodal hypersurfaces and to remove the time-step error within statistical uncertainties. For a system consisting of light atoms such as the acrolein some care has to be taken for properly reproducing the electron-nucleus cusp both for the core and valence electrons. Regarding the core region, we have replaced the $1s$ atomic orbitals (oxygen and carbon atoms) expanded over the Gaussian basis set by the $1s$ Slater-type orbitals given in Clementi and Roetti's tables.²⁵ On the other hand, the valence molecular orbitals are also modified at short nuclear distances to impose the nuclear cusp; we do that using a short- r representation of the radial part of orbitals under the form $c(1+\alpha r^2+\beta r^3)\exp(-\gamma r)$, in the same spirit as in Ref. 26. For each trial wave function and simulation, the calculations are extensive and have been carried over a large number of processors, the total statistics representing about 10^9 Monte Carlo steps.

C. Basis sets

Three Gaussian basis sets of increasing size have been considered. They are extracted from the ANO (atomic natural orbital) basis sets of Widmark *et al.* presented in Ref. 27. Basis set 1 consists of $(14s, 9p) \rightarrow [3s, 2p]$ for the oxygen and carbon atoms and $(8s) \rightarrow [2s]$ for H (44 atomic basis functions). Basis set 2 is given by $(14s, 9p, 4d) \rightarrow [3s, 2p, 1d]$ for O and C and $(8s, 4p) \rightarrow [2s, 1p]$ for H (76 basis functions). Basis set 3 is given by $(14s, 9p, 4d, 3f) \rightarrow [4s, 3p, 2d, 1f]$ for O and C and $(8s, 4p, 3d) \rightarrow [3s, 2p, 1d]$ for H (176 basis functions).

IV. RESULTS

A. Configuration interaction

SCF, CASSCF, and configuration interaction single and double (CISD) calculations for the model geometry are presented in Table I. We also present equation-of-motion coupled-cluster single and double (EOM-CCSD) calculations to get an alternative estimate of the transition energy. Note that the largest calculations presented here are the CAS(6,5)-CISD. For these calculations the transition energies are similar and vary between 3.42 and 3.59 eV. The EOM-CCSD calculations vary between 3.51 and 3.63 eV. Consequently, an estimate for the gap of about 3.5 eV at this geometry appears reasonable. In what follows, we will refer to this value as the reference energy.

Let us now comment in more detail on the results obtained. First, let us begin with the calculations at the SCF and CASSCF levels (no treatment of the dynamic correlation effects). At the SCF level [one determinant for the closed-shell ground state of symmetry A' and a two-determinant CAS(2,2) structure for the open-shell excited state to recover the A'' symmetry] the gap is found too small (about 2.80 eV), in error of about 20%. Note that the result obtained with the small basis (basis 1) is rather different from those obtained with the two other basis sets. However, results with bases 2 and 3 are very similar. This observation turns out to be true for all data presented below, thus indicating that finite basis set effects are marginal here for basis sets of a quality comparable to basis 2.

TABLE I. All-electron *ab initio* calculations of the ground- and first-excited-state energies of the acrolein molecule using different levels of theory. The geometry of the molecule is the model geometry described in the text.

	E_0 (a.u.)	E_1 (a.u.)	$\Delta=E_1-E_0$ (eV)
CASSCF			
SCF for E_0 ; CAS(2,2) for E_1 basis 1	-190.703 362 12	-190.609 505 39	2.55
SCF for E_0 ; CAS(2,2) for E_1 basis 2	-190.811 565 58	-190.707 449 19	2.83
SCF for E_0 ; CAS(2,2) for E_1 basis 3	-190.835 585 73	-190.732 824 05	2.80
CAS(2,2) SA basis 1	-190.690 552 31	-190.575 940 43	3.12
CAS(2,2) SA basis 2	-190.804 270 04	-190.680 399 63	3.37
CAS(2,2) SA basis 3	-190.823 777 95	-190.701 483 01	3.33
CAS(6,5) ^a SA basis 1	-190.766 391 54	-190.643 706 13	3.34
CAS(6,5) ^a SA basis 2	-190.870 615 36	-190.741 889 78	3.50
CAS(6,5) ^a SA basis 3	-190.889 590 34	-190.762 087 12	3.47
CAS(6,5) ^a SS basis 1	-190.774 808 28	-190.648 067 78	3.45
CAS(6,5) ^a SS basis 2	-190.881 577 16	-190.748 017 29	3.63
CAS(6,5) ^a SS basis 3	-190.900 822 19	-190.768 835 60	3.59
CASSCF-CISD			
SR-CISD basis 1 (SS)	-191.056 529 56	-190.936 638 09	3.26
SR-CISD basis 2 (SS)	-191.339 091 15	-191.216 253 17	3.34
SR-CISD basis 3 (SS)	-191.484 469 42	-191.364 258 78	3.27
CAS(2,2)-CISD basis 1 (SA)	-191.053 161 81	-190.927 502 65	3.42
CAS(2,2)-CISD basis 2 (SA)	-191.335 107 51	-191.205 936 13	3.51
CAS(2,2)-CISD basis 3 (SA)	-191.479 768 06	-191.352 997 62	3.45
CAS(2,2)-CISD basis 1 (SS)	-191.057 939 72	-190.936 935 25	3.29
CAS(2,2)-CISD basis 2 (SS)	-191.341 344 83	-191.216 673 57	3.39
CAS(2,2)-CISD basis 3 (SS)	-191.487 157 72	-191.364 723 44	3.33
CAS(6,5)-CISD basis 1 (SA)	-191.080 410 05	-190.953 688 31	3.42
CAS(6,5)-CISD basis 2 (SA)	-191.365 186 07	-191.235 393 68	3.53
CAS(6,5)-CISD basis 1 (SS)	-191.082 792 09	-190.954 568 33	3.49
CAS(6,5)-CISD basis 2 (SS)	-191.368 843 45	-191.236 840 21	3.59
EOM-CCSD			
Basis 1			3.51
Basis 2			3.63
Basis 3			3.61

^aFifty-two determinants for the ground state and 48 determinants for the excited state.

Using the “minimal” active space consisting of the oxygen lone pair and π_{CO}^* orbital [SA-CAS(2,2) calculation] the gap is seriously increased up to the value of about 3.3 eV. When the full “chemically relevant” active space is employed [CAS(6,5) calculations] the reference value for the gap is approximately obtained. Note the difference of results for the SS and SA calculations. In the first case the gap found is found to be slightly too large by about 0.1 eV. In the second case the gap obtained is close to the correct value. Finally, let us comment on the impact of dynamical correlation contributions by looking at the CI results. Starting from a single SCF reference (SR-CI) the CI result (about 3.3 eV) improves the SCF result (about 2.8 eV) but is not able to recover the reference value. This illustrates clearly the necessity of introducing the nondynamical correlation contributions. At the CAS(2,2)-CISD SS level the value is slightly improved (gap of about 3.4 eV) but is still in error of about 0.1 eV. When using a CAS(2,2) reference function and a SA approach the reference value is recovered. Using a CAS(6,5) reference function does not appear to change the results, both

SS and SA approaches leading indeed to the reference value. However, because of the CAS(6,5)-CASSCF results discussed above, it should be suspected that this result is a consequence of some cancellation of errors between missing dynamic and nondynamic correlation effects.

B. Fixed-node diffusion Monte Carlo

Our all-electron FN-DMC calculations for the ground- and first-excited-state energies of the acrolein (model geometry) are presented in Table II. Trial wave functions having various nodal patterns have been used. The trial wave functions have been built from SCF, SS-CASSCF, and SA-CASSCF Slater part with molecular orbitals optimized (in the deterministic *ab initio* sense) using the three basis sets of increasing sizes. Monte Carlo simulations have been performed to reach the 0.05–0.10 eV accuracy on the transition energies.

A first important remark is the great quality of the FN-DMC total energies. For example, the best QMC value ob-

TABLE II. All-electron FN-DMC calculations of the ground- and first-excited-state energies of the acrolein molecule using different nodal structures. The geometry of the molecule is the model geometry described in the text.

	E_0 (a.u.)	E_1 (a.u.)	$\Delta=E_1-E_0$ (eV)
QMC			
FN-DMC[nodes: SCF for E_0 ; CAS(2,2) for E_1]			
Basis 1	-191.814 ± 0.0045	-191.690 ± 0.0023	3.37 ± 0.14
Basis 2	-191.819 ± 0.0020	-191.708 ± 0.0042	3.02 ± 0.13
Basis 3	-191.729 ± 0.0037	-191.608 ± 0.0021	3.29 ± 0.12
FN-DMC[nodes: CAS(2,2)SA]			
Basis 1	-191.803 ± 0.0015	-191.665 ± 0.0013	3.76 ± 0.05
Basis 2	-191.841 ± 0.0031	-191.716 ± 0.0042	3.40 ± 0.14
Basis 3	-191.763 ± 0.0021	-191.634 ± 0.0022	3.51 ± 0.08
FN-DMC[nodes: CAS(6,5) ^a SS]			
Basis 1	-191.795 ± 0.0033	-191.663 ± 0.0034	3.59 ± 0.13
Basis 2	-191.755 ± 0.0022	-191.603 ± 0.0031	4.14 ± 0.10
Basis 3	-191.744 ± 0.0048	-191.596 ± 0.0021	4.03 ± 0.14
FN-DMC[nodes: CAS(6,5) ^a SA]			
Basis 1	-191.791 ± 0.0026	-191.663 ± 0.0025	3.48 ± 0.10
Basis 2	-191.719 ± 0.0027	-191.592 ± 0.0026	3.46 ± 0.10
Basis 3	-191.739 ± 0.0034	-191.611 ± 0.0023	3.48 ± 0.11

^aFifty-two determinants for the ground state and 48 determinants for the excited state.

tained here for E_0 is -191.841 ± 0.003 [FN-DMC with CAS(2,2)-SA nodes and basis 2 in Table II]. To compare with, we have performed CCSD(T) calculations with large basis sets, the results obtained being as follows: $E_0 = -191.410\ 671\ 04$ (using cc-pCVDZ), $E_0 = -191.598\ 624\ 99$ (cc-pCVTZ), and $E_0 = -191.651\ 392\ 55$ (using cc-pCVQZ). This result exemplifies the fact that QMC is a highly accurate method for computing total energies, a point already emphasized in Sec. I. A second important remark is that the fixed-node error magnitude as a function of the nodal pattern used (the nodes are changed when using different levels of theory and basis sets) is large at the scale of our problem. For E_0 the higher and lower values are $-191.719(3)$ and $-191.841(3)$, respectively. This makes a variation of $0.122(4)$ a.u., that is, 3.3 eV. For E_1 the variation is 3.4 eV. As seen, the range of the fixed-node energy variation is of the order of the gap itself. This result illustrates clearly the need of some “constructive correlation” between the fixed-node error on both energy components if some meaningful result for the transition energy is desired. However, as already pointed out, this fundamental problem is not specific to QMC but is present in any electronic structure method. For example, in the case of the best CAS(2,2)-CISD calculations presented in Table I, the variation of the total energies as a function of the basis set used is about 11.6 eV, more than three times the FN-DMC result and the gap in energy itself! Another important remark regarding the FN-DMC results of Table II is that the fixed-node total energies does not necessarily improve (i.e., decrease) as the size of the basis set is increased. This result is a nice illustration of the fundamental point already stressed in Sec. I regarding the

fact that decreasing the total variational energy does not necessarily improve the nodes of the trial wave function (see also comment in Ref. 18).

Using the SCF nodes, the QMC gap obtained varies between 3.02 and 3.37 eV. Such values obtained with monodeterminantal wave functions are reminiscent of the SR-CI calculations results presented above. Using CASSCF nodes the value of the gap is increased. With the SA-CAS(2,2) nodal pattern values close to the reference gap are obtained. However, the variations of the results as a function of the basis set are large, namely, 0.36 eV. At the SS-CAS(6,5) level the variations are still larger (0.55 eV) and the average value of the gap seems to be too large (3.92 eV). This is also reminiscent of the SS-CAS(6,5) CASSCF calculations which gives a slightly too large value. Finally, with the SA-CAS(6,5) nodes the results obtained are much more coherent: Remarkably, the variations of the results as a function of the basis set are almost suppressed and the average value is excellent.

A few general comments are now in order. As seen from our results the quality of the nodes of the trial wave function plays indeed a central role. Let us insist that imposing approximate nodes is the sole source of systematic error within the FN-DMC framework (the statistical error is controllable by making sufficient long simulations). In the case of the acrolein molecule, using “monodeterminantal” or “SCF” nodes leads to too small transition energies, although a large part of the correlation energy is recovered via FN-DMC. This result is also true in extensive *ab initio* CISD calculations based on a *monoconfigurational* reference wave function. This important result suggests that there probably exists some relation between the nature of the correlation energy recovered by FN-DMC and the nature of the nodes employed. To be more precise, using SCF nodes the DMC process would recover essentially the dynamic correlation effects and very little of the nondynamic correlation component. To recover this last contribution, we really need nodes which have some “multiconfigurational” character. Physically, such statement makes sense but, mathematically, the situation is much less clear. Note that this idea is supported by some recent calculations done by Caffarel and Ramirez-Solis²⁸ on the chromium dimer at the equilibrium distance. It is known that the electronic structure of this molecule is very hard to recover and that Cr_2 is considered as a real nightmare for standard methods of quantum chemistry. In particular, the ground-state wave function has a very strong multiconfigurational character. It has been shown that using SCF nodes a very small fraction of the binding energy is recovered by FN-DMC. This result is similar to what has been obtained by Scuseria²⁹ using SR CCSD(T) calculations using very large basis sets. Here, also, by using “monoconfigurational” nodes in FN-DMC it seems that only the dynamic correlation contribution is recovered.

Another remark is that “SA” CASSCF nodes appear effective to get the correct estimate transition energy. Such a result can be understood by the fact that using the same set of molecular orbitals for the two states allows large compensations of the fixed-node error components corresponding to configuration space regions where the nodal structure is

TABLE III. CI and FN-DMC calculations of the transition energy at experimental equilibrium geometry. Comparison with experiment.

	E_0 (a.u.)	E_1 (a.u.)	$\Delta = E_1 - E_0$ (eV)
FN-DMC[nodes:CAS(6,5)SA] basis 3	-191.8504 ± 0.0020	-191.7086 ± 0.0023	3.86 ± 0.07
CAS(2,2)-CISD basis 1 (SA)	$-191.058\ 675\ 38$	$-190.923\ 190\ 83$	3.69
CAS(2,2)-CISD basis 2 (SA)	$-191.342\ 283\ 92$	$-191.201\ 061\ 17$	3.84
CAS(2,2)-CISD basis 3 (SA)	$-191.487\ 441\ 01$	$-191.348\ 531\ 05$	3.78
CAS(6,5)-CISD basis 1 (SA)	$-191.085\ 252\ 53$	$-190.949\ 179\ 07$	3.70
CAS(6,5)-CISD basis 2 (SA)	$-191.371\ 580\ 70$	$-191.230\ 307\ 15$	3.84
Experimental results			$3.69 - 3.75^a$

^aReferences 30–32.

common to both states and not primarily involved in the excitation process. For the acrolein molecule we have found that by using a minimal active space the correct value is recovered but the sensitivity of the value to the basis set is important. When the active space contains all molecular orbitals which are critical in the excitation process, this sensitivity appears to be much less important. Due to the local character of these excitations, we expect that such a result could extend to a large class of organic compounds and, more generally, to any system where a chemically active space can be properly defined. Note that, to the best of our knowledge, the first use of SA-CASSCF wave functions for FN-DMC has been done by Schautz *et al.*^{14,15} In these works, SA-CASSCF wave functions have been introduced essentially to avoid the so-called root flipping problem occurring in MCSCF (multi-configurational-self-consistent-field) calculations (optimization of a state in the presence of lower states of the same symmetry). Here, the motivation is different: we employ a SA approach to get two CASSCF wave functions (of different symmetry and thus always orthogonal) constructed from a common set of optimized molecular orbitals. In this way, we can expect a maximal similarity between the nodal hypersurfaces of both states and, thus, a minimization of the fixed-node error on the energy difference.

Finally, in Table III the CI and FN-DMC results at the experimental equilibrium geometry²⁰ are presented. The largest CI calculation [CAS(6,5)-CISD basis 2 (SA)] leads to a value of 3.84 eV. The FN-DMC result is 3.86 ± 0.07 eV, in full agreement with the *ab initio* transition energy. To the best of our knowledge, the experimental data of the literature fall into the range (3.69, 3.75) eV.^{30–32} According to these data, the *ab initio* value is found to be slightly greater than expected. The FN-DMC value is also slightly greater. However, considering the statistical character of the result, there is a probability of about 6% that our transition energy falls into the previous experimental interval.

V. SUMMARY AND PERSPECTIVES

In this work we have presented FN-DMC calculations of the energy gap of a prototypical electronic transition in a simple organic molecule having a carbonyl group. To elucidate the impact of the fixed-node approximation on the computation of electronic energy differences and, more specifically, on the possible existence of *compensation of errors*,

we have performed FN-DMC simulations under various conditions. These conditions include basis sets of various sizes, CASSCF wave functions with different active spaces, and molecular orbitals optimized for each state separately or molecular orbitals common to both states. Changing these conditions leads to changing the nodal hypersurfaces and, therefore, the magnitude of the fixed-node error. We emphasize that, in contrast with some other groups^{14–17} we propose here not to change the nodal structure of the various *ab initio* trial wave functions used [in other words, no optimization of the determinantal part in Eq. (3)]. Besides avoiding the optimization of many (hundreds) of parameters (always a not-so-easy task, particularly for large systems), our major motivation is to avoid as much as possible the loss of the coherence between the two nodal patterns. In agreement with the common wisdom of the domain, it has been found that the impact of each of the previous factors is very important. More precisely, by changing the various conditions the fixed-node error on both total energies can vary by an amount which is of the order of magnitude of the energy difference. This result—quite common in standard DFT or *ab initio*-wave function based methods—confirms the fact that any realistic FN-DMC calculation must be based on a large and controlled compensation of errors. In other words, the error made on the location of the nodes for a given state must be tightly correlated with the error made for the other state. To achieve this, we have proposed to use the same set of optimized molecular orbitals for describing the two states involved in the transition (the so-called SA approach of *ab initio* approach). By doing this the total energies obtained are less accurate but we introduce some “coherence” between the nodal shapes of the two states. Our FN-DMC results show, at least for the system studied, that this compensation works very well. Indeed, it has been found that in a SA calculation using a chemically meaningful active space, the energy gap is nearly independent of the basis set despite the fact that fixed-node errors on separate total energies vary substantially. Such a result is particularly interesting since it suggests that meaningful results can be obtained by using a simple strategy based on standard and compact *ab initio* trial wave functions without resorting to large-scale optimizations which will become increasingly difficult for large systems. However, to validate our approach it is clear that the next step will consist in investigating larger molecular systems.

ACKNOWLEDGMENTS

We would like to thank Dr. Sophie Hoyau for helpful references and IDRIS (CNRS, Orsay), CCRT (CEA/DAM, Ile-de-France), and CALMIP (Université de Toulouse) for computational support.

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