Intracule functional models. V. Recurrence relations for two-electron integrals in position and momentum space†

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The approach used by Ahlrichs [Phys. Chem. Chem. Phys., 2006, 8, 3072] to derive the Obara-Saika recurrence relation (RR) for two-electron integrals over Gaussian basis functions, is used to derive an 18-term RR for six-dimensional integrals in phase space and 8-term RRs for three-dimensional integrals in position or momentum space. The 18-term RR reduces to a 5-term RR in the special cases of Dot and Posmom intracule integrals in Fourier space. We use these RRs to show explicitly how to construct Position, Momentum, Omega, Dot and Posmom intracule integrals recursively.

1. Introduction

Since their introduction as basis functions by Boys,1 most quantum chemistry calculations have relied on the evaluation of molecular integrals over Gaussian-type orbitals (GTOs). Boys also suggested that integrals over functions of higher angular momentum can be obtained from those over functions of lower angular momentum by differentiation with respect to the Cartesian centres of the GTOs. Contributions by Pople and Hehre,2 Dupuis, Rys and King,3–5 and McMurchie and Davidson6 improved the original Boys’ algorithm but a major advance occurred when Obara and Saika introduced7,9 their recurrence relations (RRs).‡ Recursive schemes are now employed in almost all modern algorithms10 for calculating molecular integrals11 for they facilitate the development of algorithms, for integrals of arbitrarily high angular momentum, that are both easier to implement and more efficient than explicit formulae obtained by Boys differentiation. In a recent paper in this journal,12 Ahlrichs used an elegant algebraic construction to derive a generalization of the Obara-Saika RR under mild assumptions. In that paper, he wrote, “Although the treatment given in sections 2 and 3 can be generalized to some extent, the author has not pursued this in detail”. It is the pursuit of such a generalization that led to our present work.

Most algorithm development has focused on integrals over operators of the form $g(u)$, where $u$ is the interelectronic separation, and the resulting techniques are therefore useful for computing two-electron repulsion integrals (ERIs) over the Coulomb operator $u^{-1}$, integrals over attenuated Coulomb operators13 or damped Coulomb potentials,14 and the integrals required in R1215,16 and geminal17 methods. More general operators in position and/or momentum space have received much less attention but are our primary concern here.

Intracules, or two-electron probability distribution functions, are useful tools for the study of electron-electron interactions. They contain information about the relative position18,19 $u = r_1 - r_2$ or momentum20 $v = p_1 - p_2$ of electrons or, more recently, the dot product21,22 $x = u \cdot v$. It has also been found that the correlation energy of a molecular system can be estimated by contracting one of its intracules with a suitable kernel, in an approach called intracule functional theory (IFT).23–25 However, with the exception of the Position intracule (which is closely related to ERIs), RRs have not been presented for intracule integrals. As a result, the efficiencies of current schemes for constructing intracules leave much to be desired and this has seriously limited their range of application. One particular application is the analysis of the effects of electron correlation, and it is well known that basis functions of high angular momentum are required to effectively model the interelectronic cusp in multi-determinantal approaches. Efficient RRs for intracule integrals would be of great benefit to such studies.

If $\Psi(r_1,\ldots,r_N)$ is an $N$-electron wavefunction, its spinless 2nd-order density matrix26 is

$$
\rho_2(r_1, r_1', r_2, r_2') = \int \Psi^*(r_1, r_2, r_3, \ldots, r_N) \times \Psi(r_1', r_2', r_3, \ldots, r_N) dr_3 \ldots dr_N
$$

its 2nd-order Wigner distribution27 is

$$
W_2(r_1, r_2, p_1, p_2) = \frac{1}{(2\pi)^4} \int \rho_2(1 + \frac{q_1}{2}, r_1 - \frac{q_1}{2}) \times \rho_2(1 + \frac{q_2}{2}, r_2 - \frac{q_2}{2}, v) d q_1 d q_2
$$

$$
\rho_2(r_1 + \frac{q_1}{2}, r_1 - \frac{q_1}{2})
$$

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‡ A related scheme had previously been used by Schlegel for the calculation of nuclear first- and second-derivative integrals.7
and, if we regard this distribution as a bona fide probability density, a general two-electron phase-space operator $\mathcal{X}(r_1, r_2, p_1, p_2)$ has the expectation value

$$
\langle \mathcal{X} \rangle = \int W_2(r_1, r_2, p_1, p_2) \mathcal{X}(r_1, r_2, p_1, p_2) \, dr_1 \, dp_1 \, dr_2 \, dp_2
$$

(3)

Using this, we can create intracules as the expectation values of appropriate operators. For example, the operator $\mathcal{X} = \delta(r_{12} - u)$ yields the Position intracule $P(u)$, which is the probability density for the interelectronic distance $u = |r_1 - r_2|$ and, similarly, the operator $\mathcal{X} = \delta(p_{12} - v)$ gives the Momentum intracule $M(v)$, which is the probability density for the relative momentum $v = |p_1 - p_2|$. The operator $\mathcal{X} = \delta(r_{12} - u)\delta(p_{12} - v)\delta(\theta_{122} - \omega)$ is the joint quasi-probability density,27 physical properties derived from such integrals recursively, thereby extending the scope of recursive two-electron integral methodology from three-dimensional to six-dimensional space.

The next Section introduces several useful intermediates for the derivations that follow. After that, we review the key elements of Ahlrichs’ re-derivation of the Obara-Saika RR and then, using an analogous approach, we derive RR for four general forms of the $\mathcal{X}$ operator.

2. Definitions

Before deriving our RR, it is useful to define several intermediate quantities. The unnormalized Gaussian function with exponent $\alpha$, centered on $A = (A_x, A_y, A_z)$ is

$$
|a\rangle = (x - A_x)^\alpha(y - A_y)^\alpha(z - A_z)^\alpha e^{-\alpha^2 r^2}
$$

(7)

where $a = (a_x, a_y, a_z)$ is a vector of angular momentum quantum numbers. The GTOs $|b\rangle$, $|c\rangle$, and $|d\rangle$ have exponents $\beta, \gamma$, and $\delta$ and centers $B, C$, and $D$, respectively. We then define

$$
\eta = \frac{\alpha}{x + \delta} - \frac{\beta}{\beta + \gamma}
$$

(8)

$$
4\mu^2 = \frac{1}{x + \delta} + \frac{1}{\beta + \gamma} + \frac{\alpha^2}{\beta^2}
$$

(9a)

$$
\eta = \frac{1}{x + \beta} + \frac{1}{\gamma + \delta}
$$

(9b)

$$
\lambda^2 = \frac{2\delta}{x + \delta} + \frac{2\gamma}{\beta + \gamma} + \frac{4\delta^2}{\beta^2}
$$

(10a)

$$
\gamma = \frac{\beta}{x + \beta} + \frac{\gamma}{\gamma + \delta}
$$

(10b)

$$
P = \frac{2\alpha}{x + \delta} (A - D) + \frac{2\beta}{\beta + \gamma} (B - C)
$$

(11)

$$
V = \frac{2\beta}{x + \beta} (A - B) + \frac{2\gamma}{\gamma + \delta} (D - C)
$$

(12a)

$$
Q = \frac{\alpha + \delta}{x + \alpha} - \frac{\beta B + \gamma C}{\beta + \gamma} U
$$

(12b)

$$
S_{ad} = \exp \left[ -\frac{\alpha^2 |A - D|^2}{x + \delta} - \frac{\beta^2 |B - C|^2}{\beta + \gamma} \right]
$$

(13)

$$
S_{bd} = \exp \left[ -\frac{\alpha^2 |A - B|^2}{x + \beta} - \frac{\gamma^2 |C - D|^2}{\gamma + \delta} \right]
$$

3. A modified Boys recurrence relation

As a prelude to our construction of new RR, we first outline the key steps in Ahlrichs’ derivation. He begins with the Boys RR for a single GTO, viz.

$$
|a + 1_i\rangle = \hat{D}|a\rangle + \frac{a_i}{2\alpha} |a - 1_i\rangle
$$

(14)
where \( i = x, y \) or \( z \), \( 1_i = (\delta_{ix}, \delta_{iy}, \delta_{iz}) \), and \( \hat{D} \) is the scaled differential operator

\[
\hat{D} = \frac{\partial}{2\pi \partial A_i}
\]

(15)

He then defines an operator \( \hat{O}(a) \) that transforms an \( s \) function to one with angular momentum \( a \), i.e.

\[
\hat{O}(a)(0) = |a\rangle
\]

(16)

and which therefore must itself obey the RR

\[
\hat{O}(a + 1_i) = \hat{D}\hat{O}(a) + \frac{a_i}{2} \hat{O}(a - 1_i)
\]

(17)

Observing that \( \hat{O}(a) \) is the product of three operators that commute, i.e.

\[
\hat{O}(a) = \prod_{j=x,y,z} \hat{O}(a_j)
\]

(18)

he then uses (17) to show that

\[
\hat{O}(a_j) = \sum_{j=0}^{[a_j]} (2j - 1)!! \left(\frac{a_j}{2j}\right) (2j)!! \hat{D}^{a_j - 2j}
\]

(19)

He also shows that a function \( Y \) that is linear in \( A_i \), i.e.

\[
\hat{D}Y = y \quad \text{and} \quad \hat{D}Y = 0
\]

(20)

has the commutation property

\[
\hat{O}(a)Y = Y\hat{O}(a) - aY\hat{O}(a - 1)
\]

(21)

Ahrlin's confined his subsequent analysis to operators of the form \( \mathcal{Z} = g(u) \), but we will consider operators of the more general forms \( \mathcal{Z} = \mathcal{W}(u, v) \), \( \mathcal{W}(u) \), \( \mathcal{W}(v) \) or \( \delta(x - u + v) \). Because all such operators are independent of the Cartesian centers, it is clear that

\[
\hat{O}(a)\mathcal{Z} = \hat{O}(a)\mathcal{Z}
\]

(22)

Substituting this into the Boys RR

\[
\mathcal{Z}\mathcal{Z} = \hat{D}[\hat{O}(a)(b)(c)(\hat{d})[0000]_Z]
\]

(23)

and recognizing that \( \hat{O} \) and \( \hat{D} \) commute, we obtain the modified Boys RR

\[
\mathcal{Z}\mathcal{Z} = \hat{O}(a)\hat{O}(b)\hat{O}(c)\hat{O}(d)\hat{D}[0000]_Z
\]

(24)

Eqn (24) reveals the importance of the derivative of the \( [0000]_Z \) integral to the form of the corresponding “Obara-Saika-like” RR. In the following Sections, we consider several forms of the \( \mathcal{Z} \) operator and derive the corresponding RR from (24).

4. Recurrence relation for \( \mathcal{Z} = \mathcal{W}(u, v) \)

When \( \mathcal{Z} \) depends on both \( u \) and \( v \), the fundamental integral is given by

\[
[0000]_W = \frac{S_{ad}}{8(\pi + \delta)^{3/2}(\beta + \gamma)^{3/2}} \int e^{-\frac{(x^2 + y^2)}{2\sigma}} P_{uv} - Q_{uv} \mathcal{W}(u, v) dudv
\]

(25)

Applying \( \hat{D} \) to the fundamental integral, using the chain rule, yields four terms because the integral depends on the center \( A \) through the exponential factor \( S_{ad} \) and the quantities \( P^2 \), \( Q^2 \), and \( P \cdot Q \). This suggests that we define

\[
G_{lmn}(P^2, Q^2, P \cdot Q) = \left( \frac{d}{dx^2}\left( \frac{d}{dy^2}\left( \frac{d}{dz^2} \right) \right) \right)_{x, y, z}
\]

and the triple-index auxiliary integrals

\[
[0000]^{(l,m,n)}_W = S_{ad}G_{lmn}(P^2, Q^2, P \cdot Q)
\]

(27)

Applying the chain rule yields

\[
\hat{D}[0000]^{(l,m,n)}_W = \frac{\delta(D_i - A_i)}{x + \delta}[0000]^{(l,m,n)}_W + \frac{\partial P^2}{2\pi \partial A_i}[0000]^{(l+1,m,n)}_W
\]

(28)

substituting this into (24) gives

\[
(a + 1_i)abcd|Z = \hat{O}(a)\hat{O}(b)\hat{O}(c)\hat{O}(d)\left( \frac{\delta(D_i - A_i)}{x + \delta}[abcd]_{W} + \frac{\partial P^2}{2\pi \partial A_i}[abcd]_{W} + \frac{\partial Q^2}{2\pi \partial A_i}[abcd]_{W} + \frac{\partial (P \cdot Q)}{2\pi \partial A_i}[abcd]_{W} \right)
\]

(29)

and applying the commutation relation (21) four times eventually yields the 18-term RR

\[
(a + 1_i)abcd|W = \hat{O}(a)\hat{O}(b)\hat{O}(c)\hat{O}(d)\left( \frac{\delta(D_i - A_i)}{x + \delta}[abcd]_{W} + \frac{2\partial P^2}{2\pi \partial A_i}[abcd]_{W} + \frac{2\partial Q^2}{2\pi \partial A_i}[abcd]_{W} + \frac{\partial (P \cdot Q)}{2\pi \partial A_i}[abcd]_{W} \right)
\]

(30)

for \( (a + 1_i)abcd \) and \( (a + 1_i)abcd_{W} \).
Although it has ten more terms than the celebrated Obara-Saika RR, and two extra auxiliary indices, this new RR applies to integrals over a much larger class of operators. As such, it is much more general and powerful than its predecessors.

For an integral with total angular momentum

\[ L = \sum_{i=x,y,z} a_i + b_i + c_i + d_i \]  

all \((L + 1)(L + 2)(L + 3)/6\) fundamental integrals \([0000]^{(l,m,n)}\) with \(0 \leq l + m + n \leq L\) are required. In light of this, a method for generating the \(G_{l,m,n}\) recursively would be useful and should be a topic of future investigation.

In the special case of Omega intracule integrals, we have

\[ W(u,v) = \partial/\partial(t_{12} - u)(p_{12} - v)\partial/\partial\theta_{\omega} - \omega) \]

and it can be shown that

\[ G_{l,m,n}(P, Q; P \cdot Q) = \frac{\pi u^n e^{-\frac{1}{2} (p^2 - r^2) - i n r \cos \omega} \sin \omega}{(x + \delta)^{3/2}(\beta + \gamma)^{3/2}} \]

\[ \times \left( \frac{\partial}{\partial P^2} \right)^l \left( \frac{\partial}{\partial Q^2} \right)^m \left( \frac{\partial}{\partial (P \cdot Q)} \right)^n \]

\[ \int_0^\pi i_0(x + y \cos t) dt \]  

where

\[ x = P^2 u^2 - Q^2 r^2 + 2 i u v (P \cdot Q) \cos \omega \]

\[ y = 2 i u v (P^2 - Q^2)^2 \sin \omega \]

and \(i_0(x)\) is a modified spherical Bessel function.\(^36\)

5. Recurrence relation for \(Z = U(u,v)\) or \(U(v,u)\)

The 18-term RR for integrals over operators depending on both \(u\) and \(v\) seems daunting. However, for operators \(Z\) that depend on only \(u\) or only \(v\), major simplifications occur. These are realized by redefining

\[ G_{l,m,n}(U^2, V^2, U \cdot V) = \frac{\left( \frac{\partial}{\partial U} \right)^l \left( \frac{\partial}{\partial V} \right)^m \left( \frac{\partial}{\partial U \cdot V} \right)^n}{8(\alpha + \delta)^{3/2}(\beta + \gamma)^{3/2}} \]

\[ \times e^{-\frac{1}{2} u^2} e^{-\frac{1}{2} v^2} e^{-i u \theta_{\omega} - \omega} \]

\[ \times W(u,v) du dv \]

Table 1 Non-exponential FLOPs and exponential function evaluations required for a \([pppp]_\Omega\) integral class

<table>
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<tr>
<th>Algorithm</th>
<th>Boys</th>
<th>Recursion</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLOPs</td>
<td>11919</td>
<td>15647</td>
</tr>
<tr>
<td>Exp. evaluations</td>
<td>4899</td>
<td>65</td>
</tr>
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</table>

The calculation of the 81 integrals in a \([pppp]_\Omega\) class begins with the construction of the 35 fundamental integrals \([0000]^{(l,m,n)}\), where \(0 \leq l + m + n \leq 4\). Then, using the 18-term RR (30), integrals of higher angular momentum are calculated following the scheme in Fig. 1. Because \([pppp]_\Omega\) is a fairly simple class, many of the terms in the RR (30) vanish in most cases. The efficiency of recursion can be seen by comparing the FLOP (Floating-Point Operation) count required to generate the class recursively with the FLOP count of the Boys-based algorithm in the Q-CHEM software package.\(^37\) The results are summarized in Table 1, with exponential function evaluations listed separately. For this class, the FLOP cost (15647) of the recursive algorithm is 8 times smaller that than (11919) of the Boys-based scheme and the efficiency gains will be even greater for classes of higher angular momentum. The recursive approach is also much easier to implement than the laborious Boys scheme, requiring only code for the necessary \(G_{l,m,n}\) integrals.
and then deriving an alternative 18-term RR (see ESI†). Then, for \( \mathcal{X} = \mathcal{Y}(u) \) or \( \mathcal{Y}(v) \), the alternative 18-term RR reduces to the 8-term RRs

\[
[(a + 1)abcd]_U^{(l)} = \frac{\beta(B_i - A_i)}{\alpha + \beta} \frac{[(a - 1)abcd]_U^{(l)}}{\alpha + \beta} + \frac{U_j}{\alpha + \beta} [abcd]_U^{(l+1)}
\]

\[
+ \frac{a_i}{2(\alpha + \beta)} \frac{[(a - 1)abcd]_U^{(l+1)}}{\alpha + \beta} + \frac{b_i}{2(\alpha + \beta)} [a(b - 1)cd]_U^{(l)}
\]

\[
+ \frac{b_i}{2(\alpha + \beta)} \frac{[a(b - 1)cd]_U^{(l+1)}}{\alpha + \beta} - \frac{\epsilon_i}{2(\alpha + \beta)\sqrt{\gamma + \delta}} |ab(c - 1)d|_U^{(l+1)}
\]

\[
- \frac{\epsilon_i}{2(\alpha + \beta)(\gamma + \delta)} |ab(c - 1)d|_U^{(l+1)} - \frac{d_i}{2(\alpha + \beta)} \frac{[(a - 1)abcd]_U^{(l+1)}}{\alpha + \beta} + \frac{\eta_i}{2(\alpha + \beta)} |ab(c - 1)d|_U^{(l+1)}
\]

\[
[(a + 1)abcd]_V^{(m)} = \frac{\beta(B_i - A_i)}{\alpha + \beta} \frac{[abcd]_V^{(m)}}{\alpha + \beta} + \frac{2\beta V_j}{\alpha + \beta} [abcd]_V^{(m+1)}
\]

\[
+ \frac{a_i}{2(\alpha + \beta)} \frac{[(a - 1)abcd]_V^{(m)}}{\alpha + \beta} + \frac{2a_i}{(\alpha + \beta)^2} \frac{[(a - 1)abcd]_V^{(m+1)}}{\alpha + \beta}
\]

\[
+ \frac{b_i}{2(\alpha + \beta)} \frac{[a(b - 1)cd]_V^{(m)}}{\alpha + \beta} - \frac{2b_i}{(\alpha + \beta)^2} \frac{[a(b - 1)cd]_V^{(m+1)}}{\alpha + \beta}
\]

\[
- \frac{2c_i}{(\alpha + \beta)(\gamma + \delta)} |ab(c - 1)d|_V^{(m+1)} + \frac{2d_i}{(\alpha + \beta)(\gamma + \delta)} \frac{[(a - 1)abcd]_V^{(m+1)}}{\alpha + \beta}
\]

\[
(36a)
\]

where the fundamental integrals are given, respectively, by

\[
[0000]_U^{(l)} = S_{ab} \frac{\pi^{3/2}}{\alpha + \beta} \left(\begin{array}{c}
\frac{\omega}{\beta f}
\end{array}\right)^l \int e^{-\omega^2 u^2} \mathcal{Y}(u) \mathcal{I}(u) du
\]

\[
= S_{ab} G_1(U^2)
\]

\[
(37a)
\]

\[
[0000]_V^{(m)} = S_{ab} \frac{\pi^{3/2}}{\alpha + \beta} \left(\begin{array}{c}
\frac{\omega}{\beta f}
\end{array}\right)^m \int e^{-\omega^2 r^2 + V^2} \mathcal{Y}(v) \mathcal{I}(v) dv
\]

\[
= S_{ab} G_m(V^2)
\]

\[
(37b)
\]

The RR (36a) for \( \mathcal{X} = \mathcal{Y}(u) \) is a generalization of the Obara-Saika RR and the fact that

\[
\frac{\partial U^2}{2\alpha \partial A_i} = \frac{\partial U^2}{2\beta \partial B_i}
\]

\[
(38)
\]

leads to the existence of a two-term “horizontal” RR

\[
[(a + 1)abcd]_U^{(l)} = [ab + 1)abcd]_U^{(l)} + (B_i - A_i)[abcd]_U^{(l+1)}
\]

\[
(39)
\]

which transfers angular momentum from center \( A \) to center \( B \).

The RR (36b) for \( \mathcal{X} = \mathcal{Y}(v) \) appears similar to (36a) but differs in that

\[
\frac{\partial V^2}{2\alpha \partial A_i} = \frac{\partial V^2}{2\beta \partial B_i} + 2V_i
\]

\[
(40)
\]

As a consequence, the “horizontal” relation for momentum integrals is the four-term RR

\[
[(a + 1)abcd]_V^{(m)} = [ab(c + 1)d]_V^{(m)} - [ab(c + 1)d]_V^{(m)} + [abc(d + 1)]_V^{(m)} - (A_i - B_i + C_i - D_i)[abcd]_V^{(m)}
\]

\[
(41)
\]

The striking asymmetry between (39) and (41) arises from the fact that both the position and the momentum integrals are over basis functions that are centered in position space.

For an integral with total angular momentum \( L \), all \( L + 1 \) fundamental integrals \([0000]_U^{(l)}\) with \( 0 \leq l \leq L \), or \([0000]_V^{(m)}\) with \( 0 \leq m \leq L \), are required. Before a scheme for generating the \( G_1(U^2) \) or \( G_m(V^2) \) recursively would be useful.

In the special case where \( \mathcal{X} = g(u) \), one finds

\[
G_1(U^2) = \frac{4\pi^{5/2}}{(\alpha + \beta + \gamma + \delta)^{3/2}} \left(\begin{array}{c}
\frac{\partial}{\partial U^2}
\end{array}\right) \int_0^\infty u^2 e^{-\nu^2 u^2} \mathcal{I}_0(2\nu^2 U u) g(u) du
\]

\[
(42)
\]

where \( \mathcal{I}_0(x) = x^{-1} \sin x \). In the important case of Coulomb integrals, we have \( g(u) = 1/u \) and one obtains

\[
G_1(U^2) = \frac{2\nu^{5/2}}{\nu^2 (\alpha + \beta + \gamma + \delta)^{3/2}} F_1(U^2)
\]

\[
(43)
\]

where \( F_1(T) \) is the Boys function

\[
F_1(T) = \int_0^1 t^{2l} e^{-Tr^2} dt
\]

\[
(44)
\]

For Position intracule integrals, we have \( g(u) = \delta(r_{12} - u) \) and therefore

\[
G_1(U^2) = \frac{4\pi^{5/2}\nu^2 e^{-\nu^2 u^2}}{(\alpha + \beta + \gamma + \delta)^{3/2}} \left(\begin{array}{c}
\frac{\partial}{\partial U^2}
\end{array}\right) \left[ \exp(-\nu^2 U^2) \mathcal{I}_0(2\nu^2 U u) \right]
\]

\[
(45)
\]

In the special case where \( \mathcal{X} = f(v) \), one finds

\[
G_m(V^2) = \frac{4\pi^{5/2}\nu^2}{(\alpha + \beta + \gamma + \delta)^{3/2}} \left(\begin{array}{c}
\frac{\partial}{\partial V^2}
\end{array}\right) m \int_0^\infty v^2 e^{-\nu^2 v^2} \mathcal{I}_0(2\nu^2 V v) f(v) dv
\]

\[
(46)
\]

where \( \mathcal{I}_0(x) = x^{-1} \sin x \). For Momentum intracule integrals, we have \( f(v) = \delta(p_{12} - v) \) and therefore

\[
G_m(V^2) = \frac{4\pi^{5/2}\nu^2 e^{-\nu^2 v^2}}{(\alpha + \beta + \gamma + \delta)^{3/2}} \left(\begin{array}{c}
\frac{\partial}{\partial V^2}
\end{array}\right) m \left[ \exp(\nu^2 V^2) \mathcal{I}_0(2\nu^2 V v) \right]
\]

\[
(47)
\]
6. Recurrence relation for $\mathcal{Z} = \delta(x - u \cdot v)$

Although the 18-term RR (30) is applicable to integrals over $\mathcal{Z} = \delta(x - u \cdot v)$, enormous simplifications occur if we move into Fourier space. By substituting (2) into

$$D(x) = \int W_{2}(r_{1},r_{2},p_{1},p_{2})\delta(x - u \cdot v)dr_{1}dr_{2}dip_{1}dip_{2}$$

(48)

and then replacing the delta function by its Fourier representation and integrating over $p_{1}$, $p_{2}$, $q_{1}$ and $q_{2}$, one can show that it can be recast as

$$D(x) = \frac{1}{2\pi} \int \rho_{2}(r,r + ku,r + u + ku,r + u)e^{ikx}drudk$$

(49)

and it follows that its Fourier transform is

$$\tilde{D}(k) = \int \rho_{2}(r,r + ku,r + u + ku,r + u)dru$$

(50)

The fundamental Dot intracule integral in Fourier space, or $k$-space, is, given by

$$\begin{split}
\langle 0000 \rangle_{\tilde{D}} &= \frac{\pi^{3}S_{ad}}{[\langle x + \delta \rangle(\beta + \gamma)]^{3/2}} \exp(T)
\end{split}$$

(51)

where

$$T = \frac{\mu^{2}P^{2} + (\eta + k)P \cdot Q - \lambda^{2}Q^{2}}{4\lambda^{2}\mu^{2} + (\eta + k)^{2}}$$

(52)

Because (51) is simply a generalized Gaussian in the centers, we can use the modified Boys RR (24) directly, without requiring auxiliary integrals. In this way, we find the 5-term RR

$$2(x + \delta)[(a + 1)abcd]_{\tilde{D}} = (2\delta(D_{1} - A_{1}) + K_{1}P_{1} + 2K_{2}Q_{1})[abcd]_{\tilde{D}}$$

(53)

where

$$K_{1} = \frac{4\mu^{2}\delta + (\eta + k)}{4\lambda^{2}\mu^{2} + (\eta + k)^{2}}$$

(54)

$$K_{2} = \frac{-\lambda^{2} + 3\delta(\eta + k)}{4\lambda^{2}\mu^{2} + (\eta + k)^{2}}$$

(55)

The surprising simplicity of this RR supports the conclusion that $D(x)$ is most efficiently constructed by forming $\tilde{D}(k)$ and then taking the inverse Fourier transform.

Bernard has shown that $D(x)$ is the $O(h)$ approximation to the exact probability density

$$X(x) = \frac{1}{2\pi} \int \rho_{2}(r,r + u \sin k, r + uc^k, r + uc \cos k)e^{ikx}drudk$$

(56)

which is known as the Posmom intracule and whose Fourier transform is

$$\tilde{X}(k) = \int \rho_{2}(r,r + u \sin k, r + uc^k, r + uc \cos k)dru$$

The fundamental Posmom intracule integral in Fourier space is

$$[0000]_{\tilde{X}} = \frac{\pi^{3}S_{ad}\text{sech}^{2}k}{[(\langle x + \delta \rangle(\beta + \gamma))]^{3/2}} \exp(T)$$

(57)

where

$$T = \frac{\mu^{2}P^{2} + (\eta + tanh k)P \cdot Q - \lambda^{2}Q^{2}}{4\lambda^{2}\mu^{2} + (\eta + tanh k)^{2}}$$

(58)

and it follows that the higher integrals also satisfy (53), but with

$$K_{1} = \frac{4\mu^{2}\delta + (\eta + tanh k)}{4\lambda^{2}\mu^{2} + (\eta + tanh k)^{2}}$$

(59)

$$K_{2} = \frac{-\lambda^{2} + 3\delta(\eta + tanh k)}{4\lambda^{2}\mu^{2} + (\eta + tanh k)^{2}}$$

(60)

7. Conclusions

The recent article by Ahlrichs provides a simple algebraic derivation of the Obara-Saika RR for a general g(\nu) and provides a general approach for the derivation of RRs for other two-electron integrals over GTOS. We have used his approach to treat integrals over more general two-electron operators in position and momentum space. The RR (30) for integrals about a phase-space operator $\Psi(\nu,v)$ has 18 terms and utilizes three-index auxiliary integrals. The new RR allows one to generate a [pppp] class at a small fraction of the cost of an earlier Boys-based algorithm. The RRs (36a) or (36b) for integrals over a position operator $\Psi(\nu)$ or a momentum operator $\Psi'(\nu)$ have 8 terms and utilize single-index auxiliary integrals, and follow easily from an alternative 18-term RR (see ESIF). The RR (53) for Fourier integrals over the dot product operator $\delta(x - u \cdot v)$ has 5 terms and does not require any auxiliary indices.

The RR provides an efficient path for calculating two-electron integrals in phase, momentum and position space and are also much easier to implement for integral classes of high angular momentum. We are incorporating them into the Q-Chem package and this will lead to significant performance improvements in the calculation of Hartree–Fock intracules of large molecules and correlated intracules of all molecules.
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