Adding electron-nuclear cusps to Gaussian basis functions for molecular quantum Monte Carlo calculations

Jörg Kussmann and Christian Ochsenfeld*

Theoretische Chemie, Universität Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany
(Received 23 May 2007; revised manuscript received 26 June 2007; published 14 September 2007)

A scheme for imposing the electron-nuclear cusp condition in molecular quantum Monte Carlo (QMC) calculations using Gaussian basis functions is presented. While the constraints proposed by Ma *et al.* [J. Chem. Phys. **122**, 224322 (2005)] have been used, in our scheme the basis functions are modified instead of the molecular orbitals. This method can also be directly applied to density matrix-based QMC calculations whose effort scales linearly for calculating the local energy [J. Kussmann *et al.*, Phys. Rev. B **75**, 165107 (2007)]. Furthermore, virtually no additional computational effort in the evaluation of the local energy arises within QMC calculations.

I. INTRODUCTION

Quantum Monte Carlo (QMC)[1–6] methods have been discussed as promising alternatives to expensive post-Hartree-Fock methods in the field of quantum chemistry. While providing CCSD(T) accuracy,[7] QMC methods also provide a relatively soft asymptotical scaling behavior with system size of $\mathcal{O}(N^3)$ for a fixed number of sampling steps. Here, it has to be stressed that the overall scaling behavior is composed of different steps: for example, within the widely used single-electron move algorithm, the prefactor of the cubically scaling update procedure of the matrix of cofactors is rather small,[6] so that a quadratic scaling $[\mathcal{O}(N^2)]$ will dominate the computational effort over a wide range of system sizes. Furthermore, the number of sampling steps increases linearly with the system size for attaining a given statistical error bar, which increases the scaling order by 1. Recent developments based on localized molecular orbitals[8–11] and also on the N-particle density matrix (N-PDM QMC)[12] can reduce the computational effort to asymptotically linear $[\mathcal{O}(N)]$ for calculating the local energy.

Within QMC calculations, the expectation value of the energy is determined as the average over a large number of electronic configurations **R**,

$$\langle E \rangle = L^{-1} \sum_{i=1}^{L} E_L(\mathbf{R}_i), \qquad (1)$$

with $E_L(\mathbf{R}) = \Psi^{T^{-1}}(\mathbf{R}) \hat{H} \Psi^T(\mathbf{R})$ as the local energy, which is calculated with a trial wave function Ψ^T, and the number of sampling steps L. QMC methods are intrinsically stochastic, i.e., the results exhibit a statistical error which is proportional to the square root of the variance of the mean value (σ^2) and to the inverse square root of the number of sampling steps ($1/\sqrt{L}$). As it will be briefly described in the following, the statistical error strongly depends on the quality of the provided trial wave function Ψ^T. In general, trial functions of Slater-Jastrow type are used which are given as a product of a single Slater determinant Ψ from a self-consistent field (SCF) calculation and a correlation factor e^U,

$$\Psi^T = \Psi e^U, \qquad (2)$$

or in terms of the N-particle trial density,[12]

$$\rho_N^T = \rho_N e^{2U}. \qquad (3)$$

Since most *ab initio* packages use Gaussian-type basis functions χ_μ, the one-electron orbitals do not account correctly for the electron-nuclear cusp[13] if an electron approaches the nucleus. When the electron-nuclear distance r goes to zero, the potential energy diverges as $-Z/r$. For a real eigenstate of the Hamiltonian $\hat{H}$, the total energy is constant within the whole configuration space, i.e., independent of the value of r. Therefore, the kinetic energy has to diverge with $r \to 0$ into the opposite direction in order to compensate for the potential energy. However, as a result of using Gaussian-type functions, the kinetic energy for $r \to 0$ is finite and therefore the local energy $E_L = \Psi^{T^{-1}} \hat{H} \Psi^T$ diverges ($E_L \to -\infty$). These instabilities at the nuclei lead to a large variance in the resulting mean value and so to a slow convergence of the sampling process.

Ma *et al.*[14] proposed a simple scheme for adding electron-nuclear cusps to one-electron molecular orbitals (MOs) $\phi_i(\mathbf{r})$. They replaced the part of the MO close to the nuclei within a cusp-correction radius r_c by an exponential function which fulfills Kato's cusp condition and ensures a well-behaved local energy. Their results have shown that this approach significantly reduces the variance σ^2 and also slightly lowers the resulting variational energy, while the computational effort is raised by a few percent only.

Within our N-PDM QMC algorithm,[12] the scheme of Ma *et al.*[14] could also be used by explicitly constructing the one-particle density matrix elements $\rho(\mathbf{r}; \mathbf{r}')$ from the MOs $\phi_i(\mathbf{r})$,

$$\rho(\mathbf{r}; \mathbf{r}') = \sum_{i \in occ} \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}'). \qquad (4)$$

However, since canonical MOs are usually delocalized over the complete nuclear frame, this construction of the density matrices would scale cubically with system size $[\mathcal{O}(N^3)]$.

In order to ensure a linear-scaling behavior for the density matrix-based QMC schemes, we propose in this work a modification of the scheme of Ma *et al.*[14] Instead of correct-

ing for the cusps at the MO level, we replace the s-type basis functions χ_μ by an exponential function within a radius r_c around the nucleus. In this way, we are able to employ this correction within the linear-scaling density matrix formulation of QMC,[12] where MOs are entirely avoided. Furthermore, no additional computational effort is introduced by this approach since the basis functions are represented by cubic splines. Note that this scheme can of course also be used within MO-based QMC calculations.

After reconsidering Kato's cusp condition in terms of the density matrix, we describe our modified cusp-correction algorithm in detail and finally present illustrative calculations.

II. ELECTRON-NUCLEAR CUSP CONDITION FOR THE N-PARTICLE DENSITY MATRIX

Considering a nucleus of charge Z at the origin and an electron at $\mathbf{r}$, the cusp condition of Kato[13] requires that the N-particle wave function Ψ depends linearly on the electron-nuclear distance r in the limit $r \to 0$,

$$\left(\frac{\partial \langle \Psi \rangle}{\partial r} \right)_{r=0} = -Z \langle \Psi \rangle_{r=0}, \tag{5}$$

with $\langle \Psi \rangle$ as the spherical average of the wave function. Reformulating this in terms of the N-particle density matrix gives

$$\left(\frac{\partial \langle \rho_N(\mathbf{R}; \mathbf{R}') \rangle_{\mathbf{R}'=\mathbf{R}}}{\partial r} \right)_{r=0} = -Z \langle \rho_N(\mathbf{R}) \rangle_{r=0}, \tag{6}$$

where $\mathbf{R}$ and $\mathbf{R}'$ represent all electronic variables. Note that the standard convention from density matrix theory is used,[15] i.e., the differential operator only acts on $\mathbf{R}$ and after this operation $\mathbf{R}'$ is replaced with $\mathbf{R}$. Similar to an SCF wave function, the N-particle density matrix is given by a determinant of a matrix containing Fock-Dirac density matrix values $\rho(\mathbf{r}; \mathbf{r}')$.[12,15] Thus, it is sufficient to impose the cusp condition upon the one-particle density:

$$\left(\frac{\partial \langle \rho(\mathbf{r}; \mathbf{r}') \rangle_{\mathbf{r}'=\mathbf{r}}}{\partial r} \right)_{r=0} = -Z \langle \rho(0) \rangle, \tag{7}$$

where $\rho(0)$ is the value for $\mathbf{r}=0$. The one-particle density matrix $\rho(\mathbf{r}; \mathbf{r}')$ is constructed using the SCF density matrix $\mathbf{P}$,

$$\rho(\mathbf{r}; \mathbf{r}') = \sum_{\mu\nu} P_{\mu\nu} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}'). \tag{8}$$

Similar to Ma et al.,[14] we split the density into a part arising from s-type basis functions centered on the corresponding nucleus ($\tilde{\rho}$) and the rest of the density (η),

$$\begin{aligned} \rho(\mathbf{r}; \mathbf{r}') &= \tilde{\rho}(\mathbf{r}; \mathbf{r}') + \eta(\mathbf{r}; \mathbf{r}') \\ &= \sum_{\mu'} \tilde{\chi}_{\mu'}(\mathbf{r}) \sum_\nu P_{\mu'\nu} \chi_\nu(\mathbf{r}') + \sum_{\mu''} \chi_{\mu''}(\mathbf{r}) \sum_\nu P_{\mu''\nu} \chi_\nu(\mathbf{r}'), \end{aligned} \tag{9}$$

where μ' denotes s-type basis functions centered on the given nucleus and μ'' all other basis functions. The cusp

condition is fulfilled if the one-particle density function $\tilde{\rho}(\mathbf{r})$ obeys Eq. (10),

$$\left(\frac{\partial \langle \tilde{\rho}(\mathbf{r}; \mathbf{r}') \rangle_{\mathbf{r}'=\mathbf{r}}}{\partial r} \right)_{r=0} = -Z[\tilde{\rho}(0) + \eta(0)]. \tag{10}$$

As in Ref. 14, we use the latter equation as the basis for the cusp correction. Note that Eq. (10) similarly holds for the one-particle reduced density matrix $\rho(\mathbf{r}; \mathbf{r}')$, i.e., for arbitrary values of $\mathbf{r}'$, since only the derivative with respect to $\mathbf{r}$ occurs in Eq. (10).

III. CUSP-CORRECTION ALGORITHM

Instead of replacing $\tilde{\rho}(\mathbf{r})$ inside a given radius r_c analogous to Ref. 14, we replace a part of the s-type functions $\chi_{\mu'}$. In order to facilitate comparability with the work of Ma et al.,[14] we use their notations, but note that the formulas in our work correspond to basis functions. Inside the radius r_c, whose determination is described later in the text, we replace the basis functions by

$$\tilde{\chi}_{\mu'}(r) = C_{\mu'} + \text{sgn}[\chi_{\mu'}(0)] \exp(p_{\mu'}(r)) = C_{\mu'} + R_{\mu'}(r), \tag{11}$$

with

$$p_{\mu'}(r) = \alpha_0^{\mu'} + \alpha_1^{\mu'} r + \alpha_2^{\mu'} r^2 + \alpha_3^{\mu'} r^3 + \alpha_4^{\mu'} r^4, \tag{12}$$

and $C_{\mu'}$ as a shift to ensure that $(\tilde{\chi}_{\mu'}(r) - C_{\mu'})$ is of one sign within r_c. Since the exponential term has the sign of the function $\text{sgn}[\chi_{\mu'}(0)]$, shifting by $C_{\mu'}$ enables us to describe a node within the correction radius r_c. The constraints to determine the coefficients in Eq. (11) are the same as those proposed by Ma et al.,[14] i.e., the basis functions have to be continuous at r_c [$X_1^{\mu'}$, $X_2^{\mu'}$, and $X_3^{\mu'}$ in Eqs. (13), (14), and (15)] and the cusp condition in Eq. (10) has to be fulfilled [$X_4^{\mu'}$ in Eq. (16)]. The last degree of freedom is used to ensure that the local energy is well behaved [$X_5^{\mu'}$ in Eq. (17)] which is described below.

$$\ln|\chi_{\mu'}(r_c) - C_{\mu'}| = p_{\mu'}(r_c) = X_1^{\mu'}, \tag{13}$$

$$\frac{1}{R_{\mu'}(r_c)} \left. \frac{d\tilde{\chi}_{\mu'}}{dr} \right|_{r_c} = p'_{\mu'}(r_c) = X_2^{\mu'}, \tag{14}$$

$$\frac{1}{R_{\mu'}(r_c)} \left. \frac{d^2\tilde{\chi}_{\mu'}}{dr^2} \right|_{r_c} = p''_{\mu'}(r) + [p'_{\mu'}(r_c)]^2 = X_3^{\mu'}, \tag{15}$$

$$\frac{1}{RP'} \left. \frac{d\tilde{\rho}(r; r')_{r'=r}}{dr} \right|_0 = p'_{\mu'}(0) = -Z \frac{\tilde{\rho}(0) + \eta(0)}{RP'} = X_4^{\mu'}, \tag{16}$$

$$\ln|\tilde{\chi}_{\mu'}(0) - C_{\mu'}| = p_{\mu'}(0) = X_5^{\mu'}, \tag{17}$$

with

$$RP' = \sum_{\mu'} R_{\mu'}(0) \sum_\nu P_{\mu'\nu}\chi_\nu(0). \qquad (18)$$

It has to be stressed that Eqs. (13)–(17) exhibit the same relationship between the constrains $X_1^{\mu'} - X_5^{\mu'}$ and the different derivatives of the polynomial $p_{\mu'}$ as in the work of Ma *et al.*[14] Therefore, one obtains the same analytical solution for the expansion coefficients $\alpha^{\mu'}$:

$$\alpha_0^{\mu'} = X_5^{\mu'}, \qquad (19)$$

$$\alpha_1^{\mu'} = X_4^{\mu'}, \qquad (20)$$

$$\alpha_2^{\mu'} = 6\frac{X_1^{\mu'}}{r_c^2} - 3\frac{X_2^{\mu'}}{r_c} + \frac{X_3^{\mu'}}{2} - 3\frac{X_4^{\mu'}}{r_c} - 6\frac{X_5^{\mu'}}{r_c^2} - \frac{X_2^{\mu'2}}{2}, \quad (21)$$

$$\alpha_3^{\mu'} = -8\frac{X_1^{\mu'}}{r_c^3} + 5\frac{X_2^{\mu'}}{r_c^2} - \frac{X_3^{\mu'}}{r_c} + 3\frac{X_4^{\mu'}}{r_c^2} + 8\frac{X_5^{\mu'}}{r_c^3} + \frac{X_2^{\mu'2}}{r_c}, \qquad (22)$$

$$\alpha_4^{\mu'} = 3\frac{X_1^{\mu'}}{r_c^4} - 2\frac{X_2^{\mu'}}{r_c^3} + \frac{X_3^{\mu'}}{2r_c^2} - \frac{X_4^{\mu'}}{r_c^3} - 3\frac{X_5^{\mu'}}{r_c^4} - \frac{X_2^{\mu'2}}{2r_c^2}. \quad (23)$$

Considering the definition of the one-particle density matrix in Eq. (9), it becomes clear that the constrain resulting from the cusp condition in Eq. (10) forces all parameters $\alpha_1^{\mu'}$ to be the same for all $\tilde{\chi}_{\mu'}$. This is due to the fact that one can factor out RP' only if all parameters $\alpha_1^{\mu'}$ are the same for all $\tilde{\chi}_{\mu'}$ in the sum over μ' in solving Eq. (16).

To obtain the parameters, we start with an initial guess for the basis functions $[\tilde{\chi}_{\mu'}(0) = \chi_{\mu'}(0)]$ and vary these values to obtain a well-behaved effective one-electron energy,

$$
\begin{aligned}
E_L^S(r) &= \tilde{\rho}(r)^{-1}\hat{h}\tilde{\rho}(r;r')_{r'=r} \\
&= \tilde{\rho}(r)^{-1}\left[-\frac{1}{2}\nabla^2 - \frac{Z_{eff}}{r}\right]\tilde{\rho}(r;r')_{r'=r} \\
&= -\frac{1}{2\tilde{\rho}(r)}\left(\sum_{\mu'}\left\{\frac{2p'_{\mu'}}{r} + p''_{\mu'}(r) + [p'_{\mu'}(r)]^2\right\}\right. \\
&\quad \left.\times R_{\mu'}(r)\sum_\nu P_{\mu'\nu}\chi_\nu(r)\right) - \frac{Z_{eff}}{r}.
\end{aligned} \qquad (24)
$$

In order to ensure the cusp condition in Eq. (10), the following equation must hold:

$$\lim_{r\to 0} \frac{-1}{\tilde{\rho}(r)}\sum_{\mu'}\frac{p'_{\mu'}(r)}{r}R_{\mu'}(r)\sum_\nu P_{\mu'\nu}\chi_\nu(r) - \frac{Z_{eff}}{r} \overset{!}{=} 0. \quad (25)$$

Considering the equations above, we obtain for the effective charge Z_{eff} in Eq. (24)

$$\frac{Z}{r}\left(1 + \frac{\eta(0)}{\tilde{\rho}(0)}\right)\overset{!}{=}0 \Rightarrow Z_{eff} = Z\left(1 + \frac{\eta(0)}{\tilde{\rho}(0)}\right). \qquad (26)$$

Similar to the work of Ma *et al.*,[14] we now vary the values of the basis functions at $r=0$ in order to minimize the square deviation from the ideal energy curve E_L^{ideal}:

$$\frac{E_L^{ideal}}{Z^2} = \beta_0 + \beta_1 r^2 + \beta_2 r^3 + \beta_3 r^4 + \beta_4 r^5 + \beta_5 r^6 + \beta_6 r^7 + \beta_7 r^8, \qquad (27)$$

with $\beta_1 = 3.258\ 19$, $\beta_2 = -15.0126$, $\beta_3 = 33.7308$, $\beta_4 = -42.8705$, $\beta_5 = 31.2276$, $\beta_6 = -12.1316$, and $\beta_7 = 1.946\ 92$. β_0 is chosen to ensure a continuous behavior of the local energy at r_c. Since there are, in general, more than only one s-type basis function centered on the corresponding nucleus, one has to use a multidimensional minimizer; in our current implementation, we use the Broyden-Fletcher-Goldfarb-Shanno algorithm.[16] Note that the energy E_L^S in Eq. (24) corresponds to the superposition of the effective local energies $E_L^{S(\phi_i)}$ for the one-electron molecular orbital ϕ_i described in Ref. 14:

$$E_L^S = \sum_{i\in occ}\tilde{\phi}_i^{-1}\hat{h}\tilde{\phi}_i = \sum_{i\in occ}E_L^{S(\phi_i)}. \qquad (28)$$

Therefore, the use of E_L^{ideal} of Ref. 14 within our scheme is justified.

The radius r_c is determined in the same way as proposed by Ma *et al.*:[14] Starting with $r_c = 1/Z$, the radius is reduced until the square deviation is smaller than $Z^2/50$. For a discussion of the influence of r_c on the variance as well as the energy, see Ref. 14.

Illustrative calculations of our scheme are presented in the final section of this work to show the performance of our cusp-correction approach.

IV. RESULTS

In this section, first exemplary calculations similar to those of Ref. 14 are presented. In all calculations, a medium-size Pople basis set (6-31G(d)) (Ref. 17) is used; the one-particle density matrices **P** are obtained from Hartree-Fock (HF) calculations with the Q-CHEM program package.[18] The automatic scheme as implemented in our package QUANTUMMC (Ref. 19) is used, i.e., no further optimization of the correction radius r_c has been applied.

First, the behavior of the local energy of D-alanine ($C_3H_7O_2N$) is sampled for an electron "tunneling" the nitrogen atom of the molecule. Starting from an arbitrarily chosen configuration, the electron with the smallest distance to the nitrogen nucleus is chosen. The electron is then moved along the vector connecting the initial electron and nuclear positions. The energy has been calculated for 1000 configurations. The results are plotted in Fig. 1. As expected, the local energy calculated with the uncorrected basis functions (full line) diverges as the distance goes to zero. The cusp-corrected basis functions, instead, yield a well-behaved local energy over the whole range of values for r (dashed line).
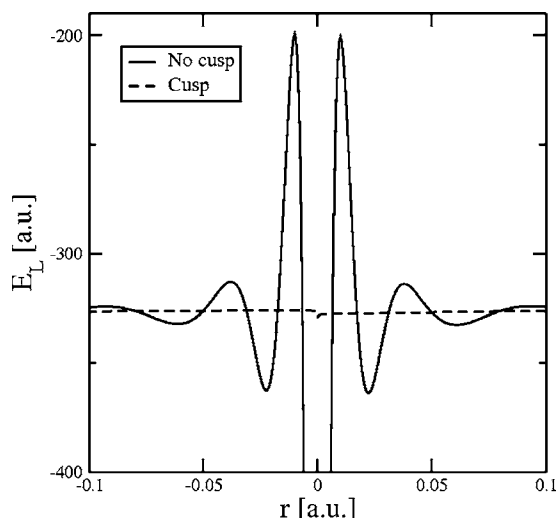
FIG. 1. "Tunneling" of an electron through the nitrogen nucleus in an alanine molecule. The local energy is shown vs the electron-nuclear distance for uncorrected (full line) and corrected (broken line) s-type basis functions.
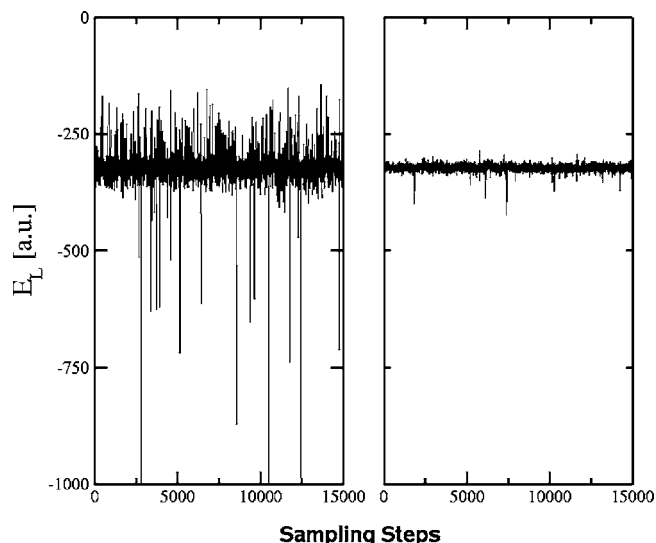

FIG. 2. Fluctuation of the local energy of an alanine molecule without (left) and with (right) cusp correction. The local energy is plotted vs the corresponding sampling step. HF trial functions expanded in a 6-31G(d) basis set have been used.

The value of the local energy over a range of 15 000 sampling steps for D-alanine is shown in Fig. 2. A correlated trial density has been used with a simple correlation factor of Boys-Handy type[20,21] to account for the electron-electron correlation. As Fig. 2 shows, the uncorrected Gaussian-type basis functions yield large negative values as a result from configurations with electrons close to a nucleus ($\lim_{r\to0} -Z/r = -\infty$). These extreme values almost completely vanish when cusp-corrected basis functions are supplied and the smaller variance is obvious in Fig. 2.

Finally, the results for several systems from the G1 set of molecules[22] are listed in Table I, which have been also studied in Ref. 14. All results are determined from 500 000 sampling steps; the trial densities were completely uncorrelated, i.e., no correlation factor was used. This means that the electron-electron divergences still remain and the lowering of the variance entirely results from the cusp correction of the basis functions. As in Ref. 14, the variance σ^2 is significantly lowered for all systems. Furthermore, the energy is slightly lowered by the correction of the basis functions,

which can be seen for the results of, e.g., LiH or C_2H_6. The presented results clearly show that our cusp-correction scheme provides a similar improvement of the QMC results as the original work of Ma *et al.*[14]

V. CONCLUSIONS

It has been shown that the modification of basis functions allows us, in analogy to the work of Ma *et al.*,[14] to account for the electron-nuclear cusp condition in molecular many-electron systems. For all test systems, the variance of the energy is significantly reduced. Therefore, energies can be obtained with small statistical errors by sampling less configurations as compared to calculations using uncorrected, Gaussian-type basis functions. Furthermore, the energy is lowered as illustrated for several systems. In contrast to the original scheme by Ma *et al.*,[14] where the correction is introduced to the molecular orbitals, the method presented in this work enables an asymptotically linear-scaling behavior for

TABLE I. Comparison of VQMC energies (E_{VQMC}) and variances (σ^2) for some test cases; in addition, the HF energies are displayed (atomic units). Calculations have been performed without correlation factors; the HF-SCF wave function is represented within a 6-31G(d) basis. VQMC results have been obtained from 500 000 sample configurations.

Molecule	E_{HF}	Not cusp corrected		Cusp corrected	
		E_{VQMC}	σ^2	E_{VQMC}	σ^2
LiH	−7.9809	−7.980(1)	7.14(2)	−7.9826(6)	1.76(1)
N_2	−108.9354	−108.9(1)	390(8)	−108.927(6)	25(1)
CO_2	−187.6284	−187.60(1)	598(9)	−187.635(9)	45(2)
SO_2	−547.1579	−547.16(6)	5239(150)	−547.16(1)	178(5)
CH_3Cl	−499.0929	−499.10(6)	7286(73)	−499.10(1)	162(5)
C_2H_6	−79.2285	−79.22(1)	214(3)	−79.237(5)	16.1(4)

the construction of the density within an N-PDM QMC algorithm.[12] Since the cusp-corrected basis functions are represented by cubic splines, our approach introduces no further computational effort as compared to the use of conventional basis functions. It has to be stressed that our cusp-correction scheme can of course also be applied to MO-based QMC calculations, although our scheme has been developed for a density matrix-based framework.

*ochsenfeld@uni-tuebingen.de

[1] D. M. Ceperley, G. V. Chester, and M. H. Kalos, Phys. Rev. B **16**, 3081 (1977).

[2] J. B. Anderson, J. Chem. Phys. **63**, 1499 (1975).

[3] P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, J. Chem. Phys. **77**, 5593 (1982).

[4] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).

[5] J. B. Anderson, *Quantum Monte Carlo: Origins, Development, Applications* (Oxford University Press, New York, 2007).

[6] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Rev. Mod. Phys. **73**, 33 (2001).

[7] S. Manten and A. Lüchow, J. Chem. Phys. **115**, 5362 (2001).

[8] S. Manten and A. Lüchow, J. Chem. Phys. **119**, 1307 (2003).

[9] A. J. Williamson, R. Q. Hood, and J. C. Grossman, Phys. Rev. Lett. **87**, 246406 (2001).

[10] D. Alfé and M. J. Gillan, J. Phys.: Condens. Matter **16**, L305 (2004).

[11] A. Aspuru-Guzik, R. Slalomón-Ferrer, B. Austin, and W. A. Lester, Jr., J. Comput. Chem. **26**, 708 (2005).

[12] J. Kussmann, H. Riede, and C. Ochsenfeld, Phys. Rev. B **75**, 165107 (2007).

[13] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[14] A. Ma, M. D. Towler, N. D. Drummond, and R. J. Needs, J. Chem. Phys. **122**, 224322 (2005).

[15] R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960).

[16] W. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in C*, 2nd ed. (Cambridge University Press, New York, 1992).

[17] W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972); J. D. Dill and J. A. Pople, *ibid.* **62**, 292 (1975); M. M. Francl, W. J. Petro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, *ibid.* **77**, 3654 (1982).

[18] Development version of the Q-CHEM program package (www.q-chem.com).

[19] J. Kussmann and C. Ochsenfeld, QUANTUMMC, a parallel quantum Monte Carlo code in C++.

[20] K. E. Schmidt and J. W. Moskowitz, J. Chem. Phys. **93**, 4172 (1990).

[21] S. F. Boys and N. C. Handy, Proc. R. Soc. London, Ser. A **310**, 43 (1969).

[22] J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtis, J. Chem. Phys. **90**, 5622 (1989).