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# A general formulation for the efficient evaluation of $n$ -electron integrals over products of Gaussian charge distributions with Gaussian geminal functions

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In this work, we present a general formulation for the evaluation of many-electron integrals which arise when traditional one particle expansions are augmented with explicitly correlated Gaussian geminal functions. The integrand is expressed as a product of charge distributions, one for each electron, multiplied by one or more Gaussian geminal factors. Our formulation begins by focusing on the quadratic form that arises in the general  $n$ -electron integral. Using the Rys polynomial method for the evaluation of potential energy integrals, we derive a general formula for the evaluation of any  $n$ -electron integral. This general expression contains four parameters  $\omega$ ,  $\theta$ ,  $\nu$ , and  $h$ , which can be evaluated by an examination of the general quadratic form. Our analysis contains general expressions for any  $n$ -electron integral over  $s$ -type functions as well as the recursion needed to build up arbitrary angular momentum. The general recursion relation requires at most  $n + 1$  terms for any  $n$ -electron integral. To illustrate the general method, we develop explicit expressions for the evaluation of two, three, and four particle electron repulsion integrals as well as two and three particle overlap and nuclear attraction integrals. We conclude our exposition with a discussion of a preliminary computational implementation as well as general computational requirements. Implementation on parallel computers is briefly discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3600745]

## I. INTRODUCTION

The quest for accurate solutions to the Schrodinger equation has been an important part of quantum chemistry throughout its history. The motivation for this is straightforward in that there are many questions in chemistry that rely on accurate treatments of molecules and their interactions. Furthermore, chemists continue to rely on accurate calculations<sup>1,2</sup> in order to measure and assess the quality of less reliable and computationally more expedient methods. The traditional approach has been to rely on some variant of a CI, CC or perturbation theory expansion. Unfortunately such expansions are slow to converge, and this slow convergence has been attributed to two factors. The first is the combinatorial dilemma whereby a full-CI for an  $n$ -electron problem and  $N$  one-electron functions scales as  $N$  factorial. The second is attributed to the slow convergence of the “partial wave expansion,” where the energy converges as  $O(l^{-3})$  with maximum orbital angular momentum  $l$  in the atomic orbital basis.

It has been known since the early days of quantum chemistry that a good representation of the cusp condition is necessary for the very accurate evaluation of wave-functions and the properties contained in them. Expansion of the wave-function in terms of geminals with explicit linear inter-electron dependence is known to provide a much more rapidly convergent solution, as demonstrated by the historic computations by Hylleras for the Helium atom<sup>3,4</sup> and by James and Coolidge for the hydrogen molecule,<sup>5</sup> subsequently extended

to the nano-Hartree level of accuracy in more modern applications of essentially their same methods.<sup>6-9</sup>

Fifty years ago Boys<sup>10</sup> and Singer<sup>11</sup> advocated the use of Gaussian geminal functions in such expansions. Their proposal was to use a Gaussian correlation factor of the form  $\exp(-\alpha r_{12}^2)$  rather than  $r_{12}$  in the trial wave-function. In the past twenty five years, straightforward variational computations using such explicitly correlated Gaussian basis functions have yielded many of the lowest Born Oppenheimer energies available today (micro-Hartree or better) for ground and excited states of two-, three-, and four-electron systems<sup>12,13</sup> including: the  $H_2$  molecule,<sup>14</sup>  $H_3^+$  and  $HeH^+$  cations,<sup>15</sup>  $H_3$ ,<sup>16</sup> the Be atom,<sup>17</sup> and the Helium dimer.<sup>18</sup> The lowest variational energy to date of the carbon atom  $^3P$  ground state has also recently been obtained using explicitly correlated Gaussian geminals.<sup>19</sup> The most computationally intensive aspect of these computations is optimization of the thousands of non-linear parameters.<sup>19</sup> The history and current status of explicitly correlated Gaussian geminals in electronic structure theory has recently been reviewed by Szalewicz and Jeziorski.<sup>20</sup>

The first application of explicitly correlated Gaussian basis functions to systems of more than four electrons was that of Pan and King in the context of second-order Møller-Plesset theory<sup>21,22</sup> reformulated a few years later by Adamowicz using explicitly correlated floating spherical Gaussians which simplifies integral evaluation.<sup>23</sup> The first-order pair correlation function in MP-2 theory lies entirely in the infinite-dimensional subspace spanned by binary products of Hartree Fock virtual orbitals, i.e., the virt-virt space. This, the strong orthogonality property, was satisfied by explicitly projecting

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the occ-occ and occ-virt components out of each individual Gaussian geminal basis function. The occ-virt components give rise to four-electron integrals which can be expressed in terms of two-electron overlap and two-electron repulsion integrals. The number of such two-electron repulsion integrals scales as  $N^4 N_{gem}^2$ , where  $N_{gem}$  is the number of geminal basis functions. Szalewicz<sup>24,25</sup> overcame this serious computational bottleneck by variationally removing the occ-virt component from the entire pair correlation function rather than projecting it out of each individual geminal basis function. The Szalewicz weak orthogonality MP-2 functional requires the evaluation of two- and three-electron repulsion integrals.

An attractive alternative to the use of Gaussian geminals is the R12 method of Kutzelnigg and Klopper<sup>26-31</sup> employing a linear  $r_{12}$  correlation factor which, unlike the Gaussian factor, can satisfy exactly the electron correlation cusp condition. Essential to the outstanding success of the R12 method has been the development of auxiliary orbital basis sets for the resolution of the identity which avoids the need to evaluate the numerous and difficult many-electron integrals. In the past twenty years, the R12 method has found wide application to highly accurate variational, coupled-cluster, and perturbation theoretic computations for many-electron molecules, and more recently has been generalized to F12 theory with correlation factors other than  $r_{12}$ , e.g.,  $\exp(-\alpha r_{12})$ .<sup>32,33</sup>

The past decade has seen a significant resurgence of interest in methods that incorporate explicit correlation into the wave-function. In 1996 Persson and Taylor proposed<sup>34</sup> a novel way of using a few Gaussian geminals in atomic and molecular calculations. A very attractive aspect of their work avoids the optimization of non-linear parameters traditionally employed in such calculations. Using only a few geminal functions (from six to nine) they demonstrated the possibility of recovering over 90% of the correlation energy with modest basis sets.

More recent work<sup>35-42</sup> by a number of authors has explored a variety of methods and models for explicit electron correlation. While an exact treatment in these methods includes the explicit evaluation of many-electron (three and four) integrals, most implementations consider the evaluation of such integrals to be computationally prohibitive. Explicit evaluation of integrals involving Gaussian geminals<sup>43</sup> has been proposed and implemented. However, virtually all calculations to date have relied on the use of the resolution of the identity in which three-electron integrals are expanded in terms of sums of products of more easily computed two-electron integrals.

Methods for the efficient evaluation of integrals over contracted Gaussian functions have been advanced throughout the computational history of quantum chemistry. While the early work of Boys<sup>44</sup> introduced the basic formulas for a Gaussian function, modern methods are generally cast in terms of one of three formulations. Most of these methods however have been restricted to the evaluation of one and two-electron integrals required in traditional orbital expansions. The work of Obara and Saika<sup>45</sup> develops recursions that build up angular momentum for each electronic charge distribution and relies on the incomplete Gamma function for the funda-

mental integrals. Several years earlier, an alternative method was proposed by McMurchie and Davidson<sup>46</sup> and relies on recursions based on Hermite Gaussian functions. Lastly, King, Rys and Dupuis suggested<sup>47-49</sup> that integrals could be evaluated by developing recursions based on orthogonal polynomials. Final integrals are evaluated as a finite sum over the roots and weights of such polynomials. While it has been suggested that all three of these approaches may be formally mapped onto each other, the use of these methods is largely dictated by personal familiarity and computational preference.

The early work of Boys<sup>10</sup> addressed the evaluation of many-electron integrals and was intended for use in very small chemical systems. In a similar vein in the 1960s Lester and Krauss<sup>50,51</sup> proposed a set of complex formulas for use in explicitly correlated wave functions. In more modern times several groups have proposed formulations for many-electron integrals. In the early 1990s Kozłowski and Adamowicz<sup>52</sup> proposed a formulation for the evaluation of multi-center and multi-particle integrals. Cencek and Rychlewski<sup>53</sup> also provided a formulation for multi-particle integrals where the focus was on functions of zero angular momentum. More recently Persson and Taylor suggested<sup>43</sup> and implemented<sup>54</sup> the evaluation of modern three-electron integrals using the formulation of McMurchie and Davidson. Most recently, Saito and Suzuki<sup>55</sup> have derived recursion formulas for the computation of many-electron integrals. Their formulation is based on the work of Obara and Saika<sup>45</sup> who had developed recursion relations for two-electron integrals. Both McMurchie Davidson and Rys polynomial methods have been applied to the evaluation of low angular momentum, four-particle integrals in recent studies of non-Born Oppenheimer effects.<sup>56</sup> In our work, we offer a general formulation for the computation of many-electron integrals. We use the methods of Rys polynomials in order to derive general formulas for the evaluation of arbitrary  $n$ -electron integrals, for both electron repulsion as well as nuclear attraction. Using this general formulation, we present explicit results for two, three and four electron integrals. These include not only formulas for the  $\lambda = 0$  case, but also the recursions required to build up arbitrary angular momentum on any center. Our analysis shows that the general recursion relation requires at most  $n + 1$  terms for an  $n$ -electron integral.

In effect, the one and two-electron operators are defined by the values of quadrature roots and weights supplied by an external routine. It follows that the entire computational machinery described in this paper is applicable without modification, to the evaluation of integrals for other one and two-electron potentials characterized by appropriate quadrature roots and weights. In particular, these computer modules can be used to evaluate the short-range perturbation potential encountered in a proposed perturbation approach to the electron correlation cusp problem.<sup>57</sup> The proposed method has been shown to converge systematically for the helium atom, yielding energies in error at the microHartree level using only the first-order perturbation wave function, and at the nanoHartree level using the second-order wave function. Applications of the method to date<sup>58</sup> have been restricted to single-center systems, largely due to the lack of efficient machinery for the evaluation of many-center, many-electron integrals.

Given the recent activity in this field, we believe that an efficient formulation and implementation of many-electron integral computation should prove quite useful, if for no other reason than to test the validity of the various approximations introduced to avoid their computation. As mentioned above virtually all calculations to date on chemically interesting molecules have been done with two approximations. The first is the use of the weak orthogonality functional originally suggested by Szalewicz, and the second is the use of the resolution of the identity in order to reduce the cost of integral evaluation. While formally the three-electron integrals required in the evaluation of the correlation energy scale as  $N^6$  the use of RI methods also scales as  $N^6$ , albeit with a much smaller prefactor.

Our work is divided into several sections. In order to make our exposition easier to follow, we develop a general integral formulation based on charge distributions, rather than individual atom centered orbitals. Only in the end are we concerned about using the traditional transfer relations in order to compute integrals with atom centered basis functions. All of these are done for uncontracted sets of functions. The problem of contracting functions, or transforming them to alternative representations is not treated here. Some of our specific cases have required extensive algebraic manipulations which we have solved using a well known symbolic algebra program<sup>59</sup> MAPLE.

Section II discusses the concepts of orbitals, geminals, charge distributions, and properties of Rys polynomials and introduces the  $\mathbf{M}$  and  $\mathbf{K}$  matrices and other notation used throughout this paper. Once geminal couplings are introduced, overlaps between charge distributions no longer factor into one-electron products. We develop the concepts of two- and three-electron overlap integrals in Sec. III, where we have found that the simple treatment of overlap integrals, albeit including a geminal coupling, offers a very convenient didactic tool for the further development of more complicated integrals. These provide a very convenient framework in which to consider general electron repulsion integrals which we treat in Sec. IV. It is in this section that our most general framework is developed that allows us to treat any set of charge distributions that is bound by some combination of Coulombic and geminal coupling. We use this general framework to treat the well known case of a two-electron repulsion integral in Sec. V. Our treatment allows us to introduce a geminal coupling into this traditional integral. In the limit of the geminal

coupling going to zero, the new expression reduces to the well known case. Section VI treats the case of the three-electron integrals. Having developed this formalism for two and three-electron integrals we next treat the four-electron integral case in Sec. VII. Here, we consider three types of such integrals. For all cases, simple expressions are presented for the zero-order integral over  $s$  type functions as well as the coefficients for the recursions required to build up angular momentum for each electron. We finally consider the nuclear attraction integrals in Sec. VIII. The reader should note that the kinetic energy integral, for which the charge distribution concept is not appropriate, is not treated in this paper.

In the concluding section, we discuss in detail the computational consequences of our approach and indicate that our approach should be very efficient and applicable to many chemically interesting molecular systems that have been inaccessible by previously employed methods.

## II. PRELIMINARY CONCEPTS

### A. Orbitals, geminals, and charge distributions

A primitive Gaussian orbital is the product of a pre-exponential factor and a Gaussian factor, both expressed with respect to the same center,

$$\phi_a(\mathbf{\Lambda}_1) = (x_1 - X_a)^{\lambda_{x1}} (y_1 - Y_a)^{\lambda_{y1}} (z_1 - Z_a)^{\lambda_{z1}} \times \exp(-\alpha_a r_{1a}^2). \quad (1)$$

Here  $\mathbf{\Lambda}_1$  is the triple of  $(\lambda_{x1}, \lambda_{y1}, \lambda_{z1})$  indices,  $(x_1, y_1, z_1)$  are Cartesian coordinates of electron 1,  $(X_a, Y_a, Z_a)$  are the coordinates of the orbital center, and  $\alpha_a$  is the exponential parameter. For an orbital, the sum  $l$  of the three  $\lambda$  values is generally referred to as the angular momentum of that function. A primitive Gaussian geminal is the following function of an inter-electron distance:

$$\eta(1, 2) = \exp(-\sigma r_{12}^2). \quad (2)$$

Note that no center and no  $\lambda$ -type indices are associated with a geminal function. We make frequent use of the well known Gaussian product rule that expresses the product of two Gaussians as another Gaussian located at their center of mass, labeled  $p$  in Eqs. (3)–(5),

$$\exp(-\alpha_a r_{1a}^2) \exp(-\alpha_b r_{1b}^2) = K_{ab} \exp(-\alpha r_p^2), \quad (3)$$

where

$$\begin{aligned} \alpha &= \alpha_a + \alpha_b, & X_p &= \frac{(\alpha_a X_a + \alpha_b X_b)}{\alpha_a + \alpha_b}, \\ K_{ab} &= \exp(-D), & Y_p &= \frac{(\alpha_a Y_a + \alpha_b Y_b)}{\alpha_a + \alpha_b}, \\ D &= \frac{\alpha_a \alpha_b}{\alpha_a + \alpha_b} R_{ab}^2, & Z_p &= \frac{(\alpha_a Z_a + \alpha_b Z_b)}{\alpha_a + \alpha_b}, \\ r_{1p}^2 &= (x_1 - X_p)^2 + (y_1 - Y_p)^2 + (z_1 - Z_p)^2, \end{aligned} \quad (4)$$



TABLE I. Charge distribution function parameters.

Electron label	Pre-exponential center label	Exponential parameter	Gaussian center label
1	A	$\alpha$	$p$
2	B	$\beta$	$q$
3	C	$\gamma$	$r$
4	D	$\delta$	$s$

A product of two orbitals, both functions of the same electron, can be expressed as a finite linear combination of charge distribution basis functions,  $\chi$ . These are products of pre-exponential and Gaussian factors whose centers generally differ,

$$\chi_p(\mathbf{A}_1) = (x_1 - X_A)^{\lambda_{x1}} (y_1 - Y_A)^{\lambda_{y1}} (z_1 - Z_A)^{\lambda_{z1}} \times \exp(-\alpha r_{1p}^2). \quad (5)$$

The pre-exponential factor is expanded about center  $A$ , usually chosen to be an orbital center. The Gaussian factor is located at the center of mass of the orbital pair.

All integral formulas derived in this paper are expressed in terms of  $\chi$ -type functions rather than orbital products. The integrand of a molecular integral contains a product of charge distribution functions, one for each electron, a multiplicative operator, and one or more geminal factors. Since three  $\lambda$ -type indices specify a  $\chi$  factor,  $3n$  indices specify an  $n$ -electron integral. Parameters in the  $n$  different  $\chi$ -functions are denoted using the notation in Table I. We denote the exponential geminal parameters as follows:  $\sigma$  couples electron 1 with 2,  $\rho$  couples electron 2 with 3, and  $\tau$  couples electron 3 with 1, when  $n=3$ , or 3 with 4, when  $n=4$ .

## B. Rys quadrature and Gaussian transform

The theory of orthogonal polynomials implies that if  $P(t^2)$  is a polynomial of degree less than  $2N$  in the variable  $t^2$  then the following integration formula applies exactly,

$$\int_0^1 dt P(t^2) e^{-ht^2} = \sum_{\alpha=1}^N W_\alpha P_x(t_\alpha^2) P_y(t_\alpha^2) P_z(t_\alpha^2), \quad (6)$$

where  $W_\alpha$  and  $t_\alpha$  are known functions of  $h$ , and  $P(t^2)$  is the product of Cartesian factors. In particular,  $t_\alpha$  is the  $\alpha$ th positive zero of the  $N$ th Rys polynomial. It is well known that traditional nuclear-attraction and electron-repulsion integrals over primitive Gaussian orbitals can be reduced to such one-dimensional integrals. In this paper, we extend the analysis to many-electron, potential energy integrals over products of geminals and charge distribution functions and show, not surprisingly, that they too reduce to integrals of the form given in Eq. (6). In our analysis, as in the original development of the Rys quadrature method,<sup>48</sup> operators for the electron–nuclear and electron–electron electrostatic interactions are expressed as Gaussian transforms,

$$\frac{1}{r_{\mu\nu}} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp(-u^2 r_{\mu\nu}^2) du. \quad (7)$$

Thus, the general,  $n$ -particle, electron repulsion integral can be expressed as follows:

$$\langle |r_{\mu\nu}^{-1}| \rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty du \langle | \exp(-u^2 r_{\mu\nu}^2) | \rangle. \quad (8)$$

Equations (7) and (8) can be generalized to treat other operators, but that is beyond the scope of this paper. Note that a charge density distribution function is separable into a product of three Cartesian factors,

$$\begin{aligned} \chi_p(\mathbf{A}_1) &= \chi_{xp}(\lambda_{x1}; x_1) \chi_{yp}(\lambda_{y1}; y_1) \chi_{zp}(\lambda_{z1}; z_1), \\ \chi_{xp}(\lambda_{x1}; x_1) &= (x_1 - X_A)^{\lambda_{x1}} \exp[-\alpha (x_1 - X_p)^2], \\ \chi_{yp}(\lambda_{y1}; y_1) &= (y_1 - Y_A)^{\lambda_{y1}} \exp[-\alpha (y_1 - Y_p)^2], \\ \chi_{zp}(\lambda_{z1}; z_1) &= (z_1 - Z_A)^{\lambda_{z1}} \exp[-\alpha (z_1 - Z_p)^2]. \end{aligned} \quad (9)$$

Geminals are similarly separable,

$$\begin{aligned} \eta(1, 2) &= \eta_x(x_1, x_2) \eta_y(y_1, y_2) \eta_z(z_1, z_2), \\ \eta_x(x_1, x_2) &= \exp[-\sigma (x_1 - x_2)^2], \\ \eta_y(y_1, y_2) &= \exp[-\sigma (y_1 - y_2)^2], \\ \eta_z(z_1, z_2) &= \exp[-\sigma (z_1 - z_2)^2]. \end{aligned} \quad (10)$$

It follows immediately that a product of charge distribution functions and geminals separates into a product of three Cartesian factors,  $g_x$ ,  $g_y$ , and  $g_z$ . The integral of this product of charge distribution functions and geminals similarly separates into a product of three integrals,  $G_x$ ,  $G_y$ , and  $G_z$ . By the same token, the integrand on the right hand side of Eq. (8) separates into a product of  $u$ -dependent  $G_x$ ,  $G_y$ , and  $G_z$  factors. These  $G_x$  integrals, which play a key role in our analysis, are defined and further discussed in Sec. II C.

## C. The $G_x$ integral

All integrals discussed in this paper require evaluation of the following  $n$ -dimensional integral, where  $n$  is the number of electrons:

$$\begin{aligned} G_x(\mathbf{A}_x) &= \int \cdots \int_{-\infty}^\infty g_x(\mathbf{A}_x; \mathbf{x}) d\mathbf{x}, \\ g_x(\mathbf{A}_x; \mathbf{x}) &= \exp[-Q_x(\mathbf{x})] \prod_{k=1, n} (x_k - X_k)^{\lambda_{xk}}, \\ \mathbf{A}_x &= (\lambda_{x1}, \lambda_{x2}, \cdots, \lambda_{xn}). \end{aligned} \quad (11)$$

Here  $\mathbf{x}$  is a vector of  $x$  coordinates of the  $n$ -electrons, and  $d\mathbf{x} = dx_1 \cdots dx_n$  is the  $n$ -dimensional volume element. The squared terms in the various exponential factors are collected together to form  $Q_x(\mathbf{x})$ ,

$$\begin{aligned} Q_x(\mathbf{x}) &= \alpha (x_1 - X_p)^2 + \beta (x_2 - X_q)^2 \cdots \\ &+ \sigma (x_1 - x_2)^2 + \cdots \end{aligned} \quad (12)$$

Thus,  $Q_x(\mathbf{x})$  is a quadratic form in the  $x$  coordinates. It is convenient to collect terms as follows:

$$Q_x(\mathbf{x}) = \mathbf{x}^\dagger \mathbf{M} \mathbf{x} - 2\mathbf{F}_x^\dagger \mathbf{x} + c_x, \quad (13)$$

where  $c_x$  is the quadratic form evaluated at the origin of the coordinate system:

$$c_x = \alpha X_p^2 + \beta X_q^2 + \dots \quad (14)$$

Elements of the  $\mathbf{M}$  matrix are obtained simply by inspection of the quadratic form  $Q(x)$ . Numerous examples are given later in this paper. Comparing Eqs. (12) and (13) reveals that  $\mathbf{F}_x$  is a column vector formed from the  $x$ -coordinates of the Gaussian centers in the  $n$  different charge distribution functions. We define  $\mathbf{X}$  to be a similar vector of  $x$ -coordinates of expansion centers of pre-exponential factors in Eq. (11),

$$\mathbf{X} = \begin{pmatrix} X_A \\ X_B \\ \dots \end{pmatrix}, \quad \mathbf{F}_x = \begin{pmatrix} \alpha X_p \\ \beta X_q \\ \dots \end{pmatrix}. \quad (15)$$

The matrices  $\mathbf{M}$  and  $\mathbf{K}$  (its inverse) are real and symmetric. A necessary and sufficient condition for convergence of the  $G_x$  integral is that  $\mathbf{M}$  be positive definite. A sufficient condition is that the exponential parameters of all charge distribution functions,  $\alpha, \beta, \dots$ , be positive, and the exponential parameters of all geminals,  $\sigma, \rho, \dots$ , be non-negative. Then no terms on the right hand side of Eq. (12) are negative, and  $Q_x(\mathbf{x})$  is everywhere non-negative. In any case,  $Q_x(\mathbf{x})$  has its minimum value at  $\mathbf{x}_{min}$  where

$$\begin{aligned} \mathbf{K} &= \mathbf{M}^{-1}, \\ \mathbf{x}_{min} &= \mathbf{K}\mathbf{F}_x, \\ Q_x(\mathbf{x}_{min}) &= c_x - \mathbf{F}_x^\dagger \mathbf{K} \mathbf{F}_x. \end{aligned} \quad (16)$$

Let  $G_x^\circ$  denote the  $G_x$  integral with all  $\lambda$  indices equal to zero,

$$G_x^\circ \equiv G_x(\mathbf{0}) = \int \dots \int \exp[-Q_x(\mathbf{x})] d\mathbf{x}. \quad (17)$$

To evaluate  $G_x^\circ$ , apply a unitary transformation which diagonalizes  $\mathbf{M}$  and thus separates  $Q_x(\mathbf{x})$  into a sum of one-electron terms,

$$Q_x(\mathbf{x}) = c_x + \sum_{i=1}^n (\bar{m}_i \bar{x}_i^2 - 2\bar{f}_i \bar{x}_i). \quad (18)$$

Here  $\bar{m}_i$  is the  $i$ th eigenvalue of  $\mathbf{M}$ , while  $\bar{f}_i$  and  $\bar{x}_i$  are the corresponding elements of the transformed  $\mathbf{F}_x$  and  $\mathbf{x}$  vectors. Then  $G_x^\circ$  becomes  $\exp(-c_x)$  times a product of  $n$  one-dimensional integrals each with the following form:

$$\int_{-\infty}^{\infty} \exp(-\bar{m} \bar{x}^2 + 2\bar{f} \bar{x}) d\bar{x} = \sqrt{\frac{\pi}{\bar{m}}} \exp\left(\frac{\bar{f}^2}{\bar{m}}\right). \quad (19)$$

Transforming back to the original coordinate system yields the useful result

$$G_x^\circ = \sqrt{\frac{\pi^n}{\det(\mathbf{M})}} \exp(-c_x + \mathbf{F}_x^\dagger \mathbf{K} \mathbf{F}_x). \quad (20)$$

Eq. (16) implies that the exponent in Eq. (20) is negative if  $Q_x(\mathbf{x})$  is everywhere positive.

Given the value of  $G_x^\circ$ , the general  $G_x(\mathbf{\Lambda}_x)$  integral can be evaluated by recursion. The recurrence relation derives from the fact that  $g_x \rightarrow 0$  as  $x_k \rightarrow \pm\infty$  for any electron. Thus,

$$\int \dots \int_{-\infty}^{\infty} \left( \frac{\partial g_x}{\partial x_k} \right) d\mathbf{x} = 0. \quad (21)$$

The partial derivative with respect to the  $x$  coordinate of electron  $k$  is

$$\begin{aligned} \left( \frac{\partial g_x(\mathbf{\Lambda}_x; \mathbf{x})}{\partial x_k} \right) &= \lambda_{xk} g_x(\lambda_{x1}, \dots, \lambda_{xk} - 1, \dots, \lambda_{xn}; \mathbf{x}) \\ &\quad - 2g_x(\mathbf{\Lambda}_x; \mathbf{x})(\mathbf{M}\mathbf{x} - \mathbf{F}_x)_k. \end{aligned} \quad (22)$$

The first term in Eq. (22) comes from differentiating the pre-exponential factor in Eq. (11), and the second term from differentiating the exponential factor using Eq. (23) below. Since the first term vanishes when  $\lambda_{xk} = 0$ , we are free to define  $g_x$  and  $G_x$  to be zero if any of its  $\lambda$  indices are negative. Differentiating Eq. (13) with respect to electron coordinates gives

$$\nabla Q_x(\mathbf{x}) = 2(\mathbf{M}\mathbf{x} - \mathbf{F}_x). \quad (23)$$

Substituting Eq. (22) into Eq. (21) and making the substitution,

$$(\mathbf{M}\mathbf{x} - \mathbf{F}_x) = \mathbf{M}(\mathbf{x} - \mathbf{X}) + (\mathbf{M}\mathbf{X} - \mathbf{F}_x), \quad (24)$$

yields after integration a linear set of equations relating  $G_x$  integrals with raised and lowered indices,

$$\begin{aligned} \sum_{j=1}^n M_{kj} G_x(\lambda_{x1}, \dots, \lambda_{xj} + 1, \dots, \lambda_{xn}) \\ = (\lambda_{xk}/2) G_x(\lambda_{x1}, \dots, \lambda_{xk} - 1, \dots, \lambda_{xn}) \\ - G_x(\mathbf{\Lambda}_x)(\mathbf{M}\mathbf{X} - \mathbf{F}_x)_k. \end{aligned} \quad (25)$$

When expressed in matrix notation this system of linear equations is

$$\mathbf{M}\mathbf{G}_x(\mathbf{\Lambda}_x^+) = \mathbf{L}_x \mathbf{G}_x(\mathbf{\Lambda}_x^-) - G_x(\mathbf{\Lambda}_x)(\mathbf{M}\mathbf{X} - \mathbf{F}_x), \quad (26)$$

where  $\mathbf{G}_x(\mathbf{\Lambda}_x^+)$  is an  $n$ -dimensional vector of  $G_x$  integrals with one raised index,

$$\mathbf{G}_x(\mathbf{\Lambda}_x^+) = \begin{pmatrix} G_x(\lambda_{x1} + 1, \lambda_{x2}, \dots) \\ G_x(\lambda_{x1}, \lambda_{x2} + 1, \dots) \\ \dots \end{pmatrix}, \quad (27)$$

and  $\mathbf{G}_x(\mathbf{\Lambda}_x^-)$  is an  $n$ -dimensional vector of  $G_x$  integrals with one lowered index,

$$\mathbf{G}_x(\mathbf{\Lambda}_x^-) = \begin{pmatrix} G_x(\lambda_{x1} - 1, \lambda_{x2}, \dots) \\ G_x(\lambda_{x1}, \lambda_{x2} - 1, \dots) \\ \dots \end{pmatrix}. \quad (28)$$

The  $\mathbf{L}_x$  matrix is diagonal with  $k$ th diagonal element equal to  $\lambda_{xk}/2$ . Recall that the  $k$ th element of the  $\mathbf{G}_x(\mathbf{\Lambda}_x^-)$  vector is zero if  $\lambda_{xk} = 0$ . Solving Eq. (26) for  $\mathbf{G}_x(\mathbf{\Lambda}_x^+)$  yields the desired recurrence relation

$$\mathbf{G}_x(\mathbf{\Lambda}_x^+) = \mathbf{K}\mathbf{L}_x \mathbf{G}_x(\mathbf{\Lambda}_x^-) + G_x(\mathbf{\Lambda}_x) \mathbf{T}_x, \quad (29)$$

where

$$\mathbf{T}_x = \mathbf{K}\mathbf{F}_x - \mathbf{X}. \quad (30)$$

The reader should note that the right-hand side of Eq. (29) is a matrix-vector product plus the product of a scalar times a vector, as the quantity  $G_x(\mathbf{\Lambda}_x)$  is a scalar; furthermore, the elements of  $\mathbf{T}_x$  are independent of the values of the  $\lambda$  indices.

The principal results of our analysis are contained in Eqs. (20) and (29). These contain general expressions for any  $n$ -electron integral over  $s$ -type functions as well as the recursion needed to build up to arbitrary angular momentum. Note that the general recursion relation requires at most  $n + 1$  terms for an  $n$ -electron integral. To evaluate any given  $G_x(\Lambda_x)$ , first compute  $G_x^\circ$  using Eq. (20), then systematically build up to higher  $\Lambda_x$  indices by repeated application of Eq. (29). Each iteration increments a  $\lambda_{xk}$  index by one unit. Note that  $G_x^\circ$  is a common factor in all  $G_x(\Lambda_x)$  integrals generated in this way, and it may be convenient to explicitly separate out this common  $G_x^\circ$  factor. In Sec. IV, for example,  $P_x$  denotes the ratio  $G_x/G_x^\circ$ .

When applying this method to the evaluation of any given class of integrals, the relevant parameters are those in Eq. (11) and Eq. (13); namely, the  $\mathbf{M}$  matrix, the  $\mathbf{X}$  and  $\mathbf{F}_x$  vectors, and the  $c_x$  constant. Inspection of the quadratic form,  $Q_x$ , reveals that geminal parameters enter only through the  $\mathbf{M}$  matrix. They make no contribution to  $\mathbf{X}$ ,  $\mathbf{F}_x$ , or  $c_x$ , so the parameters that distinguish one type of  $n$ -electron integral from another are those derived from  $\mathbf{M}$ , namely,  $\det(\mathbf{M})$  and  $\mathbf{K}$ .

### III. OVERLAP INTEGRALS

#### A. Two-electron overlap integrals

The two-electron overlap integral is a six-dimensional integral over a product of two primitive charge distribution basis functions and a geminal factor,

$$S_2(\Lambda_1, \Lambda_2, \sigma) = \int \cdots \int_{-\infty}^{\infty} d\tau_1 d\tau_2 \chi_p(\Lambda_1) \chi_q(\Lambda_2) \exp(-\sigma r_{12}^2). \quad (31)$$

A diagrammatic representation<sup>23</sup> of this integral in which charge distribution functions are represented by circles and geminals by solid lines is shown in Fig. 1. This integral can be evaluated using the methods and notation of Sec. II C:

$$\begin{aligned} S_2(\Lambda_1, \Lambda_2, \sigma) &= G_x(\Lambda_x) G_y(\Lambda_y) G_z(\Lambda_z), \\ g_x(\Lambda_x, \mathbf{x}) &= (x_1 - X_A)^{\lambda_{x1}} (x_2 - X_B)^{\lambda_{x2}} \exp[-Q_x(\mathbf{x})], \\ Q_x(\mathbf{x}) &= \alpha(x_1 - X_p)^2 + \beta(x_2 - X_q)^2 + \sigma(x_1 - x_2)^2. \end{aligned} \quad (32)$$

Here, we adopt the notation  $\mathbf{M}^\circ$  and  $\mathbf{K}^\circ$  to distinguish these matrices from corresponding  $u^2$ -dependent matrices encountered in Sec. IV:

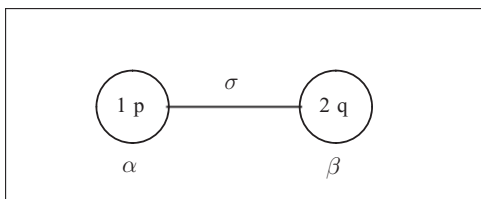


FIG. 1. A diagrammatic representation of an overlap integral between two charge distributions, coupled by a Gaussian geminal factor,  $\sigma$ . Charge distributions are represented by circles, geminal coupling by a solid line.

$$\mathbf{M}^\circ = \begin{pmatrix} \alpha + \sigma & -\sigma \\ -\sigma & \beta + \sigma \end{pmatrix}, \quad (33)$$

$$\mathbf{K}^\circ = \frac{1}{\det(\mathbf{M}^\circ)} \begin{pmatrix} \beta + \sigma & \sigma \\ \sigma & \alpha + \sigma \end{pmatrix},$$

$$\det(\mathbf{M}^\circ) = \omega,$$

$$\omega = \alpha\beta + \sigma(\alpha + \beta), \quad (34)$$

$$c_x = \alpha X_p^2 + \beta X_q^2.$$

The exponent in Eq. (20) becomes

$$\begin{aligned} v_x &= c_x - \mathbf{F}_x^\dagger \mathbf{K}^\circ \mathbf{F}_x, \\ v_x &= \left( \frac{\alpha\beta\sigma}{\omega} \right) (X_p - X_q)^2. \end{aligned} \quad (35)$$

The general relation, Eq. (29), becomes a pair of three-term recursion formulas,

$$\begin{aligned} G_x(\lambda_1+1, \lambda_2) &= (\lambda_1/2) K_{11} G_x(\lambda_1 - 1, \lambda_2) \\ &\quad + (\lambda_2/2) K_{12} G_x(\lambda_1, \lambda_2 - 1) + T_{x1} G_x(\lambda_1, \lambda_2), \\ G_x(\lambda_1, \lambda_2 + 1) &= (\lambda_1/2) K_{21} G_x(\lambda_1 - 1, \lambda_2) \\ &\quad + (\lambda_2/2) K_{22} G_x(\lambda_1, \lambda_2 - 1) + T_{x2} G_x(\lambda_1, \lambda_2), \end{aligned} \quad (36)$$

and Eq. (30) becomes

$$\begin{aligned} T_{x1} &= K_{11} \alpha X_p + K_{12} \beta X_q - X_A, \\ T_{x2} &= K_{21} \alpha X_p + K_{22} \beta X_q - X_B. \end{aligned} \quad (37)$$

When all  $\lambda$ -type indices are zero the overlap integral is

$$S_2(\mathbf{0}, \mathbf{0}, \sigma) = G_x^\circ G_y^\circ G_z^\circ = \left( \frac{\pi^2}{\omega} \right)^{3/2} \exp(-v), \quad (38)$$

where

$$v = v_x + v_y + v_z = \frac{\alpha\beta\sigma}{\omega} R_{pq}^2. \quad (39)$$

If  $\sigma$  is set to zero,  $v$  vanishes and  $S_2(\Lambda_1, \Lambda_2, 0)$  becomes the product of overlap integrals of the two uncoupled charge distribution functions. For any given positive value of  $\sigma$ , the value of  $S_2(\mathbf{0}, \mathbf{0}, 0)$  decreases monotonically to zero with increasing separation of the two charge distributions, and for any given separation decreases monotonically to zero with increasing  $\sigma$ . This is one aspect of the general principle that geminal couplings are short range.

#### B. Three-electron overlap integrals

The three-electron overlap integral is a nine-dimensional integral over a product of three primitive charge distribution basis functions, and two geminal factors represented by the diagram in Fig. 2,

$$\begin{aligned} S_3(\Lambda_1, \Lambda_2, \Lambda_3, \sigma, \rho) &= \int \cdots \int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \chi_p(\Lambda_1) \chi_q(\Lambda_2) \chi_r(\Lambda_3) \\ &\quad \times \exp(-\sigma r_{12}^2) \exp(-\rho r_{23}^2). \end{aligned} \quad (40)$$

Proceeding as for the two-electron overlap integral,

$$S_3(\mathbf{\Lambda}_1, \mathbf{\Lambda}_2, \mathbf{\Lambda}_3, \sigma, \rho) = G_x(\mathbf{\Lambda}_x) G_y(\mathbf{\Lambda}_y) G_z(\mathbf{\Lambda}_z),$$

$$g_x(\mathbf{\Lambda}_x, \mathbf{x}) = (x_1 - X_A)^{\lambda_{x1}} (x_2 - X_B)^{\lambda_{x2}} (x_3 - X_C)^{\lambda_{x3}} \exp[-Q_x(\mathbf{x})],$$

$$Q_x(\mathbf{x}) = \alpha(x_1 - X_p)^2 + \beta(x_2 - X_q)^2 + \gamma(x_3 - X_r)^2 + \sigma(x_1 - x_2)^2 + \rho(x_2 - x_3)^2.$$

It follows that

$$\mathbf{M}^\circ = \begin{pmatrix} \alpha + \sigma & -\sigma & 0 \\ -\sigma & \beta + \sigma + \rho & -\rho \\ 0 & -\rho & \gamma + \rho \end{pmatrix},$$

$$\mathbf{K}^\circ = \frac{1}{\det(\mathbf{M}^\circ)} \begin{pmatrix} (\beta + \sigma)(\gamma + \rho) + \gamma\rho & (\gamma + \rho)\sigma & \sigma\rho \\ (\gamma + \rho)\sigma & (\alpha + \sigma)(\gamma + \rho) & (\alpha + \sigma)\rho \\ \sigma\rho & (\alpha + \sigma)\rho & (\alpha + \sigma)(\beta + \rho) + \alpha\sigma \end{pmatrix},$$

$$\det(\mathbf{M}^\circ) = \omega,$$

$$\omega = (\alpha + \sigma)(\gamma + \rho)\beta + (\alpha + \sigma)\gamma\rho + (\gamma + \rho)\alpha\sigma,$$

$$c_x = \alpha X_p^2 + \beta X_q^2 + \gamma X_r^2. \quad (44)$$

The exponential part in Eq. (20) is arrived at through straightforward, but rather lengthy, algebraic manipulation,

$$v_x = c_x - \mathbf{F}_x^\dagger \mathbf{K}^\circ \mathbf{F}_x = \frac{\alpha\beta\sigma(\gamma + \rho)}{\omega} (X_p - X_q)^2$$

$$+ \frac{\gamma\beta\rho(\alpha + \sigma)}{\omega} (X_r - X_q)^2 + \frac{\alpha\gamma\sigma\rho}{\omega} (X_p - X_r)^2. \quad (45)$$

In this case, the general relation Eq. (29), becomes a set of three, four-term recursion equations.

For example, the following equation raises the  $\lambda_{x1}$  index:

$$G_x(\lambda_1 + 1, \lambda_2, \lambda_3) = (\lambda_1/2) K_{11} G_x(\lambda_1 - 1, \lambda_2, \lambda_3)$$

$$+ (\lambda_2/2) K_{12} G_x(\lambda_1, \lambda_2 - 1, \lambda_3)$$

$$+ (\lambda_3/2) K_{13} G_x(\lambda_1, \lambda_2, \lambda_3 - 1)$$

$$+ T_{x1} G_x(\lambda_1, \lambda_2, \lambda_3), \quad (46)$$

$$T_{x1} = K_{11} \alpha X_p + K_{12} \beta X_q + K_{13} \gamma X_r - X_A. \quad (47)$$

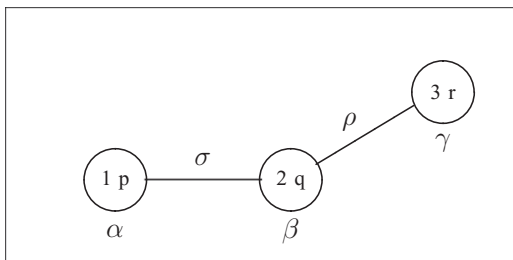


FIG. 2. A diagrammatic representation of a three-electron overlap integral, where charge distributions are coupled by two Gaussian geminal factors,  $\sigma$  and  $\rho$ . Charge distributions are represented by circles, geminal couplings by solid lines.

Analogous equations build up angular momentum on centers  $B$  and  $C$ . When all  $\lambda$ -type indices are zero the three-electron overlap integral is

$$S_3(\mathbf{0}, \mathbf{0}, \mathbf{0}, \sigma) = G_x^\circ G_y^\circ G_z^\circ = \left(\frac{\pi^3}{\omega}\right)^{3/2} \exp(-v), \quad (48)$$

where  $v$  is

$$v = \frac{\alpha\beta\sigma(\gamma + \rho)}{\omega} R_{pq}^2 + \frac{\gamma\beta\rho(\alpha + \sigma)}{\omega} R_{rq}^2 + \frac{\alpha\gamma\sigma\rho}{\omega} R_{pr}^2. \quad (49)$$

In the limit of  $\rho$  going to zero, the above overlap integral reduces to a product of a one-electron integral (with a charge distribution involving  $\gamma$ ) and the two-electron integral expressed in Eq. (38). Furthermore, the exponential parameter  $v$ , in Eq. (49) equals that in Eq. (39) when  $\rho$  is set to zero, and is greater than that in Eq. (39) for all positive  $\rho$  and  $\gamma$ . This inequality can be shown by detailed algebra, but more easily simply by recalling Eq. (16) and noting that  $Q_x(\mathbf{x})$  in Eq. (41) is never less than  $Q_x(\mathbf{x})$  in Eq. (32) and therefore it is never less than  $Q_x(\mathbf{x}_{min})$  in Eq. (32). Thus, adding a geminal to the integrand has the effect of reducing its value, and the combined effect of two geminals is greater than that of either one by itself.

#### IV. ELECTRON REPULSION INTEGRALS, CONCEPTS, AND METHODS

Various classes of two-, three-, and four-electron repulsion integrals are discussed individually in later sections of this paper. All have a common structure. The present section describes this structure and shows how it can be exploited. Let the general,  $n$ -particle, electron repulsion integral be expressed as the integral in Eq. (8) whose integrand separates



TABLE II. Various quantities that arise in the analysis of electron repulsion integrals, and whether they are or are not invariant with respect to changing electron labels in the Coulomb operator.

Dependent	$\mathbf{M}$	$\mathbf{K}$	$\theta$	$h$	$b_{ij}$	$\mathbf{K}_h$	$\mathbf{H}$	$\xi$	$\mathbf{T}_x$	$P(t^2)$
Independent	$\mathbf{M}^\circ$	$\mathbf{K}^\circ$	$\omega$	$\nu$	$a_{ij}$	$\mathbf{F}_x$	$\mathbf{X}$	$\mathbf{X}^\circ$	$\mathbf{R}_k^\circ$	

into a product of three Cartesian factors,

$$\left\| \exp(-u^2 r_{\mu\nu}^2) \right\| = G_x(\mathbf{A}_x, u^2) G_y(\mathbf{A}_y, u^2) G_z(\mathbf{A}_z, u^2). \quad (50)$$

The  $G_x$  factor is an implicit function of  $\mathbf{X}$ ,  $\mathbf{M}$ ,  $\mathbf{F}_x$ , and  $c_x$ , as discussed in Sec. II C. The notation in Eq. (50) has been modified to emphasize the dependence of  $G_x$  on  $u^2$ . The operator in Eq. (50) contributes a term  $u^2(x_\mu - x_\nu)^2$  to  $Q_x(\mathbf{x})$ . Inspection of Eqs. (12) and (13) shows that  $u^2$  makes a positive contribution to diagonal elements  $M_{\mu\mu}$  and  $M_{\nu\nu}$ , and a negative contribution to off-diagonal elements  $M_{\mu\nu}$  and  $M_{\nu\mu}$ . See for example, Eq. (94) in Sec. VI. By definition,  $\mathbf{M}^\circ$  is obtained from  $\mathbf{M}$  by setting  $u^2=0$ . It is shown in Appendix A that the determinant of  $\mathbf{M}$  is a linear function of  $u^2$ , so from any given  $\mathbf{M}$  we can extract three parameters,  $\omega$ ,  $\theta$ , and  $\xi$ , by expressing the determinant as follows:

$$\begin{aligned} \det(\mathbf{M}) &= \omega + \theta u^2 \\ &= \theta (\xi + u^2), \\ \det(\mathbf{M}^\circ) &= \omega, \\ \xi &= \frac{\omega}{\theta}. \end{aligned} \quad (51)$$

The value of  $\omega$  is independent of which pair of electrons interact through the Coulomb operator. On the other hand,  $\theta$ ,  $\mathbf{M}$ , and many other quantities, do exhibit such operator dependence. When the appropriate particle labels are thought to be obvious from the context we use the simple notation,  $\theta$ ,  $\mathbf{M}$ , etc., as in Eq. (51) above. Otherwise, notation such as  $\theta_{\mu\nu}$  and  $\mathbf{M}(\mu, \nu)$  is employed to explicitly exhibit the particle labels in the relevant Coulomb operator. Table II indicates which quantities do, and which do not, depend upon electron labels,  $\mu$  and  $\nu$ . All are independent of  $\lambda$  indices.

Recall that  $\mathbf{K}$  is the inverse of  $\mathbf{M}$ . Similarly,  $\mathbf{K}^\circ$  is defined to be the inverse of  $\mathbf{M}^\circ$ . It is shown in Appendix A that the elements of these inverse matrices can be expressed as follows:

$$\begin{aligned} K_{ij}^\circ &= \frac{a_{ij}}{\omega}, \\ K_{ij} &= \frac{a_{ij} + b_{ij} u^2}{\omega + \theta u^2}. \end{aligned} \quad (52)$$

The  $a_{ij}$  and  $b_{ij}$  elements are independent of  $u^2$ , and like  $K_{ij}$  itself, are symmetric with respect to exchange of indices,  $a_{ij} = a_{ji}$  and  $b_{ij} = b_{ji}$ , and are non-negative. We state without proof, that for any  $i = 1, 2, \dots, n$  these elements satisfy the following relationships:

$$b_{i\mu} = b_{i\nu}, \quad (53)$$

and

$$\begin{aligned} a_{i1} \alpha + a_{i2} \beta + a_{i3} \gamma + \dots &= \omega, \\ b_{i1} \alpha + b_{i2} \beta + b_{i3} \gamma + \dots &= \theta_{\mu\nu}. \end{aligned} \quad (54)$$

Equation (52) provides an entirely satisfactory representation of the  $\mathbf{K}$  matrix for numerical applications of the recursion relations.

For formal analysis, however, it is useful to re-express  $G_x^\circ(u^2)$  as a function of a new variable  $t^2$ , defined and discussed below. In particular, we show that the many-electron integral, like the more familiar two-electron repulsion integral, reduces to an integral over a Polynomial in the variable  $t^2$ . This result is summarized in Eq. (79), which is the working equation for the evaluation of all electron repulsion integrals considered in this paper.

Substitute Eq. (51) into the general expression, Eq. (20), for the zero-index  $G_x$  integral,

$$G_x^\circ(u^2) = \sqrt{\frac{\pi^n}{\theta}} (\xi + u^2)^{-1/2} \exp(-c_x + \mathbf{F}_x^\dagger \mathbf{K} \mathbf{F}_x). \quad (55)$$

Define a new integration variable,  $t$ ,

$$t = \frac{u}{(\xi + u^2)^{1/2}}, \quad dt = \frac{\xi}{(\xi + u^2)^{3/2}} du. \quad (56)$$

Integration limits,  $u=0 \rightarrow \infty$ , correspond to  $t=0 \rightarrow 1$ . Using Eq. (56), the factor of  $2/\sqrt{\pi}$  and the differential  $du$  in Eq. (8) can be combined with the pre-exponential factor in Eq. (55) and with identical factors from  $G_y$  and  $G_z$  to give the following quantity which appears in the general  $n$ -particle, electron repulsion integral:

$$\frac{2}{\sqrt{\pi}} \left[ \sqrt{\frac{\pi^n}{\theta}} (\xi + u^2)^{-1/2} \right]^3 du = \frac{2 \pi^{(3n-1)/2}}{\omega \sqrt{\theta}} dt. \quad (57)$$

Eq. (56) together with  $\omega = \theta \xi$  imply the following identity, which is valid for any  $a$  and  $b$ :

$$\frac{a + b u^2}{\omega + \theta u^2} = \frac{a}{\omega} + \left( \frac{b}{\theta} - \frac{a}{\omega} \right) t^2. \quad (58)$$

Equations. (52) and (58) imply that  $\mathbf{K}$  is a linear function of  $t^2$ ,

$$\mathbf{K} = \mathbf{K}^\circ + t^2 \mathbf{K}_h, \quad (59)$$

where  $\mathbf{K}_h$  is a symmetric  $n$ -by- $n$  matrix with elements,

$$(\mathbf{K}_h)_{ij} = \frac{b_{ij}}{\theta} - \frac{a_{ij}}{\omega}. \quad (60)$$

Eq. (59) implies that the exponent in Eq. (55) is also a linear function of  $t^2$ ,

$$c_x - \mathbf{F}_x^\dagger \mathbf{K} \mathbf{F}_x = v_x + h_x t^2, \quad (61)$$

where

$$v_x = c_x - \mathbf{F}_x^\dagger \mathbf{K}^\circ \mathbf{F}_x, \quad (62)$$

$$h_x = -\mathbf{F}_x^\dagger \mathbf{K}_h \mathbf{F}_x. \quad (63)$$

The  $v_x$  parameter in Eq. (62) has the same value as  $v_x$  in the corresponding overlap integral. The  $h_x$  parameter in Eq. (63) is non-negative. This can be proven using Eqs. (16) and (61)

which imply that  $v_x$  is the minimum value of  $Q_x$  when  $u^2$  is zero, and that  $v_x + h_x$  is the minimum value when  $u^2$  reaches infinity. The minimum value of  $Q_x$  will certainly not decrease upon addition of the  $u^2(x_\mu - x_\nu)^2$  term, so  $v_x + h_x$  is certainly not less than  $v_x$ . It is possible however, that  $h_x$  is zero. For example, when all centers  $p, q, r, \dots$  lie in the  $x = 0$  plane then  $c_x = 0$  and  $\mathbf{F}_x = \mathbf{0}$ , in which case  $v_x = h_x = 0$ .

In principle, computation of the key parameter,  $h_x$ , is a straightforward algebraic exercise involving small matrices and vectors. One can analytically invert  $\mathbf{M}$  to get  $\mathbf{K}$ ,  $\mathbf{K}^\circ$ , and  $\mathbf{K}_h$ . Then  $h_x$  can be obtained from  $\mathbf{F}_x$  and  $\mathbf{K}_h$  using Eq. (63). Performing these steps is relatively easy for two-electron integrals, but becomes increasingly tedious with increasing number of electrons and provides little insight into the resulting value of  $h_x$ . Thus, we are motivated to look for simplifications. It is shown in Appendix B that  $\mathbf{K}_h$  is a matrix of rank 1 with negative eigenvalue that can be expressed as follows:

$$\mathbf{K}_h = -\left(\frac{1}{\omega\theta}\right) \mathbf{H} \mathbf{H}^\dagger, \quad (64)$$

where  $\theta$  and  $\omega$  are given by Eq. (51), and  $\mathbf{H}$  is a column vector generated from columns  $\mu$  and  $\nu$  of the  $\mathbf{K}^\circ$  matrix,

$$\mathbf{H} = \omega \mathbf{K}^\circ \mathbf{V}. \quad (65)$$

Here  $\mathbf{V}$  is a column vector with elements  $V_\mu = 1$ ,  $V_\nu = -1$ , and all other elements zero. Substituting Eq. (64) into Eq. (63) shows that  $h_x$  is proportional to the square of the dot product of the  $\mathbf{H}$  and  $\mathbf{F}_x$  vectors,

$$h_x = \left(\frac{1}{\omega\theta}\right) (\mathbf{H}^\dagger \mathbf{F}_x)^2. \quad (66)$$

This expression for the  $h_x$  parameter is itself useful for computation, but we feel that one can better appreciate the magnitude of  $h_x$  by relating it to the  $\mathbf{R}^\circ$  centers defined below. Substituting Eq. (65) into the vector dot product formula, recalling that  $\mathbf{K}^\circ$  is a symmetric matrix, and noting the particularly simple form of the  $\mathbf{V}$  vector gives

$$\mathbf{H}^\dagger \mathbf{F}_x = \omega \mathbf{V}^\dagger \mathbf{K}^\circ \mathbf{F}_x = \omega [(\mathbf{K}^\circ \mathbf{F}_x)_\mu - (\mathbf{K}^\circ \mathbf{F}_x)_\nu]. \quad (67)$$

This result suggests that we construct a column vector  $\mathbf{X}^\circ$ , defined to be the following matrix-vector product:

$$\mathbf{X}^\circ \equiv \mathbf{K}^\circ \mathbf{F}_x. \quad (68)$$

The vector dot product in Eq. (66) can be expressed in terms of the difference between two particular elements of this vector,

$$\mathbf{H}^\dagger \mathbf{F}_x = \omega (X_\mu^\circ - X_\nu^\circ). \quad (69)$$

Thus, we find it useful to define a set of new position vectors,  $\mathbf{R}_k^\circ$ , one for each of the  $n$ -electrons,

$$\mathbf{R}_k^\circ = X_k^\circ \mathbf{i} + Y_k^\circ \mathbf{j} + Z_k^\circ \mathbf{k}. \quad (70)$$

The  $x$ -type Cartesian coordinate of  $\mathbf{R}_k^\circ$  is taken from row  $k$  of the  $\mathbf{X}^\circ$  vector. Similarly,  $Y_k^\circ$  and  $Z_k^\circ$  are taken from row  $k$  of the  $\mathbf{K}^\circ \mathbf{F}_y$  and  $\mathbf{K}^\circ \mathbf{F}_z$  vectors, respectively. If all geminal parameters are zero,  $\sigma = \rho = \tau \dots = 0$ , then  $\mathbf{X}^\circ$  reduces to  $\mathbf{X}$  in Eq. (15), and  $\mathbf{R}_k^\circ$  reduces to the Gaussian center of the charge distribution for electron  $k$ , labeled  $pqr\dots$  in Table I. If distinct centers  $p$  and  $q$  are coupled by a Gaussian geminal with

parameter  $\sigma$ , then their  $\mathbf{R}^\circ$  centers are displaced toward one another, the magnitude of the displacement increasing with increasing  $\sigma$ . The  $\mathbf{R}^\circ$  centers are properties of the charge distribution functions and geminals, independent of the Coulomb operator. In fact, they appear in expressions for matrix elements of various other operators as well, See for example, Eqs. (16), (30), and (47). Note that Eq. (47), when expressed in this notation, becomes  $T_{x1} = X_1^\circ - X_A$ , which applies to overlap integrals. Later in this paper, the  $\mathbf{R}^\circ$  centers will reappear in formulas for nuclear attraction integrals. Substituting the above results into Eq. (66) gives the final expression for the  $h$  parameter

$$h = h_x + h_y + h_z = \xi |\mathbf{R}_\mu^\circ - \mathbf{R}_\nu^\circ|^2. \quad (71)$$

Here,  $\mu$  and  $\nu$  label the electrons in the Coulomb operator,  $\xi = \omega/\theta_{\mu\nu}$ , and  $R_{\mu\nu}^2$  denotes the square of the distance between the pair of  $\mathbf{R}^\circ$  centers associated with this pair of electrons. The  $v_x$  parameter is conveniently expressed in terms of the dot-product of vectors  $\mathbf{F}_x$  and  $\mathbf{X}^\circ$ ,

$$\begin{aligned} v_x &= c_x - \mathbf{F}_x^\dagger \mathbf{X}^\circ, \\ v &= v_x + v_y + v_z. \end{aligned} \quad (72)$$

It is useful to introduce  $P_x \equiv G_x/G_x^\circ$ . The value of  $P_x$  depends upon the index vector,  $\Lambda_x$ , and the  $u^2$  variable. Recall that  $t^2$  and  $u^2$  are equivalent variables related by  $t^2 = u^2/(\xi + u^2)$ . It is more convenient to regard  $P_x$  as an explicit function of  $t^2$  rather than of  $u^2$ . So in this notation  $G_x$  becomes

$$G_x(\Lambda_x, u^2) = G_x^\circ(u^2) P_x(\Lambda_x, t^2). \quad (73)$$

The analogue of Eq. (17) is

$$P_x(\mathbf{0}, t^2) = 1, \quad (74)$$

and the analogue of Eq. (29) is

$$\mathbf{P}_x(\Lambda_x^+) = \mathbf{K} \Lambda_x \mathbf{P}_x(\Lambda_x^-) + P_x(\Lambda_x) \mathbf{T}_x. \quad (75)$$

Here,  $\mathbf{P}_x(\Lambda_x^+)$  and  $\mathbf{P}_x(\Lambda_x^-)$  are  $n$ -dimensional vectors of  $P_x$  elements, with one raised or lowered index, respectively, given by Eqs. (27) and (28) with  $P_x$  in place of  $G_x$ . Let  $\ell_x$  denote the sum of  $x$ -type lambda indices,

$$\ell_x = \sum_{k=1}^n \lambda_{xk}. \quad (76)$$

We now proceed to prove that  $P_x(\lambda_x, t^2)$  is a polynomial of degree  $\ell_x$  in the variable  $t^2$ . Proof follows by induction. Equation (74) establishes this polynomial property in the special case  $\ell_x = 0$ . Equation (75) can be manipulated to show that if the polynomial property holds for all  $P_x$  with  $\ell_x \leq \ell^\circ$  then it also holds for  $\ell_x = \ell^\circ + 1$ . First, substitute Eqs. (59) and (64) into (30) to show that  $\mathbf{T}_x$  is a linear combination of three vectors each of which is itself independent of  $t^2$ :

$$\begin{aligned} \mathbf{T}_x &= \mathbf{X}^\circ - \mathbf{X} + t^2 \mathbf{T}_{xh}, \\ \mathbf{T}_{xh} &= \mathbf{K}_h \mathbf{F}_x \\ &= -\left(\frac{\mathbf{H}^\dagger \mathbf{F}_x}{\theta\omega}\right) \mathbf{H} \\ &= -\left(\frac{X_\mu^\circ - X_\nu^\circ}{\theta_{\mu\nu}}\right) \mathbf{H}. \end{aligned} \quad (77)$$

The  $\mathbf{T}_{xh}$  vector is non-vanishing if  $h_x$  is non-zero. Now substitute Eq. (59) and Eq. (77) into Eq. (75) and note that  $\mathbf{P}_x(\Lambda_x^+)$  is given as a sum of four vectors,

$$\begin{aligned} \mathbf{P}_x(\Lambda_x^+) &= \mathbf{K}^\circ \mathbf{L}_x \mathbf{P}_x(\Lambda_x^-) + t^2 \mathbf{K}_h \mathbf{L}_x \mathbf{P}_x(\Lambda_x^-) \\ &+ P_x(\Lambda_x, t^2) (\mathbf{X}^\circ - \mathbf{X}) + t^2 P_x(\Lambda_x, t^2) \mathbf{T}_{xh}. \end{aligned} \quad (78)$$

Let  $\ell^\circ$  be the sum of indices for a particular  $\Lambda_x$  in Eq. (78), and assume that the polynomial property holds for all  $\Lambda_x$  with  $\ell(\Lambda_x) \leq \ell^\circ$ . Then the first term on the right of Eq. (78) is a vector whose elements are polynomials of degree  $\ell^\circ - 1$ , the second and third terms consist of polynomials of degree  $\ell^\circ$ , and the fourth term is a vector of polynomials of degree  $\ell^\circ + 1$ . Thus, we have established that the elements of  $\mathbf{P}_x(\Lambda_x^+)$  are polynomials of degree  $\ell(\Lambda_x) + 1$ . The argument breaks down if  $h_x = 0$ . Further analysis shows that in those special cases when  $h_x$  vanishes,  $P_x(\Lambda_x, t^2)$  is a polynomial of degree zero for all  $\Lambda_x$ .

We conclude that the  $n$ -electron repulsion integral over products of primitive charge distribution functions and geminals reduces to

$$\langle |r_{\mu\nu}^{-1}| \rangle = \frac{2\pi^{(3n-1)/2}}{\omega\sqrt{\theta}} e^{-v} \int_0^1 dt P(t^2) e^{-ht^2}, \quad (79)$$

where  $\omega$  and  $\theta$  are given by Eq. (51),  $h$  by Eq. (63) or Eq. (71),  $v$  by Eq. (62) or Eq. (72), and  $P(t^2)$  is the product of Cartesian factors,

$$P(t^2) = P_x(\Lambda_x, t^2) P_y(\Lambda_y, t^2) P_z(\Lambda_z, t^2), \quad (80)$$

where  $P_x(\Lambda_x, t^2)$  is a polynomial in the variable  $t^2$  of degree  $\ell_x$  evaluated by recursion using Eqs. (74) and (75), and the integral is evaluated by Eq. (6). Elements of the  $\mathbf{T}_x$  vector are given by Eq. (30) or Eq. (77).

The electron repulsion integral is closely related to the overlap integral over the same charge distribution and geminal functions. The resemblance becomes more apparent when the overlap integral is expressed as follows:

$$\langle | \rangle = \left( \frac{\pi^n}{\omega} \right)^{3/2} e^{-v} P(0). \quad (81)$$

The numerical values of  $\omega$  and  $v$  in Eq. (79) are the same as those in Eq. (81). This illustrates the general principle that  $\omega$  and  $v$  are characteristics of the charge distribution and geminal factors in the integrand, independent of the operator. The  $P(0)$  factor in Eq. (81) is the constant term in the polynomial,  $P(t^2)$  in Eq. (79).

## V. TWO-ELECTRON REPULSION INTEGRALS

A diagrammatic representation of an electron repulsion integral over a pair of charge distribution functions and a geminal is shown in Fig. 3,

$$I_2(\Lambda_1, \Lambda_2, \sigma) = \int \cdots \int_{-\infty}^{\infty} d\tau_1 d\tau_2 \chi_p(1) \chi_q(2) \frac{1}{r_{12}} \exp(-\sigma r_{12}^2). \quad (82)$$

Using the methods of Sec. IV to evaluate  $I_2$  shows more strength than the enemy requires, but let us follow through the steps in detail to illustrate the method. Note that the diagram in Fig. 3 resembles that in Fig. 1 but with a dotted line representing Coulombic interaction, in addition to the solid line, representing geminal coupling. By the same token, formulas for  $Q_x$ ,  $\mathbf{M}$ ,  $\det(\mathbf{M})$ ,  $\mathbf{K}$ , and,  $G_x$  resemble the corresponding formulas given for the overlap integral in Sec. III A, but with  $\sigma$  everywhere replaced by  $\sigma + u^2$ . In particular, the inverse of  $\mathbf{M}$  is

$$\mathbf{K} = \frac{1}{\det(\mathbf{M})} \begin{pmatrix} \beta + \sigma + u^2 & \sigma + u^2 \\ \sigma + u^2 & \alpha + \sigma + u^2 \end{pmatrix}. \quad (83)$$

The  $\mathbf{K}^\circ$  matrix is obtained from  $\mathbf{K}$  by setting  $u^2$  to zero. The determinant of the  $\mathbf{M}$  matrix is

$$\det(\mathbf{M}) = \alpha\beta + \sigma(\alpha + \beta) + u^2(\alpha + \beta). \quad (84)$$

Values of the  $a_{ij}$  and  $b_{ij}$  in Eq. (52) can be obtained by inspection of Eq. (83). The parametrization given in Eq. (51) combined with the above result yields

$$\begin{aligned} \omega &= \alpha\beta + \sigma(\alpha + \beta), \\ \theta &= \alpha + \beta, \\ \xi &= \frac{\alpha\beta}{\alpha + \beta} + \sigma. \end{aligned} \quad (85)$$

Elements of the  $\mathbf{K}_h$  matrix are given by Eq. (60),

$$\mathbf{K}_h = \frac{1}{\omega\theta} \begin{pmatrix} -\beta^2 & \alpha\beta \\ \alpha\beta & -\alpha^2 \end{pmatrix}. \quad (86)$$

Equations (62) and (63) give

$$v = \frac{\alpha\beta\sigma}{\omega} R_{pq}^2, \quad (87)$$

$$h = \frac{(\alpha\beta)^2}{\omega\theta} R_{pq}^2. \quad (88)$$

Note that Eq. (87) agrees with Eq. (39).

Substituting the various results above into Eq. (79) yields the following expression for the two-electron repulsion integral,

$$I_2(\Lambda_1, \Lambda_2, \sigma) = \frac{2\pi^{5/2}}{\omega\sqrt{\theta}} \exp\left[\frac{-\alpha\beta\sigma}{\omega} R_{pq}^2\right] \int_0^1 P(t^2) e^{-ht^2} dt. \quad (89)$$

The polynomial factors are generated by recursion using Eqs. (74) and (75), which reduce to a pair of three-term recurrence relations resembling Eq. (36) with  $P_x$  replacing  $G_x$  in those formulas. Using Eq. (30) and the above results for

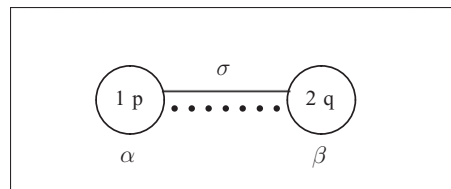


FIG. 3. A diagrammatic representation of a two-electron repulsion integral, where charge distributions are coupled by a Gaussian geminal factor,  $\sigma$ . Charge distributions are represented by circles, the geminal coupling by a solid line and the Coulombic repulsion by a dotted line.

the elements of the  $\mathbf{K}$  matrix yields the two elements of the  $\mathbf{T}_x$  vector,

$$\begin{aligned} \mathbf{T}_{x1} &= \frac{(\beta + \sigma + u^2)}{\det(\mathbf{M})} \alpha \mathbf{X}_p + \frac{(\sigma + u^2)}{\det(\mathbf{M})} \beta \mathbf{X}_q - \mathbf{X}_A, \\ \mathbf{T}_{x2} &= \frac{(\sigma + u^2)}{\det(\mathbf{M})} \alpha X_p + \frac{(\alpha + \sigma + u^2)}{\det(\mathbf{M})} \beta X_q - X_B. \end{aligned} \quad (90)$$

When  $\sigma$  is set to zero,  $I_2$  reduces to the familiar result:

$$I_2(\Lambda_1, \Lambda_2, 0) = \frac{2\pi^{5/2}}{\alpha\beta\sqrt{\alpha+\beta}} \int_0^1 P(t^2) e^{-ht^2} dt, \quad (91)$$

where,

$$h = \frac{\alpha\beta}{\alpha + \beta} R_{pq}^2. \quad (92)$$

## VI. THREE-ELECTRON REPULSION INTEGRALS

A diagrammatic representation of an electron repulsion integral over a product of three charge distribution functions and three geminals is shown in Fig. 4,

$$\begin{aligned} I_3(\Lambda_1, \Lambda_2, \Lambda_3, \sigma, \rho, \tau) &= \int \cdots \int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \chi_p(1) \chi_q(2) \chi_r(3) \\ &\times \frac{1}{r_{\mu\nu}} \exp(-\sigma r_{12}^2 - \rho r_{23}^2 - \tau r_{13}^2). \end{aligned} \quad (93)$$

For the case  $r_{\mu\nu}^{-1} = r_{12}^{-1}$  the  $\mathbf{M}$  matrix is

$$\mathbf{M}(1, 2) = \begin{pmatrix} \alpha + \sigma + u^2 + \tau & -\sigma - u^2 & -\tau \\ -\sigma - u^2 & \beta + \sigma + u^2 + \rho & -\rho \\ -\tau & -\rho & \gamma + \rho + \tau \end{pmatrix}. \quad (94)$$

The parametrization of the determinant given by Eq. (51) yields

$$\begin{aligned} \omega &= \alpha\beta\gamma + \alpha\beta(\rho + \tau) + \beta\gamma(\tau + \sigma) + \alpha\gamma(\rho + \sigma) \\ &+ (\alpha + \beta + \gamma)(\sigma\rho + \rho\tau + \tau\sigma) \end{aligned} \quad (95)$$

and  $\theta = \theta_{12}$ . Similarly, one obtains  $\theta_{\mu\nu}$  for each of the three possible Coulombic operators,

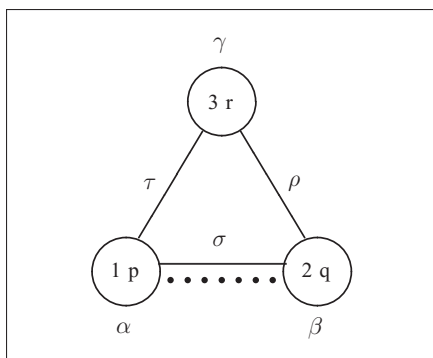


FIG. 4. A diagrammatic representation of the most general three-electron repulsion integral. Charge distributions are represented by circles, the geminal couplings by a solid lines, and the Coulombic repulsion by a dotted line.

$$\begin{aligned} \theta_{12} &= (\alpha + \beta + \gamma)(\rho + \tau) + (\alpha + \beta)\gamma, \\ \theta_{13} &= (\alpha + \beta + \gamma)(\sigma + \rho) + (\gamma + \alpha)\beta, \\ \theta_{23} &= (\alpha + \beta + \gamma)(\tau + \sigma) + (\beta + \gamma)\alpha. \end{aligned} \quad (96)$$

Elements of the inverse matrix,  $\mathbf{K}$ , are given by Eq. (52) where  $\omega$  and  $\theta$  are given above and the  $a_{ij}$  and  $b_{ij}$  values are given in Table III. The  $\mathbf{R}_k^\circ$  centers are given by Eq. (68),

$$\begin{aligned} \mathbf{R}_1^\circ &= \frac{\alpha a_{11}}{\omega} \mathbf{R}_p + \frac{\beta a_{12}}{\omega} \mathbf{R}_q + \frac{\gamma a_{13}}{\omega} \mathbf{R}_r, \\ \mathbf{R}_2^\circ &= \frac{\alpha a_{21}}{\omega} \mathbf{R}_p + \frac{\beta a_{22}}{\omega} \mathbf{R}_q + \frac{\gamma a_{23}}{\omega} \mathbf{R}_r, \\ \mathbf{R}_3^\circ &= \frac{\alpha a_{31}}{\omega} \mathbf{R}_p + \frac{\beta a_{32}}{\omega} \mathbf{R}_q + \frac{\gamma a_{33}}{\omega} \mathbf{R}_r. \end{aligned} \quad (97)$$

Note that the coefficients of the  $\mathbf{R}$  vectors given above obey the sum rules stated in Eq. (54). The  $a_{ij}$  and  $b_{ij}$  in Table III are also used to generate the  $\mathbf{K}$  matrix for use in the recursion relations in Eqs. (74) and (75).

Making the appropriate substitutions in Eq. (62) and performing some lengthy algebraic manipulations yields the  $v$  parameter in Eq. (79),

$$\begin{aligned} v &= \frac{\alpha\gamma [\tau(\beta + \sigma + \rho) + \sigma\rho]}{\omega} R_{pr}^2 \\ &+ \frac{\beta\gamma [\rho(\alpha + \sigma + \tau) + \sigma\tau]}{\omega} R_{qr}^2 \\ &+ \frac{\alpha\beta[\sigma(\gamma + \rho + \tau) + \rho\tau]}{\omega} R_{pq}^2. \end{aligned} \quad (98)$$

Similarly the  $h$  parameter can be obtained from Eq. (97) and Eq. (71).

Each of these integrals is invariant with respect to permuting electron labels since this is tantamount to simply renaming the integration variables. This permutation symmetry can be expressed in terms of the following parameter array. The first column contains an electron label; other entries in the row are labels of parameters associated with that electron,

$$\begin{pmatrix} 1 & A & p & \alpha & \rho \\ 2 & B & q & \beta & \tau \\ 3 & C & r & \gamma & \sigma \end{pmatrix}. \quad (99)$$

The expressions for the  $\omega$  and  $v$  parameters are invariant with respect to all six row permutations of this parameter array. Many of the rather complicated expressions above simplify when one or more geminal parameters are zero. We report simplified formulas for two special cases designated *Type I* or *Type II*.

### A. Three-electron repulsion: Type I

In the *Type I* integral, electron pairs 2,3 and 1,3 are geminal-coupled and the 1,2 pair interact through the Coulomb operator. This is commonly called the three-electron cyclic integral,

$$\begin{aligned} I_3(\Lambda_1, \Lambda_2, \Lambda_3, \rho, \tau) &= \int \cdots \int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \chi_p(1) \chi_q(2) \chi_r(3) \\ &\times \frac{1}{r_{12}} \exp(-\rho r_{23}^2 - \tau r_{13}^2). \end{aligned} \quad (100)$$



TABLE III. **K** matrix elements for the three-electron integral in Eq. (93).

$i j$	$a_{ij}$	$b_{ij}$ for designated operator		
		$r_{12}^{-1}$	$r_{13}^{-1}$	$r_{23}^{-1}$
1 1	$(\gamma + \tau)(\beta + \sigma) + \rho(\gamma + \tau + \beta + \sigma)$	$\gamma + \rho + \tau$	$\beta + \sigma + \rho$	$\beta + \gamma + \sigma + \tau$
2 2	$(\alpha + \sigma)(\gamma + \rho) + \tau(\alpha + \sigma + \gamma + \rho)$	$\gamma + \rho + \tau$	$\alpha + \gamma + \sigma + \rho$	$\alpha + \sigma + \tau$
3 3	$(\beta + \rho)(\alpha + \tau) + \sigma(\beta + \rho + \alpha + \tau)$	$\alpha + \beta + \rho + \tau$	$\beta + \sigma + \rho$	$\alpha + \sigma + \tau$
2 1	$\sigma(\gamma + \rho + \tau) + \rho\tau$	$\gamma + \rho + \tau$	$\sigma + \rho$	$\sigma + \tau$
3 1	$\tau(\beta + \sigma + \rho) + \sigma\rho$	$\rho + \tau$	$\beta + \sigma + \rho$	$\sigma + \tau$
3 2	$\rho(\alpha + \sigma + \tau) + \sigma\tau$	$\rho + \tau$	$\sigma + \rho$	$\alpha + \sigma + \tau$

Setting  $\sigma$  to zero in Eqs. (93)–(97) gives

$$\begin{aligned}\omega &= \alpha\beta(\gamma + \rho + \tau) + \gamma(\alpha\rho + \beta\tau) + (\alpha + \beta + \gamma)\rho\tau, \\ \theta &= (\alpha + \beta)(\gamma + \rho + \tau) + \gamma(\rho + \tau).\end{aligned}\quad (101)$$

The expression for the  $\nu$  parameter simplifies somewhat to

$$\nu = \frac{\alpha\gamma\tau(\beta + \rho)}{\omega} R_{pr}^2 + \frac{\beta\gamma\rho(\alpha + \tau)}{\omega} R_{qr}^2 + \frac{\alpha\beta\rho\tau}{\omega} R_{pq}^2. \quad (102)$$

Elements of the **K** matrix are given by Eq. (52) with the  $a_{ij}$  and  $b_{ij}$  given in Table III with  $\sigma$  set to zero. The argument to the Rys Polynomials,  $h$ , is given by (71) with  $\mathbf{R}_1^\circ$  and  $\mathbf{R}_2^\circ$  given by Eq. (97). The elements of the **T** vector required for the recursion relations are given by Eq. (30):

$$\begin{aligned}\mathbf{T}_{x1} &= K_{11}\alpha X_p + K_{12}\beta X_q + K_{13}\gamma X_r - X_A, \\ \mathbf{T}_{x2} &= K_{21}\alpha X_p + K_{22}\beta X_q + K_{23}\gamma X_r - X_B, \\ \mathbf{T}_{x3} &= K_{31}\alpha X_p + K_{32}\beta X_q + K_{33}\gamma X_r - X_C.\end{aligned}\quad (103)$$

### B. Three-electron repulsion: Type II

Electron pair 2,3 is geminal-coupled and the 1,2 pair interact through the Coulomb operator in the *Type II* integral,

$$\begin{aligned}I_3(\Lambda_1, \Lambda_2, \Lambda_3, \rho) \\ = \int \cdots \int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \chi_p(1) \chi_q(2) \chi_r(3) \frac{1}{r_{12}} \exp(-\rho r_{23}^2).\end{aligned}\quad (104)$$

The *Type II* integral can be considered to be the  $\tau = 0$  special case of *Type I*. Setting  $\sigma = \tau = 0$  in Eqs. (93)–(97) gives

$$\begin{aligned}\omega &= \alpha[\beta(\gamma + \rho) + \gamma\rho], \\ \theta &= (\alpha + \beta)(\gamma + \rho) + \gamma\rho, \\ \nu &= \frac{\beta\gamma\rho}{\beta(\gamma + \rho) + \gamma\rho} R_{qr}^2.\end{aligned}\quad (105)$$

Elements of the **K** matrix are given by Eq. (52) with the  $a_{ij}$  and  $b_{ij}$  given in Table III with  $\sigma$  and  $\tau$  set to zero. The argument to the Rys Polynomials,  $h$ , is given by Eq. (71) with  $\mathbf{R}_1^\circ$  and  $\mathbf{R}_2^\circ$  given by Eq. (97),

$$h = \frac{\omega}{\theta} |\mathbf{R}_1^\circ - \mathbf{R}_2^\circ|^2, \quad (106)$$

where

$$\begin{aligned}\mathbf{R}_1^\circ &= \mathbf{R}_p, \\ \mathbf{R}_2^\circ &= \frac{\alpha\beta(\gamma + \rho)}{\omega} \mathbf{R}_q + \frac{\alpha\gamma\rho}{\omega} \mathbf{R}_r.\end{aligned}\quad (107)$$

## VII. FOUR-ELECTRON REPULSION INTEGRALS

In this section, we consider four-electron integrals containing two geminal couplings and one Coulombic coupling. The three cases, designated *Type I*, *II*, *III*, are shown in Figs. 5–7. All are evaluated using Eq. (79) with  $n = 4$ , and all become identical when  $\rho$  is set to zero. In that limiting case the four-electron integral is equal to the product of a one-electron overlap integral on center  $s$  and a type II three-electron repulsion integral with geminal coupling parameter  $\sigma$ . This is clearly evident in all of the following expressions below:

*Type I*

$$\begin{aligned}I_4(\lambda_1, \lambda_2, \lambda_3, \lambda_4, \sigma, \rho) \\ = \int_{-\infty}^{+\infty} d\tau_1 d\tau_2 d\tau_3 d\tau_4 \chi(1) \chi(2) \chi(3) \chi(4) \\ \times \frac{1}{r_{12}} \exp[-\sigma r_{23}^2 - \rho r_{14}^2],\end{aligned}\quad (108)$$

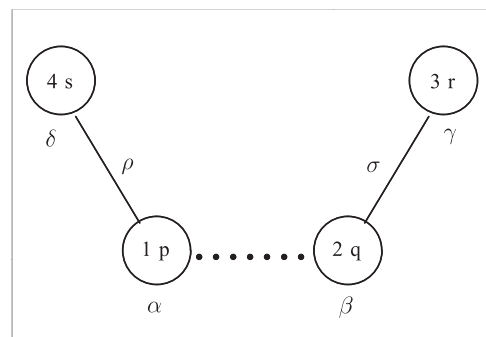


FIG. 5. A diagrammatic representation of the *Type I* four-electron repulsion integral. Charge distributions are represented by circles, the geminal couplings by a solid lines, and the Coulombic repulsion by a dotted line.

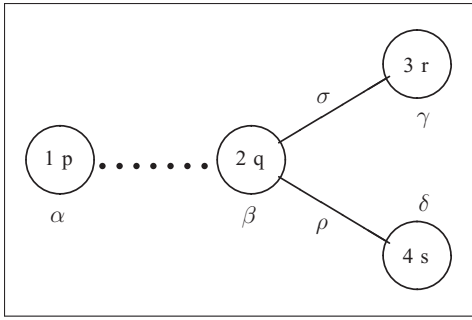


FIG. 6. A diagrammatic representation of the *Type II* four-electron repulsion integral. Charge distributions are represented by circles, the geminal couplings by a solid lines, and the Coulombic repulsion by a dotted line.

### Type II

$$I_4(\lambda_1, \lambda_2, \lambda_3, \lambda_4, \sigma, \rho) = \int_{-\infty}^{+\infty} d\tau_1 d\tau_2 d\tau_3 d\tau_4 \chi(1) \chi(2) \chi(3) \chi(4) \times \frac{1}{r_{12}} \exp[-\sigma r_{23}^2 - \rho r_{24}^2], \quad (109)$$

### Type III

$$I_4(\lambda_1, \lambda_2, \lambda_3, \lambda_4, \sigma, \rho) = \int_{-\infty}^{+\infty} d\tau_1 d\tau_2 d\tau_3 d\tau_4 \chi(1) \chi(2) \chi(3) \chi(4) \times \frac{1}{r_{12}} \exp[-\sigma r_{23}^2 - \rho r_{34}^2]. \quad (110)$$

The  $\mathbf{M}$  matrices are,

#### Type I

$$\mathbf{M} = \begin{pmatrix} \alpha + u^2 + \rho & -u^2 & 0 & -\rho \\ -u^2 & \beta + u^2 + \sigma & -\sigma & 0 \\ 0 & -\sigma & \gamma + \sigma & 0 \\ -\rho & 0 & 0 & \delta + \rho \end{pmatrix}, \quad (111)$$

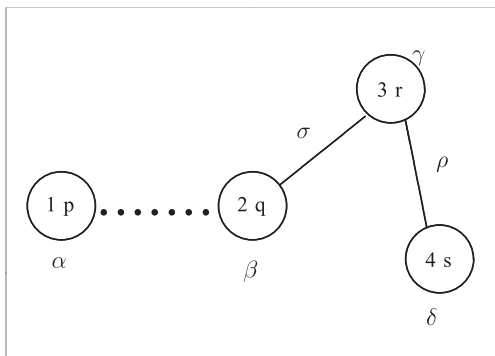


FIG. 7. A diagrammatic representation of the *Type III* four-electron repulsion integral. Charge distributions are represented by circles, the geminal couplings by a solid lines, and the Coulombic repulsion by a dotted line.

TABLE IV. Reduced variables for four-particle  $\mathbf{K}$  matrices.

	Type I	Type II	Type III
$\bar{\alpha}$	$\alpha + \delta \bar{\rho}$	$\alpha$	$\alpha$
$\bar{\beta}$	$\beta + \gamma \bar{\sigma}$	$\beta + \gamma \bar{\sigma} + \delta \bar{\rho}$	$\beta + \gamma \bar{\sigma} + \delta \bar{\sigma} \bar{\rho}$
$\bar{\sigma}$	$\frac{\sigma}{\gamma + \sigma}$	$\frac{\sigma}{\gamma + \sigma}$	$\frac{\sigma}{\gamma + \sigma + \delta \bar{\rho}}$
$\bar{\rho}$	$\frac{\rho}{\delta + \rho}$	$\frac{\rho}{\delta + \rho}$	$\frac{\rho}{\delta + \rho}$

### Type II

$$\mathbf{M} = \begin{pmatrix} \alpha + u^2 & -u^2 & 0 & 0 \\ -u^2 & \beta + u^2 + \sigma + \rho & -\sigma & -\rho \\ 0 & -\sigma & \gamma + \sigma & 0 \\ 0 & -\rho & 0 & \delta + \rho \end{pmatrix}, \quad (112)$$

### Type III

$$\mathbf{M} = \begin{pmatrix} \alpha + u^2 & -u^2 & 0 & 0 \\ -u^2 & \beta + u^2 + \sigma & -\sigma & 0 \\ 0 & -\sigma & \gamma + \sigma + \rho & -\rho \\ 0 & 0 & -\rho & \delta + \rho \end{pmatrix}. \quad (113)$$

It is convenient to introduce the reduced variables defined in Table IV. In all three cases  $\bar{\alpha}$  and  $\bar{\beta}$  reduce to  $\alpha$  and  $\beta$ , respectively, in the limit of zero  $\sigma$  and  $\rho$ .

As usual, the determinant of the  $\mathbf{M}$  matrix is expressed as

$$\det(\mathbf{M}) = \omega + u^2 \theta, \quad (114)$$

### Types I and II

$$\begin{aligned} \omega &= (\delta + \rho)(\gamma + \sigma) \bar{\alpha} \bar{\beta}, \\ \theta &= (\delta + \rho)(\gamma + \sigma) (\bar{\alpha} + \bar{\beta}), \end{aligned} \quad (115)$$

### Type III

$$\begin{aligned} \omega &= (\delta + \rho)(\gamma + \sigma + \delta \bar{\rho}) \bar{\alpha} \bar{\beta}, \\ \theta &= (\delta + \rho)(\gamma + \sigma + \delta \bar{\rho}) (\bar{\alpha} + \bar{\beta}). \end{aligned} \quad (116)$$

In all three cases the  $\xi$  parameter in Eq. (71) is

$$\xi = \frac{\omega}{\theta} = \frac{\bar{\alpha} \bar{\beta}}{\bar{\alpha} + \bar{\beta}}. \quad (117)$$

Elements of the  $\mathbf{K}$  matrices are given in Table V. Setting  $u^2 = 0$  yields matrix elements of  $\mathbf{K}^\circ$ . Note that common factors in the numerators and denominators of Eq. (52) have been removed. The  $h$  parameter in Eq. (79) is given by Eq. (71) with  $\mathbf{R}_1^\circ$  and  $\mathbf{R}_2^\circ$  centers given by Eq. (68) and Eq. (70). Explicit expressions are reported below as

#### Type I

$$\begin{aligned} \mathbf{R}_1^\circ &= \frac{\alpha}{\bar{\alpha}} \mathbf{R}_p + \frac{\bar{\rho} \delta}{\bar{\alpha}} \mathbf{R}_s, \\ \mathbf{R}_2^\circ &= \frac{\beta}{\bar{\beta}} \mathbf{R}_q + \frac{\bar{\sigma} \gamma}{\bar{\beta}} \mathbf{R}_r, \end{aligned} \quad (118)$$

TABLE V. Elements of four-particle  $\mathbf{K}$  and  $\mathbf{K}^\circ$  matrices.

	Type I	Type II	Type III
$K_{11}$	$\frac{\bar{\beta} + u^2}{(\bar{\alpha} + \bar{\beta})u^2 + \bar{\alpha}\bar{\beta}}$	$\frac{\bar{\beta} + u^2}{(\bar{\alpha} + \bar{\beta})u^2 + \bar{\alpha}\bar{\beta}}$	$\frac{\bar{\beta} + u^2}{(\bar{\alpha} + \bar{\beta})u^2 + \bar{\alpha}\bar{\beta}}$
$K_{21}$	$\frac{u^2}{(\bar{\alpha} + \bar{\beta})u^2 + \bar{\alpha}\bar{\beta}}$	$\frac{u^2}{(\bar{\alpha} + \bar{\beta})u^2 + \bar{\alpha}\bar{\beta}}$	$\frac{u^2}{(\bar{\alpha} + \bar{\beta})u^2 + \bar{\alpha}\bar{\beta}}$
$K_{22}$	$\frac{\bar{\alpha} + u^2}{(\bar{\alpha} + \bar{\beta})u^2 + \bar{\alpha}\bar{\beta}}$	$\frac{\bar{\alpha} + u^2}{(\bar{\alpha} + \bar{\beta})u^2 + \bar{\alpha}\bar{\beta}}$	$\frac{\bar{\alpha} + u^2}{(\bar{\alpha} + \bar{\beta})u^2 + \bar{\alpha}\bar{\beta}}$
$K_{31}$	$\bar{\sigma} K_{21}$	$\bar{\sigma} K_{21}$	$\bar{\sigma} K_{21}$
$K_{32}$	$\bar{\sigma} K_{22}$	$\bar{\sigma} K_{22}$	$\bar{\sigma} K_{22}$
$K_{33}$	$\bar{\sigma} K_{32} + \frac{1}{\gamma + \sigma}$	$\bar{\sigma} K_{32} + \frac{1}{\gamma + \sigma}$	$\bar{\sigma} K_{32} + \frac{1}{\gamma + \sigma + \delta \bar{\rho}}$
$K_{41}$	$\bar{\rho} K_{11}$	$\bar{\rho} K_{21}$	$\bar{\rho} K_{31}$
$K_{42}$	$\bar{\rho} K_{21}$	$\bar{\rho} K_{22}$	$\bar{\rho} K_{32}$
$K_{43}$	$\bar{\rho} K_{31}$	$\bar{\rho} K_{32}$	$\bar{\rho} K_{33}$
$K_{44}$	$\bar{\rho} K_{41} + \frac{1}{\delta + \rho}$	$\bar{\rho} K_{42} + \frac{1}{\delta + \rho}$	$\bar{\rho} K_{43} + \frac{1}{\delta + \rho}$

Type II

$$\begin{aligned} \mathbf{R}_1^\circ &= \mathbf{R}_p, \\ \mathbf{R}_2^\circ &= \frac{\beta}{\bar{\beta}} \mathbf{R}_q + \frac{\bar{\sigma}\gamma}{\bar{\beta}} \mathbf{R}_r + \frac{\bar{\rho}\delta}{\bar{\beta}} \mathbf{R}_s, \end{aligned} \quad (119)$$

Type III

$$\begin{aligned} \mathbf{R}_1^\circ &= \mathbf{R}_p, \\ \mathbf{R}_2^\circ &= \frac{\beta}{\bar{\beta}} \mathbf{R}_q + \frac{\bar{\sigma}\gamma}{\bar{\beta}} \mathbf{R}_r + \frac{\bar{\sigma}\bar{\rho}\delta}{\bar{\beta}} \mathbf{R}_s. \end{aligned} \quad (120)$$

The  $\nu$  parameter in Eq. (79), computed using Eq. (62), is reported below. Recall that  $\nu$  depends on the geminal couplings but not on the Coulombic coupling, thus  $\nu$  is the same as that for the corresponding overlap integral. In the type I integral  $\nu$  is the sum of two terms each resembling Eq. (39). For the type II and III integrals  $\nu$  resembles that in Eq. (49) with centers labeled as in Table I,

Type I

$$\nu = \frac{\alpha \delta \bar{\rho}}{\bar{\alpha}} R_{ps}^2 + \frac{\beta \gamma \bar{\sigma}}{\bar{\beta}} R_{qr}^2, \quad (121)$$

Type II

$$\nu = \frac{\beta \gamma \bar{\sigma}}{\bar{\beta}} R_{qr}^2 + \frac{\beta \delta \bar{\rho}}{\bar{\beta}} R_{qs}^2 + \frac{\gamma \delta \bar{\sigma} \bar{\rho}}{\bar{\beta}} R_{rs}^2, \quad (122)$$

Type III

$$\nu = \frac{\beta \gamma \sigma'}{\bar{\gamma}} R_{qr}^2 + \frac{\delta \gamma \bar{\rho}}{\bar{\gamma}} R_{rs}^2 + \frac{\beta \delta \sigma' \bar{\rho}}{\bar{\gamma}} R_{qs}^2, \quad (123)$$

where

$$\sigma' = \frac{\sigma}{\beta + \sigma}, \quad (124)$$

and

$$\bar{\gamma} = \gamma + \beta \sigma' + \delta \bar{\rho}. \quad (125)$$

Here,  $\bar{\gamma}$  and  $\sigma'$  for type III are analogous to  $\bar{\beta}$  and  $\bar{\sigma}$  for type II in the sense that center  $r$  with parameter  $\gamma$  in Fig. 7 is analogous to center  $q$  with parameter  $\beta$  in Fig. 6.

Angular momenta on centers  $A$ ,  $B$ ,  $C$ , or  $D$  are built, as usual, using Eqs. (74) and Eq. (75). The elements of the  $\mathbf{T}$  vector are given by Eq. (30). For example, the recurrence relation for building up angular momentum on center  $A$  is

$$\begin{aligned} P_x(\lambda_1 + 1, \lambda_2, \lambda_3, \lambda_4) &= (\lambda_1/2)K_{11} P(\lambda_1 - 1, \lambda_2, \lambda_3, \lambda_4) \\ &+ (\lambda_2/2)K_{12} P(\lambda_1, \lambda_2 - 1, \lambda_3, \lambda_4) \\ &+ (\lambda_3/2)K_{13} P(\lambda_1, \lambda_2, \lambda_3 - 1, \lambda_4) \\ &+ (\lambda_4/2)K_{14} P(\lambda_1, \lambda_2, \lambda_3, \lambda_4 - 1) \\ &+ T_{x1} P(\lambda_1, \lambda_2, \lambda_3, \lambda_4), \end{aligned} \quad (126)$$

where

$$T_{x1} = K_{11} \alpha X_p + K_{12} \beta X_q + K_{13} \gamma X_r + K_{14} \delta X_s - X_A. \quad (127)$$

## VIII. NUCLEAR ATTRACTION INTEGRALS

An  $n$ -electron nuclear attraction integral has the form of the corresponding  $n$ -electron repulsion integral and can be evaluated using very nearly the same computer code. The integral formula can be easily derived making use of the previously derived expression for the appropriate  $(n+1)$ -electron repulsion integral. Consider the integral for electron  $\mu$  ( $\mu = 1 \dots n$ ) interacting with electron  $n+1$ , where electron  $n+1$  is in a spherical Gaussian charge distribution on center  $\mathbf{R}_N$  with Gaussian exponential parameter  $\gamma$ . The spherical Gaussian reduces to a point charge in the  $\gamma \rightarrow \infty$  limit. Similarly, one obtains the integral for electron  $\mu$  interacting with a point dipole, or higher multipole moment, by building up angular momentum on center  $\mathbf{R}_N$  using the usual recurrence relations. We illustrate the method by deriving the two-electron nuclear attraction integral from the three-electron repulsion integral discussed in Sec. VI.

Consider the three-electron repulsion integral described in Fig. 4, but with the dotted line, representing Coulombic interaction, connecting electrons one and three rather than one and two. Set geminal coupling parameters  $\rho$  and  $\tau$  to zero and build up angular momentum on centers  $p$  and  $q$ , but not on center  $r$ . The resulting integral, described in Fig. 8, is that

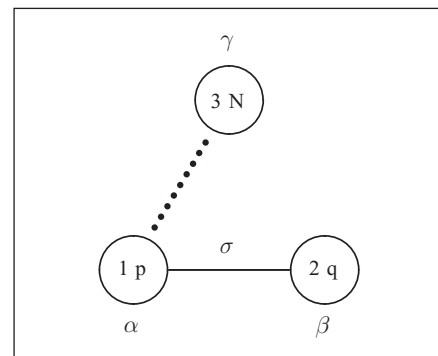


FIG. 8. A diagrammatic representation of a three-electron repulsion integral with one geminal coupling, which reduces to the two-electron nuclear attraction integral with  $\mu = 1$  in the  $\gamma \rightarrow \infty$  limit.

for geminal-coupled charge distributions on centers  $p$  and  $q$  interacting with a spherical Gaussian charge distribution on center  $r$ . This center is relabeled center  $N$  in Fig. 8 in anticipation of  $\mathbf{R}_r$  becoming the nuclear position  $\mathbf{R}_N$ . The three-electron integral Eq. (93) is rescaled by a factor of  $(\gamma/\pi)^{3/2}$  corresponding to a spherical Gaussian charge distribution at center  $\mathbf{R}_N$  with unit charge. The rescaled three-electron repulsion integral becomes the two-electron nuclear attraction integral in the  $\gamma \rightarrow \infty$  limit,

$$\langle |r_{\mu N}^{-1}| \rangle = \lim_{\gamma \rightarrow \infty} \left( \frac{\gamma}{\pi} \right)^{3/2} I_3(\mathbf{A}_1, \mathbf{A}_2, \mathbf{0}, \sigma, 0, 0). \quad (128)$$

The analysis below shows that this reduces to

$$\langle |r_{\mu N}^{-1}| \rangle = \frac{2\pi^{5/2}}{\omega\sqrt{\theta_\mu}} e^{-v} \int_0^1 dt P(t) e^{-ht^2}, \quad (129)$$

with parameters

$$\begin{aligned} \omega &= \alpha\beta + \sigma(\alpha + \beta), \\ \theta_1 &= \beta + \sigma, \\ \theta_2 &= \alpha + \sigma, \\ v &= \frac{\alpha\beta\sigma}{\omega} R_{pq}^2, \\ h &= \frac{\omega}{\theta_\mu} |\mathbf{R}_\mu^\circ - \mathbf{R}_N|^2, \end{aligned} \quad (130)$$

and the following  $\mathbf{R}_\mu^\circ$  position vectors:

$$\begin{aligned} \mathbf{R}_1^\circ &= \frac{\alpha(\beta + \sigma)}{\omega} \mathbf{R}_p + \frac{\beta\sigma}{\omega} \mathbf{R}_q, \\ \mathbf{R}_2^\circ &= \frac{\alpha\sigma}{\omega} \mathbf{R}_p + \frac{\beta(\alpha + \sigma)}{\omega} \mathbf{R}_q. \end{aligned} \quad (131)$$

The  $\mathbf{M}$  matrix for the three-electron repulsion integral with  $\mu = 1$  described in Fig. 8 is

$$\mathbf{M} = \begin{pmatrix} \alpha + \sigma + u^2 & -\sigma & -u^2 \\ -\sigma & \beta + \sigma & 0 \\ -u^2 & 0 & \gamma + u^2 \end{pmatrix}. \quad (132)$$

The determinant is

$$\det \mathbf{M} = \gamma(\omega + \theta_1 u^2) + \omega u^2. \quad (133)$$

The inverse matrix is

$$\mathbf{K} = \frac{1}{\det(\mathbf{M})} \begin{pmatrix} \theta_1(\gamma + u^2) & \sigma(\gamma + u^2) & \theta_1 u^2 \\ \sigma(\gamma + u^2) & (\gamma + u^2)\theta_2 + \gamma u^2 & \sigma u^2 \\ \theta_1 u^2 & \sigma u^2 & \omega + \theta_1 u^2 \end{pmatrix}. \quad (134)$$

In the  $\gamma \rightarrow \infty$  limit  $\mathbf{K}$  reduces to a two-by-two matrix,

$$\mathbf{K} = \frac{1}{(\omega + \theta_1 u^2)} \begin{pmatrix} \theta_1 & \sigma \\ \sigma & \theta_2 + u^2 \end{pmatrix}, \quad \text{when } \mu = 1, \gamma = \infty. \quad (135)$$

This is the appropriate  $\mathbf{K}$  matrix for generating  $P_x$  using Eqs. (74) and (75) and Eq. (37), or alternatively, for generating the  $\mathbf{G}_x$  elements using Eq. (29) and Eq. (30). Similarly, when electron 2 interacts with the nuclear charge the appropriate  $\mathbf{K}$

matrix is

$$\mathbf{K} = \frac{1}{(\omega + \theta_2 u^2)} \begin{pmatrix} \theta_1 + u^2 & \sigma \\ \sigma & \theta_2 \end{pmatrix}, \quad \text{when } \mu = 2, \gamma = \infty. \quad (136)$$

Let  $\bar{\omega}$  and  $\bar{\theta}$  denote the parameters in Sec. VI to distinguish them from  $\omega$  and  $\theta$  in Eq. (130). Setting  $\tau = \rho = 0$  in Eq. (95) and Eq. (96) gives

$$\bar{\omega} = \gamma\omega, \quad (137)$$

$$\bar{\theta} = \gamma\theta_\mu + \omega, \quad (138)$$

in agreement with Eq. (51) and Eq. (133). In the limit  $\gamma \rightarrow \infty$  the ratio,  $\xi = \bar{\omega}/\bar{\theta}$  becomes

$$\lim_{\gamma \rightarrow \infty} \xi = \frac{\omega}{\theta_\mu}. \quad (139)$$

The  $\mathbf{R}^\circ$  centers in Eq. (97) reduce to those in Eq. (131), and the first factor in Eq. (79) multiplied by the scale factor in Eq. (128) becomes

$$\lim_{\gamma \rightarrow \infty} \left( \frac{\gamma}{\pi} \right)^{3/2} \frac{2\pi^4}{\bar{\omega}\sqrt{\bar{\theta}}} = \frac{2\pi^{5/2}}{\omega\sqrt{\theta_\mu}}, \quad (140)$$

in agreement with Eq. (129). Substituting Eq. (135) into Eq. (36) and Eq. (37) yields the requisite recursion formulas. For example the elements for the  $\mathbf{T}_x$  vector become

$$\begin{aligned} \mathbf{T}_{x1} &= \frac{1}{(\omega + \theta_1 u^2)} (\theta_1 \alpha X_p + \sigma \beta X_q) - X_A, \\ \mathbf{T}_{x2} &= \frac{1}{(\omega + \theta_1 u^2)} (\sigma \alpha X_p + (\theta_2 + u^2) \beta X_q) - X_B, \end{aligned} \quad (141)$$

when  $\mu = 1$ .

The general  $n$ -electron nuclear attraction integral is

$$\langle |r_{\mu N}^{-1}| \rangle = \frac{2\pi^{(3n-1)/2}}{\omega\sqrt{\theta_\mu}} e^{-v} \int_0^1 dt P(t^2) e^{-ht^2}, \quad (142)$$

where  $\omega$  and  $v$  have the same values as for the corresponding  $n$ -electron overlap integral, and  $\theta_\mu$  and  $h$  depend upon  $\mu$ , i.e., depend upon which of the  $n$  electrons interacts with the nuclear charge. Note that  $h$  is the only parameter that depends explicitly upon the nuclear position, but the relevant values of  $u^2$  (corresponding to  $t_\alpha$  in Eq. (6)) in the  $\mathbf{K}$  matrix are functions of  $h$ , and thus implicitly dependent on  $\mathbf{R}_N$ . Finally, we note that in the limit of  $\sigma$  going to zero this integral reduces to the well known one-electron integral once the charge distribution for electron two is scaled appropriately.

## IX. COMPUTATIONAL DISCUSSION

While the exposition in Secs. V–VIII offers all of the components necessary for the evaluation of each of the respective integrals, it is by no means complete. Several key ingredients are missing. First of all our development is based on charge distributions, and not on orbitals. All of our final expressions need to be modified by the inclusion of the  $\mathbf{K}_{ab}$  factors present in Eq. (4). We have also postponed the inclusion of the horizontal recursions required to transform integrals based on charge distributions, to those based on atom centered orbitals. Lastly, the evaluation of many-electron integrals over basis functions of arbitrary angular momentum



requires us to comment on a compact and efficient evaluation of the Rys roots and weights for a vector of arguments.

### A. Rys roots and weights

The original implementation of Rys polynomials<sup>48</sup> was only focused on the evaluation of one and two-electron integrals. For any  $n$ -electron integral, composed of orbitals of angular momentum  $l$  the number of Rys roots and weights required is  $nl + 1$ . For two electron integrals, the formula becomes  $2l + 1$ , and for three electron integrals it becomes  $3l + 1$ . In order to avoid the repetitive computation of the higher order roots and weights for large numbers of arguments, we have adopted a very efficient method that consists of the following components. Using previously developed routines,<sup>47</sup> we have evaluated the roots and weights, (in quadruple precision) for arguments ranging from less than zero, up to approximately 100. We have done this for Rys polynomials ranging from one up to seventeen. This raw data allows anyone to evaluate two-electron integrals with orbitals of angular momentum up to an  $l$  value of eight, three-electron integrals with orbitals up to an  $l$  value of five, and four-electron integrals with orbitals of  $l$  value of four. The accuracy of this raw data was checked using the formulas in the original paper<sup>47</sup> and was found to be accurate to twenty significant figures for the lower roots while the values of the higher roots were found to be consistent up to 14 significant figures for the highest Rys polynomials.

Our implementation reads these tables at the beginning of a calculation and pre-computes a polynomial expansion, in terms of finite differences, for either a three or four point interpolation procedure. The procedure we have adopted is a numerical interpolation found in standard texts such as Abramowitz and Stegun<sup>60</sup> and generally referred to as the Everett formula. Asymptotically, for large values of the argument Rys polynomials behave as scaled Hermite polynomials.<sup>47</sup> Using the MAPLE program,<sup>59</sup> we have computed asymptotic formulas for the roots and weights of Rys polynomials through degree seventeen.

Given an input vector of arguments, our integral code computes the roots and weights using these standard interpolation formulas. The computational requirement here is very modest. Only five floating point operations per root are required for the three point formula. Alternatively, eight floating point operations are required for the four point formula.

Large values of the arguments require only a single multiplication for each weight, and a floating point division and subtraction for each root. Our implementation is very efficient and in contrast to the implementation done in a previous generation of computers does require some space for the tabulated finite difference expansions. Modern computers, however, have much more memory than was available to scientists forty years ago.

### B. Outline of three-electron evaluation

For any of the integral classes considered we view the evaluation of these integrals as driven by loops over charge

distributions. We provide below a brief outline of our view for the implementation focused on three-electron integrals. We consider it convenient to collect basis functions into what we call groups. This follows the development of ANO's by Almløf and Taylor in their development of atomic natural orbitals.<sup>61,62</sup> We define a group to consist of a set of primitives with a common angular momentum, and a common center. The product of two such groups forms a vector of pair charge distributions. For each of these charge distributions we compute the pair quantities given by Eq. (4).

The pair quantities are ultimately combined into sets of sextet quantities that are used for the ultimate computation of blocks of required integrals. Once these quantities are combined with the expansion of the set of geminal functions, we are able to compute the arguments to the Rys polynomials. Computation of the Rys roots and weights is accomplished by the procedure outlined above.

We next compute the elements of the  $\mathbf{K}$  matrices and the  $\mathbf{T}_x, \mathbf{T}_y, \mathbf{T}_z$  vectors used in the recursions. For the three-electron integrals the recursions produce three dimensional integrals in each of the three Cartesian directions. Products of integrals in the three Cartesian directions produce the complete  $n$ -dimensional integrals. The reader should refer to Eq. (50) in the text. The modern literature on the evaluation of two-electron integrals contains extensive discussions of both the horizontal as well as vertical recursions.<sup>63-66</sup> Ultimately, one can transform any integral involving charge distributions to ones involving atom centered basis functions by employing the well known relation

$$\chi_x(m, n) = \chi_x(m + 1, n - 1) + (X_i - X_j) \chi_x(m, n - 1). \quad (143)$$

Analogous relations apply for the remaining two Cartesian directions. Our development in terms of charge distributions implies that the angular momentum of the charge distribution is the sum of the angular momenta for the respective basis functions. Application of the recursion relationships generates a  $\chi_x(m, 0)$  where the largest value of  $m$  is the sum of the angular momenta from the respective basis functions. These transfer relations can be applied either to the three dimensional integrals, or to the full nine-dimensional integrals. The choice is a matter of computational implementation and preference. The three dimensional integrals are over primitives and have not been summed over the Rys roots. It has been argued that there is an advantage to postpone such a transformation until the full nine-dimensional integrals are available and the sum over Rys roots is completed. These can also be contracted beforehand, thereby saving significant computational effort in certain cases. Once contracted integrals are computed they should be available for any implementation that can use them.

## X. CONCLUSIONS

Historically, the computation of many-electron integrals has been considered a daunting task given the rather high scaling requirements that such computations impose, but we find reasons to adopt a more sanguine attitude. Our development

has been very general and our specific examples show that such computations should be considered a natural extension of traditional two-electron computations. Traditionally calculations that involve explicit inter-electron functions have been limited to rather small chemical systems. There is recent activity which shows interest in the application of geminal functions in variational calculations on larger chemical systems, and for a wider range of physical effects. The group of Hammes-Schiffer has recently proposed the use of geminal correlation factors in electron-proton correlation to investigate non-adiabatic effects.<sup>56</sup> Most recently, Varganov and Martinez have proposed the use of geminal-augmented multi reference based variational calculations for larger chemical systems.<sup>67</sup> These applications require the computation of both three and four electron integrals. There is also interest in the investigation molecular motion in these systems which would require the energy gradients of the potential energy with respect to nuclear coordinates. Our exposition allows for a very natural extension to the computation of such derivatives.

Experience with single particle expansions has shown that while the formal scaling of two electron integral computations behaves as the fourth power of the number of basis functions, application of realistic cutoffs to such computations reduces the power scaling to less than 2.5. The use of such computations in direct methods reduces the computational requirements even further, as implementations screen not only the magnitude of the integrals, but also the magnitude of the effective density matrices that multiply such integrals.

Our exposition shows that a careful implementation should be easily vectorizable, and very scalable. Furthermore, it is well known that a description of cusp condition is a relatively short range phenomenon. Applying such reasoning to many-electron integrals suggests that pre-screening should eliminate the computation of most integrals where charge distributions contain centers with a distance of more than one or two bond lengths. The  $K_{ab}$  factors in each pair function often is on the order of  $10^{-3}$ . In two electron computations, the product of such charge distributions mandates that the integral survives. For the case of many-electron integrals there will be three or four such factors multiplied by the  $e^{-\nu}$  factor in Eq. (79). We expect that many of these integrals can be neglected.

Finally, we consider that an efficient implementation should scale to many processors in a distributed memory environment. The work to compute each set of blocks of multi-electron integrals is totally independent, obviating the need for any communication during most of the computation. For the variational calculations mentioned above, the reduced quantities such as the Fock like matrices can be assembled only at the end of the computation. Further comments about implementation and numerical results of sample computations are available as supplementary material.<sup>68</sup>

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## APPENDIX A: ELEMENTS OF THE $\mathbf{K}$ MATRIX

Let  $\mathbf{M}^\circ$  be an  $n$ -by- $n$  real, symmetric matrix with determinant  $\omega > 0$  whose elements are independent of the variable  $u$ , and  $\mathbf{K}^\circ$  its inverse. Let  $\mathbf{M}'$  be the  $n$ -by- $n$  matrix with only four non-zero elements,

$$\begin{aligned} M'_{\mu\mu} &= M'_{\nu\nu} = 1, \\ M'_{\mu\nu} &= M'_{\nu\mu} = -1. \end{aligned} \quad (\text{A1})$$

Here  $(\mu, \nu)$  is any specified pair of distinct indices,  $1 \leq \mu < \nu \leq n$ . Matrix  $\mathbf{M}$  is the following linear combination:

$$\mathbf{M} = \mathbf{M}^\circ + u^2 \mathbf{M}', \quad (\text{A2})$$

and  $\mathbf{K}$  is its inverse.  $\mathbf{U}$  is an  $n$ -by- $n$  unitary matrix whose elements are those of an identity matrix,  $U_{ij} = \delta_{ij}$ , except for the following four elements:

$$\begin{aligned} U_{\mu\mu} &= U_{\nu\nu} = 1/\sqrt{2}, \\ U_{\mu\nu} &= -U_{\nu\mu} = 1/\sqrt{2}. \end{aligned} \quad (\text{A3})$$

The notation  $\mathbf{A}$  and  $\hat{\mathbf{A}}$  denotes a pair of matrices related by a unitary transformation,

$$\begin{aligned} \hat{\mathbf{A}} &= \mathbf{U}^\dagger \mathbf{A} \mathbf{U}, \\ \mathbf{A} &= \mathbf{U} \hat{\mathbf{A}} \mathbf{U}^\dagger, \end{aligned} \quad (\text{A4})$$

where  $\mathbf{U}$  is the particular unitary matrix in Eq. (A3) and  $\mathbf{A}$  is any  $n$ -by- $n$  matrix. It follows that  $\hat{\mathbf{M}}$  has just one non-zero matrix element,

$$\hat{M}'_{\mu\mu} = 2. \quad (\text{A5})$$

Thus  $\hat{\mathbf{M}}$  and  $\hat{\mathbf{M}}^\circ$  differ only in this one matrix element,

$$\hat{M}_{\mu\mu} = \hat{M}^\circ_{\mu\mu} + 2u^2. \quad (\text{A6})$$

Since  $\det(\mathbf{M}) = \det(\hat{\mathbf{M}})$ , and since  $u^2$  occurs in one and only one element of  $\hat{\mathbf{M}}$ , it follows that the determinant of  $\mathbf{M}$  is a linear function of the variable  $u^2$ ,

$$\det(\mathbf{M}) = \omega + u^2 \theta, \quad (\text{A7})$$

where  $\theta$  is twice the cofactor of  $\hat{M}_{\mu\mu}$ .

The  $ij$ th element of  $\hat{\mathbf{K}} \equiv \hat{\mathbf{M}}^{-1}$  is the cofactor of  $\hat{M}_{ij}$  divided by  $\det(\hat{\mathbf{M}})$ . Since  $u^2$  appears in one and only one element of  $\hat{\mathbf{M}}$ , any cofactor of  $\hat{\mathbf{M}}$  is a linear function of the variable  $u^2$ . Thus, elements of  $\hat{\mathbf{K}}$  are functions of  $u$  with the following form:

$$\hat{K}_{ij} = \frac{\hat{a}_{ij} + u^2 \hat{b}_{ij}}{\omega + u^2 \theta}. \quad (\text{A8})$$

This form is preserved under unitary transformation, so elements of  $\mathbf{K}$  are

$$K_{ij} = \frac{a_{ij} + u^2 b_{ij}}{\omega + u^2 \theta}. \quad (\text{A9})$$

Since  $\mathbf{K}$  reduces to  $\mathbf{K}^\circ$  in the  $u \rightarrow 0$  limit, and  $\omega > 0$ , elements of  $\mathbf{K}^\circ$  are

$$K_{ij}^\circ = \frac{a_{ij}}{\omega}. \quad (\text{A10})$$

## APPENDIX B: PROPERTIES OF THE K MATRIX

The identity Eq. (58) and Eq. (A8) imply that  $\hat{\mathbf{K}}$  is linear in the variable  $t^2$

$$\hat{\mathbf{K}} = \hat{\mathbf{K}}^\circ + t^2 \hat{\mathbf{K}}_h, \quad (\text{B1})$$

where  $\hat{\mathbf{K}}_h$  is a real, symmetric  $n$ -by- $n$  matrix. The analysis below establishes that  $\hat{\mathbf{K}}_h$  has one and only one non-zero eigenvector, i.e., is of rank 1, and that to within an arbitrary normalization factor, this eigenvector is simply column  $\mu$  of the  $\hat{\mathbf{K}}^\circ$  matrix.

By definition,  $\hat{\mathbf{K}}$  is the inverse of  $\hat{\mathbf{M}}$ , so

$$\begin{aligned} \mathbf{I} &= \hat{\mathbf{K}} \hat{\mathbf{M}} \\ &= (\hat{\mathbf{K}}^\circ + t^2 \hat{\mathbf{K}}_h)(\hat{\mathbf{M}}^\circ + u^2 \hat{\mathbf{M}}') \\ &= \hat{\mathbf{K}}^\circ \hat{\mathbf{M}}^\circ + t^2 \hat{\mathbf{K}}_h \hat{\mathbf{M}}^\circ + u^2 \hat{\mathbf{K}}^\circ \hat{\mathbf{M}}' + t^2 u^2 \hat{\mathbf{K}}_h \hat{\mathbf{M}}'. \end{aligned} \quad (\text{B2})$$

The first term on the right is itself the identity matrix, so the three remaining terms must cancel one another. Multiplying the sum of these three terms by  $(\xi + u^2)$  and using the identity

$$(\xi + u^2)t^2 = u^2 \quad (\text{B3})$$

yields

$$\mathbf{0} = u^2 \hat{\mathbf{K}}_h \hat{\mathbf{M}}^\circ + (\xi + u^2)u^2 \hat{\mathbf{K}}^\circ \hat{\mathbf{M}}' + u^4 \hat{\mathbf{K}}_h \hat{\mathbf{M}}'. \quad (\text{B4})$$

This result is valid for all values of  $u$ , so the coefficients of  $u^2$  and  $u^4$  must vanish individually. It follows that

$$\hat{\mathbf{K}}_h \hat{\mathbf{M}}^\circ = -\xi \hat{\mathbf{K}}^\circ \hat{\mathbf{M}}', \quad (\text{B5})$$

$$\hat{\mathbf{K}}_h = -\xi \hat{\mathbf{K}}^\circ \hat{\mathbf{M}}' \hat{\mathbf{K}}^\circ. \quad (\text{B6})$$

Recall that  $\hat{\mathbf{M}}'$  has just a single non-zero matrix element,

$$M'_{ij} = 2 \delta_{i\mu} \delta_{\mu j}. \quad (\text{B7})$$

Making this substitution in Eq. (B6) and performing the matrix multiplications yields

$$(\hat{\mathbf{K}}_h)_{ij} = -2\xi \hat{K}_{i\mu}^\circ \hat{K}_{\mu j}^\circ. \quad (\text{B8})$$

Define column vector  $\hat{\mathbf{H}}$ ,

$$\hat{\mathbf{H}} \equiv \sqrt{2} \omega \hat{\mathbf{K}}_\mu^\circ, \quad (\text{B9})$$

where  $\hat{\mathbf{A}}_\mu$  denotes column  $\mu$  of an arbitrary matrix  $\mathbf{A}$ . The  $\hat{\mathbf{K}}_h$  matrix is conveniently expressed in terms of the  $\hat{\mathbf{H}}$  vector,

$$\hat{\mathbf{K}}_h = -(\omega\theta)^{-1} \hat{\mathbf{H}} \hat{\mathbf{H}}^\dagger. \quad (\text{B10})$$

Eq. (A4) implies that

$$\begin{aligned} \mathbf{K}_h &= \mathbf{U} \hat{\mathbf{K}}_h \mathbf{U}^\dagger \\ &= -(\omega\theta)^{-1} (\mathbf{U} \hat{\mathbf{H}}) (\mathbf{U} \hat{\mathbf{H}})^\dagger. \end{aligned} \quad (\text{B11})$$

Define column vector  $\mathbf{H}$ ,

$$\begin{aligned} \mathbf{H} &\equiv \mathbf{U} \hat{\mathbf{H}} \\ &= \sqrt{2} \omega (\mathbf{U} \hat{\mathbf{K}}_\mu^\circ) \\ &= \sqrt{2} \omega (\mathbf{K}^\circ \mathbf{U})_\mu \\ &= \omega \mathbf{K}^\circ \mathbf{V}, \end{aligned} \quad (\text{B12})$$

where vector  $\mathbf{V}$  is proportional to column  $\mu$  of the  $\mathbf{U}$  matrix,

$$\mathbf{V} = \sqrt{2} \mathbf{U}_\mu. \quad (\text{B13})$$

Note that  $\mathbf{V}$  has just two non-zero elements,  $V_\mu = 1$ , and  $V_\nu = -1$ . The central results of this analysis are

$$\begin{aligned} \mathbf{K}_h &= -(\omega\theta)^{-1} \mathbf{H} \mathbf{H}^\dagger, \\ \mathbf{H} &= \omega (\mathbf{K}_\mu^\circ - \mathbf{K}_\nu^\circ). \end{aligned} \quad (\text{B14})$$

<sup>1</sup>P. R. Taylor, in *Lecture Notes in Quantum Chemistry*, edited by B. Roos (Springer Verlag, Berlin, 1992).

<sup>2</sup>T. Helgaker and P. R. Taylor, in *Modern Electronic Structure Theory*, edited by D. Yarkony (World Scientific, Singapore, 1995).

<sup>3</sup>E. Hylleras, *Z. Phys.* **48**, 469 (1928).

<sup>4</sup>E. A. Hylleras, *Z. Phys.* **65**, 209 (1930).

<sup>5</sup>H. James and A. Coolidge, *J. Chem. Phys.* **1**, 825 (1933).

<sup>6</sup>C. L. Pekeris, *Phys. Rev.* **112**, 1649 (1958).

<sup>7</sup>C. L. Pekeris, *Phys. Rev.* **115**, 1216 (1959).

<sup>8</sup>C. L. Pekeris, *Phys. Rev.* **126**, 1470 (1962).

<sup>9</sup>L. Wolniewicz, *J. Chem. Phys.* **99**, 1851 (1993).

<sup>10</sup>S. F. Boys, *Proc. R. Soc. London Ser. A* **258**, 402 (1960).

<sup>11</sup>K. Singer, *Proc. R. Soc. London Ser. A* **258**, 412 (1960).

<sup>12</sup>R. Bukowski, B. Jeziorski, and K. Szalewicz, in *Explicitly Correlated Wavefunctions in Chemistry and Physics*, edited by J. Rychlewski (Kluwer, Dordrecht, 2003), p. 185.

<sup>13</sup>J. Rychlewski and J. Komasa, in *Explicitly Correlated Wavefunctions in Chemistry and Physics*, edited by J. Rychlewski (Kluwer, Dordrecht, 2003), p. 91.

<sup>14</sup>J. Rychlewski, W. Cencek, and J. Komasa, *Chem. Phys. Lett.* **229**, 657 (1994).

<sup>15</sup>W. Cencek, J. Komasa, and J. Rychlewski, *Chem. Phys. Lett.* **246**, 417 (1995).

<sup>16</sup>J. Komasa, W. Cencek, and J. Rychlewski, *Comput. Methods Sci. Technol.* **2**, 87 (1996).

<sup>17</sup>J. Komasa, W. Cencek, and J. Rychlewski, *Phys. Rev. A* **52**, 4500 (1995).

<sup>18</sup>J. Komasa and J. Rychlewski, *Chem. Phys. Lett.* **249**, 253 (1996).

<sup>19</sup>K. L. Sharkey, S. Bubin, and L. Adamowicz, *J. Chem. Phys.* **132**, 184106 (2010).

<sup>20</sup>K. Szalewicz and B. Jeziorski, *Mol. Phys.* **108**, 3191 (2010).

<sup>21</sup>K.-C. Pan and H. F. King, *J. Chem. Phys.* **53**, 4397 (1970).

<sup>22</sup>K.-C. Pan and H. F. King, *J. Chem. Phys.* **56**, 4667 (1972).

<sup>23</sup>L. Adamowicz, *Acta Phys. Pol. A* **53**, 471 (1978).

<sup>24</sup>K. Szalewicz, B. Jeziorski, H. Monkhorst, and J. Zabolitzky, *Chem. Phys. Lett.* **91**, 169 (1982).

<sup>25</sup>K. Szalewicz, B. Jeziorski, H. Monkhorst, and J. Zabolitzky, *J. Chem. Phys.* **78**, 1420 (1983).

<sup>26</sup>W. Klopper and W. Kutzelnigg, *Chem. Phys. Lett.* **134**, 17 (1987).

<sup>27</sup>W. Kutzelnigg and W. Klopper, *J. Chem. Phys.* **94**, 1985 (1991).

<sup>28</sup>V. Termath, W. Klopper, and W. Kutzelnigg, *J. Chem. Phys.* **94**, 2002 (1991).

<sup>29</sup>W. Kutzelnigg and W. Klopper, *J. Chem. Phys.* **94**, 2020 (1991).

<sup>30</sup>W. Klopper, *Chem. Phys. Lett.* **186**, 583 (1986).

<sup>31</sup>W. Klopper, in *Modern Methods and Algorithms of Quantum Chemistry*, edited by J. Grotendorst (NIC Series, Julich, 2000), Vol. 3, pp. 181.

<sup>32</sup>W. Klopper, F. Manby, S. Te-No, and E. Valeev, *Int. Rev. Phys. Chem.* **25**, 427 (2006).

<sup>33</sup>C. Hättig, D. P. Tew, and A. Köhn, *J. Chem. Phys.* **132**, 231102 (2010).

<sup>34</sup>B. J. Persson and P. R. Taylor, *J. Chem. Phys.* **105**, 5915 (1996).

<sup>35</sup>F. R. Manby, H.-J. Werner, T. B. Adler, and A. J. May, *J. Chem. Phys.* **124**, 94103 (2006).

<sup>36</sup>A. J. May and F. R. Manby, *J. Chem. Phys.* **121**, 4479 (2004).

<sup>37</sup>S. Ten-no and F. R. Manby, *J. Chem. Phys.* **119**, 5358 (2003).

- <sup>38</sup>S. Ten-no, *Chem. Phys. Lett.* **330**, 169 (2000).
- <sup>39</sup>H.-J. Werner and F. R. Manby, *J. Chem. Phys.* **124**, 54114 (2006).
- <sup>40</sup>H.-J. Werner, T. B. Adler, and F. R. Manby, *J. Chem. Phys.* **126**, 164102 (2007).
- <sup>41</sup>D. P. Tew, W. Klopper, and F. R. Manby, *J. Chem. Phys.* **127**, 174105 (2007).
- <sup>42</sup>R. Polly, H.-J. Werner, P. Dahle, and P. R. Taylor, *J. Chem. Phys.* **124**, 234107 (2006).
- <sup>43</sup>B. J. Persson and P. R. Taylor, *Theor. Chem. Acc.* **97**, 240 (1997).
- <sup>44</sup>S. F. Boys, *Proc. R. Soc. London Ser. A* **200**, 542 (1950).
- <sup>45</sup>S. Obara and A. Saika, *J. Chem. Phys.* **84**, 3963 (1986).
- <sup>46</sup>L. E. McMurchie and E. R. Davidson, *J. Comp. Phys.* **26**, 218 (1978).
- <sup>47</sup>H. F. King and M. Dupuis, *J. Comp. Phys.* **21**, 144 (1976).
- <sup>48</sup>M. Dupuis, J. Rys, and H. F. King, *J. Chem. Phys.* **65**, 111 (1976).
- <sup>49</sup>J. Rys, M. Dupuis, and H. F. King, *J. Comp. Chem.* **4**, 154 (1983).
- <sup>50</sup>W. A. Lester, Jr. and M. Krauss, *J. Chem. Phys.* **41**, 1407 (1964).
- <sup>51</sup>W. A. Lester Jr. and M. Krauss, *J. Chem. Phys.* **42**, 2990 (1965).
- <sup>52</sup>P. M. Kozłowski and L. Adamowicz, *J. Comp. Chem.* **13**, 602 (1992).
- <sup>53</sup>W. Cencek and J. Rychlewski, *J. Chem. Phys.* **98**, 1252 (1993).
- <sup>54</sup>P. Dahle, T. Helgaker, D. Jonsson, and P. R. Taylor, *Phys. Chem. Chem. Phys.* **9**, 3112 (2007).
- <sup>55</sup>S. L. Saito and Y. ichi Suzuki, *J. Chem. Phys.* **114**, 1115 (2001).
- <sup>56</sup>A. Chakraborty, M. V. Pak, and S. Hammes-Schiffer, *J. Chem. Phys.* **129**, 014101 (2008).
- <sup>57</sup>I. Sirbu and H. F. King, *J. Chem. Phys.* **117**, 6411 (2002).
- <sup>58</sup>I. Sirbu and H. F. King, *Int. J. Quantum Chem.* **92**, 433 (2003).
- <sup>59</sup>B. W. Char, K. O. Geddes, G. H. Gonnet, B. L. Leong, M. B. Monagan, and S. M. Watt, *First Leaves: A Tutorial Introduction to Maple V* (Springer-Verlag, New York, 1992), MAPLE is a registered trademark of Waterloo Maple Software.
- <sup>60</sup>M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (U.S. Government Printing Office, Washington D.C., 1964), Vol. 55.
- <sup>61</sup>J. Almløf and P. R. Taylor, *J. Chem. Phys.* **86**, 4070 (1987).
- <sup>62</sup>J. Almløf and P. R. Taylor, *Adv. Quantum Chem.* **22**, 301 (1992).
- <sup>63</sup>R. Lindh, U. Ryu, and B. Liu, *J. Chem. Phys.* **95**, 5889 (1991).
- <sup>64</sup>P. M. Gill, *Adv. Quantum Chem* **25**, 141 (1994).
- <sup>65</sup>P. M. Gill, M. Head-Gordon, and J. A. Pople, *J. Phys. Chem.* **94**, 5564 (1990).
- <sup>66</sup>M. Dupuis and A. Marquez, *J. Chem. Phys.* **114**, 2067 (2001).
- <sup>67</sup>S. A. Varganov and T. J. Martinez, *J. Chem. Phys.* **132**, 054103 (2010).
- <sup>68</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3600745> for technical details on checking and debugging a computer implementation some sample three-electron integrals.