

Reduction of the computational effort in quantum Monte Carlo calculations with pseudopotentials through a change of the projection operators

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(Received 21 January 1992; accepted 10 March 1992)

The usual form of nonlocal pseudopotentials which project the wave function on real spherical harmonics is inconvenient in quantum Monte Carlo calculations because the projection integrals are still functions of r . It is thus necessary to calculate the integral in every point of the simulation. We circumvent this problem by transforming the pseudopotential to a form where the projection occurs on Cartesian Gaussian-type functions which makes the projection integrals independent of the electron coordinates. We applied our method to two-valence electron systems using the pure diffusion method, where the approximation in the pseudopotential is the only one present.

I. INTRODUCTION

In standard methods for atomic and molecular quantum-mechanical calculations, such as Hartree Fock (HF), the multiconfiguration self-consistent-field method (MCSCF), or the configuration interaction method (CI), a common feature is the crucial dependence on the number of electrons of the system. One possible way to overcome this problem is the introduction of pseudopotentials¹ which makes it possible to get rid of the core electrons. Today, the most frequently used form of pseudopotentials is a semilocal one with projection operators on real spherical harmonics:²

$$U_{SL} = \sum_k d_k r^{\nu_k - 2} \exp(-\xi_k r^2) + \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l |Y_{lm}\rangle \times \left(\sum_k d_{kl} r^{\nu_{kl} - 2} \exp(-\xi_{kl} r^2) \right) \langle Y_{lm}|. \quad (1)$$

The applicability of Monte Carlo methods is even more restricted by the unfavorable dependence of the computational effort on the number of electrons, see, e.g., Ref. 3. Therefore, it is quite natural to use pseudopotentials to reduce their number. Whereas, the local part of the pseudopotential is trivial to handle in Monte Carlo calculations, a direct application of the nonlocal part is not possible because the introduction of a nonlocal operator in the Hamiltonian destroys the correspondence between the Schrödinger and the Fokker-Planck equation which is necessary for the Monte Carlo simulation. Hammond, Reynolds, and Lester³ circumvent this problem by applying the pseudopotential on the antisymmetric part Ψ_T (HF or MCSCF wave function) of the trial wave function Φ_T and dividing through Ψ_T :

$$U_{SL} \rightarrow \frac{U_{SL} \Psi_T}{\Psi_T}. \quad (2)$$

This leads to a local pseudopotential which can be easily implemented in Monte Carlo methods but which is not identical with the nonlocal one and will not necessarily give the

same result.⁴ We will investigate this aspect here in detail. The main disadvantage of the aforementioned form is the cumbersome calculation of the projection integrals⁵

$$\int_{S^2} d\Omega g_A(x,y,z) Y_{lm}(x/r, y/r, z/r),$$

$$g_A(x,y,z) = (x - x_A)^n (y - y_A)^m (z - z_A)^l \exp(-ar^2), \quad (3)$$

which must be performed in every step of the simulation because they are still functions of r .

II. CHANGE OF THE PROJECTION OPERATOR

A simple way to overcome this problem is to change the projector function space from real spherical harmonics to Cartesian Gaussian-type functions (GTF) which project in a space of functions of R^3 and not in a function space on the surface of the unit sphere. This approach leads to a pseudopotential of the form

$$U_{NL} = \sum_l \sum_{ij} \Lambda_{ij}^l |g_i^l\rangle \langle g_j^l|. \quad (4)$$

The first sum goes over angular momentum quantum numbers, which means that the GTF are of s, p, d, \dots type, whereas the second sum represents the basis of the subspace on which the projection occurs. Each subspace with $l \geq 1$ contains orthogonal sets of basis functions representing the degeneracy of l . It is not efficient to try to determine the parameters Λ directly from *ab initio* calculations or experimental data because their number is too large. Therefore we follow the approach of Pelissier, Komihara, and Daudey⁶ which transform the pseudopotentials of the former Eq. (1) to the latter form Eq. (4). To be flexible enough, we use for the projectors a geometrical basis set⁷ which is large enough to be nearly complete for all atoms and which has the same exponents for all l . For practical calculations, we used 30 basis functions of $s, p,$ and d type with exponents ranging from 0.002 to 255.7 which should be sufficient to represent the valence space of all elements.

To obtain the coefficients Λ , we demand the equality of

both forms of pseudopotentials in the subspace of our basis functions. This leads to

$$\langle g_i | U_{SL} | g_j \rangle = \sum_{kl} \langle g_i | g_k \rangle \Lambda_{kl} \langle g_l | g_j \rangle \quad (5)$$

which, written in matrix notation,

$$U_{SL} = SAS \Rightarrow \Lambda = S^{-1} U_{SL} S^{-1}, \quad (6)$$

is easily solved. Taking advantage of the symmetry, this is done for each l value and in each orthogonal set separately.

Using the same localization procedure as Hammond and co-workers,³ we are led in the case of a single Slater determinant to the local pseudopotential

$$\frac{U_{NL} \Psi_T}{\Psi_T} = \sum_{n=1}^{N_{\text{val}}} \sum_{l=0}^{l_{\text{max}}} \sum_{i,j,k} |g'_i\rangle \Lambda_{ij}^l \langle g'_j | \varphi_k \rangle (\Psi_T^{-1})_{nk}, \quad (7)$$

where Ψ_T represents the Slater matrix with the elements $(\Psi_T)_{ij} = \varphi_i(j)$. The extension of this formula is trivial in the case of a MCSCF wave function.

The form of Eq. (7) has some very nice features compared with the former one of Eq. (2). The most important point is that the projection integrals on the orbitals φ are ordinary numbers and, furthermore, no longer depend on any electron coordinate. Therefore the matrix \mathbf{A} ,

$$\mathbf{A} = \begin{bmatrix} A^0 \\ A^1 \\ \vdots \\ A^{l_{\text{max}}} \end{bmatrix}, \quad (8)$$

composed of the product matrices \mathbf{A}^l ,

$$A_{ik}^l = \sum_j \Lambda_{ij}^l \langle g'_j | \varphi_k \rangle, \quad (9)$$

of the pseudopotential parameter matrix Λ and the projection integral matrix is calculated only once at the beginning of the Monte Carlo calculation. The next step consists of the calculation of the GTF for each electron and l value. Here an advantage arises from the use of equal exponents for all angular momentum quantum numbers so that the expensive exponential functions have to be calculated only for one l in every step of the simulation. Since we simulate the random walk of several configurations parallel, we obtain for each electron a matrix B^n ,

$$B^n = [B^{n0}, B^{n1}, \dots, B^{nl_{\text{max}}}], \quad (10)$$

which is, in a similar way, composed from the matrices B^{nl}

$$B_{ij}^{nl} = g'_j(r_{in}), \quad (11)$$

r_{in} representing the coordinates of the n th electron in the i th configuration. These two matrices, together with the inverse of the Slater matrix, form the contributions of the n th electron to the pseudopotentials in the various configurations:

$$\frac{U_{NL} \Psi_T}{\Psi_T} \Big|_{\text{nth conf.}} = \sum_{n,k=1}^{N_{\text{val}}} (B^n A)_{ik} [\Psi_T^{-1}(r_i)]_{nk}. \quad (12)$$

This shows that the dominating part in the calculations are matrix multiplications of comparatively large matrices which can be very efficiently vectorized on a supercomputer. It seems also worth mentioning that there is no additional computational effort if the pseudopotential and the basis functions are on different centers. In practice, the evaluation of the pseudopotential is no longer a dominating part of the total CPU time in Monte Carlo calculations. Using 30 projector functions for each l (l going from 0 to 2), the pseudopotential part of the program consumes 34% of the total CPU time on a Cray-2 in the case of Na_2 . It will be no problem to reduce the number of projector functions considerably without loss of accuracy so that we consider the mentioned fraction of CPU time as an upper limit. For systems with high symmetry, matrices of type A^l will be zero so one can eliminate these matrices and the corresponding matrices B^{nl} from the composed matrices A and B^n , respectively. This will further reduce the computational effort but was not implemented here. Equation (9) leads also to the possibility to use other forms of one-particle basis functions other than GTF, like Slater-type functions, or other more complicated forms which were shown to be extremely useful in quantum Monte Carlo calculations.⁸ In the worst case, one can perform a numerical integration for these integrals which must be done only once at the beginning of the calculation. An alternative approach to simplify the use of nonlocal pseudopotentials of the form of Eq. (1) in quantum Monte Carlo calculations can be found in Refs. 9 and 10.

III. METHOD OF CALCULATION

For our Monte Carlo calculations, we have used the pure diffusion quantum Monte Carlo method (PDMC) of Caffarel and Claverie¹¹ which is based on their derivation of the so-called full generalized Feynman-Kac formula. Applying this formula Caffarel had obtained the expression

$$\frac{\langle H \Phi_T | \exp[-(H - E_T)t] | \Phi_T \rangle}{\langle \Phi_T | \exp[-(H - E_T)t] | \Phi_T \rangle} = \lim_{T \rightarrow \infty} \frac{\int_0^T d\tau_2 [V_p(\tau) + V_p(\tau + t)] \exp(-\int_{\tau}^{\tau+t} V_p(s) ds)}{\int_0^T d\tau \exp(-\int_{\tau}^{\tau+t} V_p(s) ds)}, \quad (13)$$

$$V_p(\tau) = \frac{H \Phi_T(x_\tau)}{\Phi_T(x_\tau)},$$

for the calculation of the energy expectation value. For $t = 0$, this is just the variational energy of the trial wave function Φ_T but for the limit $t \rightarrow \infty$, this quotient represents the exact ground-state energy of the Hamiltonian. Using the standard techniques of quantum Monte Carlo, we have sam-

pled paths according to the trial wave function and calculated the functional integral for different times t . In practice, the convergence to a constant value for increasing t is very fast for good trial wave functions.

The trial wave functions used in our calculations are

composed of a Jastrow factor and a HF or MCSCF wave function:

$$\Phi_T = \prod_{i < j}^n f(r_{ij}) \Psi_T(r_1, r_2, \dots, r_n),$$

$$f(r) = \exp\left(\frac{Ar}{1 + Br}\right). \quad (14)$$

The parameter A is chosen to satisfy the cusp condition ($A = 0.5$) and B is set to 1.0 which has been found to be close to the optimal value in all calculations. It should be mentioned that, when MCSCF wave functions were used, the major part of the correlation energy in the variational case is due to the MCSCF part and not to the Jastrow factor, which means that the value of B is of minor importance.

We use a highly vectorized code on a Cray-2 supercomputer. The basis set consists of $4s, 4p$ GTF (Ref. 12) for all atoms. For the alkaline earth atoms and the alkali anions, we have calculated 100 independent configurations in configuration space. Our time step is 0.01 and the total simulation time amounts 1000 hartree⁻¹. In the case of the alkali dimers, we use the same number of configurations but time steps from 0.05 up to 0.1. The total simulation time ranges from 10 000 to 20 000 hartree⁻¹. As a starting point for our pseudopotential transformations, we use the semilocal pseudopotentials of Fuentealba *et al.*^{13,14} The MCSCF and CI calculations have been done with the program MOLPRO.¹⁵ To obtain the full CI reference values, we use even-tempered basis sets with $12s, 12p, 5d, 3f,$ and $1g$ for the alkali anions and $8s, 6p, 3d, 2f,$ and $1g$ for the alkali dimers,¹⁶ respectively. Both basis sets include diffuse as well as polarization functions.

IV. RESULTS AND DISCUSSION

Our intention in this work is not only to demonstrate the computational advantages of our approach, but also to look at the reliability of the localized pseudopotential. Christiansen⁴ has pointed out that it is necessary in some cases to use MCSCF instead of HF wave functions, even in the case of two-electron systems if pseudopotentials are used. He has shown for the Be atom the necessity to take care of the near degeneracy of the s^2 and p^2 configuration (neglect of the p^2 configuration eliminates the $l = 1$ projector from the pseudopotential). Using MCSCF wave functions, he has obtained very good agreement with experiment. Following his line, we have investigated several two electron systems which have the advantage to be free of the fixed node approximation. Another even more important property of these

TABLE I. Valence correlation energy contributions to ionization energies of alkaline earth atoms (reversed sign, mhartree).

	Be	Mg	Ca	Sr	Ba
PDMC ^{a,b}	48.1(3)	34.4(5)	30.2(6)	27.5(5)	26.0(4)
Full CI	47.9	34.7	30.1	27.7	25.9

^a Pure diffusion quantum Monte Carlo.

^b The statistical errors are given in parentheses.

TABLE II. Valence correlation energy contributions to electron affinities of the alkali atoms (reversed sign, mhartree).

	Li	Na	K	Rb	Cs
PDMC ^{a,b}	26.7(6) ^c	23.9(5)	21.3(7)	20.2(6)	19.5(8)
Full CI	27.4	24.0	21.5	20.4	19.4

^a Pure diffusion quantum Monte Carlo

^b The statistical errors are given in parentheses.

^c Addition of an excited s^2 configuration yields 27.4(3)

systems is the possibility to improve the trial wave function, significantly, through the addition of just a few configurations to the HF or MCSCF part. This allows to improve the localized pseudopotential systematically when necessary, and to estimate the effort which is necessary to obtain the correct result. In calculations with more than two electrons, the MCSCF wave function is important also for improving the fixed node approximation.¹⁷ However, here it is difficult to distinguish between these two errors because an improvement of the nodes must not result in an improvement of the local pseudopotential and vice versa. It will be a subject of further studies to look at systems with more than two electrons where the number of configurations necessary to improve the wave function significantly may quickly increase. The other approximation inherent in the algorithm is the short-time approximation but, for our systems, no indication is found that this error is significant compared to the statistical error. Thus, the only error remaining in PDMC is that coming from the localization of the pseudopotential.

At the first stage of our calculations, we look at the valence correlation energy contribution to the ionization energy of the alkaline earth atoms, see Table I. Here, we found that the incorporation of the p^2 configuration gives good results in agreement with Christiansen. All energies are within the statistical error in agreement with the extensive CI calculations of Fuentealba.¹³ Comparison with experimental values is not meaningful because we have not included polarization potentials up to now. As it has been shown,¹³ inclusion of polarization potentials is necessary to reproduce experimental values and will be the subject of further work.

A similar situation arises for the valence correlation energy contributions to the electron affinities of the alkali atoms, see Table II. As in the case of the alkaline earth atoms, we use a MCSCF wave function which contained the

TABLE III. Valence correlation energy of the alkali dimers (reversed sign, mhartree).

	Li ₂	LiNa	LiK	Na ₂	NaK	K ₂
PDMC ^{a,b}	31.3(6)	29.3(7)	28.6(8)	27.7(9)	26.9(10)	25.5(9)
VMC ^c	21.3(4)	18.7(4)	18.4(5)	16.4(2)	15.8(4)	14.5(3)
Full CI	32.6	30.0	29.4	27.6	26.4	24.5

^a Pure diffusion quantum Monte Carlo.

^b The statistical errors are given in parentheses.

^c Variational quantum Monte Carlo.

TABLE IV. Valence correlation energy of Li_2 for various MCSCF wave functions (reversed sign, mhartree).

CSF ^a	$1\sigma_g^2$	$1\sigma_g^2 1\sigma_u^2$	$1\sigma_g^2 1\pi_u^2$	$1\sigma_g^2 1\sigma_u^2 1\pi_u^2$	$1\sigma_g^2 2\sigma_g^2 1\sigma_u^2 1\pi_u^2$
PDMC ^{b,c}	29.1(9)	29.2(9)	31.3(6)	31.4(4)	32.4(3)
VMC ^d	7.5(9)	13.4(6)	21.3(4)	24.8(4)	28.6(3)

^a Configuration state functions.

^b Pure diffusion quantum Monte Carlo.

^c The statistical errors are given in parentheses.

^d Variational quantum Monte Carlo.

s^2 and the p^2 configurations. Our results show good agreement with the CI values except in the case of the Li anion. There, we have found a slight difference between Monte Carlo and CI. Addition of an additional excited s^2 configuration is sufficient to remove this discrepancy.

Finally, we look at the valence correlation energy contributions to the dissociation energies of the alkali dimers (see Table III) which is a more serious test for the method because the energy difference between the variational energy of our trial wave function and the exact energy is much larger. Here, the Li_2 molecule is especially studied, see Table IV. We have found that the HF wave function is not sufficient to reproduce the CI correlation energy. The most significant contribution not included in the HF wave function is due to the π_u configurations, however, for reproducing the CI value, it is necessary to include a second σ_g configuration. Table IV shows the convergence of both the variational and exact energy (with respect to the local pseudopotential) to the exact CI value. Here we have the case that it is necessary to add a configuration of a symmetry which is already present in the wave function to obtain the correct result. In the case of Li_2 one can also observe the reduction of the statistical error with the improvement of the wave function. Comparing the HF with the four-configuration MCSCF wave function, Table IV shows a reduction of the statistical error by a factor of 3, while the computational effort increases by a factor of 4. To obtain a similar reduction for the HF wave function, it would be necessary to take a simulation time of nine times longer. For the other alkali dimers, we have restricted ourselves to the σ_g and π_u configurations which are sufficient to reproduce the CI results within the statistical error.

V. CONCLUSIONS

The conventional semilocal approach for pseudopotentials has several serious disadvantages when applied in quantum Monte Carlo calculations; it has one significant advantage, that is, the large experience in using this form of pseudopotential in standard methods as compared to other approaches like the pseudo-Hamiltonian of Bachelet, Ceperley, and Chiochetti¹⁸ which are very effective in quantum Monte Carlo calculations. We found an efficient scheme to implement semilocal pseudopotentials in quantum Monte Carlo methods. The method proposed by us, to change the projection operator, is one possible way to improve the performance of Monte Carlo calculations with pseudopotentials.

Our results show that the localization of the pseudopotential may be a source of significant errors, not only in the case where parts of the pseudopotential are neglected due to vanishing projection integrals with the trial wave function, but also in cases where all projection operators are represented in the MCSCF wave function as was pointed out in the case of the Li_2 molecule. The use of MCSCF wave functions represent a way to improve the local pseudopotential systematically, whereby at the same time, a significant reduction of the statistical error is observed.

ACKNOWLEDGMENT

Thanks are due to Dr. M. Caffarel for supporting us with technical details of his method and for useful discussions on quantum Monte Carlo and to Dr. G. Igel-Mann for a critical reading of the manuscript. We are also grateful to Professor H. J. Werner for providing us with the program MOLPRO.

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