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Explicitly correlated second order perturbation theory: Introduction of a rational generator and numerical quadratures

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A rational generator, which fulfills the cusp conditions for singlet and triplet electron pairs, is proposed and applied to explicitly correlated second order Møller–Plesset perturbation theory calculations. It is shown that the generator in conjunction with frozen geminals improves the convergence of correlation energy without introducing any variational parameters in explicitly correlated functions. A new scheme for three-electron integrals based on numerical quadratures is also illustrated. The method is tested for the convergence of reaction enthalpies with various basis sets. © 2004 American Institute of Physics. [DOI: 10.1063/1.1757439]

I. INTRODUCTION

A fairly large basis set is required for a reliable result in molecular orbital calculations due to the correlation cusp by the Coulomb potential with singularity at electron coalescence. The cusp condition,¹ the exact wave functions obey, suggests that the Coulomb hole behaves linearly to the interelectronic distance at small r_{12} . And thus it is the main obstacle to accurate calculations that a configuration interaction (CI) expansion converges very slowly as $(L+1)^{-3}$ with the maximum angular momentum of one-electronic basis L .^{2,3} As exhibited a long time ago for the He ground state wave function,⁴ the inclusion of r_{12} terms accelerates the convergence of the partial wave expansion substantially to $(L+1)^{-7}$.⁵ It has, however, turned out that the generalization to many-electronic systems is not so straightforward because of the complex couplings of explicitly correlated functions like r_{12} and electronic interactions r_{12}^{-1} . Thus it has been one of the central issues in quantum chemistry and physics to establish useful expansions of many-electron wave functions involving interelectronic distances explicitly.

The quantum Monte Carlo (QMC) techniques have advantages in the ease of implementation as such couplings are estimated numerically. The variational Monte Carlo method usually employs a Jastrow correlation factor in a simple form like a product of two-body functions of electron–nucleus and electron–electron distances, though the importance of the three-body contribution that correlates two electrons and a nucleus has been shown for improved results.⁶ Despite the simple form of a trial function, QMC suffers from spin contamination.⁷ The reason for this is the spin dependency in the correlation factor. Antisymmetric electronic pair functions (triplet pairs) should follow the so-called p -wave cusp condition,^{3,8} which is different from the s -wave cusp condition for singlet pairs. For a factor defined as a function of spatial-spin coordinates, the inseparability of the correlations for spin antiparallel singlet and triplet pairs averages the descriptions to cause spin contamination as displacements from

those of the corresponding spin-parallel triplet pairs. The subsequent discussion in this paper explains this situation in more detail.

Explicitly correlated Gaussian functions have been employed successfully for benchmark calculations,^{9,10} ever since the functions were introduced in quantum chemistry by Boys and Singer.¹¹ The application is, however, limited to very small molecules due to the prohibitively increasing number of N -body integrals, which themselves can be estimated relatively easily in closed form algebraic expressions. The transcorrelated method^{12,13} avoids such a difficulty by the use of a similarity transformed effective Hamiltonian. The transcorrelated Hamiltonian terminates at the three-electron interaction owing to the commutability between the correlation factor and potentials. There has been a recent resurgence in the development of the method with auxiliary CI-type expansions.^{14,15} Spin-free correlation factors for the s -wave cusp condition are utilized around electron coalescences to offer improved convergences at the second order perturbation theory¹⁶ and coupled-electron pair approximation.¹⁷ Relevant progress has also been reported in density functional theory¹⁸ and QMC.¹⁹ The main drawbacks of the transcorrelated methods are that the obtained energy is not necessarily an upper bound of the true energy and that the cusp conditions cannot be fulfilled completely as in QMC.

Another class of theories utilizes two-electron functions (geminals) with strong orthogonality projection operators. In early applications of such methods, Gaussian-type geminals were employed in many-body perturbation theory.^{20,21} Further developments involving a simplification of the second order energy functional to bypass the requirement of four-electron integrals were given by Szalewicz and co-workers.²² The studies since have highlighted the treatment of three-electron integrals to transcend the restriction to small molecules. The main breakthrough is the resolution of the identity (RI) introduced by Kutzelnigg and Klopper,²³ which expands a many-electron integral into a sum of products of two-electron integrals. The R12 coupled-cluster method was also developed based on the RI approximation.^{24,25} Although

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it turned out that a very large basis set must be employed to ensure the accuracy of the RI approximation, the use of auxiliary functions makes calculations with standard orbital basis sets possible.²⁶ A comprehensive overview of the methods is given in Ref. 27. More recently, Manby utilized the density fitting (DF) technique^{28–31} to enhance the MP2-R12 method with a fractional computational cost.³² It is also shown that DF improves the convergence of the RI approximation.³³

The principal objective of this paper is to offer a generator form, which is capable of fulfilling both of the *s*-wave and *p*-wave cusp conditions. It is shown that the explicitly correlated second order perturbation theory with frozen geminals is conveniently derived based on the generator. We also demonstrate that numerical quadratures are effective in the implementation of the method containing multielectron integrals. In what follows, we present necessary formulas. Numerical results involving reaction enthalpies are presented in Sec. III.

II. THEORY

A. Rational generator

The product of a correlation factor, $\exp(G)$, and an antisymmetric wave function, Φ ,

$$\Psi = \exp(G)\Phi, \quad (1)$$

has been employed as trial functions in many places for electron correlation problems in molecules, clusters, and solids. The so-called Jastrow–Slater wave function consisting of a Jastrow factor and a single Slater determinant is quite popular in QMC calculations. The generator, G , is typically a sum of two-electron functions

$$G = \frac{1}{2} \sum_{ij}^{\neq} g(\mathbf{x}_i, \mathbf{x}_j), \quad (2)$$

where the summation indices are exclusive to each other. The two-electron function is usually of spatial-spin coordinates, $\mathbf{x}_i = (\mathbf{x}_i, \omega_i)$, and is symmetric, $g(\mathbf{x}_i, \mathbf{x}_j) = g(\mathbf{x}_j, \mathbf{x}_i)$. The choice of the spherically symmetric form, $g(\mathbf{x}_i, \mathbf{x}_j) = g(|\mathbf{x}_{ij}|)$, simplifies the implementation though the inclusion of electron–nucleus distances improves the result significantly.⁶ Additionally, the choice of Φ as a linear combination of Slater determinants turned out to be useful for a system with near degeneracy.³⁴

The exact asymptotic behavior of the geminal is given by the cusp condition of Kato¹ and its generalization of Pack and Byers-Brown without angular-averaging the relative coordinate.⁸ The results are known to be the *s*- and *p*-wave cusp conditions³

$$g(\mathbf{x}_1, \mathbf{x}_2) = \frac{r_{12}}{2(s+1)} + O(r_{12}^2), \quad (3)$$

where the quantum number of the relative coordinate takes the values $s=0$ for singlet and $s=1$ for singlet triplet pairs, respectively. Apparently, the traditional form in Eq. (2) does not suffice the above conditions since the spin antiparallel singlet and triplet pairs

$$\Phi_{ij}^{(0,0)}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \{ij\}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) [\alpha(\omega_1)\beta(\omega_2) - \beta(\omega_1)\alpha(\omega_2)], \quad (4)$$

$$\Phi_{ij}^{(1,0)}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \{ij\}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) [\alpha(\omega_1)\beta(\omega_2) + \beta(\omega_1)\alpha(\omega_2)], \quad (5)$$

are not distinguished by the generator, where $\{ij\}^{(s)}(\mathbf{r}_1, \mathbf{r}_2)$ denotes symmetric and antisymmetric spin-less pair functions

$$\begin{aligned} \{ij\}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) &= \delta_{ij} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) + \frac{1}{\sqrt{2}} (1 - \delta_{ij}) \\ &\times [\phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) + \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2)], \quad (6) \end{aligned}$$

$$\{ij\}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) - \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2)]. \quad (7)$$

The appropriate cusp conditions can be imposed only to the spin parallel triplet pairs

$$\Phi_{ij}^{(1,1)}(\mathbf{x}_1, \mathbf{x}_2) = \{ij\}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) \alpha(\omega_1) \alpha(\omega_2), \quad (8)$$

$$\Phi_{ij}^{(1,-1)}(\mathbf{x}_1, \mathbf{x}_2) = \{ij\}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) \beta(\omega_1) \beta(\omega_2). \quad (9)$$

Consequently, the resulting wave function is spin contaminated even if Φ is an eigenfunction of \hat{S}^2 .

The key for amelioration is to make use of the parity in the spatial coordinates since the difference in correlations is not originating from the spin function but from the symmetry in the spatial part. To this end, we introduce the permutation operator, p_{12} , which interchanges the labeled spatial coordinates

$$p_{12} \phi(\mathbf{r}_1) = \phi(\mathbf{r}_2) p_{12}. \quad (10)$$

The operator gives unity if there is no function concerning the labeled spatial coordinates either on the left or right of the operator

$$p_{12} c = c. \quad (11)$$

The new generator is spin free and is expressed as a sum of direct and exchange functions

$$\bar{G} = \frac{1}{2} \sum_{ij}^{\neq} \bar{G}_{ij}, \quad (12)$$

$$\bar{G}_{ij} = g^{(d)}(\mathbf{r}_i, \mathbf{r}_j) + g^{(x)}(\mathbf{r}_i, \mathbf{r}_j) p_{ij}. \quad (13)$$

This explicitly separates the weights for the singlet and triplet pairs as

$$\begin{aligned} \bar{G}_{12} \Phi_{12}^{(0,0)}(\mathbf{x}_1, \mathbf{x}_2) &= [g^{(d)}(\mathbf{r}_1, \mathbf{r}_2) + g^{(x)}(\mathbf{r}_1, \mathbf{r}_2)] \\ &\times \Phi_{12}^{(0,0)}(\mathbf{x}_1, \mathbf{x}_2), \quad (14) \end{aligned}$$

$$\begin{aligned} \bar{G}_{12} \Phi_{12}^{(1,m)}(\mathbf{x}_1, \mathbf{x}_2) &= [g^{(d)}(\mathbf{r}_1, \mathbf{r}_2) - g^{(x)}(\mathbf{r}_1, \mathbf{r}_2)] \\ &\times \Phi_{12}^{(1,m)}(\mathbf{x}_1, \mathbf{x}_2). \quad (15) \end{aligned}$$

The cusp conditions give the asymptotic behaviors

$$g_{12}^{(d)} = g^{(d)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{3}{8}r_{12} + O(r_{12}^2), \quad (16)$$

$$g_{12}^{(x)} = g^{(x)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{8}r_{12} + O(r_{12}^2). \quad (17)$$

The transcorrelated Hamiltonian simplifies the application of correlation factors as it terminates at three-body interactions, irrespective of the treatment of the Hamiltonian. Although the new generator, \bar{G} , is also commutable with potentials, nonterminating series appear in commutators with kinetic energy operators due to the inclusion of permutation operators. Further inspections are necessary in the exponentiation of the generator if it is used as in the transcorrelated method and QMC. In this work, we combine the generator with the strong orthogonality projector for many-body perturbation theory in the following section.

B. Second order perturbation theory

We derive the second order perturbation theory based on the rational generator. The derivation is closely parallel to the R12-MP2 method beyond RI.^{26,35} For a while, the standard notations, i, j, \dots , a, b, \dots , and p, q, \dots are employed for occupied, virtual, and general spin orbitals with respect to a single-reference vacuum, respectively. Additionally the virtual orbitals in the complete basis set are denoted by the Greek letters, α, β, \dots . The corresponding projectors for the occupied, given virtual and complete virtual orbitals are defined as

$$P_n = \sum_i |\varphi_i(n)\rangle\langle\varphi_i(n)|, \quad (18)$$

$$Q_n = \sum_a |\varphi_a(n)\rangle\langle\varphi_a(n)|, \quad (19)$$

$$Q_n^* = 1 - P_n = \sum_\alpha |\varphi_\alpha(n)\rangle\langle\varphi_\alpha(n)|. \quad (20)$$

We write the first order wave operator as

$$\Omega^{(1)} = \Omega_O^{(1)} + \Omega_G^{(1)}, \quad (21)$$

where $\Omega_O^{(1)}$ is the orbital-based excitation operator,

$$\Omega_O^{(1)} = \frac{1}{4} \sum_{abij} c_{ij}^{ab} a_a^+ a_b^+ a_j a_i, \quad (22)$$

$$c_{ij}^{ab} = c_{ji}^{ba} = -c_{ji}^{ab} = -c_{ij}^{ba}, \quad (23)$$

and $\Omega_G^{(1)}$ is the strong orthogonality excitation block of the rational generator with respect to the vacuum

$$\Omega_G^{(1)} = \frac{1}{2} \sum_{\alpha\beta ij} \langle\alpha\beta|\bar{G}_{12}|ij\rangle a_\alpha^+ a_\beta^+ a_j a_i. \quad (24)$$

We have not antisymmetrized the elements of $\Omega_G^{(1)}$ for later convenience. Assuming that the reference function, $\Psi^{(0)}$, is the exact Hartree–Fock (HF) solution, we obtain the second order Hylleraas energy functional of the wave operator

$$\begin{aligned} E_V^{(2)} &= \langle\Psi^{(1)}|H_0 - E^{(0)}|\Psi^{(1)}\rangle + 2\langle\Psi^{(1)}|V|\Psi^{(0)}\rangle \\ &= \sum_{i>j} \left\{ \pi_{ij} + \sum_{a>b} [2c_{ij}^{ab} \theta_{ab,ij} - (c_{ij}^{ab})^2 \right. \\ &\quad \left. \times (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) \right\}, \end{aligned} \quad (25)$$

$$\pi_{ij} = \langle[ij]|(-\bar{\kappa}_{12} + 2r_{12}^{-1})Q_1^*Q_2^*\bar{G}_{12}|[ij]\rangle, \quad (26)$$

$$\theta_{ab,ij} = \langle[ab]|\bar{\kappa}_{12} + r_{12}^{-1}|[ij]\rangle, \quad (27)$$

where the square bracket denotes antisymmetric spin pair functions

$$[pq] = \frac{1}{\sqrt{2}} [\varphi_p(\mathbf{x}_1)\varphi_q(\mathbf{x}_2) - \varphi_q(\mathbf{x}_1)\varphi_p(\mathbf{x}_2)], \quad (28)$$

and $\bar{\kappa}_{12}$ is the antisymmetric commutator between the generator and Fock operator

$$\bar{\kappa}_{12} = -\bar{\kappa}_{12}^+ = [F_1 + F_2, \bar{G}_{12}]. \quad (29)$$

Variations with respect to $\{c_{ij}^{ab}\}$ give the second order energy expression, which is a sum of the usual Møller–Plesser perturbation theory (MP2) energy and the corrections of the explicitly correlated functions

$$\begin{aligned} E_V^{(2)} &= \sum_{i>j} \left(\pi_{ij} + \sum_{a>b} \frac{\theta_{ij,ab}^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \right) \\ &= E^{(2)} - \Delta E_N^{(2)} + 2\Delta E_Z^{(2)}, \end{aligned} \quad (30)$$

$$E^{(2)} = \sum_{i>j} \sum_{a>b} \frac{\langle[ab]|r_{12}^{-1}|[ij]\rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (31)$$

$$\begin{aligned} \Delta E_N^{(2)} &= \sum_{i>j} \left(\langle[ij]|\bar{\kappa}_{12}Q_1^*Q_2^*\bar{G}_{12}|[ij]\rangle \right. \\ &\quad \left. + \sum_{a>b} \frac{\langle[ij]|\bar{\kappa}_{12}|[ab]\rangle\langle[ab]|\bar{\kappa}_{12}|[ij]\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \right), \end{aligned} \quad (32)$$

$$\begin{aligned} \Delta E_Z^{(2)} &= \sum_{i>j} \left(\langle[ij]|r_{12}^{-1}Q_1^*Q_2^*\bar{G}_{12}|[ij]\rangle \right. \\ &\quad \left. + \sum_{a>b} \frac{\langle[ij]|r_{12}^{-1}|[ab]\rangle\langle[ab]|\bar{\kappa}_{12}|[ij]\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \right). \end{aligned} \quad (33)$$

The first term of $\Delta E_N^{(2)}$ involves four-electron integrals because of the exchange term in the Fock operator. As there exist several variants conceivable for the treatment of these integrals, we use the following approximations to close the scheme through three-electron integrals in this particular work.

First, we neglect the effect of the off-diagonal block between the complementary and given virtual orbital spaces in the Fock operator, $Q_1 F_1 (Q_1^* - Q_1) = 0$, to yield the simplifications

$$\begin{aligned} \Delta E_N^{(2)} &\cong \Delta E_N'^{(2)} = \sum_{i>j} \langle[ij]|\bar{\kappa}_{12}(Q_1^*Q_2^* - Q_1Q_2) \\ &\quad \times \bar{G}_{12}|[ij]\rangle, \end{aligned} \quad (34)$$

$$\Delta E_Z^{(2)} \cong \Delta E_Z'^{(2)} = \sum_{i>j} \langle [ij] | r_{12}^{-1} (Q_1^* Q_2^* - Q_1 Q_2) \bar{G}_{12} | [ij] \rangle. \quad (35)$$

This is called the extended Brillouin condition,^{23,26} the method of which is distinguished by an asterisk in R12-MP2 theory. The reported results are very similar to those without the approximation.³⁵ For the exact generator, (with respect to the block-diagonal Fock operator), the first order equation holds in the complementary virtual space

$$(Q_1^* Q_2^* - Q_1 Q_2) (\bar{\kappa}_{12} + r_{12}^{-1}) |[ij]\rangle = 0, \quad (36)$$

to equalize the energy corrections, $\Delta E_N'^{(2)}$ and $\Delta E_Z'^{(2)}$, (virial-type theorem).³⁶ Second, the exchange operator is neglected to leave only the dominant kinetic energy part in the Fock operator as in the R12-MP2/A method

$$\bar{\kappa}_{12} \cong -\frac{1}{2} [\nabla_1^2 + \nabla_2^2, \bar{G}_{12}]. \quad (37)$$

The resulting method features the independency of the Hamiltonian partitioning, which becomes less important as the order of perturbation increases.

C. Frozen Gaussian geminals

The short-range asymptotic behaviors of the generator, \bar{G} , are given by Eqs. (16) and (17), while the geminals must be damped at a long distance because of the localized nature of fluctuation potentials.³⁷ To see this more closely, let us consider the He dimer with minimal basis. In this case, the extended Brillouin condition holds explicitly and the correction, $\Delta E_Z^{(2)}$, to the reaction energy in the limit, $r_{12} \rightarrow \infty$, is

$$\Delta E_Z^{(2)} \propto 4 \sum_{p_{APB}} \langle s_{ASB} | r_{12}^{-1} | p_{APB} \rangle \langle p_{APB} | g_{12}^{(d)} | s_{ASB} \rangle, \quad (38)$$

where s_μ and p_μ denote the localized occupied s and complete virtual p orbitals with an arbitrary spin index in the fragments $\mu = A, B$. It is found that the natural choice of $g_{12}^{(d)}$ at large inter-electronic distances is r_{12}^{-1} rather than linear r_{12} for the van der Waals decay, $\Delta E_Z^{(2)} \propto r_{12}^{-6}$. A binomial Taylor expansion shows that $\langle p_{APB} | r_{12}^{-1} | s_{ASB} \rangle$ goes as r_{12}^{-3} and is a function of local transition dipoles (and thus the coefficients are not universal but dependent on pairs). Substitution of r_{12}^{-1} into $\Delta E_N^{(2)}$ certainly brings the same asymptotic behavior. For explicitly correlated functions decaying slower than r_{12} , the long-range behavior must be discarded in some way as the unitary invariant formulation developed by Klopper.³⁸ Fortunately, the convergence of the dispersion-type correlation is much faster than that for Coulomb holes as the virtual orbitals saturate at $L_{\text{occ}} + 1$. Thus the decay of the explicitly correlated function may be faster than r_{12}^{-1} if a sufficient number of polarization functions are available. Additionally, the damping rate should be smooth and non-negative such that the commutator, $[\nabla_1^2 + \nabla_2^2, \bar{G}_{12}]$, is monotonic in the local energy fluctuation.

So far, we have not found a compact and useful function sufficing the above conditions. It is, however, shown that an appropriate range of r_{12} can be fitted accurately with a modest number of Gaussian-type geminals.³⁹ In connection with this, we have used frozen Gaussian-type geminals¹⁴

TABLE I. Gaussian exponents and coefficients of f_{12} used in the present work.

G	ζ_G	c_G
1	1000 000.0	-0.000 291 3933
2	199 473.656 25	-0.000 479 7250
3	39 789.742 1875	-0.001 148 0275
4	7 937.005 371 0938	-0.002 555 5096
5	1 583.223 510 7422	-0.005 645 8912
6	315.811 370 8496	-0.013 165 7524
7	62.996 051 7883	-0.027 383 9738
8	12.566 053 3905	-0.082 353 2790
9	2.506 596 5652	-0.136 069 3276
10	0.5	-0.058 926 3588

$$f_{12} = \sum_G^{N_G} c_G \exp(-\zeta_G r_{12}^2), \quad (39)$$

which satisfy the s -wave cusp condition approximately

$$f_{12} \cong \frac{1}{2} r_{12} + O(r_{12}^2). \quad (40)$$

The elements of the generator are then identified uniquely as

$$g_{12}^{(d)} = \frac{3}{4} f_{12}, \quad (41)$$

$$g_{12}^{(x)} = \frac{1}{4} f_{12}. \quad (42)$$

In this work, we use the geminal in Ref. 33 without scaling. The exponents are determined by the formula

$$\zeta_G = \zeta_1 \exp \left[(G-1) \frac{\ln(\zeta_1 / \zeta_{N_G})}{N_G - 1} \right], \quad (43)$$

with the number of primitive geminals, $N_G = 10$, and the range of exponents between $\zeta_1 = 10^6$ and $\zeta_{10} = 0.5$. The coefficients are optimized such that a short-range Coulomb potential with a weight Gaussian is suppressed in the similarity transformed Hamiltonian.¹⁴ The resulting parameters are given in Table I.

The generator joined with frozen geminals is particularly useful in spin-free formulation. For instance, redefining the orbital indices for spatial ones, the explicitly correlated wave operator is expressed by

$$\Omega_G^{(1)} = \frac{1}{2} \sum_{\alpha\beta ij} \langle \alpha\beta | \bar{G}_{12} | ij \rangle E_{\alpha i} E_{\beta j}, \quad (44)$$

$$\langle \alpha\beta | \bar{G}_{12} | ij \rangle = \frac{3}{4} \langle \alpha\beta | f_{12} | ij \rangle + \frac{1}{4} \langle \alpha\beta | f_{12} | ji \rangle, \quad (45)$$

where $E_{\alpha i}$ denotes the unitary group generator. Taking suitable linear combinations of pair functions, we naturally obtain the second order corrections for a closed shell system

$$\Delta E_N'^{(2)} = \sum_{s=0,1} (2s+1) (1 - \frac{1}{2}s)^2 \sum_{i \geq j} \langle \{ij\}^{(s)} | K_{12}^{(L)} (Q_1^* Q_2^* - Q_1 Q_2) f_{12} | \{ij\}^{(s)} \rangle, \quad (46)$$

$$\Delta E_Z^{(2)} = \sum_{s=0,1} (2s+1)(1-\frac{1}{2}s) \sum_{i>j} \langle \{ij\}^{(s)} | r_{12}^{-1} (Q_1^* Q_2^* - Q_1 Q_2) f_{12} | \{ij\}^{(s)} \rangle, \quad (47)$$

$$K_{12}^{(L)} = -\frac{1}{2}[\nabla_1^2 + \nabla_2^2, f_{12}] = -(\nabla_1^2 f_{12}) - (\nabla_1 f_{12}) \cdot (\nabla_1 - \nabla_2). \quad (48)$$

This is equivalent to the expression used in the previous work³³ and can be regarded as the generalization of the application of fitted r_{12} with s -wave cusp condition to the ground state wave function of the He atom.³⁹ The importance of the rational generator is, however, in the case that singlet and triplet pairs cannot be extracted so easily for more complicated reference wave functions. The strong orthogonality projector with respect to, for instance, the complete active space⁴⁰ enables us to impose the appropriate cusp conditions in multireference methods automatically. Such an application will be presented elsewhere.

The expansion of the strong orthogonality projector

$$Q_1^* Q_2^* = 1 - P_1 - P_2 + P_1 P_2 \quad (49)$$

gives explicit forms of the corrections. It is noted that only the connected term of f_{12} and $K_{12}^{(L)}$ survives in the expectation value of their product and the connectivity is attained just via the differential operators in the complete basis set limit

$$\sum_{i \geq j} \langle \{ij\}^{(s)} | K_{12}^{(L)} f_{12} | \{ij\}^{(s)} \rangle = \sum_{i \geq j} \langle \{ij\}^{(s)} | K_{12}^{(Q)} | \{ij\}^{(s)} \rangle, \quad (50)$$

$$K_{12}^{(Q)} \equiv \frac{1}{2}[K_{12}^{(L)}, f_{12}] = -(\nabla_1 f_{12}) \cdot (\nabla_1 f_{12}). \quad (51)$$

In addition to the two-electron integrals for the operators, f_{12} , $K_{12}^{(L)}$, r_{12}^{-1} , $K_{12}^{(Q)}$, and $Z_{12} \equiv f_{12} r_{12}^{-1}$, the energy corrections include the three-electron integrals in the general form

$$\langle ij | O_{12} P_2 f_{12} | k l \rangle = \sum_m \langle i j m | O_{12} f_{13} | k m l \rangle, \quad (52)$$

where O_{12} takes $K_{12}^{(L)}$ or r_{12}^{-1} . The two-electron integrals except for the operator, Z_{12} , are coincident with those in the transcorrelated method, which involves only commutators of the kinetic energy operator and f_{12} . Additionally, the integrals for f_{12}^2 should be calculated if the exchange operator is treated in $\bar{\kappa}_{12}$.

D. Numerical quadratures

The order of required integrals can be reduced by the use of numerical quadratures. For instance, electron repulsion integrals are represented as sums of two- and three-center objects over grid points

$$\langle pq | rs \rangle = \langle pr | r_{12}^{-1} | qs \rangle = \sum_g \bar{\phi}_p(\mathbf{r}_g) \phi_q(\mathbf{r}_g) \langle r | r_{1g}^{-1} | s \rangle, \quad (53)$$

where $\bar{\phi}_p(\mathbf{r}_g)$ denotes weighted orbitals of the quadrature

$$\bar{\phi}_p(\mathbf{r}_g) = w(\mathbf{r}_g) \phi_p(\mathbf{r}_g), \quad (54)$$

and $\langle r | r_{1g}^{-1} | s \rangle$ denotes electric field integrals

$$\langle p | r_{1g}^{-1} | q \rangle = \int d\mathbf{r}_1 \phi_p(\mathbf{r}_1) \phi_q(\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_g|^{-1}. \quad (55)$$

The scaling of the first integral transformation in an MP2 calculation is reduced to $N^2 OG$ from $N^4 O$ for the numbers of occupied and general functions, O and N , respectively, and that of grid points, G . This reduction is advantageous if $G \ll N^2$. Moreover the disk storage requirement can be avoided by the accumulation of the transformed integrals on the fly. If the weighted orbitals are replaced by a least square fitting operator, Eq. (53) reduces to the expression used in the pseudospectral method.⁴¹ The pseudospectral method, however, assumes the completeness of one electronic basis and the convergence is poor for a system with large energy fluctuations in the physical space, e.g., a correlated calculation with a small basis set. Efficient numerical integration schemes have been developed in density functional theory. For a reasonable accuracy (in the order of μE_h), the required number of grid points ranges from 1000 to 30 000 per atom, which is 10–100 times as large as those employed in the pseudospectral method. This is the price we have to pay in the present implementation. In addition to the expression of two-electron integrals without differential operators as in Eq. (53), those for $K_{12}^{(L)}$ can be expressed by

$$\langle pq | K_{12}^{(L)} | rs \rangle = \sum_g \bar{\phi}_p(\mathbf{r}_g) [\phi_r(\mathbf{r}_g) \langle q | A_{1g} | s \rangle + \mathbf{g}_r(\mathbf{r}_g) \cdot \langle q | \mathbf{B}_{1g} | s \rangle], \quad (56)$$

$$A_{1g} = -(\nabla_1^2 f_{1g}) - (\nabla_1 f_{1g}) \cdot \nabla_1, \quad (57)$$

$$\mathbf{B}_{1g} = -(\nabla_1 f_{1g}), \quad (58)$$

$$\mathbf{g}_p(\mathbf{r}_g) = [\nabla \phi_p(\mathbf{r}_g)]. \quad (59)$$

The numerical grid should integrate the spherical harmonics for all $l \leq L$ accurately with the maximum angular momentum of the integrand L . The octahedral grids of Lebedev, whose numbers, $(L+1)^2/3$, are near minimum, are efficient especially for nonlinear molecules. More flexible but less efficient grids are constructed by using the polar coordinate, $0 \leq \theta \leq \pi$ and $0 \leq \phi \leq 2\pi$. The number of grid points led to is $(L+1)^2/2$, i.e., $(L+1)/2$ for θ and $L+1$ for ϕ . In the explicitly correlated MP2 method, the two-electron integrals involve at least two occupied orbitals. Thus the grid in the expressions of two-electron integrals should exactly integrate the spherical harmonics at least up to $L=2(L_{\text{occ}}+L_{\text{bas}})$ for the maximum angular momentum quantum numbers of the occupied shells and given basis set, L_{occ} and L_{bas} , respectively. For molecules, the use of fuzzy Voronoi polyhedra⁴² is crucial for accurate numerical integration. In this case, the required number of grid points increases for the divided amplitudes of different atoms. Later refinements to gridding are given in the literature.^{43–46}

The main advantage of numerical integrations in the explicitly correlated method is that the three-electron integrals can be calculated accurately as

TABLE II. Errors of MP2 and MP2-geminal energies for the HF molecule with different grids.

cc-pCVTZ	(N_R, N_θ)	MP2		MP2-geminal			
		Numerical	Analytical	QD1	QD2	RI	DF
Uncontracted	Reference ^a	-0.343 652 59	-0.343 652 59	-0.381 875 69	-0.381 875 69	-0.383 458 20	-0.381 708 37
	(96,24)	0.000 000 00	(0.000 000 00)	0.000 000 00	0.000 000 00	(-0.001 582 51)	(0.000 167 32)
	(48,24)	-0.000 000 05	...	0.000 000 23	-0.000 000 10
	(36,24)	-0.000 001 67	...	0.000 012 90	-0.000 004 27
	(96,12)	0.000 001 67	...	-0.000 005 35	-0.000 001 91
	(48,12)	0.000 001 60	...	-0.000 005 11	-0.000 001 99
	(36,12)	0.000 000 38	...	0.000 006 03	-0.000 005 14
	(96,9)	-0.000 030 78	...	0.000 084 35	-0.000 159 86
	(48,9)	-0.000 030 80	...	0.000 084 23	-0.000 159 67
	(36,9)	-0.000 034 37	...	0.000 106 41	-0.000 171 07
Contracted	Reference ^a	-0.339 829 80	-0.339 829 80	-0.381 266 31	-0.381 266 31	-0.386 113 27	-0.364 552 38
	(96,24)	0.000 000 00	(0.000 000 00)	0.000 000 00	0.000 000 00	(-0.004 846 96)	(0.016 713 93)
	(48,24)	-0.000 000 02	...	0.000 000 15	-0.000 000 07
	(36,24)	-0.000 001 72	...	0.000 012 81	-0.000 003 81
	(96,12)	0.000 001 40	...	-0.000 005 46	-0.000 001 74
	(48,12)	0.000 001 37	...	-0.000 005 30	-0.000 001 81
	(36,12)	-0.000 000 06	...	0.000 005 83	-0.000 004 44
	(96,9)	-0.000 027 00	...	0.000 084 10	-0.000 161 85
	(48,9)	-0.000 026 98	...	0.000 083 97	-0.000 161 70
	(36,9)	-0.000 030 36	...	0.000 105 48	-0.000 171 97

^aReference MP2 energies. Numerical MP2 and MP2-geminal of QD1 and QD2 uses the grid with $N_R = 144$ and $N_\theta = 36$. The numbers in parentheses are the deviations from the reference energies of numerical integrations.

$$\langle ij|r_{12}^{-1}P_2f_{12}|kl\rangle = \sum_g \sum_m \bar{\phi}_i(\mathbf{r}_g)\phi_k(\mathbf{r}_g)\langle j|r_{1g}^{-1}|m\rangle \times \langle m|f_{1g}|l\rangle, \quad (60)$$

$$\langle ij|K_{12}^{(L)}P_2f_{12}|kl\rangle = \sum_g \sum_m \bar{\phi}_i(\mathbf{r}_g)[\phi_k(\mathbf{r}_g)\langle j|A_{1g}|m\rangle + \mathbf{g}_i(\mathbf{r}_g)\cdot\langle j|\mathbf{B}_{1g}|m\rangle]\langle m|f_{1g}|l\rangle. \quad (61)$$

In this case, the grids should integrate the spherical harmonics accurately for $l=6L_{\text{occ}}$ that is usually smaller than the requirement in two-electron integrals, $2(L_{\text{occ}}+L_{\text{bas}})$, for a molecule without a heavy atomic element. If the outermost occupied shell is filled completely, just the spherical average over m survives to reduce the requirement to $l=4L_{\text{occ}}$. The orbital indices in an integral are coincident in the MP2 method. Hence the accumulation involving the three-electron integrals in Eqs. (60) and (61) scales as O^3G , which is cheaper than the integral transformation of the three-center objects. In the first method of the present MP2 with explicitly correlated geminal (MP2 geminal), only three-electron integrals are treated numerically (QD1). Alternatively, all of the two- and three-electron integrals can be calculated by the numerical quadratures (QD2). The formulas for the required three-center integrals are given in Appendix B. The progress in this work is that the integrals for the spherically symmetric operators, $-(\nabla_{1g}^2 f_{1g})$ and $-(\nabla_{1g} f_{1g})\cdot(\nabla_{1g} f_{1g})$, are calculated as efficiently as the usual two-electron operators like r_{1g}^{-1} without increments of additional angular momentum indices for the differentiations.

III. RESULTS AND DISCUSSION

A. Convergence of numerical integrations

We preliminarily check the convergence of numerical integrations for the diatomic HF molecule using the product grid along with the augmented correlation-consistent aug-cc-pCVTZ basis set.⁴⁷⁻⁴⁹ The bond distance is taken from the optimized result at the all-electron correlated coupled-cluster single double (triple) (CCSD(T))/cc-pCVQZ level.⁵⁰ The maximum angular momentum indices, $L_{\text{occ}}=1$ and $L_{\text{bas}}=3$, lead to the minimum number of grid points, $n_\phi=9$, for a saturated result in the ϕ coordinate. In the C_{2v} alignment, the number increases to $n_\phi=12$ as the minimum multiple of 4. Thus the accuracy of numerical integration is a function of the numbers of the radial and θ angular grids, n_R and n_θ . The grid with $n_R=144$ and $n_\theta=36$ gives very accurate results, which are taken as reference values. Table II shows the calculated MP2 energies to eight decimal places in the Hartree atomic unit. With the reference grid, there is no deviation both in the MP2 and MP2-geminal energies between the numerical and analytical treatments of two-electron integrals. As the convergence of three-electron integrals is faster than that of two-electron integrals under the present condition, the reference MP2-geminal energies are considered to be exact within the given decimal places.

In addition to QD1 and QD2, we show the results of RI²³ and DF in conjunction with RI.³³ Both of the methods involve no approximations except for three-electron integrals. In the result with uncontracted basis, the absolute displacements from the reference MP2-geminal energy are $1.58mE_h$ and $0.17mE_h$ for RI and DF, respectively. Thus the decomposition of DF is by 1 order of magnitude more accurate than

TABLE III. Convergence of the MP2 energy for the first selection with cc-pCVXZ sets (mE_h).

Method	System	X=D	(%)	X=T	(%)	X=Q	(%)	X=5	(%)	Limit ^b
MP2 ^a	CH ₂ (¹ A ₁)	-146.21	(69.66)	-186.40	(88.81)	-199.91	(95.24)	-204.04	(97.21)	-209.9
	H ₂ O	-241.35	(66.65)	-317.51	(87.69)	-342.64	(94.63)	-350.59	(96.82)	-362.1
	NH ₃	-192.81	(59.71)	-287.16	(88.93)	-307.68	(95.29)	-314.34	(97.35)	-322.9
	HF	-242.81	(63.13)	-332.03	(86.33)	-361.32	(93.95)	-370.10	(96.23)	-384.6
	N ₂	-382.83	(71.30)	-477.87	(89.00)	-510.79	(95.14)	-520.07	(96.87)	-536.9
	CO	-362.99	(69.84)	-459.46	(88.41)	-493.03	(94.87)	-502.49	(96.69)	-519.7
	Ne	-228.30	(58.83)	-329.10	(84.80)	-361.51	(93.15)	-370.93	(95.58)	-388.1
	F ₂	-476.06	(64.28)	-642.57	(86.76)	-696.69	(94.07)	-712.28	(96.18)	-740.6
	Ave. %	...	65.4	...	87.6	...	94.5	...	96.6	...
	MP2-geminal ^a	CH ₂ (¹ A ₁)	-196.76	(93.74)	-206.38	(98.33)	-208.75	(99.45)	-209.42	(99.77)
H ₂ O		-337.57	(93.33)	-354.93	(98.02)	-359.61	(99.31)	-361.23	(99.76)	-362.1
NH ₃		-304.89	(94.42)	-317.39	(98.29)	-321.02	(99.41)	-322.49	(99.87)	-322.9
HF		-357.89	(93.06)	-376.24	(97.83)	-381.74	(99.26)	-383.61	(99.74)	-384.6
N ₂		-509.30	(94.86)	-528.94	(98.52)	-534.33	(99.52)	-536.00	(99.83)	-536.9
CO		-492.35	(94.74)	-512.11	(98.54)	-517.37	(99.75)	-518.94	(99.85)	-519.7
Ne		-361.18	(93.06)	-379.25	(97.72)	-385.00	(99.20)	-387.01	(99.72)	-388.1
F ₂		-692.36	(93.49)	-725.96	(98.02)	-735.84	(99.36)	-739.07	(99.79)	-740.6
Ave. %		...	93.8	...	98.2	...	99.4	...	99.8	...
R12-MP2/A' ^c		CH ₂ (¹ A ₁)	-198.69	(94.66)	-205.50	(97.90)	-208.96	(99.55)	-209.31	(99.72)
	H ₂ O	-337.74	(93.27)	-353.83	(97.72)	-358.49	(99.00)	-360.53	(99.57)	-362.1
	NH ₃	-303.28	(93.92)	-316.43	(98.00)	-320.32	(99.20)	-321.93	(99.70)	-322.9
	HF	-358.77	(93.28)	-374.27	(97.31)	-379.35	(98.63)	-381.65	(99.23)	-384.6
	N ₂	-509.90	(94.97)	-527.57	(98.26)	-533.64	(99.39)	-536.06	(99.84)	-536.9
	CO	-491.97	(94.66)	-510.78	(98.28)	-517.03	(99.49)	-519.04	(99.87)	-519.7
	Ne	-233.73 ^d	(60.22)	-368.48	(94.94)	-381.17	(98.21)	-386.37	(99.55)	-388.1
	F ₂	-692.40	(93.49)	-722.36	(97.54)	-731.48	(98.77)	-736.90	(99.50)	-740.6
	Ave. %	...	94.0	...	97.4	...	99.0	...	99.6	...

^aMP2 and MP2-geminal results using numerical quadratures. h functions are not included for X=5.

^bReferences 26 and 50.

^cReference 26.

^dThe value is excluded in Ave. %. See the text.

RI in accordance with the previous work.³³ Contrarily, the error in DF with the contracted basis, $16.71mE_h$, is more than three times larger than that of RI, $4.85mE_h$. This is because the DF includes duplicated approximations for the product of orbitals and the completeness insertion. Although the convergence of each approximation in DF is better than that of the conventional RI, i.e., $2L_{occ}$ and $3L_{occ}$,³³ respectively, the net error of DF amounts to the one larger than RI with the less flexible basis set. In either case, the contracted basis set is not suitable for a precise estimate of three-electron integrals. The accuracy of the numerical integration is mostly dominated by n_θ rather than n_R . As far as the series, $n_R=48$ and 96 are concerned, the results of grids with $n_\theta=24, 12$, and 9 are accurate at least to $1\mu E_h$, $10\mu E_h$, and $200\mu E_h$, respectively. These accuracies are acceptable for many applications in chemistry.

B. Selection of small molecules

A benchmark study on the molecules, CH₂(¹A₁), H₂O, NH₃, HF, N₂, CO, Ne, and F₂ was carried out with the auxiliary-function based MP2-R12 methods.²⁶ The present MP2-geminal method is applied to the same systems for comparison with the R12 results. We present only all-electron correlated results with cc-pCVXZ (X=D,T,Q,5) and their augmented variants, aug-cc-pCVXZ (X=D,T,Q,5). The current program handles up to g -basis functions and h func-

tions are not included in calculations for X=5. The QD2 method of the medium grid with the parameters, $n_R=48$, $n_\theta=12$, and $n_\phi=24$, is employed throughout the calculations. The errors of the numerical integrations are expected to be less than $0.1mE_h$ for the systems treated in this paper. All geometrical parameters are taken from Ref. 50.

The results of MP2, MP2-R12/A',²⁶ and MP2-geminal for the series of cc-pCVXZ and aug-cc-pCVXZ are given in Tables III and IV. MP2-R12/A' and MP2-geminal neglect the exchange operator in commutators, though the present method further assumes the extended Brillouin condition. In addition to the difference in the forms of explicitly correlated functions, i.e., linear r_{12} and linear combination of Gaussian-type geminals, MP2-R12/A' optimizes the linear coefficients based on the unitary invariant formulation.³⁸ The results of the explicitly correlated methods show markedly better convergence over the conventional MP2. The MP2-geminal with aug-cc-pCVTZ recovers more than 99% of the MP2 energy in the complete basis set limit.^{26,51} It is noted that k functions or even higher angular momentum components are necessary in the standard orbital expansion to attain an equivalent accuracy.⁵² In the MP2-R12/A' result of Ne with cc-pCVDZ, the Jacobian in the unitary invariant formulation involves the negative eigen values with the small basis set, and thus the Hylleraas energy functional is not optimized appropriately.⁵³ Thus a direct comparison between MP2-R12/A' and MP2-

TABLE IV. Convergence of MP2 energy for the first selection with aug-cc-pCVXZ sets (mE_h).^a

Method	System	X=D	(%)	X=T	(%)	X=Q	(%)	X=5	(%)	Limit
MP2	CH ₂ (¹ A ₁)	-151.81	(72.32)	-188.71	(89.90)	-201.00	(95.86)	-204.52	(97.44)	-209.9
	H ₂ O	-259.24	(71.59)	-324.15	(89.52)	-345.64	(95.46)	-351.58	(97.09)	-362.1
	NH ₃	-237.70	(73.62)	-292.09	(90.46)	-309.85	(95.96)	-315.10	(97.58)	-322.9
	HF	-263.64	(68.55)	-339.83	(88.36)	-364.84	(94.86)	-371.11	(96.23)	-384.6
	N ₂	-394.41	(73.46)	-483.19	(90.00)	-513.59	(95.66)	-520.93	(97.03)	-536.9
	CO	-376.35	(72.42)	-464.80	(89.44)	-495.70	(95.38)	-503.23	(96.83)	-519.7
	Ne	-249.90	(64.39)	-337.29	(86.91)	-365.16	(94.09)	-371.83	(95.81)	-388.1
	F ₂	-510.65	(68.95)	-655.76	(88.54)	-702.68	(94.88)	-713.82	(96.38)	-740.6
	Ave. %	...	70.7	...	89.1	...	95.3	...	96.8	...
	MP2-geminal	CH ₂ (¹ A ₁)	-200.22	(95.39)	-207.82	(99.01)	-209.32	(99.72)	-209.64	(99.88)
H ₂ O		-350.45	(96.78)	-359.35	(99.24)	-361.35	(99.79)	-361.74	(99.90)	-362.1
NH ₃		-311.67	(96.52)	-320.54	(99.27)	-322.23	(99.79)	-322.83	(99.98)	-322.9
HF		-373.14	(97.02)	-381.27	(99.13)	-383.65	(99.75)	-384.16	(99.89)	-384.6
N ₂		-516.02	(96.11)	-531.85	(99.06)	-535.58	(99.75)	-536.43	(99.91)	-536.9
CO		-500.42	(96.29)	-514.78	(99.05)	-518.39	(99.75)	-519.22	(99.91)	-519.7
Ne		-376.02	(96.89)	-383.79	(98.89)	-386.72	(99.65)	-387.55	(99.86)	-388.1
F ₂		-717.44	(96.87)	-733.91	(99.10)	-738.66	(99.74)	-739.80	(99.89)	-740.6
Ave. %		...	96.5	...	99.1	...	99.7	...	99.9	...
R12-MP2/A'		CH ₂ (¹ A ₁)	-201.21	(95.86)	-207.52	(98.87)	-209.48	(99.80)	-209.87	(99.99)
	H ₂ O	-363.30	(100.33)	-359.64	(99.32)	-361.72	(99.90)	-362.15	(100.01)	-362.1
	NH ₃	-309.59	(95.88)	-320.11	(99.14)	-322.55	(99.89)	n.a. ^b	...	-322.9
	HF	-360.00	(93.60)	-380.58	(98.95)	-383.94	(99.83)	-384.67	(100.01)	-384.6
	N ₂	-514.07	(95.74)	-531.80	(99.05)	-536.01	(99.83)	-537.83	(100.17)	-536.9
	CO	-496.35	(95.51)	-514.46	(98.99)	-518.93	(99.85)	-519.84	(100.03)	-519.7
	Ne	-367.65	(94.73)	-383.94	(98.93)	-386.87	(99.68)	-388.44	(100.09)	-388.1
	F ₂	-705.67	(95.28)	-734.93	(99.23)	-739.08	(99.79)	-740.78	(100.02)	-740.6
	Ave. %	...	95.9	...	99.1	...	99.8	...	100.0	...

^aSame as Table III.^bNot available.

geminal is not fair with such a small basis set, and the Ne result is excluded for the average percentages in Table III. With this exception, the convergences of the two explicitly correlated methods are very similar to each other. It is emphasized that MP2-geminal fully replies on the cusp conditions and has no variational parameter to minimize the Hylleraas energy functional in the explicitly correlated part.

C. Reaction enthalpies

It is of interest to see how MP2-geminal improves energy differences. Comprehensive studies for atomization energies and reaction enthalpies through CCSD(T) with various basis sets have been reported.^{54,55} Here we examine the MP2 components of the reaction enthalpies. To complete the reactions, additional calculations are performed for H₂, CH₄, C₂H₄, HNC, HCN, N₂H₂, CH₂O, HNO, H₂O₂, HOF, CO₂ and O₃ using the same scheme and the basis sets through cc-pCVQZ. The geometrical parameters optimized at CCSD(T)/cc-pCVQZ are taken from Ref. 55 for O₃ and from Ref. 50 for the others. The calculated energy components are given in Table V. The asymptotic limits of MP2 energies are estimated accurately by the two-point extrapolation scheme, pcV(XY)Z,⁵⁶ where X and Y are cardinal numbers of basis sets used for the extrapolation. The total energies of MP2-geminal with aug-cc-pCVQZ are slightly higher than the extrapolated results of pcV(56)Z. The differences involve the incompleteness of the Hartree-Fock energies with the basis set amounting at most to 3.7mE_h for H₂O₂.

Table VI summarizes the MP2 contributions to the reaction enthalpies. It is found that MP2-geminal betters the agreement of MP2 enthalpies with pcV(56)Z extrapolation. The mean displacement of MP2-geminal is less than 1 kJ/mol at aug-cc-pCVTZ, which is ~1 order of magnitude smaller than MP2 without explicitly correlated functions. The augmentation from aug-cc-pCVTZ to aug-cc-pCVQZ does not show prominent improvements in the MP2-geminal result. This might be due to slight differences between the MP2-geminal and pcV(56)Z calculations in geometrical parameters or some other reasons. The maximum displacement of MP2-geminal with aug-cc-pCVDZ, is approximately equivalent to the accuracy of orbital-based MP2 with the aug-cc-pCVQZ set.

IV. CONCLUSION

We have presented the rational generator capable of dealing with the *s*- and *p*-wave cusp conditions, which is applied to the explicitly correlated MP2 method in conjunction with frozen Gaussian-type geminals. Additionally, numerical quadratures were introduced in the implementation of the explicitly correlated method. We discussed their convergences and scaling properties for the necessary two- and three-electron integrals. Although we have used the product angular grid to examine the convergences, more efficient Lebedev quadrature will be introduced in the near future.

It is also worthwhile to investigate possible schemes for four-electron integrals with numerical quadratures. The par-

TABLE V. Convergences of the second order perturbation, HF and MP2 energies for the additional selection of molecules.^a

System	$E_V^{(2)}/mE_h$				HF/ E_h		MP2-geminal/ E_h	MP2/ E_h	
	D	AD	AT	AQ	AQ	pV6Z ^b	AQ	pcV6Z ^b	pcV(56)Z ^b
H ₂	-33.27	-33.89	-34.24	-34.23	-1.133 46	-1.1336	-1.167 69	-1.168	-1.168
CH ₄	-260.79	-264.51	-272.34	-273.66	-40.216 37	-40.2171	-40.490 03	-40.487	-40.491
C ₂ H ₂	-429.78	-434.37	-450.93	-454.31	-76.854 66	-76.8556	-77.308 94	-77.304	-77.311
C ₂ H ₄	-457.43	-463.20	-478.49	-481.61	-78.069 67	-78.0707	-78.551 28	-78.546	-78.553
HNC	-459.73	-466.63	-482.01	-485.49	-92.899 23	-92.9003	-93.384 72	-93.379	-93.387
HCN	-472.95	-479.08	-495.10	-498.58	-92.914 65	-92.9157	-93.413 23	-93.407	-93.415
N ₂ H ₂	-543.86	-553.69	-570.69	-574.38	-110.048 33	-110.0497	-110.622 72	-110.616	-110.625
CH ₂ O	-533.53	-544.02	-559.52	-563.06	-113.921 67	-113.9234	-114.484 73	-114.478	-114.487
HNO	-580.40	-592.50	-609.33	-613.26	-129.847 94	-129.8498	-130.461 20	-130.454	-130.464
H ₂ O ₂	-647.17	-668.17	-686.00	-690.08	-150.848 58	-150.8523	-151.538 66	-151.533	-151.544
HOF	-666.83	-690.20	-707.49	-711.94	-174.819 68	-174.8230	-175.531 62	-175.524	-175.536
CO ₂	-817.70	-832.72	-855.98	-861.74	-187.722 54	-187.7252	-188.584 29	-188.574	-188.588
O ₃	-1005.76	-1027.41	-1052.42	-1058.88	-224.362 72	-224.3661	-225.421 61	-225.410	-225.427

^aD, AD, AT and AQ abbreviate the cc-pCVDZ and aug-pCVXZ (X=D,T,Q) sets, respectively.^bReference 54.

tial wave convergence of the commutator between the generator and exchange operator is $(L+1)^{-5}$.²³ The MP2-R12 method employed integrals with two indices of auxiliary functions.²⁶ In the case of numerical quadratures, however, at least one electronic coordinates of the Coulomb operator should be integrated explicitly due to the divergent form of the potential at a coincident grid point. The method incorporating with RI³⁵ is therefore more practical to this secondary contribution though some inspection is necessary for accuracy.

Most of the other explicitly correlated methods optimize two-electron basis set parameters. The present result implies that the gain of such optimization is small and the matter of basis set incompleteness is essentially recovered by imposing the appropriate cusp conditions. This feature is important for various extensions of explicitly correlated methods. The uni-

tary invariant formulation requires O^6 scaling, which is tractable in MP2 and coupled-cluster (CC) theory. The method, however, becomes formidable when the occupation spreads in the entire orbital space as in CC linear response theory. The explicit use of cusp condition was discussed in the initial R12 method for the He-like atoms.⁵ The rational generator supplies a more general and robust principle for many applications.

Finally we mention the performance of the present method. The use of numerical quadratures becomes more advantageous as the system size increases. With our preliminary code, the MP2-geminal calculation of C₂H₂ with the aug-cc-pCVQZ set took 687 CUP seconds on a 1.6 GHz Centrino notebook computer with the allowance of 240 MB memory, while an additional 1047 and 1204 s were required

TABLE VI. MP2 components of reaction energies.^a

Reaction	MP2				MP2-geminal				MP2
	D	AD	AT	AQ	D	AD	AT	AQ	pcV(56)Z ^a
CO+H ₂ → H ₂ CO	-7.9	-16.0	-24.9	-26.9	-20.8	-25.5	-27.6	-27.4	-27.7
HNC → HCN	-33.2	-31.9	-33.2	-33.8	-34.7	-32.7	-34.4	-34.4	-34.2
H ₂ O+F ₂ → HOF+HF	20.0	16.7	14.4	12.7	13.7	11.9	11.8	11.6	11.9
N ₂ +3H ₂ → 2NH ₃	200.5	2.4	-13.1	-16.6	-1.8	-14.8	-17.1	-16.2	-17.3
N ₂ H ₂ → N ₂ +H ₂	-7.2	3.4	10.4	12.2	3.4	9.9	12.1	12.0	12.3
C ₂ H ₂ +H ₂ → C ₂ H ₄	18.6	14.4	16.2	16.9	14.7	13.3	17.5	18.1	18.0
CO ₂ +4H ₂ → CH ₄ +2H ₂ O	58.7	23.3	5.3	3.3	38.9	7.6	5.1	6.1	4.7
CH ₂ O+2H ₂ → CH ₄ +H ₂ O	16.0	1.0	-8.5	-9.9	4.5	-8.3	-9.7	-9.2	-9.8
CO+3H ₂ → CH ₄ +H ₂ O	8.1	-15.0	-33.4	-36.8	-16.3	-33.8	-37.2	-36.6	-37.5
HNC+3H ₂ → CH ₄ +NH ₃	124.8	24.9	13.7	12.7	18.6	12.0	13.0	14.1	13.3
H ₂ O ₂ +H ₂ → 2H ₂ O	-7.9	-16.0	-24.9	-26.9	-20.8	-25.5	-27.6	-27.4	-27.7
HNO+2H ₂ → H ₂ O+NH ₃	119.4	9.6	-1.2	-4.5	11.7	-4.8	-5.5	-4.9	-5.7
C ₂ H ₂ +3H ₂ → 2CH ₄	31.5	23.2	21.7	23.2	21.0	18.4	23.5	25.3	25.0
CH ₂ +H ₂ → CH ₄	-65.9	-67.3	-75.2	-77.6	-80.8	-79.8	-79.8	-79.0	-79.4
F ₂ +H ₂ → 2HF	44.2	28.0	21.3	16.4	25.8	13.2	14.7	14.6	14.6
2CH ₂ → C ₂ H ₄	-144.8	-143.4	-155.8	-161.6	-167.8	-164.8	-165.0	-165.3	-165.9
O ₃ +3H ₂ → 3H ₂ O	277.7	231.2	212.5	205.6	243.8	204.1	202.4	203.5	203.0
$\langle \Delta E \rangle$	46.7	12.9	3.6	1.2	11.5	2.1	0.4	0.5	...
ΔE_{\max}	217.8	28.2	10.1	4.3	40.8	6.6	1.5	1.4	...

^aSame as Table V.

for the conventional self-consistent field and MP2 calculations without numerical integrations. Most of the CPU time in the MP2-geminal step is spent for the calculation of kernel functions for $K_{1g}^{(Q)}$ and Z_{1g} (see Appendix B). Currently, these functions are computed explicitly and accumulated inside the loop(s) over primitive geminals. The development of interpolation schemes for the functions will improve this step significantly. This line of work is in progress.

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APPENDIX A: CONNECTION TO THE TRANSCORRELATED METHOD

Let us start with the CC equations for the similarity transformed Hamiltonian

$$\langle \phi | \tilde{H} \exp(T) | \phi \rangle = E_N, \quad (\text{A1})$$

$$\langle \chi_l | \tilde{H} \exp(T) | \phi \rangle_c = 0, \quad (\text{A2})$$

$$\tilde{H} = \exp(-\bar{G}_N) H \exp(\bar{G}_N), \quad (\text{A3})$$

where χ_l denotes excited determinants, T is in the usual excitation operator form, and \bar{G}_N is the generator without the vacuum amplitude

$$\bar{G}_N = \bar{G} - \langle \phi | \bar{G} | \phi \rangle. \quad (\text{A4})$$

Assigning first order in perturbation to \bar{G}_N , the order-by-order expansion of the CC equations supplies the second order energy expression

$$E_N^{(2)} = \langle \phi | [H_0, \bar{G}_N] (\bar{G}_N + T^{(1)}) | \phi \rangle + \langle \phi | VT^{(1)} | \phi \rangle, \quad (\text{A5})$$

and the first order wave operator equation

$$\langle \chi_l | [H_0, T^{(1)}] | \phi \rangle = -\langle \chi_l | V + [H_0, \bar{G}_N] | \phi \rangle. \quad (\text{A6})$$

The excitations by the generator and cluster operator are divided into singles and doubles components

$$\bar{G}_N | \phi \rangle = (\bar{G}_1 + \bar{G}_2) | \phi \rangle, \quad (\text{A7})$$

$$T^{(1)} | \phi \rangle = (T_1^{(1)} + T_2^{(1)}) | \phi \rangle. \quad (\text{A8})$$

The assumption that the HF reference is the exact solution of H_0 eliminates the sum of singles in the complete basis

$$[H_0, \bar{G}_1 + T_1] | \phi \rangle = 0, \quad (\text{A9})$$

to leave just the double substitutions as meaningful terms

$$E_N^{(2)} = \langle \phi | [H_0, \bar{G}_N] \bar{G}_2 | \phi \rangle + \langle \phi | ([H_0, \bar{G}_N] + V) T_2^{(1)} | \phi \rangle. \quad (\text{A10})$$

Substitution of the explicit expression of the first order amplitudes

$$\langle a_a^+ a_b^+ a_j a_i \phi | T^{(1)} | \phi \rangle = \frac{\langle [ab] | r_{12}^{-1} + \bar{\kappa}_{12} | [ij] \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (\text{A11})$$

we arrive at the second order energy expression

$$\begin{aligned} E_N^{(2)} &= \sum_{i>j} \left(\langle [ij] | \bar{\kappa}_{12} Q_1^* Q_2^* \bar{G}_{12} | [ij] \rangle \right. \\ &\quad \left. + \sum_{a>b} \frac{\langle [ij] | \bar{\kappa}_{12} + r_{12}^{-1} | [ab] \rangle \langle [ab] | r_{12}^{-1} + \bar{\kappa}_{12} | [ij] \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \right) \\ &= E^{(2)} + \Delta E_N^{(2)}. \end{aligned} \quad (\text{A12})$$

The obtained correction is just that in Eq. (32) with the opposite sign. The transcorrelated method essentially treats the kinetic energy part of the electron correlation and is connected to the Hylleraas type expansion via the virial-type theorem. For a nonperturbative treatment, \tilde{H} is generally nonterminating due to the permutation operators in the generator. However, the use of the s -wave cusp condition, irrespective of the spin multiplicities of pair functions,

$$\bar{G}_{12} = \frac{1}{2} r_{12} + O(r_{12}^2), \quad (\text{A13})$$

brings terminating and nontrivial expansions because triplet pairs have no amplitude at coalescence. In this case, the increment by an augmentation of basis set is not necessarily negative especially for a geminal in which the r_{12} behavior is extrapolated to long-range distances, although the asymptotic limit is identical to the Hylleraas energy functional.

APPENDIX B: INTEGRAL EVALUATION

All of the operators in the three-center integrals required in the present explicitly correlated MP2 theory are expressed by Gaussian-type functions

$$f_{1g} = \sum_G^{N_g} c_G \exp(-\zeta_G r_{1g}^2), \quad (\text{B1})$$

$$-(\nabla_1 f_{1g}) = -\sum_G^{N_g} c_G [\nabla_1 \exp(-\zeta_G r_{1g}^2)], \quad (\text{B2})$$

$$-(\nabla_1 f_{1g}) \cdot \nabla_1 = -\sum_G^{N_g} c_G [\nabla_1 \exp(-\zeta_G r_{1g}^2)] \cdot \nabla_1, \quad (\text{B3})$$

$$-(\nabla_1^2 f_{1g}) = -\sum_G^{N_g} c_G (4\zeta_G^2 r_{1g}^2 - 6\zeta_G) [\exp(-\zeta_G r_{1g}^2)], \quad (\text{B4})$$

$$\begin{aligned} -(\nabla_1 f_{1g}) \cdot (\nabla_1 f_{1g}) &= -\sum_{GG'}^{N_g} 4\zeta_G \zeta_{G'} c_G c_{G'} r_{1g}^2 \\ &\quad \times \exp[-(\zeta_G + \zeta_{G'}) r_{1g}^2], \end{aligned} \quad (\text{B5})$$

$$r_{1g}^{-1} = \frac{2}{\sqrt{\pi}} \int_0^\infty du \exp(-u^2 r_{1g}^2), \quad (\text{B6})$$

$$Z_{12} = \frac{2}{\sqrt{\pi}} \sum_G^{N_g} c_G \int_0^\infty \exp[-(\zeta_G + u^2) r_{1g}^2]. \quad (\text{B7})$$

First, we present formulas for the basic integrals

$$\begin{aligned}
 (\mathbf{n}|\mathbf{l}|\bar{\mathbf{n}}) &= \int d\mathbf{r} \varphi_c(\mathbf{r}-\mathbf{R}; \zeta, \mathbf{n}) \varphi_c(\mathbf{r}-\mathbf{r}_g; \zeta_T, \mathbf{l}) \\
 &\quad \times \varphi_c(\mathbf{r}-\bar{\mathbf{R}}; \bar{\zeta}, \bar{\mathbf{n}})
 \end{aligned}
 \tag{B8}$$

of Cartesian Gaussian functions

$$\varphi_c(\mathbf{r}; \zeta, \mathbf{n}) = x^n y^n z^n \exp(-\zeta r^2). \tag{B9}$$

The Cartesian orbitals are transformed to spherical Harmonics after the calculation of integrals in each of the shell pairs. For the basic integrals, the Obara–Saika recurrence relations^{57,58} reduce to

$$\begin{aligned}
 (\mathbf{n}+1_\kappa:) &= [(\mathbf{P}-\mathbf{R})_\kappa + (\mathbf{r}_g-\mathbf{P})\Theta(\zeta_T)](:) \\
 &\quad + \frac{1-\Theta(\zeta_T)}{2Z} [n_\kappa(\mathbf{n}-1_\kappa:) + \bar{n}_\kappa(\bar{\mathbf{n}}-1_\kappa:) \\
 &\quad + l_\kappa(\mathbf{l}-1_\kappa:)],
 \end{aligned}
 \tag{B10}$$

$$\begin{aligned}
 (\mathbf{l}+1_\kappa:) &= (\mathbf{P}-\mathbf{r}_g)[1-\Theta(\zeta_T)](:) + \frac{1-\Theta(\zeta_T)}{2Z} [n_\kappa(\mathbf{n} \\
 &\quad -1_\kappa:) + \bar{n}_\kappa(\bar{\mathbf{n}}-1_\kappa:) + l_\kappa(\mathbf{l}-1_\kappa:)],
 \end{aligned}
 \tag{B11}$$

where the colons in parentheses abbreviate unchanged indices from $(\mathbf{n}|\mathbf{l}|\bar{\mathbf{n}})$, and the parameters are defined by

$$Z = \zeta + \bar{\zeta}, \tag{B12}$$

$$\mathbf{P} = \frac{\zeta \mathbf{R} + \bar{\zeta} \bar{\mathbf{R}}}{Z}, \tag{B13}$$

$$\Theta(\zeta_T) = \frac{\zeta_T}{Z + \zeta_T}. \tag{B14}$$

The integral over s functions is given by

$$(\mathbf{0}|\mathbf{0}|\bar{\mathbf{0}})^{(0)} = S_1^{(0)} [1-\Theta(\zeta_T)]^{3/2} \exp[-T\Theta(\zeta_T)], \tag{B15}$$

$$S_1^{(0)} = \left(\frac{\pi}{Z}\right)^{3/2} \exp\left[-\frac{\zeta\bar{\zeta}}{Z}(\mathbf{R}-\bar{\mathbf{R}})^2\right], \tag{B16}$$

$$T = Z(\mathbf{P}-\mathbf{r}_g)^2. \tag{B17}$$

The above equations are independent in each Cartesian component, $\kappa = x, y, z$, which can be calculated separately for a given ζ_T or a discrete quadrature point as in the Rys polynomial.⁵⁹ Since only Θ is dependent on the exponent, ζ_T , in the recurrence relations, summations over the Gauss operators $\exp(-\zeta_T r_{1g}^2)$ lead to the contracted recurrence relations

$$\begin{aligned}
 (\mathbf{n}+1_\kappa:)^{(m)} &= (\mathbf{P}-\mathbf{R})_\kappa[:]^{(m)} + (\mathbf{r}_g-\mathbf{P})[:]^{(m+1)} \\
 &\quad + \frac{1}{2Z} [[:]]_\kappa^{(m)},
 \end{aligned}
 \tag{B18}$$

$$(\mathbf{l}+1_\kappa:)^{(m)} = (\mathbf{P}-\mathbf{r}_g)([:]^{(m)} - [:]^{(m+1)}) + \frac{1}{2Z} [[:]]_\kappa^{(m)}, \tag{B19}$$

$$\begin{aligned}
 [[:]]_\kappa^{(m)} &= n_\kappa([(\mathbf{n}-1_\kappa:)]^{(m)} - [(\mathbf{n}-1_\kappa:)]^{(m+1)}) \\
 &\quad + \bar{n}_\kappa([\bar{(\mathbf{n}}-1_\kappa:)]^{(m)} - [\bar{(\mathbf{n}}-1_\kappa:)]^{(m+1)}) \\
 &\quad + l_\kappa([\mathbf{l}-1_\kappa:]^{(m)} - [\mathbf{l}-1_\kappa:]^{(m+1)}),
 \end{aligned}
 \tag{B20}$$

for the auxiliary integrals

$$(\mathbf{n}|\mathbf{l}|\bar{\mathbf{n}})^{(m)} = \int \omega^{(O)}(\zeta_T) \Theta^m(\zeta_T) (\mathbf{n}|\mathbf{l}|\bar{\mathbf{n}}) d\zeta_T, \tag{B21}$$

where $\omega(\zeta_T)$ is an arbitrary weight function characterizing the spherically symmetric operator

$$O = \int \omega^{(O)}(\zeta_T) \exp(-\zeta_T r_{1g}^2) d\zeta_T. \tag{B22}$$

The angular momentum indices are increased from the kernel functions

$$[O]^{(m)} \equiv [\mathbf{0}|\mathbf{0}|\bar{\mathbf{0}}]^{(m)} = S_1^{(0)} \int \omega^{(O)}(\zeta_T) \xi_m(T, \zeta_T) d\zeta_T, \tag{B23}$$

$$\xi_m(T, \zeta_T) = \Theta^m(\zeta_T) [1-\Theta(\zeta_T)]^{3/2} \exp[-T\Theta(\zeta_T)]. \tag{B24}$$

The functions for f_{12} and electric field operators are

$$[f_{12}]^{(m)} = S_1^{(0)} \sum_G c_G \xi_m(T, \zeta_G), \tag{B25}$$

$$[r_{1g}^{-1}]^{(m)} = \frac{2S_1^{(0)}}{\sqrt{\pi}} F_m(T), \tag{B26}$$

$$F_m(T) = \int_0^1 dt t^{2m} \exp(-Tt^2). \tag{B27}$$

The integrals for $(\nabla_{1g} f_{1g})$ and $(\nabla_{1g} f_{1g}) \cdot \nabla_1$ can also be calculated from $[f_{12}]^{(m)}$, since the first derivative of Gaussian-type functions are related to those with different angular momentum indices

$$\begin{aligned}
 \frac{\partial}{\partial r_\kappa} \varphi_c(\mathbf{r}; \zeta, \mathbf{n}) &= -2\zeta \varphi_c(\mathbf{r}; \zeta, \mathbf{n}+1_\kappa) \\
 &\quad + n_\kappa \varphi_c(\mathbf{r}; \zeta, \mathbf{n}-1_\kappa).
 \end{aligned}
 \tag{B28}$$

Substituting this into Eq. (B19) with the aid of

$$\zeta_T [1-\Theta(\zeta_T)] = Z\Theta(\zeta_T), \tag{B29}$$

we obtain the expression for the differential operator integrals

$$\begin{aligned}
 \left[\mathbf{n} \left| \frac{\partial f_{12}}{\partial (\mathbf{r}_{1g})_\kappa} \right| \bar{\mathbf{n}} \right]^{(m)} &= -2Z(\mathbf{P}-\mathbf{r}_g) [\mathbf{n}|f_{12}|\bar{\mathbf{n}}]^{(m+1)} \\
 &\quad - n_\kappa [\mathbf{n}-1_\kappa | f_{12} | \bar{\mathbf{n}}]^{(m+1)} \\
 &\quad - \bar{n}_\kappa [\mathbf{n} | f_{12} | \bar{\mathbf{n}}-1_\kappa]^{(m+1)}.
 \end{aligned}
 \tag{B30}$$

The integrals

$$\left[\mathbf{n} \left| \frac{\partial f_{12}}{\partial (\mathbf{r}_{1g})_\kappa} \frac{\partial}{\partial (\mathbf{r}_{1g})_\kappa} \right| \bar{\mathbf{n}} \right]^{(m)}$$

reduce to the same form by Eq. (B28).

The integrals for the operators, $(\nabla_{1g}^2 f_{1g})$ and $(\nabla_{1g} f_{1g}) \cdot (\nabla_{1g} f_{1g})$, can be evaluated by the applications of the recurrence relations after the differentiation of the Gauss operator. However, there exist more efficient methods using the fact

that the operators are spherically symmetric. The integrals with the square distance operator is identical to the derivative with respect to the Gaussian exponent

$$(\mathbf{n}|r_{1g}^2 \exp(-\zeta_T r_{1g}^2)|\bar{\mathbf{n}}) = -\frac{\partial}{\partial \zeta_T} (\mathbf{n}|\exp(-\zeta_T r_{1g}^2)|\bar{\mathbf{n}}). \quad (\text{B31})$$

Since the recurrence relation Eq. (B18) does not contain any exponent, ζ_T , except for the auxiliary integrals, it is applicable to the contracted object

$$[\mathbf{n}|r_{1g}^2 O|\bar{\mathbf{n}}]^{(m)} = -\int d\zeta_T \omega^{(O)}(\zeta_T) \frac{\partial}{\partial \zeta_T} \Theta^m(\zeta_T) \times (\mathbf{n}|\exp(-\zeta_T r_{1g}^2)|\bar{\mathbf{n}}). \quad (\text{B32})$$

Using the relation

$$-\frac{\partial \Theta(\zeta_T)}{\partial \zeta_T} \frac{\partial}{\partial \Theta(\zeta_T)} = -\frac{[1 - \Theta(\zeta_T)]^2}{Z} \frac{\partial}{\partial \Theta(\zeta_T)}, \quad (\text{B33})$$

along with Eqs. (B4), (B5), (B23), and (B29) in the above differentiation, we obtain

$$[-(\nabla_{1g}^2 f_{1g})]^{(m)} = -4Z\{T[f_{1g}]^{(m+2)} - (\frac{3}{2} + m) \times [f_{1g}]^{(m+1)}\}, \quad (\text{B34})$$

$$[-(\nabla_{1g} f_{1g}) \cdot (\nabla_{1g} f_{1g})]^{(m)} = -\frac{1}{Z} \left(T[f_{1g}'^2]^{(m)} + \frac{3}{2} [f_{1g}'^2]^{(m)} - m[f_{1g}'^2]^{(m-1)} \right), \quad (\text{B35})$$

$$f_{1g}'^2 = 4 \sum_{GG'} \zeta_G \zeta_{G'} \exp[-(\zeta_G + \zeta_{G'}) r_{1g}^2], \quad (\text{B36})$$

$$[O]^{(m)} = [O]^{(m)} - [O]^{(m+1)}, \quad (\text{B37})$$

$$[O]^{(m)} = [O]^{(m)} - [O]^{(m+1)}. \quad (\text{B38})$$

Thus the integrals for these operators can be calculated as those for spherically symmetric operators, f_{1g} and r_{1g}^{-1} , just by replacing the kernel functions.

It is relatively easy to show that the kernel functions for Z_{1g} are essentially linear combinations of those for Coulomb integrals. In this way, the integrals required in the present explicitly correlated method are of different kernel functions but mostly with coincident linear coefficient of the recurrence relations. Such integrals are efficiently calculated by use of fixed-root polynomials⁶⁰

$$[O]^{(m)} = \sum_{\alpha} R_{\alpha}^m W_{\alpha}^{(O)}, \quad (\text{B39})$$

where the R_{α} are root positions, $W_{\alpha}^{(O)}$ are the corresponding weights for the operator O , and α ranges from 0 to the maximum value of m . In the Rys polynomial method,⁵⁹ both roots and weights are variables and thus the order of the polynomial is 1/2 of the present fixed-root polynomial method. The latter is, however, more advantageous for the present purpose because the target integrals are expressed as the Cartesian

components independent of operators multiplied by the weights

$$[\mathbf{n}|O|\bar{\mathbf{n}}]^{(0)} = \sum_{\alpha} I_x(R_{\alpha}) I_y(R_{\alpha}) I_z(R_{\alpha}) W_{\alpha}^{(O)}. \quad (\text{B40})$$

The integrals for different operators are calculated simultaneously with different weights characterizing the operators. In this case, the rate-determining step is the generation of the kernel functions, especially for $[-(\nabla_{1g} f_{1g}) \cdot (\nabla_{1g} f_{1g})]^{(m)}$ and $[Z_{1g}]^{(m)}$ rather than the increments of angular momentum indices and contractions over the quadrature points.

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