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A systematic study on the fixed-node and localization error in quantum Monte Carlo calculations with pseudopotentials for group III elements

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Abstract

Short-time fixed-node pure diffusion quantum Monte Carlo (PDMC) calculations with pseudopotentials for the group III elements B, Al, Ga and In have been carried out in order to study the capability of multireference trial wavefunctions to reduce the fixed-node and localization error. For this purpose PDMC energies for the ^2P and ^4P states of the neutral atoms and for the ^1S state of the positive ions have been compared with the results of MRCI calculations. For these simple systems, we demonstrate the possibility of a systematic reduction of these errors by adding supplementary configurations to the trial wavefunction.

1. Introduction

Pseudopotentials represent an efficent way to overcome the limitations concerning the number of particles in quantum Monte Carlo methods. Unfortunately, the semi-local Ansatz to pseudopotentials introduces an additional approximation in quantum Monte Carlo calculations which originates from the necessary localization of the non-local part [1]. The localization can be achieved through an auxiliary wavefunction, so that the localized and non-local pseudopotentials are equivalent with respect to the energy expectation value of the auxiliary wavefunction. With regard to the fixed-node approximation it is necessary that the nodal surfaces of the auxiliary and trial wavefunction agree [2]. Therefore, the trial wavefunction [2,3] or its antisymmetric part [1,4] are common choices for the auxiliary wavefunction. We have chosen as in a previous paper [4] the antisymmetric part, not only for technical reasons, but also with respect to the fact that pseudopotentials are adjusted on the basis of independent particle models, such as Hartree–Fock (HF) and Dirac–Fock, or on experimental results for one-particle valence states [5]. The inclusion of a correlation factor in the auxiliary wavefunction does not necessarily result in an improvement of the localized pseudopotential. In some cases it is essential to go beyond HF because otherwise one would lose important parts of the pseudopotential [6]. We will discuss this point in detail in the following sections.

The fixed-node approximation is, as already mentioned, closely related to the localization problem. Multiconfiguration self-consistent field (MCSCF) wavefunctions offer a way for a controllable and systematic improvement of both approximations. To

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study this possibility we have chosen the group III elements for which we expect sensitive reactions with regard to improvements of the auxiliary and trial wavefunctions. Schmidt and Moskowitz [7] found in the case of the B atom (^{2}P) a large discrepancy between the correlation energy obtained with a HF wavefunction multiplied by an optimized symmetric correlation function and the exact correlation energy. This error is comparable to that observed for the Be atom (^{1}S) where it is well known [8] that the nodes of the HF wavefunction are rather poor approximations due to near-degeneracy effects. There is no fixed-node approximation for the Be atom in Monte Carlo calculations with pseudopotentials but these effects also strongly influence the localization of the pseudopotential [6]. Therefore, we expected a rather similar behaviour of the group III elements with respect to both approximations in Monte Carlo calculations with pseudopotentials.

Another important reason for considering three electron systems is the possibility of carrying out multireference configuration interaction (MRCI) calculations with higher accuracy than the expected statistical error in the Monte Carlo calculations.

This enables a quantitative estimate for the sum of the fixed-node and localization error for each particular Monte Carlo calculation. Without these reference energies it would be necessary to consider energy differences between various states and compare these differences with experimental results. Such comparisons would imply an additional source of error as the pseudopotential approach itself is naturally just an approximation. We will discuss this point in detail in section 4.

2. Methods of calculation

For our quantum Monte Carlo calculations we used the PDMC method developed by Caffarel and Claverie [9] in the way described in ref. [4]. The semi-local pseudopotentials from Igel-Mann et al. [5] were first brought into a form where the projection occurs on Cartesian Gaussian-type functions (GTFs) [4]. To take care of core polarization effects which are of increasing importance in the row B, Al, Ga and In, the pseudopotentials were supplemented by an effective polarization potential,

$$V_{\mathrm{pol}} = -\tfrac{1}{2}\alpha_{\mathrm{D}}\boldsymbol{E}^2\,, \quad \boldsymbol{E} = \sum_i \frac{\boldsymbol{r}_i}{r_i^3} C(r_i, \delta)\,,$$

$$C(r, \rho) = 1 - \exp(-\delta r^2)\,. \qquad (1)$$

The analytic form is due to Müller et al. [10] and was first applied in connection with pseudopotentials by Fuentealba et al. [11]. In Eq. (1) the parameter α_{D} represents the static dipole polarizability of the atomic core. V_{pol} contains a cut-off function $C(r, \delta)$ with parameter δ in order to restrict the sphere of action to the valence region.

Both parameters α_{D} and δ were taken from Igel-Mann et al. [5]. Because of its local form there is no difficulty in incorporating the core polarization potential in Monte Carlo calculations.

The determination of the HF and MCSCF wavefunctions used within the PDMC calculations, as well as the calculations of MRCI reference energies, were carried out with the program MOLPRO [12] which was extended to allow for a self-consistent treatment of polarization potentials by one of us (AN). In our Monte Carlo calculations we used 4s4p GTF basis sets [13] supplemented, when necessary, by d-type GTFs. To take care of the electron–electron cusp, the trial wavefunctions Φ_{T},

$$\Phi_{\mathrm{T}}(1,2,3) = f(1,2) f(1,3) f(2,3) \Psi(1,2,3)\,,$$

$$f(i,j) = \exp[\alpha r_{ij}/(1 + r_{ij})]\,, \qquad (2)$$

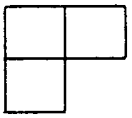
were composed of a HF or MCSCF wavefunction Ψ and a Jastrow factor f with $\alpha = 0.5$ for antiparallel and $\alpha = 0.25$ for parallel spins [14].

The MRCI calculations were carried out with 12s12p6d4f2g even tempered GTF basis sets where the underlying parameters originate from Chakravorty et al. [15]. In the case of neutral atoms the MRCI calculations were based on CASSCF (complete active space SCF) calculations, where the valence shell together with the next higher s, p and d shells formed the active space. It is a matter of course that for the positive ions a single–double CI based on the HF configuration was sufficient.

PDMC calculations were carried with time steps ranging from 0.005 h^{-1} for B up to 0.02 h^{-1} for In. Taking into account detailed balance [16] for each step of the simulation, we observed no time-step dependence within the statistical error bars.

3. Selection of the trial wavefunctions

Our intention was to study the ^{2}P ground and ^{4}P excited states of the atoms and the ^{1}S ground state of the positive ions for the elements B, Al, Ga and In. For the ^{2}P ground state it is reasonable to expect that the nodes of the HF wavefunctions are not sufficient to reproduce the MRCI energies. Therefore, it seems natural in analogy to the Be atom to extend the trial wavefunction by s→p double excitations. As will be shown in section 4 this results indeed in a considerable improvement but there still remains a significant discrepancy. CASSCF calculations for the B atom show that a large improvement with respect to the correlation energy is feasible through the inclusion of the 3d shell in the active space. To allow for excitations into d orbitals within the MCSCF wavefunctions used in the Monte Carlo calculations seems promising for two reasons. First it enters a qualitative new feature into the trial wavefunctions with possibly significant influence on the nodal structure. In the second place it is important with respect to the auxiliary wavefunctions used for the localization of the pseudopotential because the d orbitals are needed for the localization of the d projectors which become of increasing importance with ascending atomic number. The most important configurations are represented by single and double excitations from the doubly occupied s orbital and the singly occupied p_z orbital into the d shell and the p_x or p_y orbitals. Since the configurations are eigenfunctions to the angular momentum operator, they are easily generated by angular momentum coupling of the p and d orbitals to an eigenfunction with $l=1$ and $m=0$ [17]. In view of their application in quantum Monte Carlo calculations it is necessary to have the correct permutation symmetry for the particles. This can be achieved by applying the appropriate Young diagram,



, (3)

in two different ways to the angular momentum eigenfunctions [17]. Each way represents a specific spin-coupling as can be seen by combining the spatial parts of the wavefunction with appropriate spinfunctions [18]. Summing up we have used three different types of trial respectively auxiliary wavefunctions for the ^{2}P state in the course of our Monte Carlo calculations,

$$\begin{aligned}
&\Psi_{\mathrm{HF}}(1,2|3)=|\mathrm{s}(1)\mathrm{p}_z(2)|\mathrm{s}(3)\,,\\
&\Psi_{\mathrm{2CSF}}(1,2|3)=c_1\,\Psi_{\mathrm{HF}}(1,2|3)+c_2\,\Psi_{\mathrm{s}\to\mathrm{p}}(1,2|3)\,,\\
&\Psi_{\mathrm{4CSF}}(1,2|3)=c_1\,\Psi_{\mathrm{HF}}(1,2|3)+c_2\,\Psi_{\mathrm{s}\to\mathrm{p}}(1,2|3)\\
&\quad+c_3\,\Psi^{\mathrm{A}}_{\mathrm{s,p}\to\mathrm{p,d}}(1,2|3)+c_4\,\Psi^{\mathrm{B}}_{\mathrm{s,p}\to\mathrm{p,d}}(1,2|3)\\
&\Psi_{\mathrm{s}\to\mathrm{p}}(1,2|3)=|\mathrm{p}_x(1)\mathrm{p}_z(2)|\mathrm{p}_x(3)\\
&\quad+|\mathrm{p}_y(1)\mathrm{p}_z(2)|\mathrm{p}_y(3)\,,\\
&\Psi^{\mathrm{A}}_{\mathrm{s,p}\to\mathrm{p,d}}(1,2|3)=\sqrt{\tfrac{3}{10}}\\
&\quad\times(|\mathrm{s}(1)\mathrm{p}_x(2)|\mathrm{d}_{xz}(3)+|\mathrm{s}(1)\mathrm{d}_{xz}(2)|\mathrm{p}_x(3)\\
&\quad+|\mathrm{s}(1)\mathrm{p}_y(2)|\mathrm{d}_{yz}(3)+|\mathrm{s}(1)\mathrm{d}_{yz}(2)|\mathrm{p}_y(3))\\
&\quad+\sqrt{\tfrac{2}{5}}(|\mathrm{s}(1)\mathrm{p}_z(2)|\mathrm{d}_{2z^2-x^2-y^2}(3)\\
&\quad+|\mathrm{s}(1)\mathrm{d}_{2z^2-x^2-y^2}(2)|\mathrm{p}_z(3))\,,\\
&\Psi^{\mathrm{B}}_{\mathrm{s,p}\to\mathrm{p,d}}(1,2|3)=\sqrt{\tfrac{3}{10}}\\
&\quad\times(|\mathrm{p}_x(1)\mathrm{d}_{xz}(2)|\mathrm{s}(3)+|\mathrm{s}(1)\mathrm{d}_{xz}(2)|\mathrm{p}_x(3)\\
&\quad+|\mathrm{p}_y(1)\mathrm{d}_{yz}(2)|\mathrm{s}(3)+|\mathrm{s}(1)\mathrm{d}_{yz}(2)|\mathrm{p}_y(3))\\
&\quad+\sqrt{\tfrac{2}{5}}(|\mathrm{s}(1)\mathrm{d}_{2z^2-x^2-y^2}(2)|\mathrm{p}_z(3)\\
&\quad+|\mathrm{p}_z(1)\mathrm{d}_{2z^2-x^2-y^2}(2)|\mathrm{s}(3))\,.
\end{aligned}\tag{4}$$

In the case of the Al atom d excitations were already considered by Christiansen [19] without specifying the utilized configurations.

As an example for a high-spin system we considered the ^{4}P state. The electron correlation in these states is dominated by the Pauli repulsion which is already present in the HF wavefunction. Therefore, it was no surprise that we got reasonable results for HF nodal surfaces within our Monte Carlo calculations.

In the case of the positive ions we expected a situation similar to that found for the alkaline earth atoms. Therefore, we used as trial respectively auxiliary wavefunctions, beside HF, MCSCF wavefunctions which take care of the s, p near-degeneracy [4].

4. Results and discussion

The results of the PDMC calculations can be discussed in various ways. As the first step it is important to get an idea of the absolute error of the total energy due to the fixed-node approximation and the localization of the pseudopotential. Unfortunately, it is impossible to separate these errors in a strict sense. Therefore, we will confine ourselves to a quantitative discussion of the net effect and to some qualitative arguments concerning the partition with respect to the different errors. To be more precise we are interested in the discrepancy between the eigenvalues of the model Hamilton operator including the semi-local pseudopotential and the PDMC energies obtained within the discussed approximations. The eigenvalues can be approximated with sufficient accuracy by the energies obtained from MRCI calculations. Table 1 shows the obtained energy differences for the various elements and states. The localization procedure, as already mentioned, leads to the elimination of the non-local d potential from the pseudopotential for all auxiliary wavefunctions without d orbitals. Therefore, it is useful to compare not only with MRCI calculations obtained with the complete semi-local pseudopotential, but also with MRCI energies obtained for the semi-local pseudopotential without the d potential. In order to estimate the significance of the d potential it is necessary to consider two different factors. The first factor applies to the absolute values of the pseudopotential parameters, keeping in mind that they are determined from a one-particle model where electron correlation is absent. Another important factor descends from the relative weights of the CSFs including d excitations in the auxiliary wavefunction. Both factors are not necessarily related, e.g. in the case of the B atom there exists a significant contribution of d excitations to the correlation energy; on the other hand, the coefficient of the d potential is too small [5] for a perceptible effect on the energy.

For the ^{2}P ground state we observe a general trend for all types of wavefunctions that is a decrease of the energy differences (PDMC versus MRCI) in the sequence B, Al, Ga and In. All wavefunctions exhibit a sign inversion in the energy differences within the above sequence. This behaviour results in part from a change of sign of the d potential which is attractive for Al but ascendingly repulsive for Ga and In. The HF wavefunctions yield rather large errors for B and In whereby in the first case the error is due to the fixed-node approximation and in the second case it is mainly due to the neglect of the d potential. In going from HF to 2CSF wavefunctions we find as expected a significant improvement for the B atom but for Al, Ga and In an increase in the energy of approximately

Table 1
Energy differences (E_h) between PDMC energies obtained with various trial respectively auxiliary wavefunctions and the MRCI reference energies for the ^{2}P and ^{4}P states of the neutral atoms as well as the ^{1}S state of the positive ions. The values in parentheses refer to MRCI calculations without the non-local d potential in the pseudopotential. Statistical errors are given in parentheses behind the energy differences

Ψ	B	Al	Ga	In
^{2}P				
HF	0.017 (2)	0.0023 (12)	−0.0022 (12)	−0.0059 (9)
2CSF	0.0059 (11)	0.0044 (10)	0.0002 (9)	−0.0032 (9)
	(0.0059)	(0.0039)	(0.0021)	(0.0002)
4CSF	0.0033 (14)	0.0024 (9)	−0.0002 (9)	−0.0019 (8)
^{4}P				
HF	0.0012 (10)	0.0015 (10)	−0.0005 (5)	−0.0008 (7)
	(0.0012)	(0.0011)	(0.0005)	(0.0006)
^{1}S				
HF	0.0243 (11)	0.0008 (10)	−0.0017 (11)	−0.0045 (5)
2CSF	0.0004 (9)	0.0005 (5)	−0.0002 (6)	−0.0011 (6)
	(0.0004)	(0.0005)	(0.0003)	(0.0000)

2 mE_h is observed. Presuming an improvement in the nodal surfaces in going from HF to 2CSF wavefunctions this result originates probably from changes in the localized p potential. It should be noticed that in contrast to the fixed-node error it is not possible to apply the variational principle to the localization error; therefore, an improvement of the localized pseudopotential need not result in a decreasing energy.

It is justifiable to assume that a comparison with MRCI calculations without the d potential yields the remaining error caused by the fixed-node approximation which decreases as expected in the sequence B, Al, Ga and In. We will consider our results obtained with the 4CSF wavefunctions where a slight improvement can be observed for B, Al and In. While for the first two elements the remaining error is probably due to the fixed-node approximation, it seems to originate in the case of In from a still insufficient localization of the d potential. For the Ga atom the 2CSF wavefunction already yields the desired result but it must be due to a compensation of errors because the neglect of the repulsive d potential must result in a lower energy which is compensated by the fixed-node error. The 4CSF wavefunction represents an improvement with respect to both errors which is why the energy undergoes no change. It should be noticed with respect to the discussion above that we are dealing with rather small effects whereby statistical errors are attached to the energy differences. Nevertheless, we expect that the observed trends were not affected by statistical fluctuations.

For the ^4P states electron correlation is much less important because of the Pauli repulsion between all electrons which is already present at the HF level. For this reason the neglect of the d potential has no serious consequences with respect to the energy. Therefore, we found for our PDMC calculations with HF wavefunctions only minor variations from the MRCI energies.

In addition to the neutral atoms, PDMC calculations were carried out for the ^1S state of the positive ions which resemble strongly the alkaline earth atoms. The HF wavefunction for B exhibits a significant error due to the neglect of the p potential. For the other ions the use of HF wavefunctions results in much smaller errors which are mainly due to the change of sign for the p potential which is attractive in the case of B but repulsive in the other cases with p shells in the core. PDMC calculations with the 2CSF wavefunctions yield good agreement with CI results whereby in all cases the neglect of the d potential had nearly no consequences.

5. Comparison with experiment

The use of various trial respectively auxiliary wavefunctions within the PDMC calculations results in a noticeable spread of errors. To get an idea up to which magnitude an error can be tolerated, it is important to determine the error inherent in the pseudopotential approach. Therefore, we have calculated ionization and excitation energies and compared them with experimental results.

The ionization energies of the atoms with respect to the ground states are listed in Table 2. There is a satisfactory agreement between experimental and calculated results. Looking a little bit closer it turns

Table 2
Comparison of ionization energies (eV) obtained from PDMC and MRCI calculations with experimental values. MRCI results are listed with (pol.) and without (no pol.) polarization potential. The PDMC ionization energies with polarization potential refer to different combinations of trial respectively auxiliary wavefunctions. Statistical errors are given in parentheses

	PDMC (^2P–^1S)			MRCI		
	HF [a]–HF	2CSF [a]–2CSF	4CSF [a]–2CSF	no pol.	pol.	exp. [b]
B	8.52 (8)	8.18 (5)	8.25 (6)	8.30	8.33	8.30
Al	5.99 (6)	5.92 (4)	5.98 (4)	6.04	6.03	5.99
Ga	5.88 (6)	5.85 (4)	5.86 (4)	5.88	5.86	6.00
In	5.54 (4)	5.56 (4)	5.52 (4)	5.53	5.50	5.79

[a] Abbreviations refer to the wavefunctions Ψ in (4). [b] Ref. [20].

Table 3
Comparison of $^2P \rightarrow {}^4P$ excitation energies (eV) obtained from PDMC and MRCI calculations with experimental values. MRCI results are listed with (pol.) and without (no pol.) polarization potential. The PDMC excitation energies with polarization potential refer to different combinations of trial respectively auxiliary wavefunctions. Statistical errors are given in parentheses

	PDMC ($^2P \rightarrow {}^4P$)			MRCI		
	HF [a]→HF	2CSF [a]→HF	4CSF [a]→HF	no pol.	pol.	exp. [b]
B	3.17 (8)	3.48 (6)	3.55 (6)	3.61	3.60	3.58
Al	3.55 (6)	3.49 (5)	3.54 (5)	3.47	3.57	3.61
Ga	4.72 (5)	4.65 (4)	4.66 (4)	4.31	4.67	4.78
In	4.42 (4)	4.35 (4)	4.31 (4)	3.78	4.28	4.53

[a] Abbreviations refer to the wavefunctions Ψ in (4). [b] Ref. [21].

out that the influence of the polarization potential on this property is nearly negligible.

In nearly all cases we got energy differences between the PDMC and MRCI results which are of the same order of magnitude or considerably smaller than the error inherent in the pseudopotential approach, represented by the differences between MRCI and experimental ionization energies. Only in the case of the B atom we observe for the PDMC calculations with HF wavefunctions a significant deviation. For Al we find a close agreement between our results and those obtained by Christiansen [19].

Other interesting experimental properties which are within the reach of Monte Carlo methods are excitation energies into states with symmetries different from the ground state for which the ^2P into ^4P excitation is a typical example (Table 3). In contrast to the ionization energies there is a strong influence of the core polarization on the excitation energies. As before, the localization and fixed-node error is of the same order of magnitude or considerable smaller than the error of the underlying semi-local pseudopotential and polarization potential.

6. Conclusions

We have investigated in a systematic manner the interactions between the localization and fixed-node error both inherent in Monte Carlo calculations with pseudopotentials. Both errors are due to an inappropriate choice of the trial respectively auxiliary wavefunction.

Therefore, we tried to reduce these errors by utilizing the MCSCF method which allowed for systematic improvements by adding additional configurations. Our results show that at least for these simple systems a controllable improvement is possible. We could also demonstrate for the calculated properties that Monte Carlo specific errors are just of the same order of magnitude or considerable smaller than the error due to the semi-local pseudopotential approximation.

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