A simple algebraic derivation of the Obara–Saika scheme for general two-electron interaction potentials

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A new derivation is presented for the recursion relation of Obara and Saika (OS) for two-electron integrals over Gaussian basis functions for general interaction potentials $g(r_{12})$, where r_{12} denotes the interelectronic distance. The decisive vertical OS recursion is proved directly from the recursion relation for Gaussian basis functions and the structure of the primitive integral expression for *s* functions. The resulting simple formulae greatly facilitate extensions of OS-based codes for Coulomb interactions to general *g*, which has already proved useful in implementations. The present derivation further extends the validity of the OS recursion beyond interactions covered so far.

1. Introduction

The use of GTOs (Gaussian type orbitals) as basis functions and the availability of efficient algorithms to compute all necessary integrals is essential for contemporary molecular electronic structure theory. Much effort has thus been devoted to the development of fast integral codes. A remarkable level of efficiency had been reached in the late seventies with the work of Dupuis, Rys and King (DRK),[1–3] McMurchie and Davidson (MD),[4] and Pople and Hehre (PH)[5] to mention some popular procedures. Saunders[6] has presented a good review covering the developments up to about 1982. The field then lay 'dormant'[7] until Obara and Saika (OS)[8] derived a recursion relation, consisting essentially of a single equation for the computation of a complete batch of integrals. Similar techniques had actually been used before by Schlegel[9] to construct efficient algorithms for integral derivatives. The OS scheme made it easy to implement and optimize the code for high efficiency. The paper of OS also opened the way for a better understanding of the structure behind integral evaluations and led to numerous further studies, *e.g.* ref. 7,10–13. These resulted in the discovery of additional recursion relations, clarified the connections between different algorithms, and led to more efficient codes. A review of these developments has been given by Gill,[14] to which the reader is referred for a detailed account.

The present work first describes an algebraic derivation, based on operator equations, of OS recursion relations, which uses only the recursion formula for Gaussian basis functions together with the structure of the integral expression for *s* functions. This is much simpler and more direct than the derivation of OS based on the Laplace transform of $1/r_{12}$, which could be considered an unnecessary detour. Dunlap[15] has given an algebraic derivation of three-center two-electron integrals over solid spherical harmonics, as opposed to Cartesian Gaussians, and has mentioned that 'It is tedious, but straightforward, to extend this approach to four centers, thereby extending the method of OS from Cartesian Gaussians to spherical harmonic Gaussians'. The present treatment of Cartesian Gaussians for four-center integrals turns out to be extremely simple and holds for quite general interaction potentials $g(r_{12})$. May and Manby[16] have mentioned that the OS recursion and its derivation hold for any $g(r_{12})$ for which a Laplace transformation can be found. The present treatment extends the validity of OS beyond this condition under very mild assumptions.

General interactions of the type $g(r_{12})$, other than the $1/r_{12}$ originally considered by OS, occur in various computational procedures. We mention the following examples: explicit R12 theories[17,18] as well as its extension to damped Coulomb interactions,[19] attenuated Coulomb interaction procedures,[20] or the 'anti-Coulomb' operator, $g(r_{12}) = r_{12}$, required for an optimal approximation of the potential caused by a given charge distribution.[21] The necessary integral routines have typically been obtained by modifications of existing algorithms,[20] or by an MD procedure,[17,19] to give just few examples. A detailed account has been given in the review by Gill.[14]

Obara and Saika have, in a remarkable and elaborate paper, extended their recursion relations to more general interactions besides scalar potentials $g(r_{12})$.[22] The resulting equations do not demonstrate the crucial fact that the case $g(r_{12})$ can be treated by very minor modifications of an existing OS code for $g(r_{12}) = 1/r_{12}$, as will be shown below. Weber and Daul[23] have considered the damped Coulomb interaction, see section 5, and have shown that the OS scheme holds in this case as well. OS-type recursions have also been derived by Ten-no in the treatment of three-electron integrals occurring in explicitly-correlated methods, and for wave functions including terms $e^{-\gamma r_{12}}$.[24,25] In a very recent work Saunders[26] has extended the OS scheme to more general types of Gaussian basis functions, the separable polynomial Gaussians.

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The following section provides the necessary definitions. The main result of this work, the derivation of a vertical recursion relation, is presented thereafter. This is then extended to the case of general quantum numbers in section 4. For the sake of completeness, we also collect the expression for intermediate quantities required to extend OS codes to the most common interaction potentials, section 5.

2. Definitions and notation

We consider unnormalized atom-centered GTOs specified by the orbital exponent α, the center $\boldsymbol{A}$, and quantum numbers $\boldsymbol{a} = (a_x,a_y,a_z)$

$$|\boldsymbol{a}\rangle = \phi_a(\boldsymbol{r}) = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} e^{-\alpha|\boldsymbol{r}-\boldsymbol{A}|^2}. \quad (1)$$

In the short hand notation $|\boldsymbol{a}\rangle$, we have suppressed the other parameters since we consider a batch of integrals and are mainly interested in the dependence on $\boldsymbol{a}$. The functions ϕ_b, ϕ_c, ϕ_d are defined in the same way with orbital exponents β, γ, δ, at centers $\boldsymbol{B}$, $\boldsymbol{C}$, $\boldsymbol{D}$, and quantum numbers $\boldsymbol{b}$, $\boldsymbol{c}$, $\boldsymbol{d}$. The two-electron integral in question is defined as

$$I(\boldsymbol{ab}|\boldsymbol{cd}) = \int \phi_a(\boldsymbol{r}_1)\, \phi_c(\boldsymbol{r}_2)\, g(r_{12})\, \phi_b(\boldsymbol{r}_1)\, \phi_d(\boldsymbol{r}_2) \mathrm{d}\tau \quad (2)$$

for general interaction potentials g. With the usual definitions:

$$\zeta = \alpha + \beta, \quad \eta = \gamma + \delta, \quad \rho = \frac{\zeta\eta}{\zeta + \eta}, \quad (3)$$

$$\boldsymbol{P} = \frac{\alpha\boldsymbol{A} + \beta\boldsymbol{B}}{\zeta}, \quad \boldsymbol{Q} = \frac{\gamma\boldsymbol{C} + \delta\boldsymbol{D}}{\eta}, \quad (4)$$

$$T = \rho|\boldsymbol{P} - \boldsymbol{Q}|^2, \quad (5)$$

$$S_{ab} = e^{-\frac{\alpha\beta}{\zeta}|\boldsymbol{A}-\boldsymbol{B}|^2}, \quad S_{cd} = e^{-\frac{\gamma\delta}{\eta}|\boldsymbol{C}-\boldsymbol{D}|^2}, \quad (6)$$

one gets the basic integral

$$I_0 = I(00|00) = \left(\frac{\pi}{\zeta + \eta}\right)^{\frac{3}{2}} S_{ab} S_{cd} G_0(\rho, T) \quad (7)$$

with

$$G_0(\rho,T) = \int e^{-\rho|\boldsymbol{r}-\boldsymbol{P}+\boldsymbol{Q}|^2} g(r) d^3\boldsymbol{r}. \quad (8)$$

Eqn (7) is obtained from eqn (2) by a variable transformation to $\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)$ and $\boldsymbol{r} = (\boldsymbol{r}_1 - \boldsymbol{r}_2)$, and integration over $\boldsymbol{R}$. G_0 depends only on ρ and $|\boldsymbol{P} - \boldsymbol{Q}|^2$; it is more convenient to take ρ and T as variables. As mentioned above, G_0 can be analytically evaluated for various cases of interest, for which explicit expressions will be given in section 5.

Integrals over functions with higher angular momentum can be obtained by recursion as is well known, *e.g.*:

$$\hat{D} = \frac{\partial}{2\alpha\partial A_x}, \quad (9)$$

$$|\boldsymbol{a} + \boldsymbol{1}_x\rangle = \hat{D}|\boldsymbol{a}\rangle + \frac{a_x}{2\alpha}|\boldsymbol{a} - \boldsymbol{1}_x\rangle, \quad (10)$$

$$I((\boldsymbol{a} + \boldsymbol{1}_x)\boldsymbol{b}|\boldsymbol{cd}) = \hat{D} I(\boldsymbol{ab}|\boldsymbol{cd}) + \frac{a_x}{2\alpha} I((\boldsymbol{a} - \boldsymbol{1}_x)\boldsymbol{b}|\boldsymbol{cd}), \quad (11)$$

with $\boldsymbol{1}_i = (\delta_{ix},\delta_{iy},\delta_{iz})$ for $i = x,y,z$. In fact, eqn (11) holds for any arbitrary operator, not just multiplicative. We will further need the definition

$$G_n(\rho, T) = \left(-\frac{\partial}{\partial T}\right)^n G_0(\rho, T), \quad (12)$$

and the following easily verified equations:

$$\hat{D} S_{ab} = (P_x - A_x) S_{ab}, \quad (13)$$

$$\hat{D} G_k(\rho, T) = -\frac{\rho}{\zeta}(P_x - Q_x) G_{k+1}(\rho, T), \quad (14)$$

$$\hat{D}(P_x - A_x) = -\frac{\beta}{2\alpha\zeta}, \quad \hat{D}(P_x - Q_x) = \frac{1}{2\zeta}. \quad (15)$$

It is appropriate at this stage to consider the validity of the present derivation: it is only required that G_0 exists, is sufficiently differentiable with respect to T, and that integration and differentiation can be interchanged, *i.e.* the step from (10) to (11). This is more general than previous derivations of OS schemes and even covers exponentially increasing cases as $g(r_{12}) = e^{r12}$.

3. A vertical recursion relation

The derivations presented in this section have been motivated by the aim to give a direct proof of recursion relations that are based solely on (11) and are thus valid for general interactions. It will now be shown for a special class of integrals how this equation leads to an explicit integral expression from which the desired recursion follows directly. We start with the definition of an operator $\hat{M}_n$, with $\hat{D}$ and α as in (9)

$$\hat{M}_n = \sum_{i=0}^{\left[\frac{n}{2}\right]} (2i - 1)!! \binom{n}{2i} (2\alpha)^{-i} \hat{D}^{n-2i}, \quad (16)$$

which obeys the recursion relation

$$\hat{M}_{n+1} = \hat{M}_n \hat{D} + \frac{n}{2\alpha} \hat{M}_{n-1} \quad (17)$$

as is verified by induction with $\hat{M}_0 = 1$. This is (10) in operator form and we have

$$|n,0,0\rangle = \hat{M}_n|0,0,0\rangle. \quad (18)$$

The operators $\hat{M}_n$ fulfil another relationship of importance for the present work. Let Y be linear in the sense

$$\hat{D} Y = \mu, \quad (19)$$

where μ is constant, then

$$\hat{M}_n Y = Y\hat{M}_n + n\mu\hat{M}_{n-1}. \quad (20)$$

For a proof of (20) one inserts the commutator

$$\hat{D}^{n-2i} Y = Y\hat{D}^{n-2i} + (n-2i)\mu\hat{D}^{n-2i-1} \quad (21)$$

into (16) and uses standard equations for binomial coefficients. The rest of the present paper relies entirely on the definition (16) of $\hat{M}_n$ and eqn (17) and (20).

For a special class of integrals one then has an explicit expression

$$I_n = I((n,0,0)0|00) = \hat{M}_n I_0 \quad (22)$$

since this fulfils (11) as a consequence of (17). For the derivation of a recursion relation, it is convenient to define

$$I_n^{(m)} = I^{(m)}((n,0,0)0|00) = \hat{M}_n\left(\frac{\pi}{\zeta+\eta}\right)^{\frac{3}{2}} S_{ab}S_{cd}G_m(\rho,T). \quad (23)$$

The $I_n^{(m)}$ represent true integrals only for $m = 0$; as a consequence of (17) they also obey the recursion relation (11).

Let us now consider $\hat{D}I_n^{(m)} = \hat{M}_n\hat{D}I_0^{(m)}$. From (13), (14), and (23) one first gets

$$\hat{D}I_0^{(m)} = (P_x - A_x)I_0^{(m)} - \frac{\rho}{\zeta}(P_x - Q_x)I_0^{(m+1)}. \quad (24)$$

The commutator relationships (20) for $Y = (P_x - A_x)$ and $Y = (P_x - Q_x)$ together with (15) leads to

$$\hat{D}I_n^{(m)} = \hat{M}_n[\hat{D}I_0^{(m)}] = (P_x - A_x)I_n^{(m)} - \frac{\rho}{\zeta}(P_x - Q_x)I_n^{(m+1)} - \frac{n\beta}{2\alpha\zeta}I_{n-1}^{(m)} - \frac{n\rho}{2\zeta^2}I_{n-1}^{(m+1)}. \quad (25)$$

We finally combine (17) and (25) and get

$$I_{n+1}^{(m)} = (P_x - A_x)I_n^{(m)} - \frac{\rho}{\zeta}(P_x - Q_x)I_n^{(m+1)} + \frac{n}{2\zeta}I_{n-1}^{(m)} - \frac{n\rho}{2\zeta^2}I_{n-1}^{(m+1)}. \quad (26)$$

This is the desired recursion formula, which has been proved under the following assumptions on g: G_0 exists, is differentiable in T, and (11) follows from (10).

4. Recursion relations for general quantum numbers

The derivations of the preceding section are readily extended to the general case; it is mainly necessary to be more specific with the variables on which $\hat{M}$ depends. In analogy to (16), one defines

$$\hat{M}(n,\tau,X) = \sum_{i=0}^{[\frac{n}{2}]}(2i-1)!!\binom{n}{2i}(2\tau)^{-i}\left(\frac{\partial}{2\tau\partial X}\right)^{n-2i}, \quad (27)$$

which also obeys, see (17),

$$\hat{M}(n+1,\tau,X) = \hat{M}(n,\tau,X)\frac{\partial}{2\tau\partial X} + \frac{n}{2\tau}\hat{M}(n-1,\tau,X). \quad (28)$$

The operators $\hat{M}(n,\tau,A_i)$, $i = x, y, z$, commute with each other, facilitating the formation of

$$\hat{M}(\boldsymbol{a}) = \prod_{i=x,y,z}\hat{M}(a_i,\alpha,A_i) \quad (29)$$

since the ordering in the product is irrelevant. In $\hat{M}(\boldsymbol{a})$ we have suppressed α and $\boldsymbol{A}$ since they are obvious from the context. We then define

$$I^{(m)}(\boldsymbol{ab}|\boldsymbol{cd}) = \hat{M}(\boldsymbol{a})\hat{M}(\boldsymbol{b})\hat{M}(\boldsymbol{c})\hat{M}(\boldsymbol{d})I_0^{(m)}, \quad (30)$$

with $I_0^{(m)}$ from (23) (note that $\hat{M}_0 = 1$). The operators in (30) commute again. The case $m = 0$ corresponds to a true integral $I^{(0)}(\boldsymbol{ab}|\boldsymbol{cd}) = I(\boldsymbol{ab}|\boldsymbol{cd})$ since (30) fulfils (11) by virtue of (28).

For the derivation of the recursion formula, one proceeds as in the preceding section and considers an increase of angular momentum on one of the centers, *e.g.* the transition from $\boldsymbol{a}$ to $(\boldsymbol{a}+1_i)$, since other indices are analogous. Using (28), one has to consider $\hat{M}(\boldsymbol{a})\frac{\partial}{2\alpha\partial A_i}\hat{M}(\boldsymbol{b})\hat{M}(\boldsymbol{c})\hat{M}(\boldsymbol{d})$. The additional differentiation commutes with the $\hat{M}$ operators and can be applied directly on $I_0^{(m)}$, as in (24). One then brings the factors $(P_i - A_i)$ and $(P_i - Q_i)$ to the left of all $\hat{M}$ operators in using the commutator relationship (21) and its corresponding analogues. Commuting $(P_i - A_i)$ with $\hat{M}$ gives contributions from the i component of $\hat{M}(\boldsymbol{a})$ and $\hat{M}(\boldsymbol{b})$, whereas for $(P_i - Q_i)$ one gets contributions from the i component of all operators. The final result is eqn (39) of OS, which is now proved for general $g(r_{12})$; the only change required is the replacement of F_n, (40) below, by G_n (12):

$$\begin{aligned} I^{(m)}((\boldsymbol{a}+\boldsymbol{1}_i)\boldsymbol{b}|\boldsymbol{cd}) =& (P_i - A_i)I^{(m)}(\boldsymbol{ab}|\boldsymbol{cd}) \\ &- \frac{\rho}{\zeta}(P_i - Q_i)I^{(m+1)}(\boldsymbol{ab}|\boldsymbol{cd}) \\ &+ \frac{a_i}{2\zeta}[I^{(m)}((\boldsymbol{a}-\boldsymbol{1}_i)\boldsymbol{b}|\boldsymbol{cd}) \\ &- \frac{\rho}{\zeta}I^{(m+1)}((\boldsymbol{a}-\boldsymbol{1}_i)\boldsymbol{b}|\boldsymbol{cd})] \\ &+ \frac{b_i}{2\zeta}[I^{(m)}(\boldsymbol{a}(\boldsymbol{b}-\boldsymbol{1}_i)|\boldsymbol{cd}) \\ &- \frac{\rho}{\zeta}I^{(m+1)}(\boldsymbol{a}(\boldsymbol{b}-\boldsymbol{1}_i)|\boldsymbol{cd}) \\ &+ \frac{c_i}{2(\zeta+\eta)}I^{(m+1)}(\boldsymbol{ab}|(\boldsymbol{c}-\boldsymbol{1}_i)\boldsymbol{d}) \\ &+ \frac{d_i}{2(\zeta+\eta)}I^{(m+1)}(\boldsymbol{ab}|\boldsymbol{c}(\boldsymbol{d}-\boldsymbol{1}_i)) \end{aligned} \quad (31)$$

The most important case is the one where angular momentum is increased on a single center only

$$\begin{aligned} I^{(m)}((\boldsymbol{a}+\boldsymbol{1}_i)0|00) =& (P_i - A_i)I^{(m)}(\boldsymbol{a}0|00) \\ &- \frac{\rho}{\zeta}(P_i - Q_i)I^{(m+1)}(\boldsymbol{a}0|00) \\ &+ \frac{a_i}{2\zeta}[I^{(m)}((\boldsymbol{a}-\boldsymbol{1}_i)0|00) \\ &- \frac{\rho}{\zeta}I^{(m+1)}((\boldsymbol{a}-\boldsymbol{1}_i)0|00)], \end{aligned} \quad (32)$$

since this appears indispensable. One may further employ the recursion in which angular momentum is raised on the third center (in addition to the one on center $\boldsymbol{A}$)

$$\begin{aligned} I^{(m)}(\boldsymbol{a}0|(\boldsymbol{c}+\boldsymbol{1}_i)0) =& (Q_i - C_i)I^{(m)}(\boldsymbol{a}0|\boldsymbol{c}0) \\ &+ \frac{\rho}{\eta}(P_i - Q_i)I^{(m+1)}(\boldsymbol{a}0|\boldsymbol{c}0) \\ &+ \frac{c_i}{2\eta}[I^{(m)}(\boldsymbol{a}0|(\boldsymbol{c}-\boldsymbol{1}_i)0) \\ &- \frac{\rho}{\eta}I^{(m+1)}(\boldsymbol{a}0|(\boldsymbol{c}-\boldsymbol{1}_i)0)] \\ &+ \frac{a_i}{2(\zeta+\eta)}I^{(m+1)}((\boldsymbol{a}-\boldsymbol{1}_i)0|\boldsymbol{c}0). \end{aligned} \quad (33)$$

The remaining integrals are best obtained from a transfer relationship, *e.g.*

$$I((\boldsymbol{a}+\boldsymbol{1}_i)\boldsymbol{b}|\boldsymbol{cd}) = I(\boldsymbol{a}(\boldsymbol{b}+\boldsymbol{1}_i)|\boldsymbol{cd}) + (B_i - A_i)I(\boldsymbol{ab}|\boldsymbol{cd}), \quad (34)$$

which also applies for contractions and provides a convenient and efficient way to get all integrals from $I(\boldsymbol{a}0|\boldsymbol{c}0)$. Eqn (34) holds for all multiplicative potentials, but not if g is replaced by an arbitrary operator.[27]

The recursion (33) can be replaced by a horizontal recursion which redistributes angular momentum between centers $\boldsymbol{A}$ and $\boldsymbol{C}$ and permits one to get $I(\boldsymbol{a}0|\boldsymbol{c}0)$ from $\boldsymbol{I}(10|00)$ for $\boldsymbol{I} = 0,(\boldsymbol{a}+\boldsymbol{b})$[11,12]

$$\begin{aligned} I(\boldsymbol{a}0|(\boldsymbol{c}+\boldsymbol{1}_i)0) =& [(Q_i - C_i) + \frac{\zeta}{\eta}(P_i - A_i)]I(\boldsymbol{a}0|\boldsymbol{c}0) \\ &+ \frac{a_i}{2\eta}I((\boldsymbol{a}-\boldsymbol{1}_i)0|\boldsymbol{c}0) + \frac{c_i}{2\eta}I(\boldsymbol{a}0|(\boldsymbol{c}-\boldsymbol{1}_i)0) \\ &- \frac{\zeta}{\eta}I((\boldsymbol{a}+\boldsymbol{1}_i)0|\boldsymbol{c}0). \end{aligned} \quad (35)$$

Eqn (35) is valid for arbitrary potentials g since it follows from the translational invariance of integrals applied to $I(\boldsymbol{a}0|\boldsymbol{c}0)$

$$\left(\frac{\partial}{\partial A_i} + \frac{\partial}{\partial B_i} + \frac{\partial}{\partial C_i} + \frac{\partial}{\partial D_i}\right) I(\boldsymbol{a}0|\boldsymbol{c}0) = 0, \quad (36)$$

together with (10) and the transfer relationship to eliminate terms with angular momentum on centers $\boldsymbol{B}$ and $\boldsymbol{D}$. Eqn (35) can also be derived from (33).[11] The horizontal recursion (35) leads to a favorable flop count for higher angular momentum functions,[10,11] and is more efficient in this case, *e.g.* correlated treatments. Eqn (35) offers little advantage over (33) in Hartree Fock or density functional calculations since relatively few f or g functions are used and the overwhelming majority of integral batches concerns cases where the sum of angular momenta is less or equal to four.

Eqns (32) and (33) have been proved by Weber and Daul[23] for the Coulomb case with damping $-e^{-\omega r_{12}^2}$. The case $g(r_{12}) = r_{12}$ has been considered repeatedly since it is of importance for the approximation of the Coulomb potential[21] and in R12 theories. Klopper and Röhse[28] derived a recursion similar to (32), and Valeev and Schaefer[27] one similar to (33); the equations include integrals over r_{12} as well as over $1/r_{12}$, which is different from the present work.

5. Explicit expressions for G_0

An implementation of the procedures presented above requires explicit expressions for G_0, eqn (8). For a generalization of an OS program one has only to adapt G_0 and its derivatives, (12), which are typically evaluated in a single subroutine. G_0 can, of course, be obtained by the comparison of the present expression for I_0, eqn (7), with literature results cited in the text. For the sake of completeness we collect G_0 for various $g(r_{12})$, which are conveniently obtained from the definition of G_0, eqn (8). This covers well known cases together with new ones.

The trivial cases of the delta function and the overlap lead to

$$g(r) = \delta(\boldsymbol{r}) : G_0(\rho,T) = e^{-T}, \quad (37)$$

$$g(r) = 1 : G_0(\rho,T) = \left(\frac{\pi}{\rho}\right)^{\frac{3}{2}}, \quad (38)$$

and the well known Coulomb case to

$$g(r) = r^{-1} : G_0(\rho,T) = \frac{2\pi}{\rho}F_0(T), \quad (39)$$

where F_n denote Boys' functions

$$\begin{aligned} F_n(T) &= \int_0^1 t^{2n}e^{-Tt^2}\mathrm{d}t = \sum_{i=0}^{\infty}\frac{(-T)^i}{(2i+2n+1)i!} \\ &= e^{-T}(2n-1)!!\sum_{i=0}^{\infty}\frac{(2T)^i}{(2i+2n+1)!!}. \end{aligned} \quad (40)$$

The damped two-electron integrals resulting from

$$\tilde{g}(r) = e^{-\omega r^2}g(r) \quad (41)$$

lead to $\tilde{G}_0(\rho,T,\omega)$, which is obtained from the definition of G_0, eqn (8), as

$$\tilde{G}_0(\rho,T,\omega) = e^{\frac{-\omega T}{\rho+\omega}}G_0\left(\rho+\omega, \frac{T\rho}{\rho+\omega}\right), \quad (42)$$

where G_0 corresponds to the interaction potential g. The last two equations provide a simple and systematic procedure to go from $g(r)$ to $r^2g(r)$, since one only has to take the partial derivative with respect to ω at $\omega = 0$:[19]

$$g(r) \to r^2g(r) : G_0(\rho,T) \to \frac{T}{\rho}\left[G_0 + \frac{\partial G_0}{\partial T}\right] - \frac{\partial G_0}{\partial \rho}. \quad (43)$$

Together with (38) and (39) this yields, *e.g.*

$$g(r) = r : G_0(\rho,T) = \frac{2\pi}{\rho^2}[(1+T)F_0(T) - TF_1(T)], \quad (44)$$

$$g(r) = r^2 : G_0(\rho,T) = \sqrt{\frac{\pi^3}{\rho^5}}\left(T + \frac{3}{2}\right). \quad (45)$$

For other g we first reduce (8) to a one-dimensional integral by integrating over angles in spherical coordinates with the direction of $(\boldsymbol{P}-\boldsymbol{Q})$ as z axis

$$G_0(\rho,T) = \frac{2\pi}{\rho^{\frac{3}{2}}\sqrt{T}}\int_0^{\infty} g\left(\frac{y}{\sqrt{\rho}}\right)ye^{-y^2-T}\sinh(2y\sqrt{T})\mathrm{d}y. \quad (46)$$

Expanding sinh in a power series yields

$$G_0(\rho,T) = \frac{4\pi}{\rho^{\frac{3}{2}}}e^{-T}\sum_{i=0}^{\infty}a_i\frac{2^{2i}}{(2i+1)!}T^i \quad (47)$$

$$a_i = \int_0^{\infty} g\left(\frac{y}{\sqrt{\rho}}\right)y^{(2i+2)}e^{-y^2}\mathrm{d}y. \quad (48)$$

eqn (48) can be easily evaluated for many g, *e.g.*

$$g(r) = r^{\alpha}, \alpha > -3 : a_i = \frac{1}{2\sqrt{\rho^{\alpha}}}\Gamma\left(i + \frac{\alpha+3}{2}\right). \quad (49)$$

The representation (47) for G_0 is numerically stable if $g \geq 0$ (or $g \leq 0$), since the coefficients a_i are then of the same sign. Eqn (47) defines a holomorphic function in T with $T = \infty$ as only singularity provided $g(r)$ does not increase too strongly for large r. This condition holds even if $g(r)$ increases like e^r. One can thus use (47) to get approximations for G_0, *e.g.* within small intervals of T, which is usually done anyway for the sake of efficiency.

From eqn (46)–(48) one gets the following integral directly, which is needed for the computation of lower bounds for energies:

$$g(r) = r^{-2} : G_0(\rho, T) = \frac{2\sqrt{\pi}^3}{\sqrt{\rho}} e^{-T} F_0(-T). \qquad (50)$$

This involves F_0 with negative argument, which is related to Dawson's integral $D(x)$[29]

$$D(x) = e^{-x^2} \int_0^x e^{t^2} \mathrm{d}t = x e^{-x^2} F_0(-x^2). \qquad (51)$$

With the damping considered by Gill and Adamson[20] one has

$$g(r) = \frac{1 - \mathrm{erf}(\omega r)}{r} : G_0(\rho, T)$$
$$= \frac{2\pi}{\rho} F_0(T) - \frac{2\pi}{\rho} \frac{\omega}{\sqrt{\omega^2 + \rho}} F_0\left(\frac{\omega^2 T}{\omega^2 + \rho}\right), \qquad (52)$$

the additional term arising from $\mathrm{erf}(\omega r)$ follows directly by integration of (42) with G_0 from (39). Eqn (52) is slightly more complicated than (42), both dampings are very similar asymptotically for large r, but (41) may be of advantage since it has a smaller effect near $r = 0$.

All examples considered so far display a simple structure of G_0, one has to deal only with $F_n(T)$, a function of a single variable. The reason is essentially that a_i, (48), factorize into a function of i multiplied by a term in ρ which is independent of i. This picture is essentially maintained in the damped Coulomb interactions (42) and (52). The situation is entirely different for the case

$$\tilde{g}(r) = e^{-\gamma r} g(r) \qquad (53)$$

considered by Ten-no.[25] In eqn (46) and (48) there is no factorization of the kind found so far, and the evaluation of G_0, *e.g.* from (46), becomes more complicated as discussed by Ten-no.

6. Summary

Treatments of molecular integrals, *e.g.* over GTOs, invariably have to cope with the numerous necessary definitions given in section 2. The main results of the present work can be summarized as follows.

(i) A direct and short derivation of a vertical recursion formula for special integrals, eqn (26), based solely on the recursion for GTOs (10).

(ii) The derivation does not refer to the explicit form of the interaction potential $g(r_{12})$, thus extending the OS scheme to general interactions. The only change required is the replacement of $F_n(T)$ (40) by $G_n(\rho,T)$ (12).

(iii) The validity of the OS recursion has been proved under the mild assumptions that G_0 exists, is differentiable in T, and integration and differentiation can be interchanged, eqn (10) and (11).

(iv) In section 4, it was demonstrated that these results are easily extended to all integrals, again without limitations on the form of $g(r_{12})$.

(v) With the explicit formulae collected in section 5 it is very easy to extend an OS-based code for $g(r_{12}) = 1/r_{12}$ to arbitrary potentials $g(r_{12})$ without losing efficiency. This has been demonstrated for two examples: an extension of the TURBOMOLE[30] code to damped Coulomb interactions (42) for four-center integrals and an implementation[31] of (44) for three-center integrals required in RI-MP2-R12 theories, the latter with considerably increased efficiency as compared to a previous implementation.[32]

The considerations presented in this work concerned only multiplicative operators $g(r_{12})$. The representation of integrals given in (30), however, is valid even for arbitrary operators replacing g in (2), which may turn out to be useful in future work. The above derivation of recursion relations depends crucially on (24) and this will not hold in general. Although the treatment given in sections 2 and 3 can be generalized to some extent, the author has not pursued this in detail. In cases of some importance, integrals involving more general operators can be expressed as linear combinations of integrals over $g(r_{12})$. To give an example, in explicit R12 theories one needs integrals over $[r_{12},\Delta_1]$; the treatment of this case, as discussed in ref. 19, 27 and 28 is easily carried over to the present method.

The situation is similar for the general recursion formulae derived by Obara and Saika.[22] That treatment deals with integrals which include (besides the Gaussians): $g(r_{12})$ representable by a Laplace transform, terms obtainable by certain limiting processes to generate a delta function or powers of $(x - a_x)$ *etc.*, or partial derivatives with respect to coordinates of electrons or centers of Gaussians (the former is trivially converted to the latter). All these cases yield integrals covered in the present work or linear combinations of integrals resulting from differentiation with respect to centers, which only changes quantum numbers. One would thus first compute the necessary integrals and then the required linear combinations, whereas the general OS scheme gets the final integrals directly. The general recursion is more complicated and costly, however, and it remains to be established which procedure is preferable.

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