J. Phys. Chem. A **2004,** *108,* 1305−1311

Guiding Function and Basis Function Optimization in Correlation Function Quantum Monte Carlo Calculations of Vibrational Excited States in Molecules

Frederico V. Prudente,*,† Luis S. Costa,‡ and Paulo H. Acioli‡

Instituto de Física, Universidade Federal da Bahia, Campus Universitário de Ondina,
40210-340, Salvador, Bahia, Brazil, and Instituto de Fısica, Universidade de Brasília, CP 04455,
70919-970, Brasília, DF, Brazil

Received: August 29, 2003; In Final Form: November 20, 2003

In this paper we discuss some aspects regarding the role of the guiding function and the optimization process in obtaining vibrational spectra of molecules using correlation function quantum Monte Carlo method. We start with the guiding function most used in these calculations and verify how its parameters affect the integration of the matrix elements involved in the problem. We then study how the optimization process influences the accuracy of the results. The results point out that there is an optimum parameterization of the guiding function, which in turn gives better accuracy and lower statistical errors. They also indicate that in order to improve the accuracy of the higher excited states, one should include them in the optimization process.

1. Introduction

The quantum Monte Carlo methods (QMC) have been pointed out as an alternative to the traditional methods for computing excited states of molecular systems with many degrees of freedom.[1−10] There are different QMC methodologies that have been proposed and utilized within this context.[11] The main advantage of the use of stochastic methods is that the computational effort does not grow exponentially with the number of atoms. Thus, allowing to study systems with more than four atoms without major modifications.

One of the QMC methods that has been most used to compute vibrational and ro-vibrational spectra of molecular systems is the correlation function quantum Monte Carlo (CFQMC) method.[5,6,12−18] This method combines the conventional basis set approach with QMC techniques (variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC)) for multidimensional integral sampling (see ref 11 for a comprehensive review). The CFQMC method has reached accuracy of about 1% or less for the systems studied, within a few wavenumbers ($\approx$10 cm^{-1}). But one wishes to reach spectroscopic accuracy of the standard methods for tri- and tetraatomic systems (less than 1 cm^{-1}) and to calculate properties of highly excited states. To achieve these goals two important aspects have to be considered: the proper integration of the multidimensional integrals, where the guiding function plays an important role; and the quality of the trial basis functions. The quality of the basis functions can be approached from two different points of view, the first one is its functional form, and the second one is the optimization procedure.

The aim of this work is two-fold: first the study of the role of the guiding function in the integral sampling and second the study of the optimization procedure of the free parameters of a given trial basis set. The functional form of the basis functions will not be explored here; however, it has been the central subject in recent papers.[12,19] For the purpose of this paper, we perform a systematic study at the VMC level of two diatomic systems: the Morse potential parameterized for the H_2 molecule and a two minima model potential. We seek to utilize the simplicity of the systems to better understand these two important aspects of the CFQMC procedure. Our final goal is to establish a simple procedure to allow the calculation of the excited states of polyatomic molecules with spectroscopic accuracy using the CFQMC method. The paper is organized as follows. In the next section we briefly present the CFQMC method. In section 3 we introduce the trial wave function and the guiding function used in this work and discuss the optimization procedure. In section 4 we present our results, and in the last section we make our final remarks.

2. Correlation Function Quantum Monte Carlo

In this section we summarize the CFQMC method to obtain the vibrational energy levels of molecular systems. We remember that the method is general and can be applied, a priori, to solve any quantum system. The vibrational energy levels of a molecular system are obtained by solving the following eigenvalue problem:

$$\hat{H}\Phi(\mathbf{R}) = E\Phi(\mathbf{R}) \tag{1}$$

The Hamiltonian operator associated with the relative motion of particles (excluding the kinetic energy of the center of mass) is given as[20]

$$\hat{H} = -\sum_{i=1}^{N-1} \frac{\hbar^2}{2\mu_i} \nabla_{\rm i}^{\,2} + V(\mathbf{R}) \tag{2}$$

where μ_i is the ith reduced mass, ∇_i^2 are the Laplacians in three-dimensional (3D) Cartesian coordinates, $\mathbf{R} = (\mathbf{R}^1, \mathbf{R}^2, \cdots, \mathbf{R}^{N-1})$ is the vectorial representation of the $(N-1)$ 3D vectors $\mathbf{R}^i$ written in Cartesian coordinates, $V(\mathbf{R})$ is the potential energy surface (PES), and E and $\Phi(\mathbf{R})$ are the eigenvalue and the eigenfunction of $\hat{H}$. It is important to point out that the removal

---

* Corresponding author. E-mail: prudente@ufba.br.
† Universidade Federal da Bahia.
‡ Universidade de Brasília.

10.1021/jp036575a CCC: $27.50

of the center of mass term and even the use a particular coordinate system choice is arbitrary and the present procedure is valid for any choice.

Within the spirit of the Rayleigh−Ritz variational principle, the problem is transformed into finding the stationary solutions of the functional $J[\Phi]$ given by

$$J[\Phi] = \int \Phi^*(\mathbf{R})(\hat{H} - E)\, \Phi\, (\mathbf{R})\, d\mathbf{R} \tag{3}$$

To obtain the eigenenergies and the eigenfunctions numerically, the wave function is first expanded using a finite basis set $\{f_\alpha(\mathbf{R})\}$

$$\Phi(\mathbf{R}) = \sum_{\alpha=1}^{M} c_\alpha f_\alpha(\mathbf{R}) \tag{4}$$

where $\{c_\alpha\}$ are the expansion coefficients and M is the number of elements of the basis set. Then, $J[\Phi]$ is required to be stationary under variations of such coefficients. The variational procedure converts the problem into that of solving a generalized eigenvalue problem

$$\mathbf{Hc} = E\mathbf{Sc} \tag{5}$$

where $\mathbf{c}$ is the vector of coefficients,

$$H_{\alpha\beta} = \int f_\alpha^*(\mathbf{R})\hat{H} f_\beta(\mathbf{R})\, d\mathbf{R} \tag{6}$$

are the Hamiltonian matrix ($\mathbf{H}$) elements, and

$$S_{\alpha\beta} = \int f_\alpha^*(\mathbf{R}) f_\beta(\mathbf{R})\, d\mathbf{R} \tag{7}$$

are the overlap matrix ($\mathbf{S}$) elements. An essential key of the variational procedure is how to compute these integrals with high precision.

The CFQMC consists of employing the quantum Monte Carlo techniques (VMC or DMC) to evaluate the multidimensional integrals (eqs 6 and 7). It differs from the usual QMC methods[21] because it allows one to calculate directly various excited states of the system. Usually, the calculation of the eigenvalues for a given Hamiltonian using the CFQMC method is done in two steps: a VMC step, where a good simple approximation to the excited eigenfunctions $\{f_\alpha\}$ is used; and a DMC step, where the solutions of the variational diagonalization procedure are used as the basis functions. This procedure was proposed by Bernu et al.[6] to reduce the round-off errors and the number of basis functions used in the calculation.

The first step (VMC) is to compute the Hamiltonian and overlap matrix elements (eq 6 and eq 7, respectively) using the Metropolis algorithm.[22] For this purpose, we have to introduce in eqs 6 and 7 an assistant probability distribution $\Psi(\mathbf{R})$, which is named guiding function. The Hamiltonian and the overlap matrix elements are rewritten as

$$H_{\alpha\beta} = \int |\Psi(\mathbf{R})|^2 F_\alpha(\mathbf{R}) F_\beta(\mathbf{R}) E_{L\beta}(\mathbf{R})\, d\mathbf{R} \tag{8}$$

and

$$S_{\alpha\beta} = \int |\Psi(\mathbf{R})|^2 F_\alpha(\mathbf{R}) F_\beta(\mathbf{R})\, d\mathbf{R} \tag{9}$$

where

$$F_\alpha(\mathbf{R}) = \frac{f_\alpha(\mathbf{R})}{\Psi(\mathbf{R})} \tag{10}$$

and

$$E_{L\beta}(\mathbf{R}) = \frac{\hat{H} f_\beta(\mathbf{R})}{f_\beta(\mathbf{R})} \tag{11}$$

is the local energy associated with the f_β basis function. The integral equations 8 and 9 are then evaluated using the random walk $\{\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_p\}$ generated according to the probability distribution $P(\mathbf{R}) = |\Psi(\mathbf{R})|^2$ as follows:[28]

$$H_{\alpha\beta} = \frac{1}{p} \sum_{i=1}^{p} F_\alpha(\mathbf{R}_i) F_\beta(\mathbf{R}_i) E_{L\beta}(\mathbf{R}_i) \tag{12}$$

and

$$S_{\alpha\beta} = \frac{1}{p} \sum_{i=1}^{p} F_\alpha(\mathbf{R}_i) F_\beta(\mathbf{R}_i) \tag{13}$$

where p is the number of random walk steps. In this procedure, each calculated Hamiltonian and overlap matrix element has a statistical uncertainty which offers an estimate of the precision of the integral calculations. For eqs 12 and 13, the statistical errors associated with a VMC calculation are given by[28]

$$\mathrm{Er}(H_{\alpha\beta}) = \frac{1}{\sqrt{p}} \left[\sum_{i=1}^{p} \frac{(F_\alpha(\mathbf{R}_i) F_\beta(\mathbf{R}_i) E_{L_\beta}(\mathbf{R}_i))^2}{p} - \left(\sum_{i=1}^{p} \frac{F_\alpha(\mathbf{R}_i) F_\beta(\mathbf{R}_i) E_{L_\beta}(\mathbf{R}_i)}{p} \right)^2 \right]^{1/2} \tag{14}$$

and

$$\mathrm{Er}(S_{\alpha\beta}) = \frac{1}{\sqrt{p}} \left[\sum_{i=1}^{p} \frac{(F_\alpha(\mathbf{R}_i) F_\beta(\mathbf{R}_i))^2}{p} - \left(\sum_{i=1}^{p} \frac{F_\alpha(\mathbf{R}_i) F_\beta(\mathbf{R}_i)}{p} \right)^2 \right]^{1/2} \tag{15}$$

It is important to point out that the guiding function is responsible for the efficiency of the Metropolis integration.

The second step (DMC) is to "project" the basis functions $\{\phi_\alpha\}$ (where $\{\phi_\alpha\}$ are the solutions of the previous step) using the operator $C(\hat{H}) = \exp(-\tau\hat{H}/2)$. This second step is very important to improve the accuracy of the spectra, within the same set of trial wave functions. However, as we are more interested in the basis function optimization we restricted ourselves to the VMC step. We will not discuss the diffusion Monte Carlo version of CFQMC any further, and a complete description of the method can be found in refs 5, 11, and 13.

3. Trial Basis Set and Guiding Functions

3.1. General Aspects. The procedure to build the trial basis set $\{f_\alpha\}$ and the guiding function $\Psi(\mathbf{R})$ will depend on the characteristics of the quantum system. However, some general aspects must always be considered, independent of the physical system. (i) The guiding function must be positively defined and nonzero wherever the potential is finite, in order to avoid large statistical fluctuations. Moreover, it is important to reflect the properties of the ground and excited states considered in the calculation. (ii) The trial basis functions need to be generated in a simple fashion. The trial functions (and their derivatives) must be easy to evaluate and must permit an easy generalization for any multidimensional system. It is also important that a linear combination of these basis functions describe reasonably well the ground and excited states of the system. We will address here these issues for vibrational excited states of molecules. Examples of trial basis functions and guiding functions for other quantum problems (including rotational motion) can be found in refs 11, 23−25.

3.2. Vibrational States. In CFQMC applications there have been a few basis functions used to describe the ground and excited vibrational state eigenfunctions.[6,12,13,19] In this work we have explored only one of them as we are more interested in the optimization procedure and not in the particular functional form of the basis functions. Moreover, the optimization procedure, which we will discuss in subsection 3.4, is general and can be employed for all previously utilized basis sets. The trial basis functions used in the present paper are the ones used by Acioli and Soares Neto.[13] This basis set has been widely used to treat di-, tri-, and tetraatomic molecules.[11] Defining $\{S_\nu\}$ as the vibrational coordinate set and $N_{\max}$ the number of these coordinates, S_ν^0 as the value of the νth coordinate in the minimum of the PES, and $\Delta S_\nu = S_\nu - S_\nu^0$, the basis set is given by

$$f_\alpha = \exp\Big(\sum_{\nu,\eta} \Delta S_\nu A_{\nu\eta} \Delta S_\eta\Big) \prod_{\nu=1}^{N_{max}} \Delta S_\nu^{\;n_\nu(\alpha)} \qquad (16)$$

where the $\{A_{\mu\nu}\}$ are the parameters that will be optimized in order to improve the accuracy of the excited states, and α represents the set of exponents n_ν that defines the f_α function. Note that the basis set (eq 16) is defined considering that there is one minimum in the PES. In subsection 4.2 we will discuss the difficulties and present a strategy to deal with a two-minima PES.

3.3. Guiding Function. Another open problem is the choice of the guiding function $\Psi(\mathbf{R})$ which satisfies the properties mentioned above. In particular, one wants the guiding function to be large wherever any excited basis function is large and small only when all basis functions are small. Bernu et al.[6] proposed a simple form that has been used in all CFQMC rovibrational calculations, that is:

$$\Psi(\mathbf{R}) = (f_0(\mathbf{R}))^{1/n} \qquad (17)$$

where $f_0(\mathbf{R})$ is the vibrational ground-state basis function ($n_\nu = 0\ \forall\ \nu$) given by

$$f_0(\mathbf{R}) = \exp\Big(\sum_{\nu,\eta} \Delta S_\nu A_{\nu\eta} \Delta S_\eta\Big) \qquad (18)$$

The parameter n in eq 17 is very important in our study. This parameter controls the shape of the guiding function; it means that when n changes, the width of the function $\Psi(\mathbf{R})$ is modified. This parameter is set according to the number of desired excited states. To ensure correct integration of all states included in the calculation, for example, Bernu et al.[6] proposed that the parameter n could be chosen of the following way:

$$n = \Gamma^{1/2} \qquad (19)$$

where Γ is the order of the highest excited local mode exponents n_ν desired in the calculation.

Our first goal in this paper is to explore the properties of the guiding function of the form of eq 17 and the role of the parameter n to assert an accurate integration sampling for the Morse potential. For this, we will discuss the size and distribution of the statistical errors of the Hamiltonian and overlap matrix elements (eqs 14 and 15), and we will compare these CFQMC results with those obtained from a numerically "exact" integration (using the conventional numerical quadrature rules) for the same basis set. Moreover, we will analyze the behavior of the guiding function to obtain the excited vibrational states accurately in the case where the potential curve has more then one minimum.

3.4. Excited States Optimization. Another aspect that we want to stress is how the optimization of the nonlinear parameters $\{A_{\mu\nu}\}$ of the basis set influences the description of excited states. In traditional ground state QMC calculations, one usually minimizes the total energy of the system (the average value of the local energy ($E_L[\Psi] = H\Psi/\Psi$)) with respect to the square of the guiding function. Umrigar et al.[26] have shown that the minimization of the variance of the local energy can be a powerful strategy to optimize the trial ground-state function. In another paper, Bressanini and Reynolds[28] have discussed some interesting aspects of the VMC method as well as the different ways to optimize the ground-state trial wave function parameters at the VMC level. In most ground-state QMC calculations one minimizes the local energy and/or its variance.

Ceperley and Bernu[5,6] have proposed the same procedure in the CFQMC method. That is, they minimize the local energy (or its variance) of the trial ground-state wave function $f_0(\mathbf{R})$ (eq 18) and use these parameters in the excited-state calculation. Brown et al.[12] have minimized the energy of a few excited states. Silva and Acioli[19] have used this procedure in their study of trial basis sets for determination of vibrational spectra using CFQMC. Recently, Nightingale and Melik-Alaverdian[27] have proposed a different procedure for excited states optimization, based in the minimization of the sum of the squared residuals with respect to eigenenergies.

In this work we propose a procedure similar to those proposed by Brown et al. We start from the minimization with respect to the ground state, using the Umrigar et al. procedure. We then optimize the nonlinear parameters $\{A_{\mu\nu}\}$ with respect to the energy of the first n_{exc} excited states, minimizing the functional

$$F[\{A_{\mu\nu}\}] = \sum_{i=1}^{n_{\text{exc}}} E_i[\{A_{\mu\nu}\}] - E_0[\{A_{\mu\nu}\}] \qquad (20)$$

where $\{E_i[\{A_{\mu\nu}\}]\}$ are the eigenvalues of the generalized eigenvalue problem (eq 5) for a short VMC calculation. The difference with respect to the work of Brown et al. is that here we try to understand qualitatively the effect of the number of excited states included in the optimization procedure in the accuracy of the calculation. For this, we will study the difference of the CFQMC calculations from the exact eigenvalues as a function of the number of excited states included in the minimization (n_{exc}). We will also study the shape of the ground-state trial wave function (eq 18) as a function of n_{exc} in the optimization procedure and the behavior when we increase the number of basis functions.

4. Results

4.1. Morse Potential (H_2). In this section we discuss the results for the vibrational spectrum of the Morse potential

$$V(r) = D_e\{1 - \exp[-\beta(r - r_{\text{eq}})]\}^2 \qquad (21)$$

with $D_e = 0.1744$, $\beta = 1.02764$, $r_e = 1.40201$, and for the reduced mass we used $\mu = 918.57635$. These parameters

TABLE 1: Difference between the Exact Vibrational States of the Morse Potential (H_2) and the CFQMC Ones Calculated Using Different Number of Excited States in the Optimization[a]

	|c|CFQMC							
ν	$n_{exc} = 0$	$n_{exc} = 3$	$n_{exc} = 5$	$n_{exc} = 7$	$n_{exc} = 10$	$n_{exc} = 12$	$n_{exc} = 16$	exact
0	0.02(0.91)	0.01(0.52)	0.01(0.62)	0.02(0.56)	0.00(0.54)	0.06(0.77)	−0.04(0.57)	2165.95
1	0.03(0.69)	0.02(0.43)	0.01(0.59)	0.03(0.46)	0.00(0.30)	0.03(0.58)	−0.60(0.84)	6308.60
2	0.04(0.78)	0.01(0.40)	0.01(0.48)	0.01(0.41)	−0.06(0.33)	−0.02(0.51)	−5.25(2.00)	10198.93
3	−0.05(0.69)	0.00(0.35)	0.02(0.38)	0.00(0.38)	−0.36(0.41)	−0.45(0.62)	−18.01(4.49)	13836.94
4	−2.85(0.87)	0.00(0.32)	0.02(0.35)	−0.01(0.37)	−1.44(0.74)	−2.51(1.02)	−37.23(6.99)	17222.63
5	−46.42(2.70)	−0.39(0.34)	0.00(0.41)	−0.04(0.36)	−3.61(1.24)	−6.86(1.63)	−82.44(6.49)	20356.00
6	−330.88(6.29)	−10.05(1.22)	−0.12(0.39)	−0.13(0.38)	−6.19(1.85)	−12.26(2.94)	−194.30(7.81)	23237.05
7	−1190.18(10.88)	−113.50(5.31)	−2.37(0.62)	−0.35(0.44)	−10.09(1.74)	−17.69(4.15)	−364.27(13.02)	25865.79
8	−2787.06(14.99)	−592.08(15.29)	−43.53(2.24)	−15.82(1.52)	−19.54(1.75)	−26.00(4.23)	−525.09(29.80)	28242.20

[a] Numbers in parentheses denote the error bars and the results are in cm^{-1}.

describe the H_2 molecule and are given in atomic units. For this case, the vibrational eigenvalues (in atomic units) assume the following analytical form[30]

$$E_n = D_e\left(n + \frac{1}{2}\right)\sqrt{\frac{2\beta^2}{D_e\mu}} - \left(n + \frac{1}{2}\right)^{1/2}\frac{\beta^2}{2\mu} \qquad n = 0, 1, ... \quad (22)$$

under the condition

$$n < \frac{\sqrt{2\mu D_e}}{\beta} - \frac{1}{2} \quad (23)$$

This leads to a total of 17 vibrational bound states.

The first and important aspects analyzed are the size of the statistical error and the accuracy of the CFQMC results as a function of the exponent n in the guiding function (eq 17). For this, we have used 21 basis functions to compute the eigenvalues of H_2 by employing the CFQMC procedure and using an "exact" quadrature integration (EQI) of eqs 6 and 7 as a comparison. For each $n = 3$, 4, 6, 8, 10, 15, and 20 in the guiding function, the CFQMC eigenvalues and the respective statistical error bars ($E_\nu^{QMC} \pm \text{Er}(E_\nu^{QMC})$) were computed from 32 different random walks where we set for each of them a different seed for the random number generator as well as a different starting point. The results[31] indicate that the relative errors between the EQI and the CFQMC for all 21 eigenvalues ($\Delta E_\nu = (E_\nu^{EQI} - E_\nu^{QMC})/E_\nu^{EQI}$) and the respective relative statistical error bars ($Er(E_\nu^{QMC})/E_\nu^{EQI}$) depend strongly on n. For certain eigenvalues, the difference among the statistical error bars for different n can arrive up to 10^2. For example, for the 16th excited state, we have obtained that the relative statistical error bars are 2.5×10^{-2}, 4.0×10^{-3}, 1.1×10^{-3}, 7.4×10^{-4}, 4.9×10^{-4}, 4.9×10^{-4}, and 3.9×10^{-4} for $n = 3$, 4, 6, 8, 10, 15, and 20, respectively. Moreover, we have observed that for $n = 3$ the CFQMC eigenvalues are well below those obtained from the "exact" quadrature integration; this difference for the 8th excited state is ≈ 124 cm^{-1}, while for the 15th excited state it is ≈ 264 cm^{-1}. This is due to the fact that the matrix elements associated with the higher excited basis functions are poorly integrated, as we will discuss below. Although for $n = 8$ the results look already satisfactory (with the relative statistical error bars around 10^{-4}), the best results are achieved for $n = 20$ considering both the relative errors and the statistical error bars. Another important aspect to point out is that the statistical error of a given state indicates very well the precision of the result because the relative errors are always inside of the statistical error bars. Using the previoulsy defined rule of thumb of Bernu et al. (eq 19), the parameter n should be approximately 4, for the 21 basis functions that we used in this calculation.

To understand the direct relationship between the integration of $H_{\alpha\beta}$ and $S_{\alpha\beta}$ matrix elements and the final CFQMC results (eigenvalues and statistical error bars), we have calculated the following quantity[32]

$$\Delta\left(\frac{H_{\alpha\alpha}}{S_{\alpha\alpha}}\right) = \frac{(H_{\alpha\alpha}^{EQI}/S_{\alpha\alpha}^{EQI} - H_{\alpha\alpha}^{QMC}/S_{\alpha\alpha}^{QMC})}{H_{\alpha\alpha}^{EQI}/S_{\alpha\alpha}^{EQI}} \quad (24)$$

with the respective statistical error bars given by

$$\text{Er}\left(\frac{H_{\alpha\alpha}^{QMC}}{S_{\alpha\alpha}^{QMC}}\right) = \frac{S_{\alpha\alpha}^{QMC}\,\text{Er}(H_{\alpha\alpha}^{QMC}) - H_{\alpha\alpha}^{QMC}\,\text{Er}(S_{\alpha\alpha}^{QMC})}{(S_{\alpha\alpha}^{QMC})^2} \quad (25)$$

for each diagonal element of the Hamiltonian and overlap matrix ($\text{Er}(H_{\alpha\alpha}^{QMC})$ and $\text{Er}(S_{\alpha\alpha}^{QMC})$ are given by eqs 14 and 15, respectively). This way we can highlight the quality of the integration of each matrix element. For example, the statistical errors of the $H_{\alpha\alpha}/S_{\alpha\alpha}$ for the first diagonal element are 6.1×10^{-4}, 6.7×10^{-4}, 7.4×10^{-4}, 8.0×10^{-4}, 8.4×10^{-4}, 9.3×10^{-4}, and 1.0×10^{-3} for $n = 3$, 4, 6, 8, 10, 15, and 20, respectively, while those for the 9th diagonal element are 1.9×10^{-3}, 1.1×10^{-3}, 1.0×10^{-3}, 9.4×10^{-4}, 9.2×10^{-4}, 9.1×10^{-4}, and 9.3×10^{-4}, and for the 18th diagonal element the statistical errors are 9.9×10^{-3}, 4.6×10^{-3}, 2.2×10^{-3}, 1.4×10^{-3}, 1.1×10^{-3}, 1.0×10^{-3}, and 9.9×10^{-4}, respectively. These indicate that for the highly excited basis functions the integration is done better for $n \geq 8$, while for the first diagonal elements the ones for $n \leq 6$ are a little better. So, it is important to balance between these two opposite situations (particularly, in our analysis from now on we decided to use $n = 10$). Moreover, we can note that the relative error in the eigenvalues is, in general, of the same order of magnitude of the relative error in the integration of the **H** and **S** matrix elements.

Now we turn our attention to the optimization procedure discussed in subsection 3.4. In Table 1 we display the difference between the CFQMC and the exact eigenvalues of the first nine states as a function of the number of excited states included in the optimization (n_{exc} in eq 20). All CFQMC results are computed using 21 basis functions. The average difference of the CFQMC results from the exact ones for these states are 484.5, 79.6, 5.1, 1.8, 4.6, 7.3, and 137.4 cm^{-1}, for $n_{exc} = 0$, 3, 5, 7, 10, 12, and 16, respectively, while the average statistical errors are 4.3, 2.7, 0.7, 0.5, 1.0, 1.8, and 8.0 cm^{-1}.

One can see that the inclusion of more states improves the accuracy of the results up to an ideal n_{exc}, in this case $n_{exc} = 7$. This can be better seen in Figure 1. In this figure we plot the difference of the CFQMC results from the exact ones for the first 12 bound states of the system as a function of n_{exc}. The

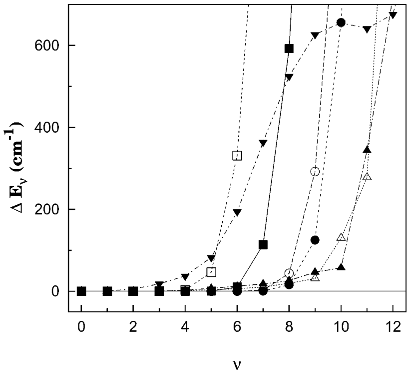

Figure 1. Difference of the CFQMC and exact vibrational energy levels of the Morse potential for different excited states optimized parameters (first 13 states): (empty square) $n_{\text{exc}} = 0$, (full square) $n_{\text{exc}} = 3$, (empty circle) $n_{\text{exc}} = 5$, (full circle) $n_{\text{exc}} = 7$, (empty up triangle) $n_{\text{exc}} = 10$, (full up triangle) $n_{\text{exc}} = 12$, and (full down triangle) $n_{\text{exc}} = 16$.

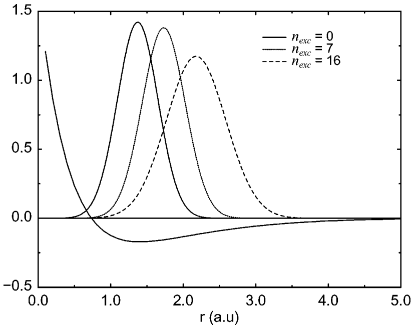

Figure 2. Trial ground-state wave functions for different number of excited states included in the optimization procedure.

trend is that the higher excited states improve as n_{exc} grows. However, the low and intermediate states are worsened after a threshold $n_{\text{exc}} \approx 10$.

To understand this trend we plot the ground-state trial function ($n_\nu(i) = 0$ in eq 16) for $n_{\text{exc}} = 0$, 7, and 16 in Figure 2. For $n_{\text{exc}} = 0$ the function is centered near the minimum of the well; as we increase n_{exc} the function is centered at larger interatomic separations and becomes broader. To improve the higher excited states, the basis sets need to describe the states at larger interatomic separations. But as the function becomes broader and off centered, the approximation of the low-lying states is worse. The optimum parameters, for this trial wave function, will be a balance of these two regimes. For the case studied the optimum result is achieved when we include seven excited states in the optimizations procedure. Moreover, we reach the spectroscopic accuracy ($\Delta E_\nu < 1$ cm^{-1}) for the first eight states using only 21 basis functions.

However, the optimum parameters for the problem using 21 basis functions will not be the best parameters for a basis set with a larger number of functions. This aspect can be seen in Table 2, where we show the differences of the CFQMC results calculated using 31 basis functions from the exact ones for different optimized parameters ($n_{\text{exc}} = 7$, 12, and 16). In this case, we can see that the better results are from the $n_{\text{exc}} = 12$. The average difference for the 12 first states are 31.9, 0.4, and 8.1 cm^{-1} for $n_{\text{exc}} = 7$, 12, and 16, respectively. And the average statistical errors are 2.5, 0.8, and 4.1 cm^{-1}, respectively. Note that we obtain the spectroscopic accuracy for the first 11 states using the optimized parameters for $n_{\text{exc}} = 12$. In Figure 3, we display the differences of our CFQMC results with $n_{\text{exc}} = 12$ optimized parameters from the exact ones for the first 13 states as a function of the number of the basis functions. This is an indication that one needs to be very careful before pointing out a general rule about this behavior. However, we note that this optimization procedure yields more accurate results and goes toward our main goal of reaching spectroscopic accuracy with QMC.

TABLE 2: Difference between the CFQMC and Exact Vibrational States of the Morse Potential (H_2) for CFQMC Calculations Using 31 Basis Functions with Different Number of Excited States in the Optimization[a]

	CFQMC			
n	$n_{\text{exc}} = 7$	$n_{\text{exc}} = 12$	$n_{\text{exc}} = 16$	exact
0	−0.1(0.5)	0.0(0.8)	−0.1(0.2)	2165.9
1	0.0(0.6)	0.0(0.5)	−0.2(0.6)	6308.6
2	0.0(0.6)	0.0(0.4)	−0.1(0.4)	10198.9
3	0.0(0.6)	0.0(0.4)	0.0(0.2)	13836.9
4	0.0(0.5)	0.0(0.4)	0.2(0.2)	17222.6
5	0.0(0.5)	0.0(0.4)	1.1(0.7)	20356.0
6	0.0(0.6)	0.0(0.3)	4.4(1.8)	23237.1
7	0.0(0.6)	0.0(0.4)	9.8(3.5)	25865.8
8	0.0(0.6)	0.1(0.4)	14.4(5.1)	28242.2
9	2.7(0.9)	0.3(0.8)	17.5(8.3)	30366.3
10	49.4(3.6)	0.6(1.3)	21.3(12.6)	32238.1
11	330.8(15.0)	4.1(3.9)	28.5(15.3)	33857.5

[a] Numbers in parentheses denote the error bars and the results are in cm^{-1}.

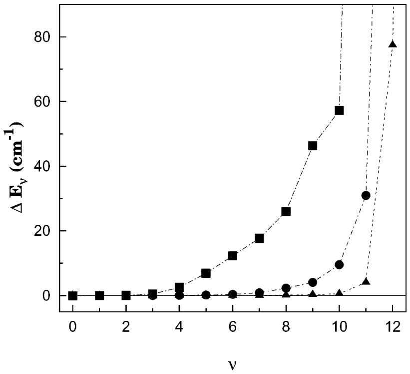

Figure 3. Difference between the CFQMC with $n_{\text{exc}} = 12$ optimized parameters and exact vibrational energy levels of the Morse potential for different number of the basis functions (first 13 states): (full square) 21 basis functions, (full circle) 26 basis functions, and (full up triangle) 31 basis functions.

4.2. Two Minima Model Potential. Now we focus our attention in a model potential that has more than one minimum. This type of potential is very important in physical chemistry due to the fact that these potentials are related to systems that have different isomeric forms, such as HCN and HCCH. The model potential that we proposed is given by

$$V(r) = D_1(1 - e^{-\beta_1(r-r_1)})^2 - D_1 - D_2 e^{-\beta_2(r-r_2)^2} \quad (26)$$

with $D_1 = 4.0$, $\beta_1 = 0.2$, $r_1 = 7.5$, $D_2 = 2$, $\beta_2 = 0.09$, and $r_2 = 25.0$ (arbitrary units). We used $\mu = 1.0$ and $\hbar = 1.0$. The potential is shown in Figure 4.

The focus in this system is the study of the role of the guiding function to accurately obtain all the excited states. This system has three different sets of states. The first is a set mostly localized in the first well, which we call the Morse states. The second is mostly localized in the second minimum, which we call the harmonic states. The third set is composed of states with amplitude in both wells, which we call mixed states. The guiding function and the basis functions should be flexible enough to describe all the states.

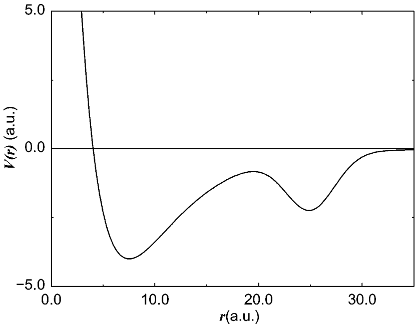

Figure 4. Modified two-minima potential from the eq 26.

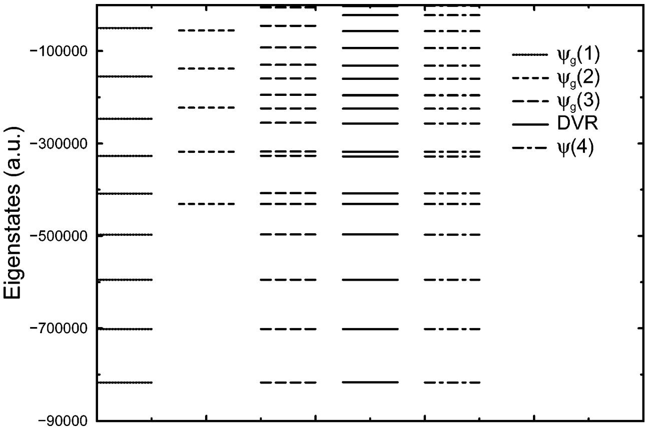

Figure 5. Vibrational spectra of the modified potential with different guiding and basis functions.

We use $n = 8$ in the guiding function (eq 17) and 21 basis functions of the type

$$f_{\alpha}(r) = (r - r_e)^{n_{\alpha}} e^{-A(r-r_e)^2} \qquad (27)$$

In the first calculation we used the basis functions and the guiding function centered in the first well: $A = 0.2525$ and $r_e = 7.59$. In the second calculation we used the basis functions and the guiding function centered in the second well: $A = 0.2$ and $r_e = 24.664$. In the third calculation we used a function centered between wells: $A = 0.2$ and $r_e = 8.17$.

The results are shown on Figure 5. The exact results are 17 bound states and they were obtained employing the discrete variable representation (DVR) method. The DVR method is a useful approach to solve the Schrödinger equation and has been used in many different subjects.[33−38] Particularly, we use 800 equally spaced DVR grid points (which were developed by Colbert and Miller[33]) and integrate in the interval $r = [0.0, 100.0]$ (in arbitrary units). In the first CFQMC calculation we obtained 9 bound states, in the second one we obtained 5 bound states, and in the third one we obtained 16 states. This shows that in order to describe a system with more than one minimum, both the guiding function and the trial basis set need to be broad enough and should be centered in a region so that they reasonably describe all the states of interest.

To describe the bound states of the system we propose a different basis set which is composed of a set of functions centered in the first well and another set centered in the second well. These basis functions are given by

$$f_{\alpha} = (r - r_{e_1})^{n_{\alpha_1}} e^{-A_1(r-r_{e_1})^2} + (r - r_{e_2})^{n_{\alpha_1}} e^{-A_2(r-r_{e_2})^2} \qquad (28)$$

We used a guiding function given by eqs 17 and 27 with r_e chosen to be centered between wells.

We used 21 basis functions centered in each well. The parameters for the function centered in the first well $r_{e_1} = 7.59$ and $A_1 = 0.12$, for the second set we used $r_{e_2} = 26.0$ and $A_2 = 0.05$. For the guiding function we used $A = 0.05$ and $r_e = 8.5$. This expansion produces a better integration as we can see in the results, the spectra of the right side in Figure 5, which display all 17 bound states. This kind of wave functions can also be used in the simple one minimum potential and should improve the quality of the highly excited states.

5. Concluding Remarks

In this paper we have presented a systematic study of the influence of the guiding function in the integration sampling and of the optimization procedure of the trial basis function parameters considering a small set of excited states in order to obtain vibrational spectra with spectroscopic accuracy using correlation function quantum Monte Carlo method. We studied two simple one-dimensional models, the Morse potential and a modified Morse potential, with an additional Gaussian minimum.

We have made several conclusions. (i) There is an optimum value of the exponent parameter n of the guiding function in eq 17. This value depends of the number of the excited states considered but it is larger than the square root of the number of excited states included in the basis set. (ii) The procedure of optimizing only the ground state is good to describe the low lying states of the system. However, to describe higher excited states one should include an excited-state optimization. Moreover, given a basis set, there is an optimum number of excited states that should be included in the optimization procedure. (iii) When we increase the number of basis functions it becomes clear that this number is smaller than the total number of basis functions. (iv) If the problem is more complex, with more than one minimum, both the guiding function and the trial basis set must be flexible enough and have non-negligible amplitude in all the regions of interest.

Although we restricted ourselves to simple one-dimensional problems, all the conclusions drawn for both the guiding function and the optimization of excited states should apply for systems with more dimensions. Preliminary calculations for the water molecule show that this is indeed the case.

Acknowledgment. F.V.P. and P.H.A. thank “Conselho Nacional de Desenvolvimento Científico e Tecnológico” (CNPq-Brazil) for financial support.

Supporting Information Available: Two tables of expanded results data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Suhm, M. A.; Watts, R. O. *Phys. Rep.* **1991**, *204*, 293.
(2) Caffarel, M.; Claverie, P.; Mijoule, C.; Andzelm, J.; Salahub, D. R. *J. Chem. Phys.* **1989**, *90*, 990.
(3) Buch, V. *J. Chem. Phys.* **1992**, *97*, 726.
(4) Blume, D.; Lewerenz, M.; Whaley, K. B. *J. Chem. Phys.* **1997**, *107*, 9067.
(5) Ceperley, D. M.; Bernu, B. *J. Chem. Phys.* **1988**, *89*, 6316.
(6) Bernu, B.; Ceperley, D. M.; Lester, W. A., Jr. *J. Chem. Phys.* **1990**, *93*, 552.
(7) Blume, D.; Greene, C. H. *J. Chem. Phys.* **2000**, *113*, 4242.
(8) Bertini, L.; Mella, M.; Bressanini, D.; Morosi, G. *J. Phys. B: At. Mol. Opt. Phys.* **2001**, *34*, 257.
(9) Needs, R. J.; Kent, P. R. C.; Porter, A. R.; Tower, M. D.; Rajagopal, G. *Int. J. Quantum Chem.* **2002**, *86*, 218.
(10) Bohm, M. C.; Schulte, J.; Ramirez, R. *J. Phys. Chem. A* **2002**, *106*, 3169.

(11) Prudente, F. V.; Costa, L. S.; Acioli, P. H. *J. Phys. B: At. Mol. Opt. Phys.* **2000**, *33*, R285.

(12) Brown, W. R.; Glauser, W. A.; Lester, W. A., Jr. *J. Chem. Phys.* **1995**, *103*, 9721.

(13) Acioli, P. H.; Soares Neto, J. J. *J. Mol. Struct.: THEOCHEM* **1999**, *464*, 145.

(14) Prudente, F. V.; Acioli, P. H.; Soares Neto, J. J. *J. Chem. Phys.* **1998**, *109*, 8801.

(15) Acioli, P. H.; Costa, L. S.; Prudente, F. V. *Chem. Phys. Lett.* **2000**, *321*, 121.

(16) Prudente, F. V.; Acioli, P. H. *Chem. Phys. Lett.* **1999**, *302*, 249.

(17) Acioli, P. H.; Costa, L. S.; Prudente, F. V. *J. Chem. Phys.* **1999**, *111*, 6311.

(18) Costa, L. S.; Prudente, F. V.; Acioli, P. H. *Phys. Rev. A* **2000**, *61*, n.012506.

(19) Silva, W. B.; Acioli, P. H. *J. Chem. Phys.* **2001**, *114*, 9720.

(20) Kuppermann, A. *Adv. Mol. Vib. Col. Dyn.* **1994**, *2B*, 117.

(21) Ceperley, D. M.; Mitas, L. *Adv. Chem. Phys.* **1996**, *93*, 1.

(22) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, A. N.; A. H. Tellerand Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.

(23) Jones, M. D.; Ortiz, G.; Ceperley, D. M. *Phys. Rev. E* **1997**, *55*, 6202.

(24) Alexander, S. A.; Coldwell, R. L.; Monkhost, H. J.; Morgan, J. D., III *J. Chem. Phys.* **1991**, *95*, 6622.

(25) Kwon, Y.; Ceperley, D. M.; Martin, R. M. *Phys. Rev. B* **1996**, *53*, 7377.

(26) Umrigar, C. J.; Wilson, K. G.; Wilkins, J. W. *Phys. Rev. Lett.* **1988**, *60*, 1719.

(27) Nightingale, M. P.; Melik-Alaverdian, V. *Phys. Rev. Lett.* **2001**, *87*, n. 043401.

(28) Bressanini, D.; Reynolds, P. J. *Adv. Chem. Phys.* **1999**, *105*, 37.

(29) Morse, P. M. *Phys. Rev.* **1929**, *34*, 57.

(30) Pauling, L.; Wilson, E. B. *Introduction to Quantum Mechanics*; McGraw-Hill: New York, 1935.

(31) The complete set of these results are presented in Table 1 of the Supporting Information due to the length.

(32) The complete set of these results are presented in Table 2 of the Supporting Information due to the length.

(33) Colbert, D. T.; Miller, W. H. *J. Chem. Phys.* **1992**, *96*, 1982, 34.

(34) Muckerman, J. T. *Chem. Phys. Lett.* **1990**, *173*, 200.

(35) Prudente, F. V.; Costa, L. S.; Soares Neto, J. J. *J. Mol. Struct. (THEOCHEM)* **1997**, *394*, 169.

(36) Costa, L. S.; Prudente, F. V.; Acioli, P. H.; Soares Neto, J. J.; Vianna, J. D. M. *J. Phys. B: At. Mol. Opt. Phys.* **1999**, *32*, 2461.

(37) Light, J. C.; Carrington, T., Jr. *Adv. Chem. Phys.* **2000**, *114*, 263 2000.

(38) Prudente, F. V.; Riganelli, A.; Varandas, A. J. C. *Rev. Mex. Fis.* **2001**, *47*, 568 2001.