

A spline approach to trial wave functions for variational and diffusion Monte Carlo

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We describe how to combine the variational Monte Carlo method with a spline description of the wave function to obtain a powerful and flexible method to optimize electronic and nuclear wave functions. A property of this method is that the optimization is performed ‘locally’: During the optimization, the attention is focused on a region of the wave function at a certain time, with little or no perturbation in far away regions. This allows a fine tuning of the wave function even in cases where there is no experience on how to choose a good functional form and a good basis set. After the optimization, the splines were fitted using more familiar analytical global functions. The flexibility of the method is shown by calculating the electronic wave function for some two and three electron systems, and the nuclear wave function for the helium trimer. For ${}^4\text{He}_3$, using a two-body helium–helium potential, we obtained the best variational function to date, which allows us to estimate the exact energy with a very small variance by a diffusion Monte Carlo simulation.

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I. INTRODUCTION

Most methods that solve the Schrödinger equation start by expanding the wave function using a basis set of analytical functions of some sort.

In practice, however, it is not possible to use a complete basis set, and one is forced to use a truncated basis, losing flexibility. The chosen basis set might be more suitable to describe some regions of space than others, for example it might be designed to describe the tail of the wave function at the expense of the core region or vice versa. Although with a careful choice of basis functions it is possible to have a balanced description in all the regions of space, the optimization process (usually the minimization of the energy or its variance) might still favor a particular region.

The key point to observe here is that the most commonly used basis sets, Slater or Gaussian functions for example, are global in nature, therefore the modification of a parameter during the optimization process modifies the wave function everywhere. This is true whether we are modifying a linear parameter or a nonlinear one. The optimization process is global, in the sense that at each step the whole shape of the wave function in configuration space changes. This is a direct consequence of the choice of using a basis set of analytic global functions, since in this way we cannot associate a particular parameter of the wave function with a given region

of space, although of course some regions are more affected by certain parameters and less affected by others.

This approach is widely used and has been very successful in providing accurate wave functions; however it makes difficult the fine-tuning of the wave function since it prevents a local optimization in a chosen region of space. This might be particularly desirable in cases where there is little guidance on how to choose the correct shape of the basis functions or a good trial wave function form. In these cases, one would like to be able to optimize a region of the wave function without spoiling it in other regions.

The finite element method¹ (FEM) has been developed to offer an alternative to global basis set methods. The region of solution is divided into elements, and local functions are defined within the elements to represent the wave function in that particular region of space. This method has been mainly implemented for Hartree–Fock (HF) and second-order Moller–Plesset calculations of atoms. This application of the FEM to atoms is fairly simple, since the elements are used only to model the radial coordinate for each orbital, while the angular variables can be expressed by spherical harmonics. With some modifications, the method can be used to perform HF calculations for linear molecules. However, if one wishes to introduce explicitly the interelectronic distances in the trial wave function, this method encounters the same difficulties in evaluating integrals as any other basis set method. The best way to optimize and evaluate properties of explicitly correlated trial wave functions is to use a Monte Carlo method.^{2–7} It would be desirable to combine the power of Monte Carlo methods in treating correlated functions with

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the flexibility of using a locally defined basis set. A widely used set of functions that are locally defined to interpolate a set of points are spline functions.⁸

In this paper we describe how spline functions and quantum Monte Carlo methods (QMC) can be combined to create a flexible trial wave function form that is amenable of local optimization. This method allows us to compute optimal wave functions for a given functional form and to investigate the shape of the basis functions.

The outline of the paper is as follows: In Sec. II we describe the main properties of spline functions, and give a brief summary of the Monte Carlo algorithm that is used to evaluate the energy and to optimize the wave function. In Sec. III we describe the application of this method to some atomic and molecular systems. In Sec. IV we show how this algorithm is not restricted to electronic systems, but can be used to give a good description of quantum clusters, and we apply it to the He₃ cluster, obtaining the best variational result to date. Using the optimized wave function we compute the exact ground state energy using the diffusion Monte Carlo (DMC) method. Finally, in Sec. V we discuss the method, its capabilities, and give some suggestions on possible directions for future work.

II. THEORY

Spline functions are simple piecewise polynomial functions and are well described in many books on numerical approximations.⁸ They are often used to build an interpolating function through N points. A different polynomial is used to join each pair of adjacent points, and special care is required to join smoothly the various polynomials, forcing the derivatives up to a given order to match at the points. The *cubic splines*, so called because a third-order polynomial is used to interpolate two adjacent points, are the simplest type of spline functions. To interpolate N points we need $N-1$ third-degree polynomials

$$p_i(x) = a_i x^3 + b_i x^2 + c_i x + d_i, \quad i = 1, \dots, N-1, \quad (1)$$

i.e., $4(N-1)$ parameters. We can fix the coefficients by requiring that where two polynomials join, they have the same value, the same first derivative, and the same second derivative. These conditions give $4N-6$ equations with $4N-4$ unknown coefficients, so two more conditions must be specified to describe the derivatives at the end points. In the so-called *natural cubic splines*, a very common approach, the second derivatives at the end points are set to zero, giving $4N-4$ linear equations in $4N-4$ variables that can be solved to find the coefficients. We decided not to impose any particular value to the derivatives at the end points, rather those are two more parameters that can be optimized to give a better wave function.

An important property is that the time needed to connect N points by splines scales linearly with N . This ensures that the trial wave function can be efficiently assembled and computed.

In the past, spline functions have been used to build approximate solutions of the Schrödinger equation, often in combination with the basis set approach.⁹⁻¹⁶ However, in those cases, like in the FEM approach, the crucial property

needed was the ability to compute analytically the overlap integrals and the Hamiltonian matrix elements. For example, using splines to describe the radial part of the atomic orbitals in HF calculations can lead to a simplification of the calculation. Since splines are polynomials, all the integrals are available. A disadvantage of this method is that the N points defining the spline implicitly define a grid for the integration, and like in all grid integration methods the computational cost scales as N^D , where D is the number of dimensions in configuration space. The fact that the integration can be performed analytically and not numerically is immaterial here, since for each element of the grid a different integral must be evaluated. In this paper we show how, in combination with Monte Carlo methods, splines can be successfully employed to build explicitly correlated functions avoiding the N^D computational cost scaling. An earlier attempt to use spline functions within a Monte Carlo method is due to Lowther and Coldwell,¹⁷ however they used splines to model only a small part of a the helium dimer wave function while here we attempt to model the whole wave function for a variety of systems.

A. Variational Monte Carlo

An integration method well suited for high dimensional spaces is the Monte Carlo method.^{18,19} Its practical application to the computation of the variational energy of a given trial wave function is called variational Monte Carlo (VMC). Since it is well described in the literature²⁰⁻²² we summarize here only the main points and redirect the reader to the vast literature on the subject for more technical details and for a review of the applications of this method.

The VMC approach is a very powerful technique that estimates the energy and all the desired properties of a given trial wave function without any need to compute analytically the matrix elements. For this reason, it poses no restrictions on the functional form of the trial wave function, requiring only the evaluation of the wave function value, its gradient, and its Laplacian, and these are easily computed. The essential idea, as in classical statistical mechanics, is the ability to write the desired property $\langle O \rangle$ of a system as an average over an ensemble,

$$\langle O \rangle = \frac{\int P(\mathbf{R}) O(\mathbf{R}) d\mathbf{R}}{\int P(\mathbf{R}) d\mathbf{R}}, \quad (2)$$

given some specific probability distribution $P(\mathbf{R})$. If $\langle O \rangle$ is a quantum expectation value, $P(\mathbf{R})$ is the wave function squared: $\Psi^2(\mathbf{R})$.

The essence of VMC basically a stochastic numerical integration scheme, is the creation of a distribution $P(\mathbf{R})$ proportional to $\Psi^2(\mathbf{R})$. This is usually done by a random walk in configuration space using a Metropolis algorithm²³ or a Langevin algorithm.²⁴ Once such a distribution is established, expectation values of various quantities can be sampled. The expectation value of the energy for any trial wave function form, for example, can be estimated by averaging the local energy $H\Psi/\Psi$ during the simulation

$$\begin{aligned} \langle \hat{H} \rangle &= \frac{\int \Psi^2(\mathbf{R}) E_L(\mathbf{R}) d\mathbf{R}}{\int \Psi^2(\mathbf{R}) d\mathbf{R}} \cong \frac{1}{M} \sum_{i=1}^M E_L(\mathbf{R}_i) \\ &= \frac{1}{M} \sum_{i=1}^M \frac{\hat{H}\Psi(\mathbf{R}_i)}{\Psi(\mathbf{R}_i)}, \end{aligned} \quad (3)$$

where M is the number of sampled points.

B. Spline description of the wave function

The general idea of our method is to describe the trial wave function using a set of points in configuration space, also called “knots,” and using spline functions to build a continuous and differentiable function. In particular we write the wave function as a product of functions of a single variable, each one described by splines. The optimization process modifies the values of the function at those points, and eventually some other degrees of freedom that the spline definition gives us, like the derivatives at the end points. To avoid any unfavorable scaling with the number of dimensions, we use the VMC method to estimate the trial energy. Note that the parameters of the wave function that can be optimized, the values of the function at the knots, are thus directly related to different regions of space. This allows the optimization to be local, in the sense defined above.

We will use a simple example to explain the practical implementation of this algorithm: consider the hydrogen atom in its ground state, since it is an S state its wave function depends only on r , the electron nucleus distance. We then approximate $\Psi(r)$ using cubic splines connecting N points (see Fig. 1). The wave function must be defined in the range $0 \leq r < \infty$, while the cubic splines can be defined only for finite values of r , so they can only be used to approximate the function between the first and the last point. Therefore, we must augment the spline description with an analytical function that describes the wave function beyond the last point and is joined smoothly with the last polynomial. We call this function the “tail function” since it is used to describe the tail of $\Psi(r)$. In practice, this means that we must have some free parameters in the tail function so that it can be adjusted to join smoothly to the last point. We have tried several tail functions for various systems, e.g., $ar^b e^{cr}$ or $(a + br)e^{cr}$, where a , b , and c are the free parameters. However we have found that, if at the last point the wave function is already very small, there is no noticeable difference in using the simpler exponential ae^{cr} , although in this case the second derivative at the joining point might not be continuous. Of course, for the simple case of the hydrogen atom, the tail function used is also the correct one, but this is by no means a requisite of the method. If we wish to study states with different angular momentum, e.g., the state described by the $3d_{xy}$ orbital, we simply write the wave function as $\Psi = xyf(r)$ and use splines to build $f(r)$. The extension of this method to many electron systems is trivial and we will give concrete examples in Sec. III.

As mentioned in a previous paragraph, specifying the value of the wave function at the N knots is not sufficient to completely define the cubic splines: we still have to define the derivative values at the end points (there are four values

involved: two first derivatives and two second derivatives, but only two are independent). Rather than fix them to some particular value, like in the natural spline approach, we decided to leave these parameters free, and to optimize them during the process. In particular we chose to optimize the two first derivatives at the end points. Another valid approach would be to fix the derivative at the initial point so that the spline satisfies the cusp conditions,²⁵ since these are exactly known.

C. Optimization of the trial wave function

We now have a complete description of $\Psi(r)$, and we are left with the task of optimizing all the parameters: the N wave function values at the chosen points and the two derivatives. The optimization is performed using the standard *fixed sample sigma minimization* algorithm, described by Umrigar, Wilson, and Wilkins.² This method dates back to Frost²⁶ and Conroy²⁷ and is the standard way to optimize trial wave functions using VMC. Briefly, the mean square deviation of the local energy $H\Psi/\Psi$ is minimized, rather than the energy itself, since this leads to a numerically more stable process. The fluctuation of the local energy $\sigma^2(H) = \langle H^2 \rangle - \langle H \rangle^2$ is computed using an ensemble of points (or *walkers*) distributed in configuration space. We need to distinguish between $\sigma(H)$, which is the sigma of the Hamiltonian operator computed using a given trial function, and the standard deviation of the computed variational energies, which is a measure of the uncertainty associated with a given expectation value estimated using a Monte Carlo algorithm, and is usually written in parentheses after the estimated value.

The optimization process alters the value of the wave function at the various spline knots, trying to generate a better function. In principle, even the position of the knots can be optimized, but for simplicity we keep them fixed. After the optimization has produced a new function, a VMC simulation is performed to estimate the new trial energy and to generate a new ensemble of walkers, to be used eventually in a new optimization. Usually convergence is achieved in three or four steps.

Figure 1 shows the effect of altering the value of the function at a single point (the open circle); the altered wave function is shown by the dotted line. This example clearly shows the local properties of spline functions: the further away we are from the perturbed point, the less important is the perturbation. The two wave functions are already indistinguishable three points away from the perturbation. This means that the optimization process is able to improve locally a wave function without the risk to deteriorate it elsewhere.

The locality (or more precisely, quasilocality) of spline functions can also be exploited to improve the computational efficiency of the optimization process. In the fixed ensemble optimization, whenever a single parameter is modified, the entire wave function must be recomputed for all the walkers in the ensemble, since in principle all the walkers can have their value changed drastically. In our approach, however, when we optimize the value at a knot, we know that the wave function will be modified only in the surrounding re-

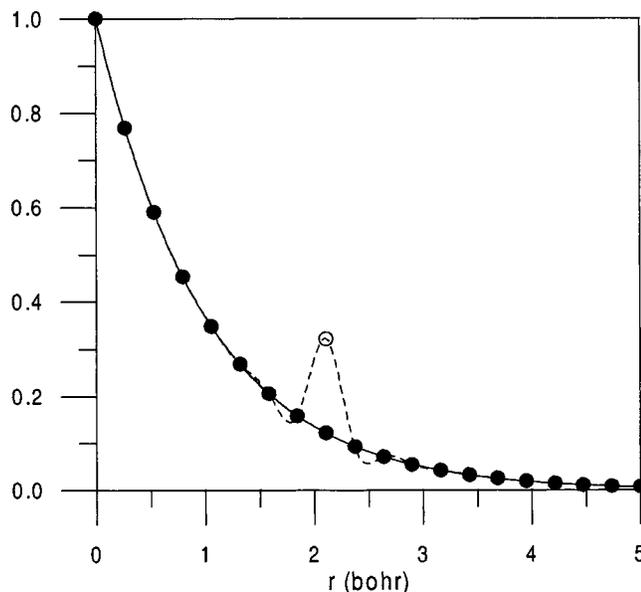


FIG. 1. Solid line: cubic spline description of the ground state of the hydrogen atom. Dashed line: wave function perturbed at a single knot.

gions. Since the spline knots and the walkers are never changed during an optimization, at the start of the process it is possible to assign all the walkers that are within a certain range to each knot. The practical range to use depends on the system under study and the number of points and can be found quickly with a little trial and error. The result is that when a parameter is optimized, we only need to recompute the wave function value for those walkers directly within the chosen range and not for all.

Of course, this introduces an approximation into the optimization, but it can be minimized at will, by enlarging the range: a range too small will result into an uncontrolled approximation, while a too large one will lose all the speed-up. A value can be chosen to gain speed during the optimization, but without altering it too much. It must be noted that no such approximation is introduced during the estimation of the energy of a VMC run, so it does not introduce any bias on the properties evaluation.

An immediate extension of this approach would be to use higher polynomials to join two adjacent points. We might use fourth degree polynomials (quartic splines), for example. In this case we have $5(N-1)$ parameters to fix; as an extension of the cubic case, we might also impose the continuity of the third derivative at all the points; another possibility is to consider the added degrees of freedom simply as parameters to optimize during the process, improving the wave function form. A third, promising approach that we are currently exploring, is the possibility of using the extra degrees of freedom offered by fourth degree polynomials to enforce a strictly local optimization. In particular, we might require that, when optimizing the value at a particular knot, only the region of wave function included between this and the two neighbor points be modified: the outside polynomials are rigorously unchanged, while in the cubic case the perturbation was only decreasing very fast.

Consider the optimization of a given point: two fourth

TABLE I. Spline wave function optimization for the hydrogen atom.^a

	$\langle H \rangle$	$\sigma(H)$
Initial spline	-0.305 0(19)	1.198
First optimization	-0.499 78(7)	0.031
Final optimization	-0.500 02(5)	0.014

^aEnergies in hartree.

degree polynomials join at this point, with ten parameters to fix. Two parameters are assigned by requiring the two polynomials to have the new value at the joining point, another two by requiring that at this point the two curves have the same first and second derivative. The remaining six parameters can be fixed by demanding that the value, first derivative, and second derivative of the two adjacent knots do not change. The two end points can be treated similarly. In this way, the optimization can be strictly local, with no approximations.

It must be noted that each walker during the optimization contributes only to two knots, regardless of the total number of knots: In this case, the optimization cost is completely independent of the number of points. This means that the quality of the wave function description can be increased without too much optimization cost (the fact that the cost of a single optimization pass is the same regardless of the number of points does not mean that the minimum will be reached with the same number of steps. Presumably, the more parameters we have the more steps we need to reach the minimum). However, if there are too many points with too few walkers, it is likely that some points will have too few or no walkers in their range, preventing a meaningful optimization.

III. ONE AND FEW ELECTRON SYSTEMS

As a first check of the algorithm, we optimized a wave function for the hydrogen atom in its ground state. We used 15 knots equally spaced between 0 and 10 bohr and 1000 walkers. The starting cubic spline functions were generated taking an exponential function and randomly modifying its value at those 15 points. The resulting wave function, as can be seen in Table I, gives a very bad energy and a $\sigma(H)$ of 1.198 (this should be zero for the exact wave function). However, after the first optimization step, the new wave function is greatly improved, both in the energy and in the fluctuations of the local energy. After the second and last optimization step, the energy is statistically indistinguishable from the exact one and $\sigma(H)$ is very small.

The extension to more electrons is very easy: For a two electron atom we can write the ground state wave function using the interparticle distances r_1 , r_2 , and r_{12} , and choose the functional form to which apply the spline Monte Carlo algorithm.

In the simplest case one could use the restricted HF ansatz and write $\Psi = f(r_1)f(r_2)$. Correlation between the two electrons can be introduced by using a function of the form $\Psi = f(r_1)f(r_2)g(r_{12})$ where we have multiplied the HF wave function by a correlation factor. Not requiring the two electrons to share the same orbital leads to the following

TABLE II. Spline wave functions for two-electron atoms.^a

	Z=1	Z=2	Z=3
One term	$E = -0.526\,97(1)$ $\sigma(H) = 0.041$	$E = -2.903\,06(3)$ $\sigma(H) = 0.096$	$E = -7.279\,34(9)$ $\sigma(H) = 0.157$
Two terms		$E = -2.903\,55(2)$ $\sigma(H) = 0.093$	
NR limit	-0.527 75	-2.903 72	-7.279 91

^aEnergies in hartree.

functional form: $\Psi = (f_1(r_1)f_2(r_2) + f_2(r_1)f_1(r_2))g(r_{12})$ where now f_1 , f_2 , and g are independent functions that can be described using splines.

We chose the last functional form and used 10 knots to build each function. The simulations and optimizations were performed using 5000 walkers. Table II shows the results for the cases $Z=1, 2$, and 3 . In all cases, the optimized energy is less than 1 mhartree away from the nonrelativistic (NR) limit. This shows that spline functions can efficiently exploit the chosen correlated functional form. We might ask ourselves the reasons for the remaining difference between the exact energy and the computed one. Of course, the most important source of difference is the functional form: It is not possible to go beyond a certain limit energy for a given functional form. This is similar to what happens in HF calculations, where it is impossible to get a lower energy than the HF limit, regardless of the basis set. Two other possible sources of errors are the use of a too small number of spline knots, so the function is not flexible enough, and the fact that the chosen optimization process does not minimize the energy, but rather the $\sigma(H)$. We then performed the simulations doubling the number of knots, with essentially no gain in the energy. In our experience, for these small systems the optimization of the sigma is almost as good as the optimization of the energy, so this means that the algorithm should have reached the limit of the given functional form. In order to go beyond this functional form, three-body correlation must be included. To test this hypothesis on He, we improved the functional form using a linear combination of two terms similar to the first one, with completely independent functions. This is a way to include implicitly three-body correlation. The energy shown in Table II, $-2.903\,55(2)$ hartree, is better than the single term result, and is only 0.0002 hartree away from the nonrelativistic limit.

This example shows a very useful property of the algorithm: the ability to “explore” different functional forms. This can be particularly important for systems where there is little experience on how to build a good trial wave function.

The applicability of the method is by no means restricted to atoms: We optimized a spline wave function for the hydrogen molecule in the ground state at the equilibrium distance of 1.4012 bohr using the ansatz $\Psi = (1 + \hat{P}_{12})(1 + \hat{i})f_1(r_{1a})f_2(r_{1b})f_3(r_{2a})f_4(r_{2b})g(r_{12})$ with four electron-nucleus functions and one electron-electron function. In the above equation, \hat{P}_{12} is the permutation operator, \hat{i} is the inversion operator, while a and b are the nuclei. We used 10 knots to describe the electron-nucleus functions and 20 to describe the electron-electron function. The optimized en-

TABLE III. Spline and analytical wave functions for the lithium atom.^a

	$\langle H \rangle$	$\sigma(H)$
$\Psi = \hat{A}f_1(r_1)f_2(r_2)f_3(r_3)$	-7.440 8(1)	1.17
$\Psi = \hat{A}f_1(r_1)f_1(r_2)f_2(r_3)g_1(r_{12})g_2(r_{13})g_2(r_{23})$	-7.474 14(2)	0.29
$\Psi = \hat{A}f_1(r_1)f_2(r_2)f_3(r_3)g_1(r_{12})g_2(r_{13})g_3(r_{23})$	-7.477 04(9)	0.27
As above with f =Padé and g =Jastrow	-7.476 6(2)	0.19
HF limit	-7.437 69	
NR limit	-7.478 07	

^aEnergies in hartree.

ergy is $-1.173\,97(3)$ hartree with a $\sigma(H)$ of 0.051, to be compared with the nonrelativistic limit of $-1.174\,47$ hartree.

To show that the algorithm presented here is equally applicable in other coordinate systems we studied the hydrogen molecule using elliptic coordinates, obtaining statistically similar results. For other systems the use of a different coordinate system might be more convenient and might allow recovering more correlation energy.

We already explained in a previous section why so far the use of splines in fully correlated calculations has been mainly restricted to one- and two-electron systems. Here we show that, due to the use of QMC integration, our method has no restriction of this sort.

We consider the lithium atom as the prototype of a many-electron system. The power of the algorithm to test different functional forms can be put to a more stringent test with the lithium atom than with a two-electron system. Of course, as the number of particles in a system increases, so does the number of possible functional forms. For example in the lithium case we might consider a class of “restricted” forms, where the two core electrons are described with identical functions, and a class of “unrestricted” forms, where we allow an independent description. For an explicitly correlated wave function, this has effects also on the correlation factors.

As an example, we chose three representative functional forms. The simplest example of function beyond the restricted HF description is $\Psi = \hat{A}f_1(r_1)f_2(r_2)f_3(r_3)$, where we give complete freedom to the three orbitals. Note in Table III that, although we have not yet introduced any correlation factor, we are already recovering some correlation energy. This is an artifact of the definition of the HF limit, where a restricted function is used. To recover the remaining correlation energy, a correlation factor g must be introduced that describes the instantaneous electron-electron correlation. The second form we tried, $\Psi = \hat{A}f_1(r_1)f_1(r_2)f_2(r_3) \times g_1(r_{12})g_2(r_{13})g_2(r_{23})$, was built starting from the restricted HF wave function and multiplying it by two different correlation factors. As can be seen in Table III, the energy greatly improved, but we have still 4 mhartrees to recover. In other words, the correlation factors helped the description of the electronic correlation, but cannot compensate fully for the lack of flexibility in the electron-nucleus description.

In the last function, $\Psi = \hat{A}f_1(r_1)f_2(r_2)f_3(r_3)g_1(r_{12}) \times g_2(r_{13})g_3(r_{23})$, we assumed a different function for each electron and for each pair, with six functions to optimize. The simulations were performed with 5000 walkers. The re-

TABLE IV. Spline and analytical wave functions for the He_2^+ molecule.^a

	$\langle H \rangle$	$\sigma(H)$
$\Psi = \hat{A} f_1(r_{1a}) f_2(r_{1b}) f_3(r_{2a}) f_4(r_{2b})$ $\times f_5(r_{3a}) f_6(r_{3b}) g_1(r_{12}) g_2(r_{13}) g_3(r_{23})$	-4.9914(3)	0.18
As above with f =Padé and g =Jastrow	-4.9905(1)	0.17
HF limit	-4.9227	
NR limit	-4.9945	

^aEnergies in hartree.

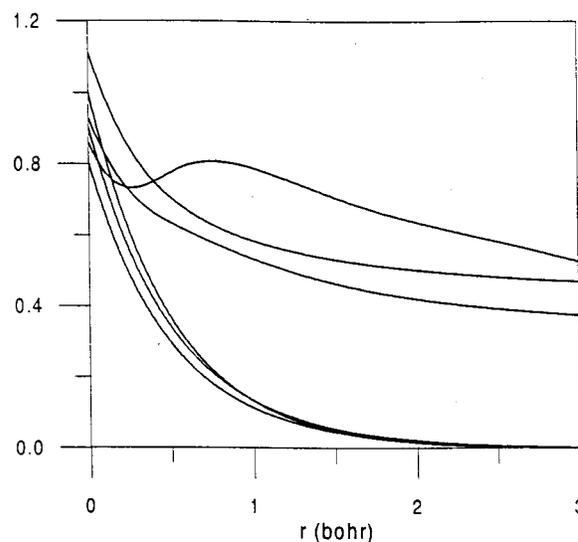
sult in Table III shows that the added flexibility in the trial wave function recovered almost all the remaining correlation energy. In our opinion, the remaining millihartree of correlation energy might be due to three- and four-body effects that are not present in the chosen functional form.

We have chosen three simple functional forms, which by no means exhaust all the possibilities. Of course the exact energy for the lithium atom is already known, and very accurate analytical functions can be built, e.g., using Hylleraas functions or Slater determinant and Jastrow factors. However, the study of few electron systems can be very useful to answer questions that naturally arise when investigating many electron systems. It is not known, for example, how much can be gained in a correlated function allowing each electron to occupy a different orbital. The lithium example above seems to suggest that the gain is substantial, but for more complicated systems the question remains to be answered. As a second example, simple VMC calculations are usually performed using the same Jastrow correlation factor for all like spin electrons. It is not known how much can be gained by using a different correlation factor for each electron–electron distance, as we did above.

The exploration of these questions for few and many electron systems will be the subject of a future work.

As final electronic system, we studied the He_2^+ molecular ion. We chose to describe the ground state at the internuclear distance of 2.0625 bohr using six electron–nucleus and three electron–electron functions: $\Psi = \hat{A} f_1(r_{1a}) f_2(r_{1b}) \times f_3(r_{2a}) f_4(r_{2b}) f_5(r_{3a}) f_6(r_{3b}) g_1(r_{12}) g_2(r_{13}) g_3(r_{23})$. The results are shown in Table IV. Again, this algorithm is able to exploit fully the freedom of the functional form, obtaining a variational energy only 3 mhartrees away from the nonrelativistic limit.

It might be desirable, after the spline has been thoroughly optimized, to find a good analytical approximation with few parameters. This can be very useful, especially for systems where no good basis set exists, to investigate new shapes for global basis functions. It can also reduce the computational cost to study a similar system, where a new optimization process must be performed: One can start optimizing the analytical wave function and then use the spline model to increase the flexibility. We tried to find a good analytical model that could accurately describe the optimized spline for the lithium atom that we obtained using the third functional form previously described. To do so we performed a least-squares fit using various analytical models. For the electron–nucleus functions, we found that the model

FIG. 2. The six electron–nucleus spline functions for the He_2^+ molecule.

$$f(r) = \exp\left(\frac{ar + br^2}{1 + cr}\right), \quad (4)$$

a generalized Padé, was the best compromise between a good least-squares fit and a small number of parameters. The simplified form obtained setting $c=1$ was only slightly worse. The reason why this form is a good choice to describe $1s$ orbitals is that for small values of r this function resembles e^{ar} , while for large r it resembles $e^{(b/c)r}$: so, with different exponents, it can simultaneously accommodate the cusp at the nucleus and the exponential decay for large r . This model is very good also at describing the helium $1s$ orbitals. Surprisingly, this model can accurately describe even a $2s$ orbital like in lithium: In fact, if we allow a to be positive and b to be negative, the function rises through a maximum and then decays to zero like a $2s$ orbital. For the electron–electron functions we found, reassuringly, that the well-known Jastrow function was the best among two parameter models. We performed a VMC simulation and optimization using the analytical model found for the same functional form for lithium: we used three Padé functions [Eq. (4)] to describe the electron–nucleus functions and three Jastrow factors for electron–electron correlation. As can be seen in Table III, this function is only slightly worse than the spline we started with, but with less parameters. It is interesting to note that, while the spline function and the analytical function have very similar energies, their $\sigma(H)$ are quite different. A possible explanation is that the optimization of the spline function was not complete, and that the analytical wave function has a smooth second derivative, while the second derivative of a cubic spline is composed by segments.

Figure 2 shows the final electron–nucleus splines for the He_2^+ molecular ion. Five out of six functions resemble $1s$ orbitals, but the last function shows a very interesting feature—there is a local maximum at about 0.9 bohr. We checked that this is not an artificial feature or a spurious result from a bad optimization: If we eliminate this feature,

the energy systematically increases. The spline algorithm is trying to push some electronic density in between the two nuclei and exploits the local freedom of the splines to increase the wave function in this region.

Finally we fitted the splines and then optimized an analytical function for the He_2^+ molecular ion using Padé and Jastrow functions. As discussed above, the Padé was able to fit function f_5 reproducing the maximum between the nuclei, but could not at the same time reproduce the cusp. Nevertheless, we obtained an energy (see Table IV) only 1 mhartree worse.

IV. APPLICATION TO NUCLEAR WAVE FUNCTIONS: THE HELIUM TRIMER $^4\text{He}_3$

While there is now substantial experience on the construction of very good functional forms for electronic wave functions for atoms and molecules, this is not the case in the rapidly growing field of atomic and molecular clusters.²⁸ Given a potential energy surface that describes the interaction of all the present species, very little is known about how to build an accurate and compact functional form. For these systems, the proposed method should be an invaluable help for testing new functional forms and new trial wave functions, especially in those cases where impurities are present in the cluster.

As a testing ground for our algorithm, we used the helium trimer cluster. This system has been the subject of many recent investigations,^{29–31} however a good compact description of its ground state is still lacking. We assumed, as customary in studying helium clusters, only two-body interactions and used the recently proposed Tang–Toennies–Yiu (TTY) potential³² for the helium–helium interaction.

Many calculations have been performed on this system, both using standard *ab initio* and quantum Monte Carlo methods. Recent calculations on small helium clusters^{29,33,34} used a trial wave function of the form

$$\Psi = \exp\left(\sum_{ij} \varphi(r_{ij})\right), \quad (5)$$

where

$$\varphi(r_{ij}) = p_1 r_{ij} + p_0 \ln r_{ij} + p_5 r_{ij}^{-5} + p_2 r_{ij}^{-2}. \quad (6)$$

This kind of functional form has been chosen to satisfy some reasonable boundary conditions and has been used with success in the past for various kinds of quantum clusters. In principle, one could add to φ higher (negative or positive) powers of r_{ij} or more complicated terms. However, there is little guidance on how to choose the best terms, and for a different system it might be necessary to add more terms to Eq. (6) to obtain good results.

One can note that the wave function of Eq. (5) can be written as a product of two-body wave functions

$$\Psi = \exp\left(\sum_{i<j} \varphi(r_{ij})\right) = \prod_{i<j} e^{\varphi(r_{ij})} = \prod_{i<j} f(r_{ij}), \quad (7)$$

where f is the same for all the interactions due to the permutational symmetry of the system. This functional form might be thought of as analogous to the restricted Hartree–Fock

model used in electronic systems. While only two fermions can be associated to the same function, since the ^4He atom is a boson, in this picture there is no restriction to the number of pairs that can be associated to the same function.

The function f is a monodimensional function, defined for positive values, and we can describe it as a spline as described above. We used 15 nodes from 0 to 85 bohr using Eq. (6) as the starting point, and a tail function of the type

$$e^{-kr}. \quad (8)$$

After a few standard VMC optimizations using 15 000 walkers, we obtained a variational energy of $-0.0868(2) \text{ cm}^{-1}$. If we consider that the starting wave function had an energy of $-0.0797(5) \text{ cm}^{-1}$ and that the exact energy, estimated by Lewerenz²⁹ with a diffusion Monte Carlo simulation, is $-0.0872(4) \text{ cm}^{-1}$, we can appreciate how this simple algorithm is fully able to exploit the given functional form, and to come very close to the estimated ground state energy. We believe that the energy of our spline function is close to the limit energy of the functional form [Eq. (7)]. Future work will be devoted to trying to find a good analytical form that fits very well the spline we have obtained, and to use it with different, and larger systems. We finally used the spline function in diffusion Monte Carlo simulation to estimate the exact energy, obtaining $-0.08772(8) \text{ cm}^{-1}$, statistically equal to the one previously found by Lewerenz. However, since our trial wave function behaves much better, we obtained a smaller variance.

V. CONCLUSIONS

The method we presented appears to be powerful and flexible. We have just started experimenting and studying it. We showed here how it can be applied to the study of atoms and molecules, or to atomic and molecular clusters, where there is still not enough experience on how to write an accurate and compact trial wave function. Applications to other systems are trivial. This algorithm can also be used to investigate the limit energy and the best wave function for a given functional form. For example, it is still not known for helium, and other clusters, the importance of three-body effects, or put in another way what is the limit energy for a wave function product of two-body terms. Once the method has generated a good wave function, if desired, it should be possible to find an analytical global function that approximates the splines. In this view, this method is the first exploratory step of systems where good analytical trial functions are not yet available. Even more interesting is the description of the trial wave function for mixed atom–molecule clusters where the anisotropy of the interaction potential introduces more complexity in the physics of these aggregates.

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