ANALYTICAL WAVEFUNCTIONS FROM QUANTUM MONTE CARLO SIMULATIONS

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Abstract

We present a method for extracting analytical wavefunctions for atoms and molecules from the sampling of the exact wavefunction provided by quantum Monte Carlo (QMC) methods. The parameters in the trial wavefunctions are optimized minimizing the total square deviation between the trial and the exact wavefunction. The least squares optimized wavefunction gives energy and other properties in good agreement with the exact values. The optimized wavefunction can be used to compute properties not easily accessible to QMC simulations.

1. Introduction

An exact wavefunction can be calculated by solving the Schrodinger equation only for very simple systems, in general one is restricted to approximated wavefunctions.

One adopts a trial wavefunction $\Psi(\mathbf{R}|\mathbf{c})$, where $\mathbf{c}$ represents the vector of the adjustable parameters, and finds the vector $\mathbf{c}$ for which $\Psi(\mathbf{R}|\mathbf{c})$ best describes the exact ground state wavefunction $\phi(\mathbf{R})$ of the Hamiltonian operator H. To make the problem mathematically more tractable, usually the function $\Psi(\mathbf{R}|\mathbf{c})$ is written as a linear combination of basis functions.

So far the problem is not yet well defined, since one has to specify what is meant by "best approximation". Several different criteria are available, and they lead to different approximated analytical wavefunctions.

The most common practice is to use the variational principle and to minimize the expectation value of the energy

$$\langle H \rangle = \frac{\int \Psi^*(\mathbf{R}|\mathbf{c}) H \Psi(\mathbf{R}|\mathbf{c}) d\mathbf{R}}{\int \Psi^*(\mathbf{R}|\mathbf{c}) \Psi(\mathbf{R}|\mathbf{c}) d\mathbf{R}} \tag{1}$$

with respect to the parameter vector **c**. In order to carry out this approach one has to compute overlap integrals and integrals involving one and two particles operators over the basis set. This fact severely limits the freedom of choice of the basis functions and one is usually forced to introduce the orbital approximation, i.e. to use products of monoelectronic functions.

Another possible approach, rarely used in the past[1,2], is the minimization of the functional

$$\sigma^2(H) = \frac{\int \Psi^*(\mathbf{R}|\mathbf{c})(H - \langle H \rangle)^2 \Psi(\mathbf{R}|\mathbf{c}) d\mathbf{R}}{\int \Psi^*(\mathbf{R}|\mathbf{c}) \Psi(\mathbf{R}|\mathbf{c}) d\mathbf{R}} \tag{2}$$

or related quantities.

The task of computing integrals involving not only H, but also H^2, makes this approach even more difficult to carry out than the previous one. However this optimization method has recently gained some popularity for its efficiency when used in combination with Variational Monte Carlo methods[3,4,5], which allows one to avoid the analytical integration.

Recently a new class of methods, collectively called *quantum Monte Carlo* methods (QMC), has gained popularity among chemists and physicists for their ability to compute energies and other properties with great accuracy. These methods, which we will not discuss here since they have been reviewed in details elsewhere[6], do not give an analytical description of the exact wavefunction like the above mentioned methods; rather, they directly sample $\phi(\mathbf{R})$, i.e. they generate a set of points in configuration space distributed according to the exact wavefunction. Using these points it is easy to estimate the energy of the system and other properties.

However one of the weaknesses of QMC methods is that one should store all the configurations sampled by the walkers, that is an enormous amount of data, to save the information gathered during the simulation of the Schrodinger equation. Otherwise, to estimate a property not computed during a simulation, the only solution is to run again the same simulation.

In a very low dimensional configuration space (1D or 2D) one could divide the configuration space in boxes and build a histogram-like approximation of the exact wavefunction binning the points produced by the QMC process. At the end of the simulation one could use this numerical wavefunction to compute the properties. One could also fit the histogram with an analytical function and compute analytically the observables. In these ways the information is compressed in a manageable form. This approach, feasible in 1D or 2D, becomes very inefficient if the configuration space has more than two degrees of freedom. It would be useful to have a method that "stores" the information on the exact wavefunction gathered by the QMC simulation in an analytical, even if approximated, wavefunction.

Here we present a general algorithm to extract an approximated analytical wavefunction from a QMC simulation even for multidimensional systems.

The algorithm attempts to fit the sampled wavefunction with a given trial wavefunction through the minimization of their total square deviation

$$q^2(\mathbf{c}) = \int (\phi(\mathbf{R}) - \Psi(\mathbf{R}|\mathbf{c}))^2 d\mathbf{R} \tag{3}$$

We will show how our method exploits the ensemble of points generated by the QMC process to compute the integrals required by the least squares procedure.

In all the calculations reported below we used the Diffusion Monte Carlo (DMC) method, but this technique can be used with any "flavor" of QMC.

2. The Least Squares Procedure (LSQ)

Let us assume as functional form for our trial wavefunction a linear combination of *N* basis functions

$$\Psi(\mathbf{R}|\mathbf{c}) = \sum_{i=1}^{N} c_i \chi_i(\mathbf{R}) \tag{4}$$

where the functions $\chi_j(\mathbf{R})$ (considered real here for simplicity) are not necessarily a product of monoelectronic functions, but can be explicitly correlated functions.

The best $\Psi(\mathbf{R}|\mathbf{c})$ can be obtained substituting Eq. 4 into Eq. 3, taking the derivatives with respect to c_i and setting them to zero to find the stationary point. It is easy to show that the coefficient vector **c** that minimizes the total square deviation between the trial and the exact wavefunction is the solution of the linear system

$$\mathbf{Sc} = \mathbf{b} \tag{5}$$

where **S** is the matrix of the overlap integrals $S_{ij} = \int \chi_i(\mathbf{R})\chi_j(\mathbf{R})d\mathbf{R}$ between the basis functions and **b** is the vector of the overlap integrals between the exact wavefunction and the basis functions

$$b_i = \int \phi(\mathbf{R})\chi_i(\mathbf{R})d\mathbf{R} \tag{6}$$

Quantum Monte Carlo methods sample the exact wavefunction generating a set of points distributed according to $\phi(\mathbf{R})$, this means that the integrals b_i can be easily estimated in a QMC simulation by

$$b_i \cong \frac{1}{M}\sum_{i=1}^{M}\chi_i(\mathbf{R}_i) \tag{7}$$

where M is the number of configurations generated by the simulation.

If the overlap matrix is available, the linear system of Eq. 5 can be solved to obtain the coefficients c_i. The coefficients of Eq. 4 are considered independent, since the approximate wavefunction can be normalized *a posteriori* by simply rescaling all the coefficients.

When the overlap integrals are not analytically integrable, one can compute them by a Monte Carlo method, introducing however another source of uncertainty in the final coefficients.

A point worth noting here is that our method requires only the ratios between the b_i and not their absolute magnitude. Since the b_i are estimated using the same random walk, we are implicitly using a sort of correlated sampling[7] : this reduces the length of the walk required to get meaningful values of the coefficients.

The *Importance Sampling* technique[8] is often used in QMC simulations to improve the convergence of the energy estimator; in this case the QMC method samples the distribution $\phi(\mathbf{R})\Psi_G(\mathbf{R})$, where $\Psi_G(\mathbf{R})$ is a guiding function, and the estimate of the b_i must be modified as follows

$$b_i \cong \frac{1}{M}\sum_{i=1}^{M}\frac{\chi_i(\mathbf{R}_i)}{\Psi_G(\mathbf{R}_i)} \tag{8}$$

The guiding function usually employed mimics the exact wavefunction since this choice accelerates the convergence of the energy. This choice decreases the sampling of the regions where the wavefunction is small, but these are of little interest when computing the energy. Some of the basis functions used in the fitting process might be large where the exact wavefunction is small: as a consequence the convergence of the corresponding overlap integrals might be slow. The introduction of standard importance sampling could slow down even more the convergence, at the same time accelerating the convergence of the b_i of those basis functions whose overlap integral with the guiding function is large. Since the basis functions may have very different shapes, it is not possible to find a single guiding function that helps the convergence of all the integrals.

The optimization of nonlinear parameters, for example exponents in the basis functions, requires a slightly different formulation. Let $\Psi(\mathbf{R}|\mathbf{c})$ be a normalized trial wavefunction, where $\mathbf{c}$ represents the vector of adjustable parameters. The problem

$$\min_{\mathbf{c}} \int (\phi(\mathbf{R}) - \Psi(\mathbf{R}|\mathbf{c}))^2 d\mathbf{R} \tag{9}$$

is equivalent to the minimization of

$$\int \Psi^2(\mathbf{R}|\mathbf{c}) d\mathbf{R} - 2\int \phi(\mathbf{R})\Psi(\mathbf{R}|\mathbf{c}) d\mathbf{R} \tag{10}$$

since the normalization integral of the exact wavefunction does not depend on $\mathbf{c}$.

Having computed the overlap integrals over the basis set, a QMC estimate of Eq. 10 is available at each step of the simulation, so it is possible to set up a nonlinear optimization process similar to the ones used by other authors[3,5]. The quantity computed using Eq. 10 varies slightly on changing the non linear parameters of the trial wavefunction: so its minimization is more difficult than other expectation values, for example the variance of the local energy. Instead of using a small number of walkers, like

in similar minimization processes, to get an accurate estimate of Eq. 10 we were forced either to use larger sets (10000 walkers) or to compute average values of the integrals by short QMC simulations. A non linear parameter can be easily optimized interpolating values of Eq. 10 computed by correlated sampling in a single simulation. To optimize many non linear parameters one could adopt a multi dimensional minimization algorithm. In this work we checked the feasibility of the algorithm only on the helium ground state trial wavefunction, having one non linear parameter.

If we impose the normalization of the trial wavefunction (a condition that is not required for the existence of the minimum of Eq. 3) the problem is equivalent to

$$\max_{\mathbf{c}} \int \phi(\mathbf{R})\Psi(\mathbf{R}|\mathbf{c})d\mathbf{R} \tag{11}$$

so the minimization of the total square deviation (Eq. 3) is equivalent to the maximization of the overlap between the exact wavefunction and the normalized trial function.

3. Weighted least squares (WLSQ)

Given a basis set of finite size, it is obviously impossible to accurately reproduce the wavefunction sampled by the QMC process in every region of space. We can improve the approximate description of the exact wavefunction in some region of space only at the expense of the description in some other region. It is easy to modify the least squares procedure to increase the quality of the description in some region of interest. This can be useful if one is interested in a particular feature of the wavefunction, like the tails or the region around the nuclei. To do so, it is sufficient to include an appropriate weight in the total square deviation

$$q^2(\mathbf{c}) = \int w(\mathbf{R})(\phi(\mathbf{R}) - \Psi(\mathbf{R}|\mathbf{c}))^2 d\mathbf{R} \tag{12}$$

Following the derivation of Eq. 5 it is easy to show that now **S** is the weighted overlap matrix (i.e. $S_{ij} = \int w(\mathbf{R})\chi_i(\mathbf{R})\chi_j(\mathbf{R})d\mathbf{R}$) and **b** is the vector of the weighted overlaps between the exact wavefunction and the basis functions

$$b_i = \int w(\mathbf{R})\phi(\mathbf{R})\chi_i(\mathbf{R})d\mathbf{R} \tag{13}$$

The weight can be a function that selects only a region of space (i.e. 1 for points inside the region and 0 outside) or can be a function that weights different regions of space differently.

4. Comparing the variational and the least squares wavefunction

It is interesting to investigate the connection between the LSQ wavefunction and a variationally optimized wavefunction with the same basis.

Since we optimize our trial wavefunction using a least squares fitting procedure, the resulting wavefunction will be equal to the variational one only if we use a complete basis set, in which case both methods give the exact wavefunction. In practice we can work only with incomplete basis sets, so the LSQ wavefunction and the variational wavefunction will differ. For a given basis we might wonder how much the LSQ wavefunction is different from the variational wavefunction. Eckart[9] derived a formula relating the total square deviation q^2 to the variational energy $\langle H \rangle$. Expanding the trial wavefunction in series of the eigenfunctions of the Hamiltonian, it can be shown that

$$q^2 - \frac{q^4}{4} = \left(\langle H \rangle - E_0\right)\left(\frac{\sum_{i=1}^{\infty} a_i^2 E_i}{\sum_{i=1}^{\infty} a_i^2} - E_0\right)^{-1} \tag{14}$$

where E_i is the energy of the i-th state of the same symmetry as the ground state.

If the basis is flexible enough, the total square deviation is small and so $q^4 << q^2$; if also the contaminations from high-lying states can be neglected, the above equation can be approximated by

$$q^2 \cong \frac{\langle H \rangle - E_0}{E_1 - E_0} \tag{15}$$

So for good basis functions the minimization of the total square deviation is almost equivalent to the minimization of the expectation value of the energy: in conclusion we can expect the LSQ wavefunction to be similar to the variational one, and their energies and properties to be comparable.

The LSQ wavefunction does not automatically satisfy the virial theorem. If for some reasons one needs a trial wavefunction with the correct virial, the same procedure used for

the variational wavefunctions, i.e. scaling of all the coefficients including the nonlinear ones[10], can be applied, at least for atomic wavefunctions. Since the scaling procedure is equivalent to the minimization of the energy with respect to the scaling parameter, it is interesting to note that the application of this procedure to a LSQ wavefunction can be seen as a mixing of the variational and the LSQ methods.

5. Calculations

The Monte Carlo process might be unable to correctly sample the exact wavefunction for the presence of some bias, like the *time step bias*, caused by the use of a finite time step in DMC simulations: consequently the fitted wavefunction and its expectation values might be affected.

All the simulations reported in this paper are affected by a small time step bias; it is possible to eliminate it, either by using an extrapolation scheme[11] or by using a different simulation method[12,13,14]. We did not do so since the time steps employed were very small and the time step bias should be negligible enough for the purposes of this paper, i.e. to show the capabilities of the LSQ algorithm.

In the following we report examples of the application of the method to a model problem and to atomic and molecular systems. All the simulations were stopped after having checked that the b_i integrals had converged and their variance was 3-4 orders of magnitude smaller than the b_i values.

5.1. Particle in the box

We used the ground state of the particle in the box as a test of our algorithm. Since this is a one dimensional model, we can compare the fitted wavefunction and its properties with the sampled wavefunction, which can be accumulated during the simulation by using a grid with a sufficiently small mesh.

The DMC simulation of the ground state of a particle of unitary mass in a box was performed using 1000 walkers, 1000 blocks, 1000 steps long and a time step of 0.001 hartree^{-1}. The position of the particle was restricted to the interval [-1,+1], which was divided into boxes 0.001 bohr long to accumulate a numerical representation of the exact wavefunction. The bias introduced by the presence of the nodes was eliminated as shown

by Anderson[15]. As trial wavefunction we chose a linear combination of orthogonal polynomials $P_{2k}(x)$ of even order, with boundary conditions $P_{2k}(-1)=P_{2k}(+1)=0$

$$\Psi_N(\mathbf{R}) = \sum_{k=1}^{N} a_{2k} P_{2k}(x) \tag{16}$$

Table 1 lists some expectation values of $\Psi_1(\mathbf{R})$ and $\Psi_2(\mathbf{R})$, the first two approximations, along with values computed using the numerical wavefunction accumulated during the simulation.

Table 1. Particle in the box: energy and distribution moments computed using two successive least square fit approximations, Ψ_1 and Ψ_2, and the numerical QMC wavefunction.

property	Ψ_1	Ψ_2	QMC	exact
E	1.2500	1.2337	1.2337	1.2337
$\langle x^2 \rangle$	0.1429	0.1307	0.1307	0.1307
$\langle x^4 \rangle$	0.0476	0.0411	0.0411	0.0411
$\langle x^6 \rangle$	0.0217	0.0179	0.0179	0.0179

The values computed by numerical integration coincide with the exact ones to four decimal digits; this means that the time step bias and the effect of the grid discretization are very small and only affect the successive digits. As to the least squares fitted wavefunctions, the first approximating polynomial $\Psi_1(\mathbf{R})$, a polynomial of degree 2, gives rough estimates of the expectation values, the error percent increasing from 9% for $\langle x^2 \rangle$ to 21% for $\langle x^6 \rangle$. $\Psi_2(\mathbf{R})$, a sum of polynomials of degree 2 and 4, gives expectation values which agree with the exact ones to four decimal digits, and identical to those computed using the numerical wavefunction. This means that the fitting algorithm is able to accurately reconstruct the sampled wavefunction: as expected the quality of the results depends on the basis set, for the particle in the box the convergence of polynomials of even order is very fast.

5.2. He 1^1S

The problem of describing the ground state the helium atom with high-quality wavefunctions is an old one, dating back to the early days of quantum mechanics with the pioneering work done by Hylleraas[16]. Still today the calculation of a good wavefunction for the helium atom is not a trivial task. On the other hand, the simulation of the ground state of the helium atom can be done quickly and efficiently using a QMC method, so this problem is a good model to investigate the proposed algorithm on a real system.

In a previous paper[17] we fitted the QMC sampled wavefunction using a trial wavefunction for the ground state of the helium atom built from Slater type orbitals, and an Hylleraas type wavefunction using a basis set optimized by Koga[18]. The general form of the Hylleraas wavefunction is

$$\Psi_k(\mathbf{R}|\mathbf{c}) = e^{-\gamma s}\sum_{i=1}^{k} c_i s^{n_i} t^{2l_i} u^{m_i} \tag{17}$$

where $s=r_1+r_2$, $t=r_1-r_2$ and $u=r_{12}$. r_1 and r_2 are the electron-nucleus distances, while r_{12} is the interelectronic distance.

Here we extend our previous study reporting the results obtained using two different trial wavefunctions, to show the effect of improving the basis set, and of different optimization schemes.

5.2.1. Six-term Hylleraas wavefunction

We performed a DMC simulation of the ground state of the Helium atom using 6000 walkers, 1800 blocks 2000 steps long, and a time step of 0.001 hartree^{-1}.
We fitted the sampled wavefunction with a six terms Hylleraas type function[19]:

$$\Psi(\mathbf{R}|\mathbf{c}) = e^{-\gamma s}(c_0 + c_1 s + c_2 u + c_3 t^2 + c_4 s^2 + c_5 u^2) \qquad \gamma = 1.755656 \tag{18}$$

For comparison purposes we also computed the best variational function minimizing the expectation value of the energy. Some properties of the two functions are listed in Table 2.

Table 2. Helium ground state: properties computed by the variational and various LSQ wavefunctions using a Hylleraas six terms basis.

property	variational	LSQ fitting	NLSQ fitting	WLSQ fitting	exact[20]
$\langle E \rangle$	-2.9033	-2.9032	-2.9033	-2.9033	-2.9037
$\langle T \rangle$	2.9033	2.8864	2.8995	2.9009	2.9037
$\langle V \rangle$	-5.8067	-5.7896	-5.8028	-5.8041	-5.8074
$\langle r_{12}^{-2} \rangle$	1.4739	1.4767	1.4834	1.4676	1.4648
$\langle r_{12}^{-1} \rangle$	0.9460	0.9448	0.9473	0.9450	0.9458
$\langle r_{12} \rangle$	1.4219	1.4270	1.4228	1.4218	1.4221
$\langle r_{12}^{2} \rangle$	2.5111	2.5328	2.5177	2.5090	2.5164
$\langle r_1^{-1} + r_2^{-1} \rangle$	3.3764	3.3672	3.3750	3.3746	3.3766
$\langle r_1 + r_2 \rangle$	1.8592	1.8650	1.8594	1.8618	1.8589
$\langle r_1^2 + r_2^2 \rangle$	2.3871	2.4036	2.3884	2.3952	2.3870
$\langle \nabla_1 \cdot \nabla_2 \rangle$	-0.1632	-0.1629	-0.1653	-0.1540	-0.1591
$\langle \delta(r_1) \rangle$	1.8061	1.7899	1.7973	1.8095	1.8104
$\langle \delta(r_{12}) \rangle$	0.1120	0.1144	0.1148	0.1104	0.1063
A	1.9015	1.8763	1.8815	1.9078	2
B	0.3373	0.3058	0.3098	0.3508	0.5
$\langle T \rangle / \langle V \rangle$	-0.5	-0.4985	-0.4997	-0.4998	-0.5

In Table 2 and in Table 4, A and B refer to the first and the second term of the Fock expansion[21] $\Psi = 1 - A(r_1 + r_2) + B\, r_{12} + \ldots$

As expected, the energy of the variational wavefunction is better than the energy of the least squares wavefunction, but the difference is very small. The same can be said for the other properties: the differences between values computed by the LSQ wavefunction and the variational one are small. The relative errors with respect to the exact values are usually less than 1%. It should be pointed out that the exponent and the six terms of the Hylleraas basis set were explicitly optimized to get a good energy, not to fit the exact wavefunction.

To exploit the full flexibility of the basis set, and to test the capability of our algorithm to optimize non linear parameters, we optimized the exponent of the Hylleraas basis in a short simulation.

Using the optimized exponent 1.749452 we performed a longer simulation, 2050 blocks each 1000 steps long, using 6000 walkers and a time step of 0.001 hartree^{-1}.

The results of NLSQ column of Table 2 show that the exponent optimization improved all the properties, with the exception of $\langle r_{12}^{-2} \rangle$, $\langle r_{12}^{-1} \rangle$, $\delta(r_{12})$, and $\langle \nabla_1 \cdot \nabla_2 \rangle$. The properties whose improvement is larger are those requiring a good description of the regions of configuration space where electrons and nucleus are distant and as a consequence also the electrons are far from each other.

The tendency of the algorithm to improve the description of the tails of the wavefunction is confirmed by the decreasing of the exponent from 1.755656 to 1.749452, leading to a more diffuse wavefunction.

A tentative explanation of this fact could be that the least square optimization gives the same importance to all the points of the space, while the variational principle weights more the points where the wavefunction is large. As a result, the LSQ wavefunction describes slightly better the tails of the wavefunction, while the variational wavefunction gives a slightly better description near the nucleus.

To explore the ability of the algorithm to increase the quality of the approximation of the exact wavefunction in a particular region of space, we performed the fitting using a weight function, trying to describe best the region around the nucleus.

We used as weight function $w(\mathbf{R}) = e^{-\gamma(r_1+r_2)}$, $\gamma = 1.6875$, which is the best variational approximation using only the first term in the Hylleraas expansion. This choice was completely arbitrary: the only purpose of this simulation is to show the effect of giving more importance to the region around the nucleus, mimicking the effect of the variational method.

The DMC simulation of the ground state of the helium atom used 6000 walkers, 3150 blocks 1000 steps long, and a time step of 0.001 hartree^{-1}.

Comparing the observables in Table 2, we see that on going from the LSQ wavefunction to the weighted LSQ wavefunction (WLSQ), both the potential and the kinetic energy show an improvement, as well as the other properties representative of the region around the nucleus. The WLSQ wavefunction tries to give a better description of the region of the six-dimensional configuration space where the two electrons are close to the nucleus and so, indirectly, where they are close to each other. It is no surprise that this function gives property estimates similar to those of the variational wavefunction, and some even better, such as $\langle r_{12}^{-2} \rangle$, $\langle \delta(r_1) \rangle$, $\langle \delta(r_{12}) \rangle$ and the first two terms of the Fock

expansion around the nucleus. It appears that the chosen weighting function stresses the importance of the region near the nucleus even more that the variational method. The similarity between the WLSQ wavefunction and the variational one is evidenced in Table 3: it shows that the WLSQ coefficients are roughly closer to those of the variational wavefunction, than to those of the LSQ wavefunction.

Table 3. Normalized coefficients of the Hylleraas six terms wavefunction optimized using the variational, the linear least squares and the weighted least squares methods.

function	c_0	c_1	c_2	c_3	c_4	c_5
variational	1.380852	0.465753	0.155373	-0.201431	0.032636	-0.051125
LSQ fitting	1.371140	0.419364	0.157069	-0.165386	0.024964	-0.035435
WLSQ fitting	1.373280	0.481765	0.162060	-0.209023	0.037970	-0.061960

5.2.2. Twenty terms Hylleraas wavefunction

To see how the improvement of the basis set affects the quality of the LSQ fitting, and consequently of the expectation values, we performed a simulation using 20000 walkers, 2100 blocks 1000 steps long, and a time step of 0.001 hartree^{-1}: we fitted the sampled wavefunction using an Hylleraas basis set with 20 terms[22]. The expectation values of the resulting wavefunction and the exact values are showed in Table 4.

As expected the extension of the basis set improves the accuracy of the computed properties with the exception of $\langle r_{12}^{-1} \rangle$, but the convergence towards the exact values is slow. A comparison with the NLSQ fitting values evidences that the optimization of just one non linear parameter improves the results better than the addition of 14 more terms in the expansion.

Table 4. Helium ground state: properties computed with the LSQ wavefunction using a Hylleraas 20 terms basis.

property	LSQ fitting	exact[20]
$\langle E \rangle$	-2.9037	-2.9037
$\langle T \rangle$	2.8997	2.9037
$\langle V \rangle$	-5.8034	-5.8074
$\langle r_{12}^{-2} \rangle$	1.4606	1.4648
$\langle r_{12}^{-1} \rangle$	0.9443	0.9458
$\langle r_{12} \rangle$	1.4241	1.4221
$\langle r_{12}^{2} \rangle$	2.5235	2.5164
$\langle r_1^{-1} + r_2^{-1} \rangle$	3.3739	3.3766
$\langle r_1 + r_2 \rangle$	1.8613	1.8589
$\langle r_1^2 + r_2^2 \rangle$	2.3940	2.3870
$\langle \nabla_1 \cdot \nabla_2 \rangle$	-0.1585	-0.1591
$\langle \delta(r_1) \rangle$	1.8143	1.8104
$\langle \delta(r_{12}) \rangle$	0.1067	0.1063
A	1.9329	2
B	0.4061	0.5
$\langle T \rangle / \langle V \rangle$	-0.4996	-0.5

The use of the fitted wavefunction to compute properties, a shortcut one might be tempted to use to avoid the problem of sampling $\phi^2(\mathbf{R})$, a difficult task in QMC, cannot be tackled without very large basis sets and the optimization of both linear and non linear parameters.

5.3. He 1^3S

To test the method in presence of a nodal surface we performed a DMC simulation of the first triplet state of the helium atom using 10000 walkers, 1900 blocks 1000 steps long ,and a time step of 0.001 hartree^{-1}. The exact nodal surface $r_1 = r_2$ was assumed as absorbing boundary. It should be noted that the presence of a nodal surface introduces

another small bias in the simulation[23]. The sampled wavefunction was fitted using an explicitly correlated 6 terms trial wavefunction of the type

$$\Psi = (1 - P_{12}) \sum_k a_k r_1^{l_k} r_2^{m_k} r_{12}^{n_k} e^{-\alpha r_1 - \beta r_2} \tag{19}$$

where P_{12} is the permutation operator. This trial wavefunction has the correct nodal structure.

The exponential parameters were optimized variationally (α = 2.1018, β = 0.605): they were kept fixed during the fitting process. Table 5 shows some observables computed using the fitted wavefunctions along with the exact values.

Table 5. Helium first triplet state: properties computed with the LSQ wavefunction using the basis showed in the text.

property	LSQ fitting	exact[20]
$\langle E \rangle$	-2.1751	-2.1752
$\langle T \rangle$	2.1890	2.1752
$\langle V \rangle$	-4.3642	-4.3505
$\langle r_{12}^{-1} \rangle$	0.2682	0.2682
$\langle r_{12} \rangle$	4.4503	4.4475
$\langle r_{12}^2 \rangle$	23.065	23.046
$\langle r_1^{-1} + r_2^{-1} \rangle$	2.3162	2.3093
$\langle r_1 + r_2 \rangle$	5.1016	5.1009
$\langle r_1^2 + r_2^2 \rangle$	22.945	22.929
$\langle \nabla_1 \cdot \nabla_2 \rangle$	-0.0077	-0.0074
$\langle \delta(r_1) \rangle$	1.3337	1.3204
$\langle T \rangle / \langle V \rangle$	-0.5016	-0.5

The agreement with the exact values is similar to the one found for the singlet state, in particular the errors percent are of the same order of magnitude found for the ground state with the NLSQ wavefunction. We remark again that this good behaviour only partially depends on the flexibility of the trial wavefunction (a SCF like trial wavefunction would have given a much worse agreement), but mainly on the ability of the algorithm to

evenly weight the space: in fact the use of a different optimization criterion, the minimization of the variance functional in a Variational Monte Carlo calculation, gave a worse agreement in spite of the use of 34 terms in the basis set[24].

5.4. $H_2\ X\ ^1\sum_g^+$

We investigated the performance of the LSQ fitting procedure in the case of a molecule with a DMC simulation of the ground state of the hydrogen molecule at the nuclear distance of 1.4 bohr; we used 20000 walkers, 3400 blocks 1000 steps long and a time step of 0.001 hartree^{-1}. The sampled wavefunction was fitted using an explicitly correlated 24 terms trial wavefunction of James-Coolidge type[25]. The exponential parameter was not optimized, but fixed to 0.95[26]. Table 6 shows some observables computed from the LSQ wavefunction, along with the exact values.

Table 6. Hydrogen molecule ground state (R=1.4 bohr): properties computed with the LSQ wavefunction.

property	LSQ fitting	exact[27]
$\langle E \rangle$	-1.1743	-1.1745
$\langle T \rangle$	1.1739	1.1750
$\langle V \rangle$	-2.3482	-2.3495
$\langle r_{12}^{-1} \rangle$	0.5879	0.5874
$\langle r_{1A}^{-1} \rangle$	0.9126	0.9128
$\langle r_{1A} \rangle$	1.5489	1.5488
$\langle r_{1A}^{2} \rangle$	3.0368	3.0364
$\langle r_{1A} r_{1B} \rangle$	2.7041	2.7039
$\langle r_{1A} r_{2A} \rangle$	2.3208	2.3214
$\langle r_{1A} r_{2B} \rangle$	2.3841	2.3848
$\langle \delta(r_{12}) \rangle$	0.0181	0.0169
$\langle \delta(r_{1A}) \rangle$	0.2281	0.2300
$\langle T \rangle / \langle V \rangle$	-0.5001	-0.5001

The computed values are in very good agreement with the exact results and show once again that the LSQ fitting procedure is capable of extracting high quality wavefunctions from QMC simulations.

6. Conclusions

We have shown how the information on the exact wavefunction, gathered by a QMC simulation, can be stored in an approximate analytical wavefunction, whose linear and non linear parameters can be optimized by a least squares criterion. The shape of the trial wavefunction, rather than the energy, is optimized, leading to wavefunctions with energy and properties similar to those of the variational wavefunction with the same basis set. Comparisons of some expectation values of LSQ wavefunctions with the exact values confirm that the quality of the wavefunctions obtained by the least squares process is very good, in the limit of the flexibility of the basis function.

The only limitation that the method poses to the choice of the basis set is the ability to compute the overlap integrals over the basis functions. No integrals involving the Hamiltonian, usually much more difficult to compute than the overlap integrals, are required.

This method can be useful, within the frame of a QMC program, to reconstruct an analytical wavefunction by which to compute properties difficult or impossible to compute directly from the sampled wavefunction, notably operators involving differentiation or integration.

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