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PAPER

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 Davidson[6] improved the original Boys' algorithm but a major advance occurred when Obara and Saika introduced[7–9] their recurrence relations (RRs).‡ Recursive schemes are now employed in almost all modern algorithms[10] for calculating molecular integrals[11] 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 operators[13] or damped Coulomb potentials,[14] and the integrals required in R12[15,16] and geminal[17] 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 position[18,19] $\boldsymbol{u} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ or momentum[20] $\boldsymbol{v} = \boldsymbol{p}_1 - \boldsymbol{p}_2$ of electrons or, more recently, the dot product[21,22] $x = \boldsymbol{u}\cdot\boldsymbol{v}$. 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).[22–25] 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 $\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$ is an N-electron wavefunction, its spinless 2nd-order density matrix[26] is

$$\rho_2(\boldsymbol{r}_1,\boldsymbol{r}'_1,\boldsymbol{r}_2,\boldsymbol{r}'_2) = \int \Psi^*(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\ldots,\boldsymbol{r}_N) \times \Psi(\boldsymbol{r}'_1,\boldsymbol{r}'_2,\boldsymbol{r}_3,\ldots,\boldsymbol{r}_N)d\boldsymbol{r}_3\ldots d\boldsymbol{r}_N \quad (1)$$

its 2nd-order Wigner distribution[27] is

$$W_2(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2) = \frac{1}{(2\pi)^6}\int \rho_2\left(\boldsymbol{r}_1+\frac{\boldsymbol{q}_1}{2},\boldsymbol{r}_1-\frac{\boldsymbol{q}_1}{2},\boldsymbol{r}_2+\frac{\boldsymbol{q}_2}{2},\boldsymbol{r}_2-\frac{\boldsymbol{q}_2}{2}\right)e^{i(\boldsymbol{p}_1\cdot\boldsymbol{q}_1+\boldsymbol{p}_2\cdot\boldsymbol{q}_2)}d\boldsymbol{q}_1d\boldsymbol{q}_2 \quad (2)$$

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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 $\mathscr{Z}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2)$ has the expectation value§

$$\langle \mathscr{Z} \rangle = \int W_2(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2)\mathscr{Z}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{p}_1 d\boldsymbol{p}_2 \quad (3)$$

Using this, we can create intracules[21] as the expectation values of appropriate operators. For example, the operator $\mathscr{Z} = \delta(r_{12} - u)$ yields the Position intracule $P(u)$,[18,28] which is the probability density for the interelectronic distance $u = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$ and, similarly, the operator $\mathscr{Z} = \delta(p_{12} - v)$ gives the Momentum intracule $M(v)$,[20,29] which is the probability density for the relative momentum $v = |\boldsymbol{p}_1 - \boldsymbol{p}_2|$. The operator $\mathscr{Z} = \delta(r_{12} - u)\delta(p_{12} - v)\delta(\theta_{uv} - \omega)$ gives the Omega intracule $\Omega(u,v,\omega)$,[21,30] which is the joint quasi-probability density of u, v and ω, the angle between $\boldsymbol{u}$ and $\boldsymbol{v}$. The operator $\mathscr{Z} = \delta(x - \boldsymbol{u}\cdot\boldsymbol{v})$ yields the Dot intracule $D(x)$, the quasi-probability density for $x = \boldsymbol{u}\cdot\boldsymbol{v}$.

The Obara-Saika RR generates integrals over operators of the form $\mathscr{Z} = g(u)$, which includes the position intracule. However, despite ongoing interest in observable momentum space properties such as momentum intracules,[20,29,31–33] an analogous RR for operators of the form $\mathscr{Z} = f(v)$ has not yet appeared and, consequently, most momentum intracule studies of atoms and small molecules[31–35] have been based on uncorrelated wavefunctions. The advent of an efficient RR for $\mathscr{Z} = f(v)$ would be highly beneficial for future studies using accurate correlated wavefunctions.

Although the Omega intracule, $\Omega(u,v,\omega)$, is not an experimental observable, it does contain a wealth of information regarding the relative position and momentum of electrons of a given wavefunction. In addition to providing a quantitative description of the motion of pairs of electrons, it also contains key elements leading to an intuitive understanding of electron correlation.[21] The fundamental tenet of intracule functional theory[22–25] is that the correlation energy can be recovered by contracting an intracule with an appropriate correlation kernel, $K(u,v,\omega)$, *i.e.*

$$E_{\text{corr}} = \iiint \Omega(u,v,\omega)K(u,v,\omega)du dv d\omega \quad (4)$$

and the practical success of such a theory is predicated on the availability of efficient schemes for generating the required two-electron integrals.

Expanding the wavefunction in (1) in a Gaussian one-electron basis set $\{\phi_a\}$ yields

$$\rho_2(\boldsymbol{r}_1,\boldsymbol{r}'_1,\boldsymbol{r}_2,\boldsymbol{r}'_2) = \sum_{abcd} \Gamma_{abcd}\phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}'_1)\phi_c^*(\boldsymbol{r}_2)\phi_d(\boldsymbol{r}'_2) \quad (5)$$

where Γ_{abcd} is the two-particle density matrix, and the construction of $\langle \mathscr{Z} \rangle$ therefore requires the integrals

$$\begin{aligned}[\boldsymbol{abcd}]_Z = &\frac{1}{(2\pi)^6}\int \phi_a^*\left(\boldsymbol{r}_1 + \frac{\boldsymbol{q}_1}{2}\right)\phi_b\left(\boldsymbol{r}_1 - \frac{\boldsymbol{q}_1}{2}\right) \\ &\times \phi_c^*\left(\boldsymbol{r}_2 + \frac{\boldsymbol{q}_2}{2}\right)\phi_d\left(\boldsymbol{r}_2 - \frac{\boldsymbol{q}_2}{2}\right) \\ &\times \mathscr{Z}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2)e^{i(\boldsymbol{p}_1\cdot\boldsymbol{q}_1+\boldsymbol{p}_2\cdot\boldsymbol{q}_2)}d\boldsymbol{q}_1 d\boldsymbol{q}_2 d\boldsymbol{p}_1 d\boldsymbol{p}_2 d\boldsymbol{r}_1 d\boldsymbol{r}_2\end{aligned} \quad (6)$$

§ Of course, because the Wigner distribution is not a proper probability density,[27] physical properties derived from such integrals may not be correct.

The goal of the present research is to show how to construct 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 RRs for four general forms of the $\mathscr{Z}$ operator.

2. Definitions

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

$$|\boldsymbol{a}\rangle = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z}e^{-\alpha|r-\boldsymbol{A}|^2} \quad (7)$$

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

$$\eta = \frac{\alpha}{\alpha+\delta} - \frac{\beta}{\beta+\gamma} \quad (8)$$

$$4\mu^2 = \frac{1}{\alpha+\delta} + \frac{1}{\beta+\gamma}\frac{1}{\nu^2} \quad (9a)$$

$$= \frac{1}{\alpha+\beta} + \frac{1}{\gamma+\delta} \quad (9b)$$

$$\lambda^2 = \frac{\alpha\delta}{\alpha+\delta} + \frac{\beta\gamma}{\beta+\gamma}\frac{1}{4\sigma^2} \quad (10a)$$

$$= \frac{\alpha\beta}{\alpha+\beta} + \frac{\gamma\delta}{\gamma+\delta} \quad (10b)$$

$$\begin{aligned}\boldsymbol{P} &= \frac{2\alpha\delta}{\alpha+\delta}(\boldsymbol{A}-\boldsymbol{D}) + \frac{2\beta\gamma}{\beta+\gamma}(\boldsymbol{B}-\boldsymbol{C}) \\ \boldsymbol{V} &= \frac{2\alpha\beta}{\alpha+\beta}(\boldsymbol{A}-\boldsymbol{B}) + \frac{2\gamma\delta}{\gamma+\delta}(\boldsymbol{D}-\boldsymbol{C})\end{aligned} \quad (11)$$

$$\boldsymbol{Q} = \frac{\alpha\boldsymbol{A}+\delta\boldsymbol{D}}{\alpha+\delta} - \frac{\beta\boldsymbol{B}+\gamma\boldsymbol{C}}{\beta+\gamma}\boldsymbol{U} \quad (12a)$$

$$= \frac{\alpha\boldsymbol{A}+\beta\boldsymbol{B}}{\alpha+\beta} - \frac{\gamma\boldsymbol{C}+\delta\boldsymbol{D}}{\gamma+\delta} \quad (12b)$$

$$\begin{aligned}S_{ad} &= \exp\left[-\frac{\alpha\delta|\boldsymbol{A}-\boldsymbol{D}|^2}{\alpha+\delta} - \frac{\beta\gamma|\boldsymbol{B}-\boldsymbol{C}|^2}{\beta+\gamma}\right] \\ S_{ab} &= \exp\left[-\frac{\alpha\beta|\boldsymbol{A}-\boldsymbol{B}|^2}{\alpha+\beta} - \frac{\gamma\delta|\boldsymbol{C}-\boldsymbol{D}|^2}{\gamma+\delta}\right]\end{aligned} \quad (13)$$

3. A modified Boys recurrence relation

As a prelude to our construction of new RRs, we first outline the key steps in Ahlrichs' derivation.[12] He begins with the Boys RR[1] for a single GTO, *viz.*

$$|(\boldsymbol{a}+\boldsymbol{1}_i)\rangle = \hat{D}|\boldsymbol{a}\rangle + \frac{a_i}{2\alpha}|(\boldsymbol{a}-\boldsymbol{1}_i)\rangle \quad (14)$$

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

$$\hat{D} = \frac{\partial}{2\alpha\partial A_i} \tag{15}$$

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

$$\hat{O}(\boldsymbol{a})|\mathbf{0}\rangle = |\boldsymbol{a}\rangle \tag{16}$$

and which therefore must itself obey the RR

$$\hat{O}(\boldsymbol{a}+\mathbf{1}_i) = \hat{D}\hat{O}(\boldsymbol{a}) + \frac{a_i}{2\alpha}\hat{O}(\boldsymbol{a}-\mathbf{1}_i) \tag{17}$$

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

$$\hat{O}(\boldsymbol{a}) = \prod_{i=x,y,z}\hat{O}(a_i) \tag{18}$$

he then uses (17) to show that

$$\hat{O}(a_i) = \sum_{j=0}^{\lfloor \frac{a_i}{2} \rfloor}(2j-1)!!\binom{a_i}{2j}(2\alpha)^{-j}\hat{D}^{a_i-2j} \tag{19}$$

He also shows that a function Y that is linear in A_i *i.e.*

$$\hat{D}Y = y \text{ and } \hat{D}y = 0 \tag{20}$$

has the commutation property

$$\hat{O}(a_i)Y = Y\hat{O}(a_i) - a_i y\hat{O}(a_i-1) \tag{21}$$

Ahlrichs confined his subsequent analysis to operators of the form $\mathscr{Z} = g(u)$, but we will consider operators of the more general forms $\mathscr{Z} = \mathscr{W}(\boldsymbol{u},\boldsymbol{v})$, $\mathscr{U}(u)$, $\mathscr{V}(v)$ or $\delta(x - \boldsymbol{u}\cdot\boldsymbol{v})$. Because all such operators are independent of the Cartesian centers, it is clear that

$$[\boldsymbol{abcd}]_Z = \hat{O}(\boldsymbol{a})\hat{O}(\boldsymbol{b})\hat{O}(\boldsymbol{c})\hat{O}(\boldsymbol{d})[\mathbf{0000}]_Z \tag{22}$$

Substituting this into the Boys RR

$$[(\boldsymbol{a}+\mathbf{1}_i)\boldsymbol{bcd}]_Z = \hat{D}[\boldsymbol{abcd}]_Z + \frac{a_i}{2\alpha}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_Z \tag{23}$$

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

$$[(\boldsymbol{a}+\mathbf{1}_i)\boldsymbol{bcd}]_Z = \hat{O}(\boldsymbol{a})\hat{O}(\boldsymbol{b})\hat{O}(\boldsymbol{c})\hat{O}(\boldsymbol{d})\hat{D}[\mathbf{0000}]_Z + \frac{a_i}{2\alpha}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_Z \tag{24}$$

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

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

When $\mathscr{Z}$ depends on both $\boldsymbol{u}$ and $\boldsymbol{v}$, the fundamental integral[11] is given by[21]

$$[\mathbf{0000}]_W = \frac{S_{ad}}{8(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}}\int e^{-\lambda^2u^2-\mu^2v^2-\boldsymbol{P}\cdot u-i\boldsymbol{Q}\cdot v-i\eta u\cdot v}\mathscr{W}(\boldsymbol{u},\boldsymbol{v})d\boldsymbol{u}d\boldsymbol{v} \tag{25}$$

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

$$G_{l,m,n}(P^2,Q^2,\boldsymbol{P}\cdot\boldsymbol{Q}) = \frac{\left(\frac{\partial}{\partial P^2}\right)^l\left(\frac{\partial}{\partial Q^2}\right)^m\left(\frac{\partial}{\partial(\boldsymbol{P}\cdot\boldsymbol{Q})}\right)^n}{8(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}}\int e^{-\lambda^2u^2-\mu^2v^2-\boldsymbol{P}\cdot\boldsymbol{u}-i\boldsymbol{Q}\cdot\boldsymbol{v}-i\eta\boldsymbol{u}\cdot\boldsymbol{v}}\mathscr{W}(\boldsymbol{u},\boldsymbol{v})d\boldsymbol{u}d\boldsymbol{v} \tag{26}$$

and the triple-index auxiliary integrals

$$[\mathbf{0000}]_W^{(l,m,n)} = S_{ad}G_{l,m,n}(P^2,Q^2,\boldsymbol{P}\cdot\boldsymbol{Q}) \tag{27}$$

Applying the chain rule yields

$$\hat{D}[\mathbf{0000}]_W^{(l,m,n)} = \frac{\delta(D_i-A_i)}{\alpha+\delta}[\mathbf{0000}]_W^{(l,m,n)} + \frac{\partial P^2}{2\alpha\partial A_i}[\mathbf{0000}]_W^{(l+1,m,n)} + \frac{\partial Q^2}{2\alpha\partial A_i}[\mathbf{0000}]_W^{(l,m+1,n)} + \frac{\partial(\boldsymbol{P}\cdot\boldsymbol{Q})}{2\alpha\partial A_i}[\mathbf{0000}]_W^{(l,m,n+1)} \tag{28}$$

substituting this into (24) gives

$$[(\boldsymbol{a}+\mathbf{1}_i)\boldsymbol{bcd}]_W^{(m,n)} = \hat{O}(\boldsymbol{a})\hat{O}(\boldsymbol{b})\hat{O}(\boldsymbol{c})\hat{O}(\boldsymbol{d})\left\{\frac{\delta(D_i-A_i)}{\alpha+\delta}[\mathbf{0000}]_W^{(l,m,n)} + \frac{\partial P^2}{2\alpha\partial A_i}[\mathbf{0000}]_W^{(l+1,m,n)} + \frac{\partial Q^2}{2\alpha\partial A_i}[\mathbf{0000}]_W^{(l,m+1,n)} + \frac{\partial(\boldsymbol{P}\cdot\boldsymbol{Q})}{2\alpha\partial A_i}[\mathbf{0000}]_W^{(l,m,n+1)}\right\} + \frac{a_i}{2\alpha}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_W^{(l,m,n)} \tag{29}$$

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

$$\begin{aligned}[(\boldsymbol{a}+\mathbf{1}_i)\boldsymbol{bcd}]_W^{(l,m,n)} = {} & \frac{\delta(D_i-A_i)}{\alpha+\delta}[\boldsymbol{abcd}]_W^{(l,m,n)} + \frac{2\delta P_i}{\alpha+\delta}[\boldsymbol{abcd}]_W^{(l+1,m,n)} \\ & + \frac{Q_i}{\alpha+\delta}[\boldsymbol{abcd}]_W^{(l,m+1,n)} + \frac{P_i+2\delta Q_i}{2(\alpha+\delta)}[\boldsymbol{abcd}]_W^{(l,m,n+1)} \\ & + \frac{a_i}{2(\alpha+\delta)}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_W^{(l,m,n)} \\ & + \frac{2a_i\delta^2}{(\alpha+\delta)^2}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_W^{(l+1,m,n)} \\ & + \frac{a_i}{2(\alpha+\delta)^2}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_W^{(l,m+1,n)}\end{aligned}$$

$$+\frac{a_i\delta}{(\alpha+\delta)^2}[(\boldsymbol{a}-\boldsymbol{1}_i)\boldsymbol{bcd}]_W^{(l,m,n+1)}$$
$$+\frac{2b_i\gamma\delta}{(\alpha+\delta)(\beta+\gamma)}[\boldsymbol{a}(\boldsymbol{b}-\boldsymbol{1}_i)\boldsymbol{cd}]_W^{(l+1,m,n)}$$
$$-\frac{b_i}{2(\alpha+\delta)(\beta+\gamma)}[\boldsymbol{a}(\boldsymbol{b}-\boldsymbol{1}_i)\boldsymbol{cd}]_W^{(l,m+1,n)}$$
$$+\frac{b_i(\gamma-\delta)}{2(\alpha+\delta)(\beta+\gamma)}[\boldsymbol{a}(\boldsymbol{b}-\boldsymbol{1}_i)\boldsymbol{cd}]_W^{(l,m,n+1)}$$
$$-\frac{2c_i\beta\delta}{(\alpha+\delta)(\beta+\gamma)}[\boldsymbol{ab}(\boldsymbol{c}-\boldsymbol{1}_i)\boldsymbol{d}]_W^{(l+1,m,n)}$$
$$-\frac{c_i}{2(\alpha+\delta)(\beta+\gamma)}[\boldsymbol{ab}(\boldsymbol{c}-\boldsymbol{1}_i)\boldsymbol{d}]_W^{(l,m+1,n)} \quad (30)$$
$$-\frac{c_i(\beta+\delta)}{2(\alpha+\delta)(\beta+\gamma)}[\boldsymbol{ab}(\boldsymbol{c}-\boldsymbol{1}_i)\boldsymbol{d}]_W^{(l,m,n+1)}$$
$$+\frac{d_i}{2(\alpha+\delta)}[\boldsymbol{abc}(\boldsymbol{d}-\boldsymbol{1}_i)]_W^{(l,m,n)}$$
$$-\frac{2d_i\alpha\delta}{(\alpha+\delta)^2}[\boldsymbol{abc}(\boldsymbol{d}-\boldsymbol{1}_i)]_W^{(l+1,m,n)}$$
$$+\frac{d_i}{2(\alpha+\delta)^2}[\boldsymbol{abc}(\boldsymbol{d}-\boldsymbol{1}_i)]_W^{(l,m+1,n)}$$
$$+\frac{d_i(\delta-\alpha)}{2(\alpha+\delta)^2}[\boldsymbol{abc}(\boldsymbol{d}-\boldsymbol{1}_i)]_W^{(l,m,n+1)}$$

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

$$L=\sum_{i=x,y,z}a_i+b_i+c_i+d_i \quad (31)$$

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

In the special case of Omega intracule integrals, we have $\mathscr{W}(\boldsymbol{u},\boldsymbol{v}) = \delta(r_{12}-u)\delta(p_{12}-v)\delta(\theta_{uv}-\omega)$ and it can be shown[30] that

$$G_{l,m,n}(P^2,Q^2,\boldsymbol{P}\cdot\boldsymbol{Q})=\frac{\pi u^2v^2e^{-\lambda^2u^2-\mu^2v^2-i\eta uv\cos\omega}\sin\omega}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \times\left(\frac{\partial}{\partial P^2}\right)^l\left(\frac{\partial}{\partial Q^2}\right)^m\left(\frac{\partial}{\partial(\boldsymbol{P}\cdot\boldsymbol{Q})}\right)^n \int_0^\pi i_0(\sqrt{x+y\cos t})dt \quad (32)$$

where

$$x = P^2u^2 - Q^2v^2 + 2iuv(\boldsymbol{P}{\cdot}\boldsymbol{Q})\cos\omega \quad (33)$$

$$y = 2iuv\sqrt{P^2Q^2-(\boldsymbol{P}\cdot\boldsymbol{Q})^2}\sin\omega \quad (34)$$

and $i_0(x)$ is a modified spherical Bessel function.[36]

	No. of integrals
$[ssss]_\Omega^{(4)}$	35
⇓	
$[psss]_\Omega^{(3)}$, $[spss]_\Omega^{(2)}$	90
⇓	
$[ppss]_\Omega^{(2)}$, $[psps]_\Omega^{(1)}$, $[spps]_\Omega^{(1)}$	162
⇓	
$[ppps]_\Omega^{(1)}$	108
⇓	
$[pppp]_\Omega^{(0)}$	81

Fig. 1 Order of calculation of Omega intracule integrals for $[pppp]_\Omega$ class of integrals using the 18-term RR. $[\boldsymbol{abcd}]_\Omega^{(L)}$ denotes all auxillary integrals where $0 \le l + m + n \le \boldsymbol{L}$.

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

	Algorithm	
	Boys	Recursion
FLOPs	119 191	15 647
Exp. evaluations	4899	65

The calculation of the 81 integrals in a $[pppp]_\Omega$ class begins with the construction of the 35 fundamental integrals $[\boldsymbol{0000}]_\Omega^{(l,m,n)}$, where $0 \le l+m+n \le 4$. 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 (15 647) of the recursive algorithm is 8 times smaller than that (119 191) 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.

5. Recurrence relation for $\mathscr{X} = \mathscr{U}(\boldsymbol{u})$ or $\mathscr{V}(\boldsymbol{v})$

The 18-term RR for integrals over operators depending on both $\boldsymbol{u}$ and $\boldsymbol{v}$ seems daunting. However, for operators $\mathscr{X}$ that depend on only $\boldsymbol{u}$ or only $\boldsymbol{v}$, major simplifications occur. These are realized by redefining

$$G_{l,m,n}(U^2,V^2,\boldsymbol{U}\cdot\boldsymbol{V})=\frac{\left(\frac{\partial}{\partial U^2}\right)^l\left(\frac{\partial}{\partial V^2}\right)^m\left(\frac{\partial}{\partial(\boldsymbol{U}\cdot\boldsymbol{V})}\right)^n}{8(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}}e^{-\lambda^2U^2+\mu^2V^2+\eta\boldsymbol{U}\cdot\boldsymbol{V}} \times\int e^{-\lambda^2u^2-\mu^2v^2-(2\lambda^2\boldsymbol{U}-\eta\boldsymbol{V})\cdot\boldsymbol{u}-i(\eta\boldsymbol{U}+2\mu^2\boldsymbol{V})\cdot\boldsymbol{v}-i\eta\boldsymbol{u}\cdot\boldsymbol{v}} \times\mathscr{W}(\boldsymbol{u},\boldsymbol{v})d\boldsymbol{u}d\boldsymbol{v} \quad (35)$$

and then deriving an alternative 18-term RR (see ESI†). Then, for $\mathscr{X} = \mathscr{U}(\boldsymbol{u})$ or $\mathscr{V}(\boldsymbol{v})$, the alternative 18-term RR reduces to the 8-term RRs

$$\begin{aligned}[(\boldsymbol{a}+\mathbf{1}_i)\boldsymbol{bcd}]_U^{(l)} = {} & \frac{\beta(B_i-A_i)}{\alpha+\beta}[\boldsymbol{abcd}]_U^{(l)} + \frac{U_i}{\alpha+\beta}[\boldsymbol{abcd}]_U^{(l+1)} \\ & + \frac{a_i}{2(\alpha+\beta)}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_U^{(l)} \\ & + \frac{a_i}{2(\alpha+\beta)^2}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_U^{(l+1)} \\ & + \frac{b_i}{2(\alpha+\beta)}[\boldsymbol{a}(\boldsymbol{b}-\mathbf{1}_i)\boldsymbol{cd}]_U^{(l)} \\ & + \frac{b_i}{2(\alpha+\beta)^2}[\boldsymbol{a}(\boldsymbol{b}-\mathbf{1}_i)\boldsymbol{cd}]_U^{(l+1)} \\ & - \frac{c_i}{2(\alpha+\beta)(\gamma+\delta)}[\boldsymbol{ab}(\boldsymbol{c}-\mathbf{1}_i)\boldsymbol{d}]_U^{(l+1)} \\ & - \frac{d_i}{2(\alpha+\beta)(\gamma+\delta)}[\boldsymbol{abc}(\boldsymbol{d}-\mathbf{1}_i)]_U^{(l+1)}\end{aligned} \tag{36a}$$

$$\begin{aligned}[(\boldsymbol{a}+\mathbf{1}_i)\boldsymbol{bcd}]_V^{(m)} = {} & \frac{\beta(B_i-A_i)}{\alpha+\beta}[\boldsymbol{abcd}]_V^{(m)} + \frac{2\beta V_i}{\alpha+\beta}[\boldsymbol{abcd}]_V^{(m+1)} \\ & + \frac{a_i}{2(\alpha+\beta)}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_V^{(m)} \\ & + \frac{2a_i\beta^2}{(\alpha+\beta)^2}[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_V^{(m+1)} \\ & + \frac{b_i}{2(\alpha+\beta)}[\boldsymbol{a}(\boldsymbol{b}-\mathbf{1}_i)\mathbf{c}\boldsymbol{d}]_V^{(m)} \\ & - \frac{2b_i\alpha\beta}{(\alpha+\beta)^2}[\boldsymbol{a}(\boldsymbol{b}-\mathbf{1}_i)\boldsymbol{cd}]_V^{(m+1)} \\ & - \frac{2c_i\beta\delta}{(\alpha+\beta)(\gamma+\delta)}[\boldsymbol{ab}(\boldsymbol{c}-\mathbf{1}_i)\boldsymbol{d}]_V^{(m+1)} \\ & + \frac{2d_i\beta\gamma}{(\alpha+\beta)(\gamma+\delta)}[\boldsymbol{abc}(\boldsymbol{d}-\mathbf{1}_i)]_V^{(m+1)}\end{aligned} \tag{36b}$$

where the fundamental integrals are given, respectively, by

$$\begin{aligned}[\mathbf{0000}]_U^{(l)} &= S_{ab}\frac{\pi^{3/2}\left(\frac{\partial}{\partial U^2}\right)^l}{(\alpha+\beta+\gamma+\delta)^{3/2}}\int e^{-\nu^2|\boldsymbol{u}+\boldsymbol{U}|^2}\mathscr{U}(\boldsymbol{u})d\boldsymbol{u} \\ &= S_{ab}G_l(U^2)\end{aligned} \tag{37a}$$

$$\begin{aligned}[\mathbf{0000}]_V^{(m)} &= S_{ab}\frac{\pi^{3/2}\sigma^3\left(\frac{\partial}{\partial V^2}\right)^m}{(\alpha+\beta)^{3/2}(\gamma+\delta)^{3/2}}\int e^{-\sigma^2|\boldsymbol{v}+i\boldsymbol{V}|^2}\mathscr{V}(\boldsymbol{v})d\boldsymbol{v} \\ &= S_{ab}G_m(V^2)\end{aligned} \tag{37b}$$

The RR (36a) for $\mathscr{X} = \mathscr{U}(\boldsymbol{u})$ is a generalization of the Obara-Saika RR[8] and the fact that

$$\frac{\partial U^2}{2\alpha\partial A_i} = \frac{\partial U^2}{2\beta\partial B_i} \tag{38}$$

leads to the existence of a two-term "horizontal" RR[10]

$$[(\boldsymbol{a}+\mathbf{1}_i)\boldsymbol{bcd}]_U^{(l)} = [\boldsymbol{a}(\boldsymbol{b}+\mathbf{1}_i)\boldsymbol{cd}]_U^{(l)} + (B_i - A_i)[\boldsymbol{abcd}]_U^{(l)} \tag{39}$$

which transfers angular momentum from center $\boldsymbol{A}$ to center $\boldsymbol{B}$.

The RR (36b) for $\mathscr{X} = \mathscr{V}(\boldsymbol{v})$ appears similar to (36a) but differs in that

$$\frac{\partial V^2}{2\alpha\partial A_i} = \frac{\partial V^2}{2\beta\partial B_i} + 2V_i \tag{40}$$

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

$$\begin{aligned}[(\boldsymbol{a}+\mathbf{1}_i)\boldsymbol{bcd}]_V^{(m)} = {} & [\boldsymbol{a}(\boldsymbol{b}+\mathbf{1}_i)\boldsymbol{cd}]_V^{(m)} \\ & - [\boldsymbol{ab}(\boldsymbol{c}+\mathbf{1}_i)\boldsymbol{d}]_V^{(m)} + [\boldsymbol{abc}(\boldsymbol{d}+\mathbf{1}_i)]_V^{(m)} \\ & - (A_i - B_i + C_i - D_i)[\boldsymbol{abcd}]_V^{(m)}\end{aligned} \tag{41}$$

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 $[\mathbf{0000}]_U^{(l)}$ with $0 \le l \le L$, or $[\mathbf{0000}]_V^{(m)}$ with $0 \le m \le L$, are required. As before, a scheme for generating the $G_l(U^2)$ or $G_m(V^2)$ recursively would be useful.

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

$$\begin{aligned}G_l(U^2) = {} & \frac{4\pi^{5/2}}{(\alpha+\beta+\gamma+\delta)^{3/2}}\left(\frac{\partial}{\partial U^2}\right)^l \\ & \int_0^\infty u^2 e^{-\nu^2(u^2+U^2)} i_0(2\nu^2 Uu) g(u) du\end{aligned} \tag{42}$$

where $i_0(x) = x^{-1}\sinh x$. In the important case of Coulomb integrals, we have $g(u) = 1/u$ and one obtains

$$G_l(U^2) = \frac{2\pi^{5/2}}{\nu^2(\alpha+\beta+\gamma+\delta)^{3/2}}F_l(U^2) \tag{43}$$

where $F_l(T)$ is the Boys function

$$F_l(T) = \int_0^1 t^{2l}e^{-Tt^2}dt \tag{44}$$

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

$$G_l(U^2) = \frac{4\pi^{5/2}u^2 e^{-\nu^2u^2}}{(\alpha+\beta+\gamma+\delta)^{3/2}}\left(\frac{\partial}{\partial U^2}\right)^l[\exp(-\nu^2U^2)i_0(2\nu^2Uu)] \tag{45}$$

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

$$\begin{aligned}G_m(V^2) = {} & \frac{4\pi^{5/2}\sigma^3}{(\alpha+\beta)^{3/2}(\gamma+\delta)^{3/2}}\left(\frac{\partial}{\partial V^2}\right)^m \\ & \int_0^\infty v^2 e^{-\sigma^2(v^2-V^2)} j_0(2\sigma^2 Vv) f(v) dv\end{aligned} \tag{46}$$

where $j_0(x) = x^{-1}\sin x$. For Momentum intracule integrals, we have $f(v) = \delta(p_{12} - v)$ and therefore

$$G_m(V^2) = \frac{4\pi^{5/2}\sigma^3 v^2 e^{-\sigma^2v^2}}{(\alpha+\beta)^{3/2}(\gamma+\delta)^{3/2}}\left(\frac{\partial}{\partial V^2}\right)^m[\exp(\sigma^2V^2)j_0(2\sigma^2Vv)] \tag{47}$$

6. Recurrence relation for $\mathscr{X} = \delta(x - u \cdot v)$

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

$$D(x) = \int W_2(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2)\delta(x - \boldsymbol{u}\cdot\boldsymbol{v})d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{p}_1 d\boldsymbol{p}_2 \tag{48}$$

and then replacing the delta function by its Fourier representation and integrating over $\boldsymbol{p}_1$, $\boldsymbol{p}_2$, $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$, one can show[22] that it can be recast as

$$D(x) = \frac{1}{2\pi}\int \rho_2(\boldsymbol{r},\boldsymbol{r}+k\boldsymbol{u},\boldsymbol{r}+\boldsymbol{u}+k\boldsymbol{u},\boldsymbol{r}+\boldsymbol{u})e^{ikx}d\boldsymbol{r}d\boldsymbol{u}dk \tag{49}$$

and it follows that its Fourier transform is

$$\hat{D}(k) = \int \rho_2(\boldsymbol{r},\boldsymbol{r} + k\boldsymbol{u}, \boldsymbol{r} + \boldsymbol{u} + k\boldsymbol{u}, \boldsymbol{r} + \boldsymbol{u})d\boldsymbol{r}d\boldsymbol{u} \tag{50}$$

The fundamental Dot intracule integral in Fourier space, or k-space, is given by[22]

$$[\mathbf{0000}]_{\hat{D}} = \frac{\pi^3 S_{ad}}{[(\alpha+\delta)(\beta+\gamma)]^{3/2}}\frac{\exp(T)}{[4\lambda^2\mu^2+(\eta+k)^2]^{3/2}} \tag{51}$$

where

$$T = \frac{\mu^2P^2 + (\eta+k)\boldsymbol{P}\cdot\boldsymbol{Q} - \lambda^2Q^2}{4\lambda^2\mu^2+(\eta+k)^2} \tag{52}$$

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

$$\begin{aligned}2(\alpha+\delta)[(\boldsymbol{a}+\mathbf{1}_i)\boldsymbol{bcd}]_{\hat{D}} &= (2\delta(D_i - A_i) + K_1P_i + 2K_2Q_i)[\boldsymbol{abcd}]_{\hat{D}}\\ &+ a_i\left(1+\frac{\delta K_1 + K_2}{\alpha+\delta}\right)[(\boldsymbol{a}-\mathbf{1}_i)\boldsymbol{bcd}]_{\hat{D}}\\ &+ b_i\left(\frac{\gamma K_1 - K_2}{\beta+\gamma}\right)[\boldsymbol{a}(\boldsymbol{b}-\mathbf{1}_i)\boldsymbol{cd}]_{\hat{D}}\\ &+ c_i\left(\frac{-\beta K_1 - K_2}{\beta+\gamma}\right)[\boldsymbol{ab}(\boldsymbol{c}-\mathbf{1}_i)\boldsymbol{d}]_{\hat{D}}\\ &+ d_i\left(1-\frac{\alpha K_1 - K_2}{\alpha+\delta}\right)[\boldsymbol{abc}(\boldsymbol{d}-\mathbf{1}_i)]_{\hat{D}}\end{aligned} \tag{53}$$

where

$$K_1 = \frac{4\mu^2\delta + (\eta+k)}{4\lambda^2\mu^2+(\eta+k)^2} \tag{54}$$

$$K_2 = \frac{-\lambda^2 + \delta(\eta+k)}{4\lambda^2\mu^2+(\eta+k)^2} \tag{55}$$

The surprising simplicity of this RR supports the conclusion[22] that $D(x)$ is most efficiently constructed by forming $\hat{D}(k)$ and then taking the inverse Fourier transform.

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

$$X(x) = \frac{1}{2\pi}\int \rho_2(\boldsymbol{r},\boldsymbol{r}+\boldsymbol{u}\sinh k,\boldsymbol{r}+\boldsymbol{u}e^k,\boldsymbol{r}+\boldsymbol{u}\cosh k)e^{ikx}d\boldsymbol{r}d\boldsymbol{u}dk \tag{56}$$

which is known as the Posmom intracule[38–40] and whose Fourier transform is

$$\hat{X}(k) = \int \rho_2(\boldsymbol{r}, \boldsymbol{r} + \boldsymbol{u}\sinh k, \boldsymbol{r} + \boldsymbol{u}e^k, \boldsymbol{r} + \boldsymbol{u}\cosh k)d\boldsymbol{r}d\boldsymbol{u} \tag{57}$$

The fundamental Posmom intracule integral in Fourier space is[40]

$$[\mathbf{0000}]_{\hat{X}} = \frac{\pi^3 S_{ad}\operatorname{sech}^3 k}{[(\alpha+\delta)(\beta+\gamma)]^{3/2}}\frac{\exp(T)}{[4\lambda^2\mu^2+(\eta+\tanh k)^2]^{3/2}} \tag{58}$$

with

$$T = \frac{\mu^2P^2 + (\eta+\tanh k)\boldsymbol{P}\cdot\boldsymbol{Q} - \lambda^2Q^2}{4\lambda^2\mu^2+(\eta+\tanh k)^2} \tag{59}$$

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

$$K_1 = \frac{4\mu^2\delta + (\eta+\tanh k)}{4\lambda^2\mu^2+(\eta+\tanh k)^2} \tag{60}$$

$$K_2 = \frac{-\lambda^2 + \delta(\eta+\tanh k)}{4\lambda^2\mu^2+(\eta+\tanh k)^2} \tag{61}$$

7. Conclusions

The recent article by Ahlrichs[12] provides a simple algebraic derivation of the Obara-Saika RR for a general $g(u)$ 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 $\mathscr{W}(u,v)$ has 18 terms and utilizes three-index auxiliary integrals. The new RR allows one to generate a $[pppp]_\Omega$ 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 $\mathscr{U}(\boldsymbol{u})$ or a momentum operator $\mathscr{V}(\boldsymbol{v})$ have 8 terms and utilize single-index auxiliary integrals, and follow easily from an alternative 18-term RR (see ESI†). The RR (53) for Fourier integrals over the dot product operator $\delta(x - \boldsymbol{u}\cdot\boldsymbol{v})$ has 5 terms and does not require any auxiliary indices.

The RRs provide an efficient pathway 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[37] 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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