

Explicitly correlated trial wavefunctions in quantum Monte Carlo calculations of excited states of Be and Be⁻

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Abstract

We present a new form of explicitly correlated wavefunction whose parameters are mainly linear, to circumvent the problem of the optimization of a large number of nonlinear parameters usually encountered with basis sets of explicitly correlated wavefunctions. With this trial wavefunction we have succeeded in minimizing the energy instead of the variance of the local energy, as is more common in quantum Monte Carlo methods. We have applied this wavefunction to the calculation of the energies of Be ³P (1s²2p²) and Be⁻ ⁴S^o (1s²2p³) by variational and diffusion Monte Carlo methods. The results compare favourably with those obtained by different types of explicitly correlated trial wavefunction already described in the literature. The energies obtained are improved with respect to the best variational ones found in the literature, and within one standard deviation of the estimated non-relativistic limits.

1. Introduction

The description of the electron correlation plays a central role in highly accurate quantum chemistry calculations. Mean-field methods give a qualitative description for many atomic and molecular systems, but in order to obtain quantitative results the instantaneous correlation between electrons must be taken into account. The most common way to include correlation is, starting from the Hartree–Fock picture, to approximate the exact wavefunction using MC-SCF or CI expansions. Unfortunately methods based on the orbital approximation converge very slowly to the non-relativistic limit (NRL). The reason is that these wavefunctions include the interelectronic distances only in an implicit form. Furthermore this implicit dependence is quadratic instead of linear, so the cusp conditions [1] of the exact wavefunctions are reproduced only for infinite expansions.

A very efficient and effective approach to accurately describe the local behaviour of the wavefunction when two electrons collide is the explicit inclusion of the interelectronic distances into an approximate wavefunction. Hylleraas [2], Pekeris [3], James and Coolidge [4] and Kolos and Wolniewicz [5–7] showed how to obtain very accurate results for two-electron systems by including the interelectronic distance in the wavefunction. An alternative possibility is the construction of many-particle permutational symmetry-adapted functions in hyperspherical coordinates [8, 9]. Unfortunately it is not easy to generalize these methods to many-electron systems since the resulting integrals are extremely difficult to evaluate analytically. Beyond four-electron systems, with at most two nuclei, the analytical approach becomes almost unfeasible [10, 11].

Instead of computing the integrals analytically, one could resort to a numerical method. The variational Monte Carlo (VMC) method [12, 13] is a very powerful numerical technique that estimates the energy, and all the desired properties, of a given trial wavefunction without any need to analytically compute the matrix elements. For this reason it poses no restriction on the functional form of the trial wavefunction, requiring only the evaluation of the wavefunction value, its gradient and its Laplacian, and these are easily computed. Using the VMC algorithm, essentially a stochastic numerical integration scheme, the expectation value of the energy for any form of the trial wavefunction can be estimated by averaging the local energy $\hat{H}\Psi_T(\mathbf{R})/\Psi_T(\mathbf{R})$ over an ensemble of configurations distributed as Ψ_T^2 , sampled during a random walk in the configuration space using Metropolis [14] or Langevin algorithms [15]. The fluctuations of the local energy depend on the quality of the function Ψ_T , and they are zero if the exact wavefunction is used (zero-variance principle). VMC can also be used to optimize the trial wavefunction Ψ_T , and we refer the reader to the literature for the technical details.

A popular and effective approach to building compact explicitly correlated wavefunctions is to multiply a determinantal wavefunction by a correlation factor, the most commonly used being a Jastrow factor [16]. The inclusion of the Jastrow factor does not allow the analytical evaluation of the integrals, so the use of VMC is mandatory. However, departing from the usual determinantal wavefunction form can be very fruitful [11], allowing an accurate and, at the same time, compact description of atomic and molecular systems. Very few terms are needed to reach a good accuracy, in comparison to more common wavefunction forms.

The recovery of the remaining correlation energy can be achieved using the diffusion Monte Carlo (DMC) method. Since this method is already well described in the literature, we refer the reader to the available reviews [12, 13]. We only recall here that in this method the exact, but unknown, wavefunction is interpreted as a probability density. In the fixed-node (FN) approximation [17] the nodal surfaces of the trial wavefunction Ψ_T are used to partition the space and within each region the wavefunction can be safely interpreted as a probability density. It can be shown that the FN-DMC energies are an upper bound to the exact ground state energy.

This paper is part of an ongoing project in our laboratory to develop accurate and compact wavefunctions for few-electron systems.

In our previous works [11, 18, 19] we used linear expansions of explicitly correlated wavefunctions for calculations on the ground state of few-electron systems. In all cases good VMC energies were obtained, both in infinite-nuclear-mass approximation calculations and non-adiabatic calculations. In particular we used a linear expansion of explicitly correlated exponential functions to develop accurate wavefunctions for two test systems: the beryllium atom and the lithium hydride molecule in their ground state.

Here we present a new form of explicitly correlated wavefunction and we use VMC to extend the application of a correlated trial wavefunction to excited states and five-electron systems. Furthermore we use DMC to approximate the exact energies and compare them with the estimated NRL.

We choose the Be 3P ($1s^2 2p^2$) and Be $^{-4}S^o$ ($1s^2 2p^3$) states which are involved in beryllium electron affinity determination. We compare VMC and DMC energies and variances of the energy and examine the nodal properties of the trial wavefunctions comparing FN-DMC results with the best variational calculations and the NRL estimated by Chung and coworkers [20, 21].

2. Explicitly correlated functional form

For an N -electron atomic system we write an explicitly correlated trial wavefunction [11] as

$$\Psi = \hat{A}\{f(\mathbf{r})\phi g \Theta_{S, M_s}^N\}. \quad (1)$$

In this equation \hat{A} is the antisymmetrizer operator, ϕ is a function of all the electron–nucleus distances and g is a function of all the electron–electron distances called a correlation factor. Both functions include variational parameters. Θ_{S, M_s}^N is an eigenfunction of the spin operators \hat{S}^2 and \hat{S}_z of the correct spin multiplicity. The functions ϕ and g , being dependent only on interparticle distances, are rotationally invariant. This means that their product can describe only S states, with zero angular momentum. To describe higher-angular-momentum states, it is necessary to include a function $f(\mathbf{r})$ with the correct rotational symmetry. $f(\mathbf{r})$ is a function of the Cartesian electronic coordinates (x, y, z) , but might include also the electron–nucleus distances [11]. This Ψ function might be generalized including products of the interparticle distances, that is Ψ is the two-body term of a many-body expansion of the wavefunction. It is possible to further generalize the wavefunction by taking linear combinations of such terms.

To assure a high-quality wavefunction it is particularly important that the function Ψ satisfy the cusp conditions [1], representing the behaviour of the exact wavefunction at the coalescence of two particles. It is also important to take into account the asymptotic conditions [22], which represent the behaviour when one of the particles goes to infinity.

The first type of functional form we examined is generated assuming a Padé factor $\exp[(ar + br^2)/(1 + cr)]$ for the electron–nucleus part ϕ and a Jastrow factor $\exp[a'r/(1 + c'r)]$ for the interelectronic part g :

$$\Psi = \hat{A}\left\{f(\mathbf{r}) \exp\left[\sum_i \frac{ar_i + br_i^2}{1 + cr_i}\right] \exp\left[\sum_{i < j} \frac{a'r_{ij}}{1 + c'r_{ij}}\right] \Theta_{S, M_s}^{n_e}\right\}. \quad (2)$$

In the following this wavefunction will be called Padé–Jastrow. The Padé factor is a good choice for the electron–nucleus part, because it is the best compromise between flexibility and small number of parameters. In fact this function goes as e^{ar} for $r \rightarrow 0$ and $e^{(b/c)r}$ for $r \rightarrow \infty$, so with different exponents it can accommodate both the coalescence at the nucleus and the decay for large r . It is also important to point out that this factor can accurately describe both 1s and 2s orbitals as we have shown in our previous work [11].

The main problem with linear expansions of explicitly correlated trial wavefunctions is the huge number of nonlinear parameters to optimize. In our previous work [11] for more sophisticated factors such as Padé or Jastrow we succeeded in optimizing trial wavefunctions including a maximum of two terms.

To overcome this problem we choose a second type of functional form, similar to the first one:

$$\Psi = \hat{A}\left\{f(\mathbf{r}) G(\mathbf{r}) \exp\left[\sum_i \frac{ar_i + br_i^2}{1 + cr_i}\right] \exp\left[\sum_{i < j} \frac{a'r_{ij}}{1 + c'r_{ij}}\right] \Theta_{S, M_s}^{n_e}\right\}. \quad (3)$$

We limit the expansion to a single term and so we have few nonlinear parameters to optimize. However to add extra flexibility to the wavefunction we introduce a pre-exponential

factor $G(\mathbf{r})$ written as a sum of powers of interparticle distances weighted by linear parameters:

$$G(\mathbf{r}) = \sum_p \sum_i g_p r_i^{n_p} + \sum_q \sum_{i<j} g_q r_{ij}^{n_q} + \sum_r \sum_i \sum_{j>i} g_r r_i^{n_r} r_{ij}^{o_r} + \sum_s \sum_i \sum_j g_s r_i^{n_s} r_j^{m_s} + \dots \quad (4)$$

In the following we will call equation (3) the pre-exponential wavefunction (prex).

Even if this kind of wavefunction allows us to reduce the effort for the optimization of the parameters, we recall that the CPU time needed to evaluate explicitly correlated trial wavefunctions is very large and proportional to the number of permutations generated by the antisymmetrizer. No matter what form we choose for explicitly correlated wavefunctions, they are limited to few-electron systems.

In this paper we also compare Padé–Jastrow and pre-exponential wavefunctions with a more standard form, widely used in QMC calculations [23, 24], that is the product of a determinantal function multiplied by the Schmidt–Moskowitz (SM) [25] correlation factor:

$$\Psi = \sum_l C_l \text{Det}_l^\uparrow \text{Det}_l^\downarrow \exp \left[\sum_{i<j} U_{ij}(r_i, r_j, r_{ij}) \right]. \quad (5)$$

Det^\uparrow and Det^\downarrow are the determinants for α and β electrons. The function U for atoms is given by

$$U_{ij} = \sum_k \Delta(m_k, n_k) c_k (\bar{r}_i^{m_k} \bar{r}_j^{n_k} + \bar{r}_j^{m_k} \bar{r}_i^{n_k}) \bar{r}_{ij}^{o_k} \quad (6)$$

where c_k are trial parameters and $\bar{r} = ar/(1+br)$.

The determinants are generated from *ab initio* calculations, in general SCF or MCSCF calculations, for a given basis set. Then the correlation factor is added, and its variational parameters optimized using VMC calculations.

3. Optimization of the trial wavefunctions

Our previous work [11] showed that departing from the usual determinantal wavefunction form can be very fruitful, allowing us to write very compact and at the same time very accurate wavefunctions. However it is computationally much more demanding and for this reason special care must be given to the design of an efficient method of generating and optimizing the trial wavefunction. These steps must be implemented in the most effective, fast and efficient way. The standard way to optimize a trial wavefunction using VMC is to minimize the variance of the local energy using a fixed sample of walkers; a method proposed by Frost [26] and Conroy [27] and described in detail by Umrigar *et al* [28] and by Mushinsky and Nightingale [29]. This has been proved to be numerically much more stable than the energy minimization. For our trial wavefunctions we have found very effective the minimization of the variance of the energy

$$\sigma^2(\hat{H}) = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 \quad (7)$$

or, even better, of the second moment with respect to an arbitrary parameter E_R , $\mu(E_R)$:

$$\mu(E_R) = \langle (\hat{H} - E_R)^2 \rangle = \sigma^2(\hat{H}) + \langle (\hat{H} - E_R) \rangle^2 \quad (8)$$

where the parameter E_R can be set equal to the exact energy of the system E_0 . Both $\sigma(H)$ and $\mu(E_0)$ go to zero as $\Psi_T \rightarrow \Psi_0$, where Ψ_0 is the exact eigenfunction: their values for a given trial wavefunction Ψ_T can be used to evaluate the quality of the trial wavefunction Ψ_T .

We used $\mu(E_R)$ as a cost function for the optimization of both Padé–Jastrow and SCF-MS wavefunctions.

Table 1. VMC results for the Be ground state (where prex denotes pre-exponential).

	VMC energy (Hartree)	% Correlation energy
One-term Padé–Jastrow	−14.652 8(2)	84.57
66-term prex	−14.663 3(3)	95.70
86-term prex	−14.665 1(2)	97.60
HF limit	−14.573 02	
NR limit	−14.667 35	

As to equation (2), the optimization of the first term of the expansion is usually performed starting from a trial wavefunction with a reasonable electron–electron Jastrow factor, and with the electron–nucleus functions from some standard Slater orbital basis set, or from small basis sets optimized at the SCF level. As we showed in our previous work [11], it is possible to build a trial wavefunction as a linear expansion of n terms by adding an extra term to an optimized $(n - 1)$ -term wavefunction. This procedure worked well for two- and three-electron systems with simple exponential basis sets, but not for more sophisticated Padé and Jastrow basis sets. For these reasons in this paper we optimized only one-term Padé–Jastrow functions.

Let us now consider the case of the pre-exponential trial wavefunction. The function in equation (3) can be written as a linear combination:

$$\Psi = \sum_{l=1} g_l \Phi_l \quad (9)$$

where the term Φ_l is given by

$$\Phi_l = [r_i^p \dots r_{ij}^m \dots] \Phi(\mathbf{p}). \quad (10)$$

$\Phi(\mathbf{p})$ is a single-term Padé–Jastrow function whose parameters \mathbf{p} are optimized, minimizing $\mu(E_R)$ in a preliminary step, and then are fixed during the optimization of the linear parameters.

As to the linear parameters, we succeeded in minimizing the energy instead of the variance of the local energy or the second moment $\mu(E_R)$, so we could choose the best linear parameters according to the observable we are interested in. The standard linear variational methods require the solution of the secular problem, and so the calculation of the matrix elements

$$\begin{aligned} H_{ij} &= \int \Phi_i \hat{H} \Phi_j \, d\mathbf{R} \\ S_{ij} &= \int \Phi_i \Phi_j \, d\mathbf{R}. \end{aligned} \quad (11)$$

These integrals are evaluated during a VMC simulation.

We show the main features of this pre-exponential trial wavefunction using as benchmarks the Be and Li ground states.

In table 1 we compare the energy for the Be 1S_0 ground state obtained by the one-term Padé–Jastrow function with the value calculated by the function obtained adding a pre-exponential including all the electron–nucleus and electron–electron distances and their products, a total of 66 terms. The two values evidence a large gain of correlation energy for the addition of the pre-exponential factor and further improvement is obtained adding 20 more terms, that is the third and fourth powers of the electron–nucleus and electron–electron distances, to the linear expansion. Thus the pre-exponential factor adds flexibility to the wavefunction in a very efficient way.

To examine the relative efficiency of linear and nonlinear parameters in adding flexibility to the wavefunction, for the Li ground state (see table 2) we compare the energy of a 28-term pre-exponential function with the result of a eight-term expansion of explicitly correlated

Table 2. VMC results for the Li ground state (where prex denotes pre-exponential and exp. exponential).

	VMC energy (Hartree)	% Correlation energy
8-term exp.	-7.477 5(2)	98.29
28-term prex	-7.477 70(8)	99.20
HF limit	-7.432 74	
NR limit	-7.478 06	

Table 3. Basis sets for SCF and CASSCF calculations.

System	Be ³ P	Be ⁻ ⁴ S ^o
1s	5.7	5.7
1s	4.2	4.2
2s	4.3	4.3
2s	2.4	2.4
2p	1.65	1.65
2p	0.76	0.76
2p		0.376

exponential functions, a simplified form of the Padé–Jastrow wavefunction in which both the factor ϕ and the correlation factor g are in the form $\exp(cr)$. These two trial wavefunctions give a similar gain of correlation energy, but in the pre-exponential case there are 12 nonlinear and 28 linear parameters, while the eight-term expansion of correlated exponential functions includes 48 nonlinear and eight linear parameters. In spite of the smaller number of parameters the pre-exponential function gives a better result, and its optimization process was much easier and faster.

We optimized the linear parameters also by minimization of $\mu(E_R)$. The calculated energy at the VMC level is worse than that obtained by minimization of the energy: this is obviously related to the different minima of the energy and $\mu(E_R)$.

4. Results and discussion

For Be ³P ($1s^2 2p^2$) and Be⁻ ⁴S^o ($1s^2 2p^3$) we computed SCF and CASSCF trial wavefunctions using GAMESS with the Slater orbital basis sets reported in table 3. Each orbital was fitted with six Gaussian functions. We optimized the SM correlation factor of the SCF-SM functions and the nonlinear parameters of the Padé–Jastrow and pre-exponential functions minimizing the variance of the local energy.

Beside the VMC energies, we report the variance of the local energy, given by equation (7), estimated using VMC. DMC energies were obtained by a linear fit of the energy at three time steps ($\tau = 5, 3,$ and 1 mHartree⁻¹) and extrapolation to $\tau = 0$ mHartree⁻¹.

We compare our results with the best variational energies obtained by Chung and coworkers [20, 21], who used linear expansions of Slater orbitals in the LS -coupling scheme.

4.1. Be ³P ($1s^2 2p^2$)

The calculations for the excited state Be ³P ($1s^2 2p^2$) were carried out with the following three trial wavefunctions:

- (1) a single determinantal function multiplied by a nine-term SM correlation factor;

Table 4. Be 3P ($1s^22p^2$) energies and VMC variances of the energy (where prex denotes pre-exponential).

Method	Energy (Hartree)	σ_{VMC} (H)
SCF	-14.334 0	1.68(2)
SCF-SM/VMC	-14.376 9(2)	0.48(1)
Padé/VMC	-14.393 0(1)	0.27(1)
33-term prex/VMC	-14.394 2(1)	0.22(1)
Best variational	-14.395 1086	
SCF-SM/DMC	-14.395 21(5)	
Padé/DMC	-14.395 41(7)	
33-term prex/DMC	-14.395 47(5)	
Estimated NRL	-14.395 4404	

- (2) a one-term Padé–Jastrow function;
 (3) a pre-exponential function with 33 terms.

The spin eigenfunction used for the Padé–Jastrow and pre-exponential function is $\Theta_{1,1}^4 = (\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$. The pre-factor $f(\mathbf{r})$ that defines the state symmetry is

$$f(\mathbf{r}) = x_3y_4 - x_4y_3. \quad (12)$$

The results are reported in table 4.

As to the determinantal wavefunction, we used only a single determinant, as the energy lowers by only 0.003 Hartree on going from the SCF to a CASSCF function for two electrons in an active space of two p shells (15 configurations, the highest weight of the first double excitation being equal to 0.04).

The explicit inclusion of the interelectronic distances in the wavefunction by the SM factor results in a large improvement of the quality of the wavefunction, as shown from the lowering of the energy (0.043 Hartree) and the variance of the energy (almost four times smaller) on going from SCF to SCF-SM/VMC.

A further improvement of the trial wavefunction at VMC level is found using more sophisticated functional forms [11], like the Padé–Jastrow and the pre-exponential ones. For the pre-exponential function we used a 33-term expansion, including all r_i , r_i^2 and the products $r_i r_{ij}$.

In particular in the case of the pre-exponential function we were able to optimize the linear parameters of $G(\mathbf{r})$ minimizing the energy, not the variance of the local energy, obtaining an energy 0.9 mHartree higher than the best variational one. We also notice that this wavefunction is very compact with 45 (12 nonlinear and 33 linear) variational parameters on the whole.

At DMC level already the SCF-SM wavefunction gives a lower energy than the best variational value, and 0.2 mHartree higher than the estimated NRL. This means that the nodal surfaces of this function are fairly good, at variance with the SCF-SM trial wavefunction for the Be ground state, whose energy is 11 mHartree higher than the NRL [30]. This large nodal error is due to the strong contribution of the first double excitation in improving the quality of the nodal surfaces, because of the quasi-degeneracy of the 2s and 2p orbitals.

DMC energies for Padé–Jastrow and pre-exponential functions have the estimated NRL within one standard deviation; that is, the nodal surfaces of these wavefunctions are correct and better than the SCF ones.

Table 5. Be $^4S^o$ ($1s^22p^3$) energies and VMC variances of the energy (where prex denotes pre-exponential).

Method	Energy (Hartree)	σ_{VMC} (H)
SCF	-14.326 976	1.68(1)
CASSCF	-14.334 010	1.68(1)
SCF-SM/VMC	-14.376 9(2)	0.48(1)
CASSCF-SM/VMC	-14.383 6(1)	0.48(1)
Padé/VMC	-14.403 1(2)	0.29(1)
61-term prex/VMC	-14.405 1(2)	0.21(1)
SCF-SM/DMC	-14.405 94(8)	
CASSCF-SM/DMC	-14.405 97(7)	
Best variational	-14.406 032 0	
Padé/DMC	-14.406 20(4)	
61-term prex /DMC	-14.406 20(6)	
Estimated LNR	-14.406 282 (26)	

4.2. $Be^- ^4S^o(1s^22p^3)$

The calculations for the excited state $Be^- ^4S^o$ were carried out with these four trial wavefunctions:

- (1) a single determinantal function multiplied by a nine-term Moskowitz–Schmidt correlation factor;
- (2) a multideterminantal function multiplied by a nine-term Moskowitz–Schmidt correlation factor;
- (3) a one-term Padé–Jastrow function;
- (4) a pre-exponential function $G(\mathbf{r})$ with 61 terms.

The CASSCF wavefunction for three electrons in an active space of two p shells includes 20 configurations. The two highest weights, relative to the first double and single excited configurations, are equal to 0.125 and 0.03 and indicate a more marked multiconfigurational character of the wavefunction.

As we have seen for the $Be ^3P$ state, the gain in energy and the lowering of the variance of the energy between SCF and SCF-SM are very large, while between SCF-SM and CASSCF-SM they are an order of magnitude less.

The spin eigenfunction used for the Padé–Jastrow and pre-exponential function is $\Theta_{3/2,3/2}^5 = (\alpha\beta\alpha\alpha\alpha - \beta\alpha\alpha\alpha\alpha)$. The pre-factor $f(\mathbf{r})$ that defines the state symmetry is

$$f(\mathbf{r}) = x_3y_4z_5 + x_5y_3z_4 + x_4y_5z_3 - x_3y_5z_4 - x_5y_4z_3 - x_4y_3z_5. \quad (13)$$

The results are reported in table 5.

For Be^- using the Padé and pre-exponential functions we obtained better energies and variances of the energy than the SCF-SM and CASSCF-SM ones, as already seen in the $Be ^3P$ case. In particular, with the pre-exponential function with 61 linear parameters $G(\mathbf{r})$ (all r_i , r_i^2 and the products $r_i r_{ij}$), the VMC energy is 0.9 mHartree higher than the best variational energy.

From DMC simulations we see clearly that the nodal surfaces do not change on going from the SCF to the CASSCF trial wavefunction and in both cases we have around 0.4 mHartree of nodal error.

Padé–Jastrow and pre-exponential functions have better nodal surfaces and their DMC energies have the estimated NRL within one standard deviation.

5. Conclusions

We have used explicitly correlated functional forms to improve the quality of the trial wavefunctions usually adopted to calculate the energy of a system. For the two excited states of Be and Be⁻ we obtained better non-relativistic energies with very compact trial wavefunctions compared to the best variational results.

Using a suitable pre-exponential factor we were able to improve the flexibility of the trial wavefunction without including too many nonlinear parameters: this kind of trial wavefunction allowed us to directly minimize the energy instead of the variance of the local energy. As to the computational time, the optimization of the Be⁻ five-electron trial wavefunction and the VMC calculation required around a week on a modern PC. It is not possible to compare this CPU time with calculations by correlated Gaussians as at present they are limited to four-electron systems.

Our DMC energies are in good agreement with the estimated NRL obtained by Chung and coworkers [20, 21].

From our best values for Be ³P (-14.395 47(5) Hartree) and Be⁻ ⁴S^o (-14.406 20(6) Hartree) we compute an electron affinity of 0.010 73(8) Hartree = 292(2) meV, within two standard deviations from the experimental value 295.49(25) meV [31] and the theoretical value 295.0(7) calculated by Hsu and Chung [20]. A significant comparison would require the reduction of the calculated standard deviation by one order of magnitude.

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