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Initiation of explicitly correlated Slater-type geminal theory

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Abstract

We employ the Slater-type function as a geminal basis function to incorporate the inter-electron distance in explicitly correlated theory. It is shown that the use of the Slater-type geminals confers numerical and computational advantages over the previous explicitly correlated methods. The performance of the resulting method is examined in some benchmark calculations at the second order Møller–Plesset perturbation theory. The results reveal that the Slater-type function is promising compared to the ordinary Gaussian-type geminals and linear r_{12} function.

1. Introduction

One of the main obstacles to accurate electronic structure calculations is the slow convergence of a configuration interaction (CI) expansion. The cusp conditions [1–3] suggests that the exact wave function at a small inter-electronic distance is expressed as a product of linear r_{12} and unperturbed wave functions,

$$\Psi = \left[1 + \frac{r_{12}}{2(s+1)}\right]\Phi + \mathrm{O}(r_{12}^2), \tag{1}$$

where s takes 0 and 1 for singlet and triplet pairs, respectively. However, the electronic cusp at coalescence is hardly represented by a sum of products of one-electron orbitals. As exhibited long time ago for the He ground state wave function [4], the situation is remedied substantially by introducing two-electron basis functions involving inter-electronic distances explicitly. The slow convergence is essentially in the orbital expansion of the operator product between the perturbation and correlation behavior [5] like

$$\sum_{pq} r_{12}^{-1}|pq\rangle\langle pq|r_{12} = 1, \tag{2}$$

and an analytic treatment of the product accelerates the convergence of the partial wave expansion from $(L+1)^{-3}$ to $(L+1)^{-7}$ for the maximum angular momentum of atomic orbital basis functions, L. Notwithstanding the successful applications of the Hylleraas expansion to two-electron systems, the extension of such methods to many-electronic systems is not as straightforward due to the appearance of high-rank operators.

The Gaussian-type geminals (GTGs) introduced by Boys and Singer [6,7] have been employed in many places. The best feature of GTGs is that the necessary integrals (even three- and four-electron integrals in the second order perturbation theory) can be computed in closed form algebraic expressions. A further simplification of the second order energy functional to bypass the requirement of four-electron integrals has been discussed by Szalewicz and coworkers [8]. The transcorrelated method [9,10] also introduces three-electron integrals, but no higher-rank operators arise. The number of the three-electron integrals, however, becomes prohibitively large in either case, and to maintain the integrals in full is not very advantageous.

Kutzelnigg and Klopper [11] introduced systematic approximations to represent all three- and four-electron integrals as sums of two-electron integrals using the resolution of the identity (RI) in their ingenious R12 meth-

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ods. The elimination of the many-electron integrals grants a tolerance toward large molecules, and the R12 methods have been used to calculate accurate correlation energies for a wide variety of systems. RI has also been employed in the transcorrelated and GTG calculations [12,13]. The recent developements have been concerned with the refinements of the explicitly correlated methods with linear r_{12} or GTGs. The use of auxiliary basis functions has been studied within the framework of R12 [14,15]. It also turned out that the density fitting technique is effective for the reduction of cost [16] as well as for the accuracy of the RI approximation [17]. More recently, a different expansion for three-electron integrals with numerical quadratures (QD) has been proposed [18].

The reason for the popularity of the GTG and linear r_{12} functions is the ease of the evaluation of molecular integrals. Other geminal basis functions have hardly examined in explicitly correlated electronic structure theory. However, it is should be noticed that the GTG and linear r_{12} functions are not the only useful functions, once we admit the use of RI or QD for many-electron integrals. In this letter, we present a novel strategy employing the Slater-type function. The theory is presented in the following section. We present some numerical results in Section 3. Conclusions are depicted in Section 4.

2. Explicitly correlated Slater-type geminals

In explicitly correlated electronic structure theory, the wave function is expanded into two-electron basis functions in addition to orbital products. The primary cusp condition of Kato [1] suggests such an expansion is effective for geminal basis functions with the asymptotic behavior,

$$f_{12} = \tfrac{1}{2} r_{12} + \mathrm{O}(r_{12}^2). \tag{3}$$

The inclusion of f_{12} requires two-electron integrals for operators as

$$K_{12}^{(L)} = -(\nabla_1^2 f_{12}) - (\nabla_1 f_{12}) \cdot (\nabla_1 - \nabla_2), \tag{4}$$

$$K_{12}^{(Q)} = -(\nabla_1 f_{12}) \cdot (\nabla_1 f_{12}), \tag{5}$$

$$Z_{12} = r_{12}^{-1} f_{12}, \tag{6}$$

along with f_{12} and r_{12}^{-1}. Some approximations to the commutator between the exchange operator and f_{12}, in second order Møller–Plesset perturbation (MP2) theory require integrals for f_{12}^2 [15]. Most explicitly correlated treatments to date have employed either of the linear r_{12} and GTG functions,

$$f_{12}^{(\mathrm{R12})} = \frac{1}{2} r_{12}, \tag{7}$$

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

The necessary integrals are calculated in closed form algebraic expressions for these basis functions. It is noted that the linear r_{12} is not the best function to capture the entire correlation behavior. The expression of van der Waals interactions suggests the incorrectness of long-range behavior of the ansatz [18], and the unitary invariant formulation [19] is required to eliminate the unfavorable correlation. GTG does not suffer from such a problem at large r_{12}, though the function never fulfills the condition (3) exactly. It is, however, exhibited that a suitable range of r_{12} is represented accurately by a modest number of GTGs [20]. Furthermore, the use of a short-range function will grant advantageous for the treatment of large molecules. The main disadvantage of (8) is that the computation of integrals is relatively costly especially for operators quadratic to f_{12} involving $N_G^2/2$ primitive operations.

The above situations are remedied by introducing the Slater-type geminal (STG),

$$f_{12}^{(\mathrm{STG})} = -\frac{r_c}{2} \exp\left(-\frac{r_{12}}{r_c}\right), \tag{9}$$

where r_c is a scale-length parameter. STG simplifies the quadratic operators to the exponential forms,

$$K_{12}^{(Q)} = -\frac{1}{4} \exp\left(-\frac{2r_{12}}{r_c}\right), \tag{10}$$

$$\left(f_{12}^{(\mathrm{STG})}\right)^2 = r_c^2 K_{12}^{(Q)}. \tag{11}$$

It is known that the expression of electron-repulsion integrals involves the function,

$$F_m(T) = \int_0^1 \mathrm{d}t\, t^{2m} \exp(-Tt^2) \quad (m = 0, 1, 2, \ldots). \tag{12}$$

As shown in Appendix A, all necessary integrals of STG are calculated from the special function,

$$G_m(T, U) = \int_0^1 \mathrm{d}t\, t^{2m} \exp[-Tt^2 + U(1 - t^{-2})] \quad (m = -1, 0, 1, \ldots), \tag{13}$$

instead of $F_m(T)$ for electron repulsion integrals. We apply the present STG to MP2 theory with the first order wave operator,

$$\Omega^{(1)} = \Omega_O^{(1)} + \Omega_G^{(1)}. \tag{14}$$

$\Omega_O^{(1)}$ and $\Omega_G^{(1)}$ are the usual excitation operator spanned by orbital and the strong orthogonality excitation block of the rational generator [18],

$$\Omega_G^{(1)} = \frac{1}{2} \sum_{\alpha\beta ij} \langle \alpha\beta | \bar{G}_{12} | ij \rangle E_{\alpha i} E_{\beta j}, \tag{15}$$

respectively, the indices, $i,j,\ldots$ and $\alpha,\beta,\ldots$, denote occupied and virtual orbitals in the complete basis set, and $E_{\alpha i}$ is the unitary group generator. The rational generator involves a permutation operator to distinguish the parity of pair functions, and the simplest conjunction with STG is

$$\langle\alpha\beta|\bar{G}_{12}|ij\rangle = \tfrac{3}{4}\langle\alpha\beta|f_{12}^{(\mathrm{STG})}|ij\rangle + \tfrac{1}{4}\langle\alpha\beta|f_{12}^{(\mathrm{STG})}|ji\rangle. \qquad (16)$$

The rational generator enables us to impose the s-wave and p-wave cusp conditions automatically, i.e., effectively $\bar{G}_{12} = \frac{1}{2}r_{12} + O(r_{12}^2)$ and $\bar{G}_{12} = \frac{1}{4}r_{12} + O(r_{12}^2)$ for singlet and triplet pairs, respectively. The substitution of (14)–(16) into the Hylleraas energy functional leads to the integrals for the above-mentioned operators. It will be shown elsewhere that the application of the rational generator to more sophisticated correlated methods is also straightforward.

3. Results and discussions

We present some MP2 results of the Slater-type geminal. All of the two- and three-electron integrals are calculated using a numerical quadrature with the parameters, $n_R = 48$, $n_\theta = 12$ and $n_\phi = 24$, based on the polar coordinate. Other approximations to the energy functional follow the previous work [18]. Preliminarily, we examine the r_c dependence of MP2 energy for the Ne atom using the cc-pCVXZ and aug-cc-pCVXZ (X = D,T,Q) basis sets [21–23]. Fig. 1 shows the resulting profiles. The MP2 limit is ca. −388.1 mE_h [14]. The results become less sensitive to r_c as the cardinal number increases. Some typical numbers are listed in Table 1. The nonlinear optimization with respect to r_c should be avoided from a computational point of view. The r_c dependence in the range is much smaller than the error in the conventional MP2 method for each basis set. And thus, $r_c = 1$ is used for all of the calculations henceforth.

It turns out that STG provides better results in comparison with the previous GTG and R12 methods. As an example, we show the MP2 energies for the water molecule in Table 2. The geometrical parameters optimized at CCSD(T)/cc-pCVQZ are taken from [24]. h-functions are excluded from the CV5Z basis sets except for the R12 energies because of the limitation of our current

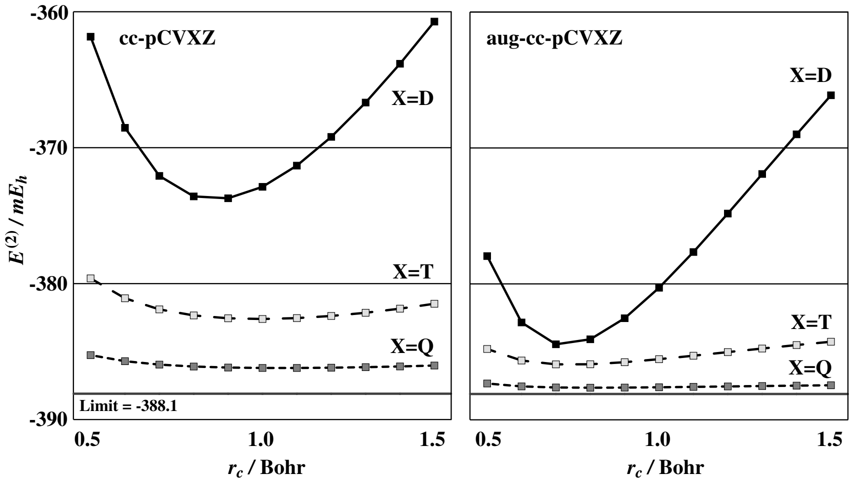

Fig. 1. Explicitly correlated MP2 energies of Ne with cc-pCVXZ and aug-cc-pCVXZ (X = D,T,Q) basis sets. The scale length parameter in the Slater-type geminal, r_c, is varied from 0.5 to 1.5 Bohr.

Table 1
MP2 and MP2-STG energies for the Ne atom (mE_h)

Basis set	MP2	(%)	MP2-STG (r_c = 1)	(%)	MP2-STG (r_c = opt)	(%)	r_c(opt)
cc-pCVXZ							
X = D	−228.30	(58.8)	−372.88	(96.1)	−373.72	(96.3)	0.9
X = T	−329.10	(84.8)	−382.60	(98.6)	−382.60	(98.6)	1.0
X = Q	−361.51	(93.1)	−386.21	(99.5)	−386.21	(99.5)	1.1
aug-cc-pCVXZ							
X = D	−249.90	(64.4)	−380.29	(98.0)	−384.44	(99.1)	0.7
X = T	−337.29	(86.9)	−385.54	(99.3)	−385.92	(99.4)	0.7
X = Q	−365.16	(94.1)	−387.61	(99.9)	−387.64	(99.9)	0.8
Lim.[a]	−388.1	(100.0)					

[a] The MP2 limit [14].

Table 2
Convergence of the MP2 energy for the water molecule with cc-pCVXZ sets (mE_h)[a]

Basis set	Method	X = D	(%)	X = T	(%)	X = Q	(%)	X = 5	(%)
cc-pCVXZ	MP2[b]	−241.35	(66.65)	−317.51	(87.69)	−342.64	(94.63)	−350.59	(96.82)
	MP2-GTG[b]	−337.57	(93.33)	−354.93	(98.02)	−359.61	(99.31)	−361.23	(99.76)
	R12-MP2/A′[c]	−337.74	(93.27)	−353.83	(97.72)	−358.49	(99.00)	−360.53	(99.57)
	R12-MP2/B[c]	−318.09	(87.85)	−348.09	(96.13)	−356.62	(98.49)	−360.12	(99.45)
	MP2-STG	−348.91	(96.36)	−357.27	(98.67)	−360.44	(99.54)	−361.60	(99.86)
	MP2-STG-10G	−348.80	(96.33)	−357.21	(98.65)	−360.38	(99.52)	−361.55	(99.85)
aug-cc-pCVXZ	MP2[b]	−259.24	(71.59)	−324.15	(89.52)	−345.64	(95.46)	−351.58	(97.09)
	MP2-GTG[b]	−350.45	(96.78)	−359.35	(99.24)	−361.35	(99.79)	−361.74	(99.90)
	R12-MP2/A′[c]	−363.30	(100.33)	−359.64	(99.32)	−361.72	(99.90)	−362.15	(100.01)
	R12-MP2/B[c]	−332.51	(91.83)	−355.84	(98.27)	−360.17	(99.47)	−361.37	(99.80)
	MP2-STG	−358.34	(98.96)	−360.69	(99.61)	−361.86	(99.93)	−362.02	(99.98)
	MP2-STG-10G	−358.23	(98.93)	−360.64	(99.60)	−361.81	(99.92)	−361.97	(99.96)

[a] The MP2 limit is −362.1 mE_h [14]. *h*-functions are absent for X = 5 except for the R12 results.
[b] Numerical MP2 and MP2-GTG results [18].
[c] Ref. [14].

program. The present MP2-STG method gives the lowest energies in most cases. The commutator between the exchange and geminal operators is neglected in all of the explicitly correlated methods except R12-MP2/B [14,18]. As the commutator contributes to the second order energy positively, the present results should involve certain amount of overshooting as the difference between the R12-MP2/A′ and /B results. It is possible to represent STG in terms of GTG approximately. We have used an even-tempered sequence of 10 component GTGs in the range of exponents between 1000 and 0.01. The coefficients $\{c_G\}$ are determined by minimizing the target function,

$$T = \int_0^\infty \left(f_{12}^{(\mathrm{STG})} - f_{12}^{(\mathrm{GTG})}\right)^2 \mathrm{d}r_{12} = \frac{1}{8} - 2\mathbf{A}^+\cdot\mathbf{c} + \mathbf{c}^+\cdot\mathbf{B}\cdot\mathbf{c}, \tag{17}$$

$$A_G = \frac{1}{2}\sqrt{\frac{\pi}{\zeta_G}}\exp\left(\frac{1}{4\zeta_G}\right)\mathrm{erfc}\left(\frac{1}{2\sqrt{\zeta_G}}\right), \tag{18}$$

Table 3
MP2 components of reaction energies (kJ/mol) with the aug-cc-pCVXZ basis sets[a]

Method	Reaction	X = D	($\lvert\Delta E\rvert$)	X = T	($\lvert\Delta E\rvert$)	X = Q	($\lvert\Delta E\rvert$)	pcV6Z[b]	($\lvert\Delta E\rvert$)	pcV(56)Z[b]
MP2[c]	R13	23.2	(1.8)	21.7	(3.3)	23.2	(1.8)	24.4	(0.6)	25.0
	R14	−67.3	(12.1)	−75.2	(4.2)	−77.6	(1.8)	−78.9	(0.5)	−79.4
	R15	28.0	(13.4)	21.3	(6.7)	16.4	(1.8)	15.5	(0.9)	14.6
	R16	−143.4	(22.5)	−155.8	(10.1)	−161.6	(4.3)	−164.4	(1.5)	−165.9
	R17	231.2	(28.2)	212.5	(9.5)	205.6	(2.6)	204.3	(1.3)	203.0
	Ave.		15.6		6.8		2.5		1.0	
MP2-GTG[c]	R13	18.4	(6.6)	23.5	(1.5)	25.3	(0.3)	–	–	25.0
	R14	−79.8	(0.4)	−79.8	(0.4)	−79.0	(0.4)	–	–	−79.4
	R15	13.2	(1.4)	14.7	(0.1)	14.6	(0.0)	–	–	14.6
	R16	−164.8	(1.1)	−165.0	(0.9)	−165.3	(0.6)	–	–	−165.9
	R17	204.1	(1.1)	202.4	(0.6)	203.5	(0.5)	–	–	203.0
	Ave.		2.1		0.7		0.4			
MP2-STG	R13	23.7	(1.3)	25.7	(0.7)	25.8	(0.8)	–	–	25.0
	R14	−78.7	(0.7)	−78.9	(0.5)	−79.0	(0.4)	–	–	−79.4
	R15	15.4	(0.8)	14.3	(0.3)	14.3	(0.3)	–	–	14.6
	R16	−164.3	(1.6)	−165.0	(0.9)	−165.7	(0.2)	–	–	−165.9
	R17	206.6	(3.6)	203.2	(0.2)	203.9	(0.9)	–	–	203.0
	Ave.		1.6		0.5		0.5			

[a] The numbers in the parentheses are absolute displacements from the two-point extrapolation results, pcV(56)Z.
[b] Ref. [25].
[c] The result of numerical MP2 and MP2-GTG [18].

$$B_{GG'} = \frac{1}{2}\sqrt{\frac{\pi}{\zeta_G + \zeta_{G'}}}. \tag{19}$$

The result of this scheme denoted as STG-10G is very similar to MP2-STG. This suggests that the cusp behavior can be represented by GTG accurately. The difference between GTG and STG-10G is in the parameterizations especially at large r_{12}. It is implied that the exponential decay improves the result to some extent in comparison with the use of a Gaussian weight function for the previous GTG falling off more quickly [12,17,18].

Finally, we test STG in the calculation of MP2 components for the last five chemical reactions in the book of Helgaker et al. [25];

$$\begin{aligned}
&\mathrm{R13: C_2H_2 + 3H_2 \rightarrow 2CH_4}\\
&\mathrm{R14: CH_2 + H_2 \rightarrow CH_4}\\
&\mathrm{R15: F_2 + H_2 \rightarrow 2HF}\\
&\mathrm{R16: 2CH_2 \rightarrow C_2H_4}\\
&\mathrm{R17: O_3 + 3H_2 \rightarrow 3H_2O.}
\end{aligned}$$

The geometrical parameters are taken from [24,25]. In Table 3, we give the resulting MP2 contributions to the reaction enthalpies with basis sets through aug-cc-pCVQZ. The absolute displacements from the two-point extrapolation result, pcV(56)Z [25], are reduced substantially in MP2-GTG and MP2-STG. The average displacement in the orbital-based MP2 with aug-cc-pCVQZ, 2.5 kJ/mol, is comparable to those in explicitly correlated calculations with the smallest basis, aug-cc-pCVDZ. It is also noticeable that the MP2-STG result with aug-cc-pCVTZ is more accurate than pcV6Z [25]. The augmentation from aug-cc-pCVTZ to aug-cc-pCVQZ does not give noticeable improvements in the results of explicitly correlated methods. This might be attributed to the error in the two-point extrapolation scheme or small differences in geometrical parameters. The accuracy of MP2-STG is slightly superior or comparable to MP2-GTG. Although there is room for the improvement of the present routine for $G_m(T, U)$, MP2-STG is faster than an MP2-GTG calculation nevertheless in all cases examined in this work.

4. Conclusion

We have presented a novel use of the STG correlation factor in explicitly correlated electronic structure theory. It is shown that all of the necessary integrals are derived from the function, $G_m(T, U)$. As a preliminarily application, we employed STG in MP2 calculations. The convergence behavior of the correlation energies and reaction enthalpies indicate the particular efficiency of the resulting method. It is also believed that STG is superior to the linear r_{12} and GTG functions from a computational point of view by virtue of its compact and short-range form.

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Appendix A. Molecular integrals of the Slater-type geminals

The two-electron integrals for a spherically symmetric operator, O_{12}, represented by the transformation,

$$O_{12} = \int_0^\infty \mathrm{d}u\,\omega^{(O)}(u)\exp(-u^2 r_{12}^2), \tag{A.1}$$

are calculated from the kernel functions,

$$(00|O_{12}|00)^{(m)} = \int_0^\infty \mathrm{d}u\,\omega^{(O)}(u)\left(\frac{u^2}{\rho + u^2}\right)^m (00|\mathrm{e}^{-u^2 r_{12}^2}|00), \tag{A.2}$$

where $\omega^{(O)}(u)$ is a weight function for the operator, $(00|\mathrm{e}^{-u^2 r_{12}^2}|00)$ denotes integrals for the Gaussian operator, $\mathrm{e}^{-u^2 r_{12}^2}$, and ρ is a parameter of the orbital exponents [26]. The kernel functions are referred to as the auxiliary integrals over s-functions for electron repulsion integrals. The key for the present implementation of STG is the equality,

$$\int_0^\infty \mathrm{d}u \exp\left(-au^2 - \frac{b}{4u^2}\right) = \frac{1}{2}\sqrt{\frac{\pi}{a}}\exp(-\sqrt{ab}), \tag{A.3}$$

which leads to

$$(00|r_{12}^{-1}\mathrm{e}^{-\zeta r_{12}}|00)^{(m)} = 2S_1^{(0)}S_2^{(0)}\left(\frac{\rho}{\pi}\right)^{1/2} G_m(T, U), \tag{A.4}$$

$$T = \rho(\mathbf{P} - \mathbf{Q})^2, \tag{A.5}$$

$$U = \frac{\zeta^2}{4\rho}, \tag{A.6}$$

where the function, $G_m(T, U)$, is given by (13), and $S_1^{(0)}$ and $S_2^{(0)}$ are overlap integrals of the first and second s-orbital pairs. Eq. (A.4) reduces to the kernel functions for electron repulsion integrals [26] in the limit, $\zeta \rightarrow 0$. The differentiation with respect to ζ gives

$$\begin{aligned}(00|\mathrm{e}^{-\zeta r_{12}}|00)^{(m)} = {} & S_1^{(0)}S_2^{(0)}(\pi\rho)^{-1/2}\\ & \times \zeta[G_{m-1}(T, U) - G_m(T, U)].\end{aligned} \tag{A.7}$$

Combining the above results with (9), we obtain

$$\begin{aligned}(00|f_{12}|00)^{(m)} = {} & -\tfrac{1}{2}(\pi\rho)^{-1/2}S_1^{(0)}S_2^{(0)}\\ & \times [G_{m-1}(T, U_L) - G_m(T, U_L)],\end{aligned} \tag{A.8}$$

$$(00|Z_{12}|00)^{(m)} = -\left(\frac{\rho}{\pi}\right)^{1/2} r_c S_1^{(0)} S_2^{(0)} G_m(T, U_L), \tag{A.9}$$

$$(00|K_{12}^{(Q)}|00)^{(m)} = -\frac{1}{2r_c}(\pi\rho)^{-1/2} S_1^{(0)} S_2^{(0)} [G_{m-1}(T, U_Q) - G_m(T, U_Q)], \tag{A.10}$$

$$U_L = \frac{1}{4\rho r_c^2}, \tag{A.11}$$

$$U_Q = 4U_L. \tag{A.12}$$

Although the integrals for $K_{12}^{(L)}$ can be calculated from (A.8), it is more efficient to estimate the contribution of the first term in $K_{12}^{(L)}$ using the relation,

$$-\nabla_1^2 f_{12} = \frac{1}{r_c}\left(2Z_{12} - \frac{f_{12}}{r_c}\right). \tag{A.13}$$

All of the necessary integrals are calculated from $G_m(T, U_L)$ and $G_m(T, U_Q)$. The reduction of the four-center integrals to the three-center ones with grid points is straightforward.

Finally we briefly mention the way to evaluate $G_m(T, U)$ used in this work. The partial integration leads to the recurrence relations,

$$G_m(T, U) = \frac{1}{2T}[(2m-1)G_{m-1}(T, U) + 2UG_{m-2}(T, U) - e^{-T}], \tag{A.14}$$

$$G_m(T, U) = \frac{1}{2U}[e^{-T} - (2m+3)G_{m+1}(T, U) + 2TG_{m+2}(T, U)]. \tag{A.15}$$

For $U = 0$, (A.14) reduces to the usual upward recurrence relation for $F_m(T)$ and is appropriate for large T. For small T and large U, the downward relation should be used. Neither of the upward and downward relations is stable when both T and U are small. In this case, $G_m(T, U)$ is calculated for all m without using the recurrence relations. As $G_m(T, U)$ satisfy the differential relation similar to $F_m(T)$, we can use the simple Maclaurin expansion for small T,

$$G_m(T, U) = \sum_{k=0} \frac{(-T)^k}{k!} G_{m+k}(0, U). \tag{A.16}$$

As $G_m(0, U)$ is related to the incomplete Gamma function as

$$G_m(0, U) = \frac{1}{2} e^U U^{m+\frac{1}{2}} \Gamma\left(-m - \frac{1}{2}, U\right), \tag{A.17}$$

the evaluation of $G_m(0, U)$ is easy for small U. For large U, we have used the continued fraction expansion formula,

$$G_m(0, U) = \frac{1}{2}\left(\frac{1}{U+}\,\frac{m+\frac{3}{2}}{1+}\,\frac{1}{U+}\,\frac{m+\frac{5}{2}}{1+}\,\frac{2}{U+}\cdots\right), \tag{A.18}$$

which turned out to be very efficient. The transformation,

$$\int_{\pm\infty}^{\sqrt{T}\pm\sqrt{U}} e^{-x^2}\,dx = \int_0^1 (\sqrt{T} \mp \sqrt{U}u^{-2}) e^{-(\sqrt{T}u \pm \sqrt{U}u^{-1})^2}\,dt, \tag{A.19}$$

leads to the relations of $G_{-1}(T, U)$ and $G_0(T, U)$ to the complementary error functions. This allows us to use (A.14) for large T. The detailed computation involving suitable ranges for formulae will be presented in a forthcoming full paper.

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