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A feasible transcorrelated method for treating electronic cusps using a frozen Gaussian geminal

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Abstract

We develop a feasible transcorrelated method for accelerating the convergence of reproducing the dynamic correlation effects with the size of one-electron basis. The effective Hamiltonian is parameterized in such a way that the Coulomb repulsion is compensated at short inter-electronic distances in terms of a frozen Gaussian geminal. The geminal is chosen to be independent of the position and orientation of pair-electrons. The extra part of the transcorrelated Hamiltonian is also short-ranged, size-consistent, and universal to the states of interest. We preliminarily applied the method to the single-reference many body perturbation theory with some pilot calculations. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In the standard ab initio molecular orbital theory, correlation energies converge very slowly with the size of one-electron basis, due to singularity of the Coulomb repulsion at $r_{12} = 0$. An attempt to mitigate this feature was first put forward by Hylleraas [1] to find a remarkable speed-up in the convergence by including functions dependent on the inter-electronic distance. Since then, various methods with correlation factors have been proposed and applied to the calculations of atoms and molecules [2–10]. These approaches are classified according to the forms of the factors (including a term linear to the inter-electronic distance or not) and the types of the excitations (with or without orthogonal projec-

tors). The second criterion is more crucial than the first, because the orthogonal projectors make the factors non-commutative with potentials.

Until today, the approach developed by Kutzelnigg, Klopper and co-workers [7,8,10], the so-called R12 method, would be of the widest applicability. The method avoids explicit evaluation of high-rank 'difficult integrals' using the resolution of identity in a complete basis set representation. Especially, the coupled-cluster (CC) R12 method of Noga et al. [9,10] enables us to reach chemical accuracy both in the basis set convergence and in the sophistication of wave function in the single reference framework. Calculations on the practical basis set limits have been reported for molecules as large as the benzene–argon van der Waals complex and ferrocene at the Moeller–Plesset second-order (MP2) perturbation theory level [11,12]. Only shortcomings are the long-range nature of effective interaction that makes the scaling property unfavorable, and the non-commutative property to the

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potential rather complicates the theoretical construction.

In the methods using correlated Gaussian-type functions [2–4,6], all the integrals can be evaluated in closed forms involving at most one-dimensional numerical integration. Despite their unsatisfactory forms for Kato's cusp condition [13], the functions have been successfully used in calculations of small molecules with high accuracy (for example, see [14]). More recently, Persson and Taylor have introduced an MP2 method [15], which incorporates the Gaussian geminal approach [4] with the R12 ansatz. They avoid tedious nonlinear optimizations using a geminal fitted to the linear r_{12} behavior. The explicit evaluation of the three-electron integrals allows us to use a one-electron basis set much smaller than those required for fulfilling the standard approximation in the R12 method [8,10]. The extension to theories beyond MP2 however includes more complicated integrals than the three-electron ones. Efficiency of the R12 method is not so much in the choice of the explicit linear behavior but in the thorough use of the completeness insertion to the difficult integrals.

In this Letter, we propose an attractive alternative, which is applicable to large-scale molecular orbital calculations. The basic idea of the approach is to employ a transcorrelated Hamiltonian with a frozen Gaussian geminal parameterized to be short-ranged. In Section 2, we illustrate the method. Results and discussions with pilot calculations are given in Section 3.

2. Method

In the transcorrelated method of Boys and Handy [2], a correlated wave function is represented by a symmetric correlation factor and a Slater determinant as

$$\Psi = \exp(F)\Phi. \tag{1}$$

The method optimizes both the factor and the determinant, approximating F to be the sum of two-electronic functions (geminals). This is a straightforward extension of the treatment of a homogeneous electron gas [16]. Use of the similarity transformed Hamiltonian, the so-called

transcorrelated Hamiltonian, $\tilde{H} = e^{-F}He^{F}$, simplifies the formal construction because of its termination at the three-body effective interaction [2]. The non-linear optimization of the factor however requires a laborious process.

Alternatively, we use a fixed geminal in the transcorrelated Hamiltonian and represent the residual correlation effects in terms of the usual correlated wave function, like the configuration interaction (CI) one, spanned by a one-electron basis. In this particular work, the geminal is assumed to be independent of positions and orientations (a function of only electronic distances),

$$F = \frac{1}{2}\sum_{i\neq j}f(r_{ij}). \tag{2}$$

One can express the geminal in the occupation number representation with a complete basis set. If we retain the full part of the operator, the similarity transformed Hamiltonian becomes

$$\tilde{H} = e^{-F}He^{F} = H + K + L, \tag{3}$$

$$K = \frac{1}{2}\sum_{pqrs}\langle pq|K_{12}|rs\rangle a_p^+ a_q^+ a_s a_r, \tag{4}$$

$$L = \frac{1}{6}\sum_{pqrstu}\langle pqr|L_{123}|stu\rangle a_p^+ a_q^+ a_r^+ a_u a_t a_s, \tag{5}$$

$$K_{12} = -\nabla_1^2 f(r_{12}) - \nabla_1 f(r_{12})\cdot\nabla_1 f(r_{12})$$
$$\qquad -\nabla_1 f(r_{12})\cdot(\nabla_1 - \nabla_2), \tag{6}$$

$$L_{123} = -3\nabla_1 f(r_{12})\cdot\nabla_1 f(r_{13}). \tag{7}$$

It is noted that the three-electronic part, L_{123}, can be further arranged to make the operator symmetric to the permutations of the three electronic indices. If we choose a factor linear to the interelectronic distance, $(1/2)r_{ij}$, the Coulomb repulsion is entirely canceled by the new two-electronic interaction [2,7]. The rapid growth of non-vanishing integrals with system size however becomes a fatal element for very large molecules.

Instead of noticing the entire behavior of the geminal, we localize it in such a way that the factor converges to unity, $e^{-f(r)}\to 1$, at large electronic separations. The conventional molecular orbital theory is fairly efficient in describing the long-

range behavior of wave functions. The localized geminal will make the three-body interaction less important; the probability of finding three-electrons within the factor radius decreases. Moreover, computational cost for the evaluation of the necessary integrals scales only linearly with system size. Abandoning exploring a suitable form of geminal for requirement, we express the factor using a frozen Gaussian geminal (FROGG),

$$f(r_{12}) = -\sum_{G}^{N_G} c_G \exp(-\zeta_G r_{12}^2). \tag{8}$$

The minus sign is for the decreasing probability of finding electrons. Although the form does not satisfy the cusp condition at $r_{12} = 0$ [13], the asymptotic behavior in this limit is considered less important for electrons interacting in the three-dimensional space. This fact supports the successful applications of the explicitly correlated Gaussian functions [4,6,14]. In this work, we optimize the coefficients and exponents such that the scalar potential part in K_{12} cancels the Coulomb interaction around $r_{12} = 0$,

$$r_{12}^{-1}w(r_{12}) - \nabla_1^2 f(r_{12}) - \nabla_1 f(r_{12}) \cdot \nabla_1 f(r_{12}) \cong 0, \tag{9}$$

where $w(r_{12})$ is a short-range weight function. We introduce an additional weight Gaussian, $w(r_{12}) = \exp(-\zeta_w r_{12}^2)$; all expressions in the least square fitting procedure are in closed forms. We show the obtained results with $\zeta_w = 5$ and $N_G = 6$ in Table 1 and Fig. 1. The effective potential (solid line) is not singular any more, whereas its long-range behavior is held in common with the Coulomb potential. With this fit, 98.7% of the short-range

Table 1
The parameters of FROGG used in this work[a]

ζ_G	c_G
0.621698	0.078215
3.371717	0.132037
14.27116	0.068633
82.76522	0.029047
605.5295	0.012063
6596.808	0.004346

[a] The exponents and coefficients are optimized with $N_G = 6$ and $\zeta_w = 5$.
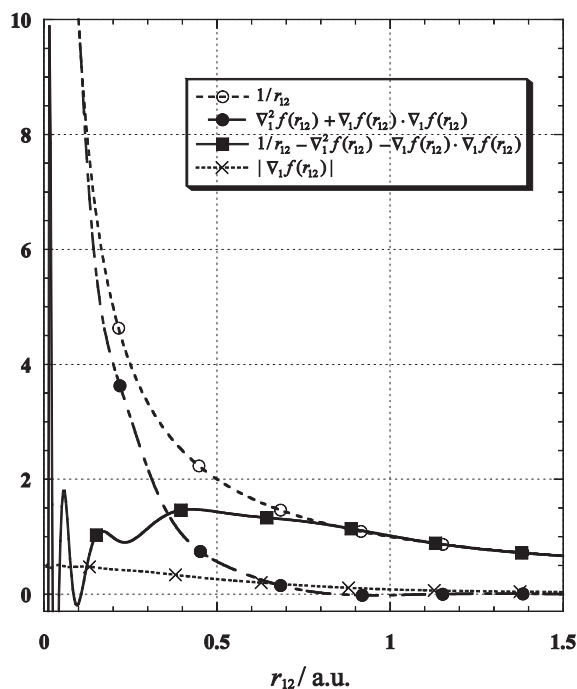

Fig. 1. Schematic representation of the optimized potentials. The bare Coulomb (dashed line) and optimized short-range Coulomb (dash–dotted line) interactions lead to the effective interaction in the transcorrelated Hamiltonian (solid line) without the singularity. The vector quantity, $\nabla_1 f(r_{12})$ (dotted line), is much less singular and included in the two- and three-electron integrals.

Coulomb energy, $\int dr_{12} r_{12}^{-1} w(r_{12})$, is compensated. The norm of the vector potential (dotted line) is a smoothly decreasing function, the asymptotic behavior of which at $r_{12} = 0$ is a good measure for the efficiency of the fit, $1/2$ being exact [2].

The present approach is based on the effective Hamiltonian in the transcorrelated form, which is parameterized to be short-ranged, size-consistent, and universal to the electronic states of interest. It is therefore applicable to most of the standard electronic structure theories. The simplest application will be to the second-order many-body perturbation theory. For this, we employ a modified MP partitioning to the transcorrelated Hamiltonian,

$$\tilde{H} = H_0^{(\text{MP})} + \tilde{V}, \tag{10}$$

where $H_0^{(\text{MP})}$ is the usual Hartree–Fock model Hamiltonian. One notes that the new perturbation,

$\tilde{V}$, is free from the Coulomb singularity. Thus the perturbation series are expected to converge quicker than the usual MP ones, if the long-range tail is reproduced well by the HF determinant. This may not be the case for electrons around the core; the orbital relaxation effects will be important. To absorb the effects, we solve the pseudo-orbital equation with a primary partitioning dropping the three-body part,

$$\langle X_\kappa^+ \phi | (H+K)\exp(\overline{T}_1) | \phi \rangle_c = 0 \quad \forall \kappa \in S, \qquad (11)$$

where c and S denote connected operators and single replacements, respectively, and $\{X_\kappa^+\}$ is a set of particle–hole excitation operators. The property of the transformed operator with $\overline{T}_1$ is discussed in detail by Koch et al. [17]. We calculate the subsequent modified perturbation energies through the second-order,

$$\overline{E}^{(0)} = \langle \phi | (H+K)\exp(\overline{T}_1) | \phi \rangle - E_{HF}, \qquad (12)$$

$$\overline{E}^{(1)} = \langle \phi | L \exp(\overline{T}_1) | \phi \rangle, \qquad (13)$$

$$\overline{E}^{(2)} = \langle \phi | \tilde{H} \exp(\overline{T}_1) T^{(1)} | \phi \rangle. \qquad (14)$$

Singles and doubles are included in the first-order wave operator,

$$\left\langle X_\kappa^+ \phi \left| \left[H_0^{(MP)}, T^{(1)} \right] \right| \phi \right\rangle$$
$$= -\langle X_\kappa^+ \phi | \tilde{H} \exp(\overline{T}_1) | \phi \rangle_c \quad \forall \kappa \in SD. \qquad (15)$$

This procedure is appropriate for the molecules of light atoms in which the two-body interactions dominate the orbital shapes. For molecules with heavy elements, the three-electronic part, L, is to be included in determining the amplitude, $\overline{T}_1$.

In this Letter, the three-electron integrals are approximated with a completeness insertion in a similar way used in the R12 methods [8,10]. The required vector integrals, $\langle pq | \nabla_1 f(r_{12}) | rs \rangle$, are intermediates of some other integrals in $\langle pq | K_{12} | rs \rangle$, and can be evaluated without extra CPU time. The integrals, $\langle pq | \nabla_1 f(r_{12}) \cdot \nabla_1 f(r_{12}) | rs \rangle$, which are quadratic to the factor, are generated in a separate loop. It is possible to combine the electron repulsion integrals with $\langle pq | K_{12} | rs \rangle$ after the generation of the model Hamiltonian. We did not take this convention for a later analysis of the perturbation energies.

3. Result and discussion

Nearly exact non-relativistic results have been reported for Be atom from CC-R12 [10] and some other theories. Firstly, we therefore apply the present approach to the atom. We use the double-zeta basis set [18] augmented with s- and p-primitives of the largest exponents taken from the atomic natural orbitals (ANO) [19] and with a d-polarization function of the exponent, 0.4. We decontract all functions and use them as a 10s6p1d primitive set for the accuracy of the completeness insertion of the three-electron integrals. The augmentation of the large exponents becomes important in the second-order energy through the operator dependent on orbital momentum, $\nabla_1 f(r_{12}) \cdot \nabla_1$. For comparison, we use the full 14s9p4d3f primitive set constructed from the same ANO set. We show the components of the correlation energies in Table 2. Only the three-electronic operator, L, contributes to the modified first-order wave operator of single replacements. The corresponding second energy is referred to as $E_{SL}^{(2)}$. We accumulated the necessary integrals in the order, the Coulomb (V), K, and L operators. Accordingly, the second-order energy is classified into three parts, $E_{DV}^{(2)}$, $E_{DK}^{(2)}$, and $E_{DL}^{(2)}$, which are the energies of only V, at least linear to K without the contribution of L, and the residual of them, respectively. The component, $E_{DV}^{(2)}$, corresponds to the conventional MP2 energy apart from the small correction of the preliminary modification with $\overline{T}_1$. One notes that the single-determinant energies, i.e., the sums of $\overline{E}^{(0)}$ and $\overline{E}^{(1)}$, cover a large amount

Table 2
Components of the perturbation energy (mE_h) of the Be atom[a]

Component	10s6p1d	14s9p4d3f
$\overline{E}^{(0)}$	−57.063	−57.046
$\overline{E}^{(1)}$	−1.671	−1.680
$\overline{E}_{SL}^{(2)}$	0.148	0.150
$\overline{E}_{DV}^{(2)}$	−66.370	−69.886
$\overline{E}_{DK}^{(2)}$	46.079	47.537
$\overline{E}_{DL}^{(2)}$	0.179	0.198
Total	−78.698	−80.727

[a] The best R12 energies are −76.248, −85.292 and −94.293 mE_h at MBPT(2) and MBPT(3) CCSD(T), respectively.

of the correlation energy. The present results lie in between the best ones of R12-MBPT(2) and R12-MBPT(3). This is accounted for by the modified perturbation free from singularity as discussed in the previous section. The transcorrelated Hamiltonian retains the full exponential of the factor including quadruples and higher excitations from the HF vacuum.

The second application is to methane, the R12 result of which is also available [10]. We used compact 10s5p1d and 11s6p2d1f primitive sets for the carbon atom derived from the correlation consistent valence double-zeta (cc-pVDZ) and triple-zeta (cc-pVTZ) basis sets [20], and augmented with s- and p-primitives of the large exponents in ANO as in the Be case. We intend to use these sizes of basis sets in practical applications to larger molecules. The primitive set for the hydrogen atoms is fixed to be 4s1p of cc-pVDZ. The results are shown in Table 3. One can see that the three-body interaction especially in the first-order energy is more important than the Be atom case. Although the completeness insertions included in $\overline{E}^{(1)}$, $\overline{E}_{SL}^{(1)}$ and $\overline{E}_{DL}^{(2)}$ seem unsaturated with the present basis sets, the difference in the total correlation energy of these components, ca. 5 mE_h, is much smaller than those in the individual contributions of $\overline{E}_{DV}^{(2)}$ and $\overline{E}_{DK}^{(2)}$. The total correlation energies are again in between the R12-MBPT(2) and R12-MBPT(3) ones. Evaluating the meagerness of the conventional MP2 energies, the present approach is particularly useful with basis sets as small as the present ones.

We have presented a part of the results of our transcorrelated method. All results are reasonable in molecules with light atoms. It is also found that the uncertainty from the approximate three-electron integrals increases when a system includes heavy atoms. For instance, the component, $\overline{E}^{(1)}$, becomes as large as the total correlation energy in the water molecule. The single energy, $\overline{E}_{SL}^{(1)}$, also becomes important with the increase of atomic numbers; the inclusion of L in determining $\overline{T}_1$ is necessary. The simplest amelioration is to employ an auxiliary basis set for the completeness insertion, which is different from the orbital set describing the wave function. The decomposed two-electron integrals include only one index for the auxiliary set, and the computational load does not increase drastically with the size of the auxiliary set. Alternatively, the three-electron integrals can be calculated explicitly using efficient recurrence relations after the contraction of the geminal [21]. The three-body interactions are important only when all electrons are in the same vicinity of an atom in the present choice of the localized geminal. Our transcorrelated Hamiltonian owns the long-range decay as the bare Hamiltonian. Thus the present approach will be suited to local correlation procedures (see Ref. [22] and references therein).

4. Conclusion

We have illustrated a feasible method for treating electronic cusps. The main features of the method are summarized as follows. We started with the transcorrelated Hamiltonian of Boys and Handy, which terminates at the three-body interaction irrespective of the choice of the anti-symmetrized part expanded by the one-electronic basis. This fact extremely simplifies the application to more sophisticated theories including the coupled-cluster and multi-reference ones. Bypassing the optimization of the correlation factor, we use a short-ranged FROGG, utilizing the coincident behavior of pair-electrons. The short-range nature of the geminal is a crucial point for the scaling property. The number of the additional integrals increases only linearly to the size of the system. Thus the combination with local basis will make

Table 3
Components of the perturbation energy (mE_h) of the methane molecule[a]

Component	10s5p1d	11s6p2d1f
$\overline{E}^{(0)}$	−112.821	−111.073
$\overline{E}^{(1)}$	−55.491	−62.544
$\overline{E}_{SL}^{(2)}$	9.012	10.331
$\overline{E}_{DV}^{(2)}$	−217.791	−243.000
$\overline{E}_{DK}^{(2)}$	93.450	113.800
$\overline{E}_{DL}^{(2)}$	5.500	7.177
Total	−278.140	−286.309

[a] The R12 energies are −273.579, −286.613 and −295.948 mE_h at MBPT(2)-A, MBPT(3) and CCSD(T), respectively.

the application to very large molecules possible. We plan to proceed with such applications.

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