

Analytical calculations of molecular integrals for multielectron **R**-matrix methods

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Closed-form analytical expressions for one- and two-electron integrals between Cartesian Gaussians over a finite spherical region of space are developed for use in *ab initio* molecular scattering calculations. In contrast with some previous approaches, the necessary integrals are formulated solely in terms of finite summations involving standard functions. The molecular integrals evaluated over the finite region of space are computed by subtracting the contributions outside the region from the integrals over all space. The latter integrals can be efficiently and accurately obtained from existing bound-state algorithms. Our approach incorporates molecular scattering calculations into current quantum chemistry programs and facilitates the unification of bound- and continuum-state calculations for both diatomic and polyatomic molecules. Multidimensional Monte Carlo numerical integrations validate the high accuracy of our closed form results for the two-electron integrals.

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I. INTRODUCTION

In the past two decades,^{1,2} collisions of electrons with molecular systems have used the **R**-matrix method to obtain scattering information, such as integral and differential cross sections for diatomic and polyatomic molecules. The application of the **R**-matrix method to electron scattering has been described in detail in Ref. 1. More recent work has focused on the use of the variational **R**-matrix scheme³ and its generalizations to highly dipolar molecules.⁴ For example, Altunata *et al.* have used an iterative Green's-function method in combination with the variational **R**-matrix treatment⁵ to calculate Rydberg and continuum electronic states of the molecule CaF, which has a highly polar ion core.⁶

In contrast to calculations of bound-state wave functions, **R**-matrix methods partition the configuration space of the scattering electron into two regions separated by a sphere of radius $r=R$. An illustration of the **R**-matrix division of configuration space is shown in Fig. 1. The **R**-matrix sphere is centered at the center of mass of the molecular target. The radius, R , of this sphere is chosen large enough to approximately enclose the molecular charge cloud. In the internal region, $r < R$, electron exchange and interelectron correlation are significant, and the combination of target molecule and scattered electron acts similarly to a bound state. Conversely, in the external region, $r > R$, electron exchange is negligible, and the scattered electron moves in the multipole potential of the target molecule. For **R**-matrix calculations, the standard quantum chemistry basis sets must be augmented with continuum or diffuse functions. These continuum functions are centered about the center of mass of the molecular target and must have significant amplitude on the **R**-matrix sphere.

Their presence accounts for the escape of the scattered electron to the external region and yields the correct asymptotic behavior of the collision wave functions.

Accurate and efficient evaluation of molecular integrals is essential to **R**-matrix calculations. Since the integration is carried out over the finite volume of the **R**-matrix sphere, the computation of the one- and two-electron integrals is significantly more difficult than their infinite-volume counterparts. Slater-type orbitals have been used in previous work^{2,7} for atomic and diatomic systems, but their applicability to general scattering problems incurs the enormous computational cost of numerical evaluation of Hamiltonian matrix elements. For polyatomic molecular systems, several atom-centered basis functions must be used, and the computation becomes prohibitively time consuming if numerical algorithms are implemented. Consequently, Cartesian Gaussian-type functions and linear combinations of Gaussians have become widely used as bound-state basis-set orbitals in molecular scattering theory.⁸ Although it is relatively easy to describe the bound-state target orbitals with Gaussian-type functions, the choice of the continuum basis set is more difficult. The continuum basis must be a good approximation to functions, which are both oscillatory and have significant amplitude on the **R**-matrix sphere. Fortunately, Nestmann and Peyerimhoff⁹ have shown that a basis set of orthogonal spherical Bessel functions can be replaced by a fit to several diffuse Gaussian-type functions. This approach reduces the problem of multidimensional numerical integration to a sum of Gaussian integrals; however, the remaining complication is the nontrivial computation of the individual matrix elements over a finite volume. These matrix elements, or integrals, must be evaluated accurately and efficiently in order to obtain reliable theoretical predictions for *ab initio* calculations of generic molecular systems.

We should mention that the efficient evaluation of molecular integrals for bound-state calculations has been a topic

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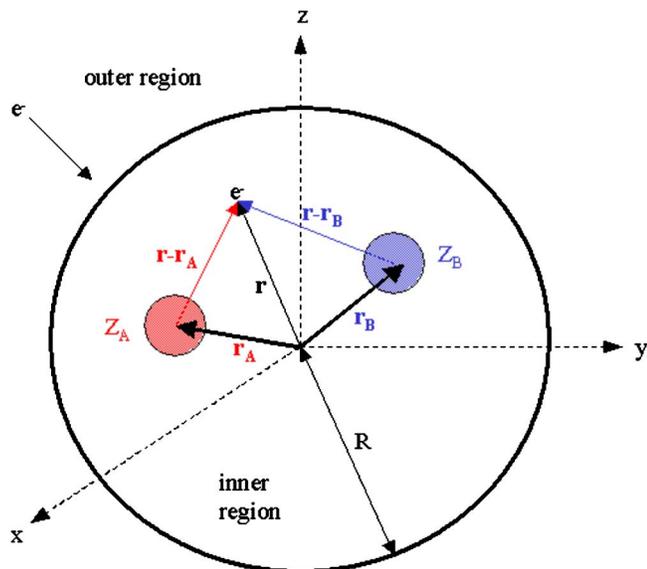


FIG. 1. Schematic diagram of a molecule enclosed by an \mathbf{R} -matrix sphere of radius R . Exchange between the scattered and atomic electrons is only important within the sphere. The bound target basis functions centered on nuclei Z_A and Z_B (only two nuclei are shown for clarity) have negligible amplitude outside the \mathbf{R} -matrix sphere. The basis functions for the scattered electron are positioned at the center of the sphere and have significant amplitude on the \mathbf{R} -matrix sphere. The various integrals of the scattered electron in the outer region must be subtracted off when evaluating Hamiltonian matrix elements over the volume inside the \mathbf{R} -matrix sphere.

of many studies for as long as 50 years.^{10–14} Most notably, the high efficiency of the Head-Gordon and Pople algorithm has allowed current programs to evaluate two-electron integrals dynamically in computer memory as needed.¹⁵ To capitalize on the high efficiency of these algorithms, the most practical modification needed to incorporate existing electronic structure programs into \mathbf{R} -matrix calculations is to subtract the contribution from the outer region of the \mathbf{R} -matrix sphere from the integrals calculated over all space. In the present work, we have used the PSI 3.2.2 software package to generate the integrals over all space for up to k -type angular-momentum basis sets.¹⁶ Since it is assumed that the bound target basis functions have negligible amplitude outside the \mathbf{R} -matrix sphere, the only matrix elements which need to be modified in the PSI 3.2.2 output are those integrations involving two or more continuum orbitals. Morgan *et al.* have briefly discussed how one might proceed to evaluate the continuum integrations in Ref. 8, but they did not present a full derivation. In the present work, we give closed-form analytic expressions for the one- and two-electron integrals of Cartesian Gaussian orbitals outside the \mathbf{R} -matrix sphere. These integrals, which are called “tail integrals,” are evaluated as finite summations over standard functions; hence, our results are accurate within computer precision. As a validating test, in Sec. VII, a multidimensional Monte Carlo integration is performed on the two-electron integrals using various angular-momentum basis functions and compared with our analytical results.

II. GENERAL EXPANSION OF CARTESIAN GAUSSIAN ORBITALS

A general unnormalized Cartesian Gaussian orbital (CGO) centered at point $\mathbf{R}_p = (X_p, Y_p, Z_p)$ is given by

$$\chi_P(p, q, r, a) = x_p^p y_p^q z_p^r e^{-ar_p^2}, \quad (1)$$

where x_p , y_p , and z_p are Cartesian components relative to the point \mathbf{R}_p where $\mathbf{r}_p = (x_p, y_p, z_p) = (x - X_p, y - Y_p, z - Z_p)$, and p , q , and r are integers greater than or equal to zero. The multipole expansion of this unnormalized CGO about the origin of the (x, y, z) coordinate system is given by¹⁷

$$\chi_P(p, q, r, a) = \sum_{l=0}^{\infty} \sum_{m=-l}^l C_{pqra}^{lm}(r) Y_{l,m}(\hat{\mathbf{r}}), \quad (2)$$

where the direction $\hat{\mathbf{r}}$ specifies the angular spherical coordinates θ and φ which uniquely defines the coordinate system of the spherical harmonic. The spherical harmonics used in the present work follow the conventional phase choice,

$$Y_{l,-m} = (-1)^m Y_{l,m}^*. \quad (3)$$

The radial function $C_{pqra}^{lm}(r)$ is derived from a Rayleigh expansion which leads to

$$C_{pqra}^{lm}(r) = 4\pi e^{-a(r^2 + R_p^2)} \sum_{i,j,k} A_{ijk}^{pqr} r^{i+j+k} \sum_{l',m'} i_{l'}(2aR_p r) \times Y_{l',m'}^*(\hat{\mathbf{R}}_p) \sum_{L,M} B_{L,M}^{LM} \langle Y_{l,m} | Y_{L,M} | Y_{l',m'} \rangle, \quad (4)$$

which is slightly modified from the expression given by Le Rouzo. The real constant A_{ijk}^{pqr} is obtained from the polynomial expansion

$$(x - X_p)^p (y - Y_p)^q (z - Z_p)^r = \sum_{i,j,k=0}^{i+j+k \leq p+q+r} A_{ijk}^{pqr} x^i y^j z^k. \quad (5)$$

The function i_l is a modified spherical Bessel function of the first kind and of order l . The complex constant B_{ijk}^{LM} is given by the expression¹⁸

$$(-1)^M B_{IJK}^{LM*} = \sqrt{\frac{2L+1}{4\pi} \frac{(L-|M|)!}{(L+|M|)!}} \times I_{\varphi}(I, J, M) I_{\theta}(I + J, K, L, M), \quad (6)$$

which is modified from Mathar's original expression to follow our phase choice. The integrals I_{φ} and I_{θ} are given by

$$I_{\varphi} = \frac{\pi}{2^{I+J-1}} i^J \sum_{\sigma=\max(0, (I-J-M)/2)}^{\min(I, (I+J-M)/2)} (-1)^{(I+J-M)/2 - \sigma} \binom{I}{\sigma} \times \binom{J}{(I+J-M)/2 - \sigma}, \quad (7)$$

and

$$I_{\theta} = \frac{2^{L+1}}{(L-|M|)!} \sum_{\nu=0}^{[(L-|M|)/2]} \left(\frac{1}{2} - \nu\right)_L \times \binom{L-|M|}{2\nu} \sum_{\sigma=0}^{(I+J+|M|)/2} \binom{(I+J+|M|)/2}{\sigma} \times \frac{(-1)^{\sigma}}{2\sigma + 1 + K + L - |M| - 2\nu}, \quad (8)$$

where the standard definition of the binomial coefficient is given by

$$\binom{a}{b} = \frac{a!}{(a-b)!b!}. \quad (9)$$

The square brackets, $[x]$, denote the largest integer less than or equal to x , and $(y)_p$ is Pochhammer's symbol, $(y)_p = y(y+1)(y+2)\cdots(y+p-1)$ for integers p and $(y)_0 = 1$. The index L in Eq. (4) decreases in steps of 2 from $i+j+k$ to 1 or 0. These basic results permit the computation of all of the various types of integrals over a finite spherical volume needed for **R**-matrix theory. From these expressions, one can evaluate overlap, kinetic, nuclear, and electron repulsion integrals analytically. The subsequent sections deal specifically with the tail integrals of one- and two-electron integrals of continuum orbitals.

III. OVERLAP TAIL INTEGRAL

The overlap tail integrals are obtained by integrating the product of two continuum CGOs from the **R**-matrix radius R to infinity. Since all the continuum CGOs are centered about the center of gravity, O , of the molecule, the product of two continuum CGOs is a single continuum CGO also located at the center of gravity,

$$\chi_{i,O}(p_i, q_i, r_i, a_i) \chi_{j,O}(p_j, q_j, r_j, a_j) = x^p y^q z^r e^{-ar^2}, \quad (10)$$

where $p = p_i + p_j$, $q = q_i + q_j$, $r = r_i + r_j$, and $a = a_i + a_j$. Since the product of the two continuum CGOs is a Gaussian located at the center of gravity, $R_p = 0$, the following relations hold for this special case:

$$A_{ijk}^{pqr} = \delta_{i,p} \delta_{j,q} \delta_{k,r}, \quad (11)$$

$$i_l(0) = \delta_{l,0}. \quad (12)$$

Therefore, the expression for the radial function reduces to the following:

$$\begin{aligned} C_{pqra}^{lm}(r) &= 4\pi e^{-ar^2} r^{p+q+r} Y_{0,0}^* \sum_{L,M} B_{pqr}^{LM} \langle Y_{l,m} | Y_{L,M} | Y_{0,0} \rangle \\ &= e^{-ar^2} r^{p+q+r} \sum_{L,M} B_{pqr}^{LM} \langle Y_{l,m} | Y_{L,M} \rangle \\ &= e^{-ar^2} r^{p+q+r} B_{pqr}^{lm}. \end{aligned} \quad (13)$$

The calculation of the overlap tail integral involves the integration of Eq. (2) from R to infinity with the radial function given by Eq. (13),

$$S_{\text{tail}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \int_{r=R}^{\infty} e^{-ar^2} r^{p+q+r} B_{pqr}^{lm} Y_{l,m}(\hat{\mathbf{r}}) d\mathbf{r}. \quad (14)$$

After integration over the angular variables, we have

$$\begin{aligned} S_{\text{tail}} &= \sqrt{4\pi} B_{pqr}^{00} \int_R^{\infty} r^{p+q+r+2} e^{-ar^2} dr \\ &= \sqrt{\pi} B_{pqr}^{00} \frac{\Gamma[1/2(p+q+r) + 3/2, aR^2]}{a^{1/2(p+q+r)+3/2}}. \end{aligned} \quad (15)$$

IV. KINETIC-ENERGY TAIL INTEGRAL

The kinetic-energy tail integrals are defined by

$$\text{KE}_{\text{tail}} = -\frac{1}{2} \int_{r=R}^{r=\infty} \chi_{i,O}(p_i, q_i, r_i, a_i) \nabla^2 \chi_{j,O}(p_j, q_j, r_j, a_j) d\mathbf{r}. \quad (16)$$

The action of the kinetic-energy operator on a continuum CGO centered about the center of gravity O is given by

$$\begin{aligned} &-\frac{1}{2} \nabla^2 (x^p y^q z^r e^{-ar^2}) \\ &= a[2(p+q+r) + 3] x^p y^q z^r e^{-ar^2} \\ &\quad - 2a^2 [x^{p+2} y^q z^r + x^p y^{q+2} z^r + x^p y^q z^{r+2}] e^{-ar^2} \\ &\quad - \frac{1}{2} [p(p-1)x^{p-2} y^q z^r + q(q-1)x^p y^{q-2} z^r \\ &\quad + r(r-1)x^p y^q z^{r-2}] e^{-ar^2}. \end{aligned} \quad (17)$$

Let $S(p, q, r, a)$ denote the overlap tail integral between $\chi_i(p_i, q_i, r_i, a_i)$ and $\chi_j(p_j, q_j, r_j, a_j)$ where $p = p_i + p_j$, $q = q_i + q_j$, $r = r_i + r_j$, and $a = a_i + a_j$. The kinetic-energy tail integral is given by the sum of seven overlap tail integrals,

$$\begin{aligned} \text{KE}_{\text{tail}} &= a_j [2(p_j + q_j + r_j) + 3] S(p, q, r, a) - 2a_j^2 [S(p \\ &\quad + 2, q, r, a) + S(p, q + 2, r, a) + S(p, q, r + 2, a)] \\ &\quad - \frac{1}{2} [p_j(p_j - 1) S(p - 2, q, r, a) + q_j(q_j - 1) \\ &\quad \times S(p, q - 2, r, a) + r_j(r_j - 1) S(p, q, r - 2, a)], \end{aligned} \quad (18)$$

where the closed analytical forms for the seven different S integrals can be found from Eq. (15).

V. NUCLEAR ATTRACTION TAIL INTEGRAL

For a nucleus centered about the point $\mathbf{r}_C = (x_C, y_C, z_C)$, the nuclear attraction tail integral is given by

$$\text{NAI}_{\text{tail}} = \int_{r=R}^{r=\infty} \chi_{i,O}(p_i, q_i, r_i, a_i) \frac{1}{|\mathbf{r} - \mathbf{r}_C|} \chi_{j,O}(p_j, q_j, r_j, a_j) d\mathbf{r}. \quad (19)$$

Using Eqs. (10) and (13), the number of Gaussians involved in the integration is reduced to one, and Eq. (19) takes the form,

$$\text{NAI}_{\text{tail}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l B_{pqr}^{lm} \int_{r=R}^{r=\infty} r^{p+q+r} e^{-ar^2} Y_{l,m}(\hat{\mathbf{r}}) \frac{1}{|\mathbf{r} - \mathbf{r}_C|} d\mathbf{r}, \quad (20)$$

where $p = p_i + p_j$, $q = q_i + q_j$, $r = r_i + r_j$, and $a = a_i + a_j$. The Coulomb term can be expressed using the well-known multipolar expansion,

$$\frac{1}{|\mathbf{r} - \mathbf{r}_C|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{l,m}^*(\hat{\mathbf{r}}) Y_{l,m}(\hat{\mathbf{r}}_C). \quad (21)$$

Since the integration of Eq. (20) is from R to infinity and the **R**-matrix radius encloses all the nuclei, thus $r_{>} = r$ and $r_{<} = r_C$; after integration over the angular variables, we have

$$\text{NAI}_{\text{tail}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} r_C^l Y_{l,m}(\hat{\mathbf{r}}_C) \times B_{pqr}^{lm} \int_R^{\infty} r^{p+q+r-l+1} e^{-ar^2} dr. \quad (22)$$

Since the index l in Eq. (22) decreases by steps of 2 from $p+q+r$ to 1 or 0, the exponent of r in the integral is always positive. Thus we have

$$\text{NAI}_{\text{tail}} = 2\pi \sum_{l=0,1}^{p+q+r} \sum_{m=-l}^l \frac{1}{2l+1} r_C^l Y_{l,m}(\hat{\mathbf{r}}_C) B_{pqr}^{lm} \times \frac{\Gamma[1/2(p+q+r-l)+1, aR^2]}{a^{1/2(p+q+r-l)+1}}, \quad \mathbf{r}_C \neq 0. \quad (23)$$

Note that the original sum in Eq. (20) is finite because it is limited by the coefficient B_{ijk}^{lm} in Eq. (23).

However, Eq. (23) is not applicable when a continuum CGO is centered about a nucleus located at the center of gravity of the molecule (i.e., this occurs in the equilibrium linear geometries of CO_2 or NO_2^+). In this special case, the Coulomb term is simply $1/r$, and Eq. (20) reduces to

$$\text{NAI}_{\text{tail}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l B_{pqr}^{lm} \int_{r=R}^{\infty} r^{p+q+r-1} e^{-ar^2} Y_{l,m}(\hat{\mathbf{r}}) dr. \quad (24)$$

After integration over the angular variables, we have

$$\begin{aligned} \text{NAI}_{\text{tail}} &= \sqrt{4\pi} B_{pqr}^{00} \int_R^{\infty} r^{p+q+r+1} e^{-ar^2} dr \\ &= \sqrt{4\pi} B_{pqr}^{00} \frac{\Gamma[1/2(p+q+r)+1, aR^2]}{a^{1/2(p+q+r)+1}}, \quad \mathbf{r}_C = 0. \end{aligned} \quad (25)$$

VI. ELECTRON REPULSION TAIL INTEGRAL

A general electron repulsion integral, evaluated over all space is given by

$$\begin{aligned} \text{ERI} &= \iint \chi_{i,A1}(p_i, q_i, r_i, a_i) \chi_{j,B1}(p_j, q_j, r_j, a_j) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &\quad \times \chi_{k,C2}(p_k, q_k, r_k, a_k) \chi_{l,D2}(p_l, q_l, r_l, a_l) d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (26)$$

where $\chi_{i,pn}$ is the i th unnormalized CGO for electron n centered at point $\mathbf{R}_{n,p} = (X_{n,p}, Y_{n,p}, Z_{n,p})$. Since only one electron can occupy a continuum orbital in the \mathbf{R} -matrix theory, we only require the two-electron tail integrals where either χ_i and χ_j are continuum orbitals or χ_k and χ_l are continuum orbitals. The latter integral is given by

$$\begin{aligned} \text{ERI} &= \iint \chi_{i,A1}(p_i, q_i, r_i, a_i) \chi_{j,B1}(p_j, q_j, r_j, a_j) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &\quad \times \chi_{k,O2}(p_k, q_k, r_k, a_k) \chi_{l,O2}(p_l, q_l, r_l, a_l) d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (27)$$

where $\chi_{i,A1}$ and $\chi_{j,B1}$ are nucleus-centered CGOs, and $\chi_{k,O2}$

and $\chi_{l,O2}$ are continuum CGOs located at the center of gravity. By definition, this integral over all space can be expanded as

$$\begin{aligned} \text{ERI} &= \int_{r_1=0}^{r_1=R} \int_{r_2=0}^{r_2=R} \chi_{i,A1} \chi_{j,B1} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_{k,O2} \chi_{l,O2} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad + \int_{r_1=0}^{r_1=R} \int_{r_2=R}^{r_2=\infty} \chi_{i,A1} \chi_{j,B1} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_{k,O2} \chi_{l,O2} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad + \int_{r_1=R}^{r_1=\infty} \int_{r_2=0}^{r_2=R} \chi_{i,A1} \chi_{j,B1} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_{k,O2} \chi_{l,O2} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad + \int_{r_1=R}^{r_1=\infty} \int_{r_2=R}^{r_2=\infty} \chi_{i,A1} \chi_{j,B1} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_{k,O2} \chi_{l,O2} d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (28)$$

However, we only require the tail integral. If we assume the nucleus-centered CGOs have negligible contribution outside the \mathbf{R} -matrix radius, the only contribution to the tail integral is

$$\begin{aligned} \text{ERI}_{\text{tail}} &= \int_{r_1=0}^{r_1=R} \int_{r_2=R}^{r_2=\infty} \chi_{i,A1}(p_i, q_i, r_i, a_i) \chi_{j,B1}(p_j, q_j, r_j, a_j) \\ &\quad \times \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_{k,O2}(p_k, q_k, r_k, a_k) \\ &\quad \times \chi_{l,O2}(p_l, q_l, r_l, a_l) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (29)$$

Using the multipolar expansion,

$$\begin{aligned} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} &= 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{l,m}^*(\hat{\mathbf{r}}_1) Y_{l,m}(\hat{\mathbf{r}}_2) \\ &= 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \frac{1}{r_{>}^{2l+1}} r_1^l Y_{l,m}^*(\hat{\mathbf{r}}_1) r_2^l Y_{l,m}(\hat{\mathbf{r}}_2). \end{aligned} \quad (30)$$

From Eq. (29) we can identify $r_{>} = r_2$ and $r_{<} = r_1$; therefore,

$$\begin{aligned} \text{ERI}_{\text{tail}} &= 4\pi \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \frac{1}{2l'+1} \left[\int_{r_1=0}^{r_1=R} r_1^{l'} Y_{l',m'}^*(\hat{\mathbf{r}}_1) \right. \\ &\quad \times \chi_{i,A1}(p_i, q_i, r_i, a_i) \chi_{j,B1}(p_j, q_j, r_j, a_j) d\mathbf{r}_1 \\ &\quad \times \int_{r_2=R}^{r_2=\infty} \frac{1}{r_2^{l'+1}} Y_{l',m'}(\hat{\mathbf{r}}_2) \chi_{k,O2}(p_k, q_k, r_k, a_k) \\ &\quad \left. \times \chi_{l,O2}(p_l, q_l, r_l, a_l) d\mathbf{r}_2 \right]. \end{aligned} \quad (31)$$

Since we are assuming the nucleus-centered CGOs have negligible amplitude outside the \mathbf{R} -matrix radius, we can extend the range of integration over \mathbf{r}_1 to all space,

$$\begin{aligned} \text{ERI}_{\text{tail}} = & 4\pi \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \frac{1}{2l'+1} \left[\int_{r_1=0}^{r_1=\infty} r_1^{l'} Y_{l',m'}^*(\hat{\mathbf{r}}_1) \right. \\ & \times \chi_{i,A1}(p_i, q_i, r_i, a_i) \chi_{j,B1}(p_j, q_j, r_j, a_j) d\mathbf{r}_1 \\ & \times \int_{r_2=R}^{r_2=\infty} \frac{1}{r_2^{l'+1}} Y_{l',m'}(\hat{\mathbf{r}}_2) \chi_{k,O2}(p_k, q_k, r_k, a_k) \\ & \left. \times \chi_{l,O2}(p_l, q_l, r_l, a_l) d\mathbf{r}_2 \right]. \end{aligned} \quad (32)$$

First consider the integration over \mathbf{r}_2 . Using Eqs. (10) and (13), the number of Gaussians involved in this integration is reduced to one and

$$\begin{aligned} & \int_{r_2=R}^{r_2=\infty} \frac{1}{r_2^{l'+1}} Y_{l',m'}(\hat{\mathbf{r}}_2) \chi_{k,O2}(p_k, q_k, r_k, a_k) \chi_{l,O2}(p_l, q_l, r_l, a_l) d\mathbf{r}_2 \\ & = \sum_{l''=0}^{\infty} \sum_{m''=-l''}^{l''} B_{pqr}^{l''m''} \int_{r_2=R}^{r_2=\infty} r_2^{p+q+r-l'-1} e^{-ar_2^2} Y_{l',m'}(\hat{\mathbf{r}}_2) \\ & \quad \times Y_{l'',m''}(\hat{\mathbf{r}}_2) d\mathbf{r}_2, \end{aligned} \quad (33)$$

where $p=p_k+p_l$, $q=q_k+q_l$, $r=r_k+r_l$, and $a=a_k+a_l$. After integration over the angular variables, we have

$$\begin{aligned} & \int_{r_2=R}^{r_2=\infty} \frac{1}{r_2^{l'+1}} Y_{l',m'}(\hat{\mathbf{r}}_2) \chi_{k,O2}(p_k, q_k, r_k, a_k) \chi_{l,O2}(p_l, q_l, r_l, a_l) d\mathbf{r}_2 \\ & = B_{pqr}^{l'm'} \int_R^{\infty} r_2^{p+q+r-l'+1} e^{-ar_2^2} dr_2 \\ & = B_{pqr}^{l'm'} \frac{\Gamma[1/2(p+q+r-l')+1, aR^2]}{2a^{1/2(p+q+r-l')+1}}. \end{aligned} \quad (34)$$

Now consider the integration over \mathbf{r}_1 . Since the range of integration is over all space, it is easiest to calculate this integral using Cartesian coordinates. The transformation between Cartesian functions to spherical harmonic functions¹⁹ is given by

$$\begin{aligned} & \int_{r_1=0}^{r_1=\infty} r_1^{l'} Y_{l',m'}^*(\hat{\mathbf{r}}_1) \chi_{i,A1}(p_i, q_i, r_i, a_i) \chi_{j,B1}(p_j, q_j, r_j, a_j) d\mathbf{r}_1 \\ & = e^{-a_i a_j (\mathbf{A} - \mathbf{B})^2 / (a_i + a_j)} \sum_{l_x+l_y+l_z=l'} \tilde{c}^*(l', m', l_x, l_y, l_z) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (x_{P1} + P1_x)^{l_x} (y_{P1} + P1_y)^{l_y} (z_{P1} + P1_z)^{l_z} \\ & \quad \times x_{A1}^{p_i} y_{A1}^{q_i} z_{A1}^{r_i} x_{B1}^{p_j} y_{B1}^{q_j} z_{B1}^{r_j} e^{-(a_i+a_j)x_{P1}^2} e^{-(a_i+a_j)y_{P1}^2} e^{-(a_i+a_j)z_{P1}^2} dx_1 dy_1 dz_1. \end{aligned} \quad (40)$$

The analysis is simpler if the other Cartesian components are also expressed in terms of \mathbf{r}_P . For example,

$$x_{A1} = x - A1_x = (x - P1_x) + (P1_x - A1_x) = x_{P1} + PA1_x, \quad (41)$$

where $PA1_x \equiv P1_x - A1_x$. Therefore

$$r^l Y_{l,m}(\hat{\mathbf{r}}) = \sum_{l_x+l_y+l_z=l} \tilde{c}(l, m, l_x, l_y, l_z) x^{l_x} y^{l_y} z^{l_z}, \quad (35)$$

where the complex constant $\tilde{c}(l, m, l_x, l_y, l_z)$ for unnormalized CGOs with $m > 0$ is given by

$$\begin{aligned} \tilde{c}(l, m, l_x, l_y, l_z) = & (-1)^m \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} \frac{1}{2^l l!} \sum_{i=0}^{(l-|m|)/2} \binom{l}{i} \\ & \times \binom{i}{(l_x+l_y-|m|)/2} \frac{(-1)^i (2l-2i)!}{(l-|m|-2i)!} \\ & \times \sum_{k=0}^{(l_x+l_y-|m|)/2} \binom{(l_x+l_y-|m|)/2}{k} \binom{|m|}{l_x-2k} \\ & \times (-1)^{(|m|-l_x+2k)/2}, \end{aligned} \quad (36)$$

which is modified from Schlegel and Frisch's original normalized expression to follow our phase choice for $m > 0$. The transformation to Cartesian functions for $m < 0$ is obtained using the phase choice given in Eq. (3).

The following identity will be very helpful in simplifying all further calculations:

$$\begin{aligned} \chi_{i,A}(0, 0, 0, a_i) \chi_{j,B}(0, 0, 0, a_j) & = e^{-a_i^2 \lambda^2} e^{-a_j^2 \lambda^2} \\ & = e^{-a_i a_j (\mathbf{A} - \mathbf{B})^2 / (a_i + a_j)} e^{-(a_i + a_j) r_P^2}, \end{aligned} \quad (37)$$

where

$$\mathbf{r}_P = \mathbf{r} - \mathbf{P} = \mathbf{r} - \frac{a_i \mathbf{A} + a_j \mathbf{B}}{a_i + a_j}. \quad (38)$$

It is also helpful to express Eq. (35) in terms of the Cartesian components of \mathbf{r}_P ,

$$\begin{aligned} r^l Y_{l,m}(\hat{\mathbf{r}}) & = \sum_{l_x+l_y+l_z=l} \tilde{c}(l, m, l_x, l_y, l_z) (x_P + P_x)^{l_x} (y_P + P_y)^{l_y} \\ & \quad \times (z_P + P_z)^{l_z}, \end{aligned} \quad (39)$$

where $x_P = x - P_x$, $y_P = y - P_y$, and $z_P = z - P_z$. Using Eqs. (37) and (39), the integral over \mathbf{r}_1 is given by

$$\begin{aligned}
& \int_{r_1=0}^{r_1=\infty} r_1^{l'} Y_{l',m'}^*(\hat{\mathbf{r}}_1) \chi_{i,A1}(p_i, q_i, r_i, a_i) \chi_{j,B1}(p_j, q_j, r_j, a_j) d\mathbf{r}_1 \\
&= e^{-a_i a_j (\mathbf{A1} - \mathbf{B1})^2 / (a_i + a_j)} \sum_{l_x + l_y + l_z = l'} \tilde{c}^*(l', m', l_x, l_y, l_z) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (x_{P1} + P1_x)^{l_x} (y_{P1} + P1_y)^{l_y} (z_{P1} + P1_z)^{l_z} (x_{P1} + PA1_x)^{p_i} \\
&\quad \times (y_{P1} + PA1_y)^{q_i} (z_{P1} + PA1_z)^{r_i} (x_{P1} + PB1_x)^{p_j} (y_{P1} + PB1_y)^{q_j} (z_{P1} + PB1_z)^{r_j} e^{-(a_i + a_j) x_{P1}^2} e^{-(a_i + a_j) y_{P1}^2} e^{-(a_i + a_j) z_{P1}^2} dx_1 dy_1 dz_1. \quad (42)
\end{aligned}$$

The notation of Eq. (42) can be condensed further and rewritten as

$$\begin{aligned}
& \int_{r_1=0}^{r_1=\infty} r_1^{l'} Y_{l',m'}^*(\hat{\mathbf{r}}_1) \chi_{i,A1}(p_i, q_i, r_i, a_i) \chi_{j,B1}(p_j, q_j, r_j, a_j) d\mathbf{r}_1 \\
&= e^{-a_i a_j (\mathbf{A1} - \mathbf{B1})^2 / (a_i + a_j)} \sum_{l_x + l_y + l_z = l'} \tilde{c}^*(l', m', l_x, l_y, l_z) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sum_{\alpha=0}^{l_x + p_i + p_j} f_{\alpha}(l_x, p_i, p_j, P1_x, PA1_x, PB1_x) x_{P1}^{\alpha} e^{-(a_i + a_j) x_{P1}^2} \\
&\quad \times \sum_{\beta=0}^{l_y + q_i + q_j} f_{\beta}(l_y, q_i, q_j, P1_y, PA1_y, PB1_y) y_{P1}^{\beta} e^{-(a_i + a_j) y_{P1}^2} \sum_{\gamma=0}^{l_z + r_i + r_j} f_{\gamma}(l_z, r_i, r_j, P1_z, PA1_z, PB1_z) z_{P1}^{\gamma} e^{-(a_i + a_j) z_{P1}^2} dx_1 dy_1 dz_1, \quad (43)
\end{aligned}$$

where $f_{\alpha}(l_x, p_i, p_j, P1_x, PA1_x, PB1_x)$ is the coefficient of x_{P1}^{α} in the expansion $(x_{P1} + P1_x)^{l_x} (x_{P1} + PA1_x)^{p_i} (x_{P1} + PB1_x)^{p_j}$. This coefficient is given by

$$f_{\alpha}(l_x, p_i, p_j, P1_x, PA1_x, PB1_x) = \sum_{a=0, l_x}^{a+b+c=\alpha} \sum_{b=0, p_i} \sum_{c=0, p_j} P1_x^{l_x - a} \binom{l_x}{a} PA1_x^{p_i - b} \binom{p_i}{b} PB1_x^{p_j - c} \binom{p_j}{c}. \quad (44)$$

Expressions for the other Cartesian components are similar.

By symmetry, only the even powers of x_{P1} , y_{P1} , and z_{P1} give nonzero contributions to the integral. The following integral is useful:

$$\int_{-\infty}^{\infty} x^{2n} e^{-\alpha x^2} dx = \frac{(2n-1)!!}{(2\alpha)^n} \sqrt{\frac{\pi}{\alpha}}, \quad (45)$$

where n is a positive integer. The integral over \mathbf{r}_1 becomes

$$\begin{aligned}
& \int_{r_1=0}^{r_1=\infty} r_1^{l'} Y_{l',m'}^*(\hat{\mathbf{r}}_1) \chi_{i,A1}(p_i, q_i, r_i, a_i) \chi_{j,B1}(p_j, q_j, r_j, a_j) d\mathbf{r}_1 \\
&= \left(\frac{\pi}{a_i + a_j} \right)^{3/2} e^{-a_i a_j (\mathbf{A1} - \mathbf{B1})^2 / (a_i + a_j)} \sum_{l_x + l_y + l_z = l'} \tilde{c}^*(l', m', l_x, l_y, l_z) \sum_{\alpha=0}^{[(l_x + p_i + p_j)/2]} f_{2\alpha}(l_x, p_i, p_j, P1_x, PA1_x, PB1_x) \\
&\quad \times \frac{(2\alpha - 1)!!}{[2(a_i + a_j)]^{\alpha}} \sum_{\beta=0}^{[(l_y + q_i + q_j)/2]} f_{2\beta}(l_y, q_i, q_j, P1_y, PA1_y, PB1_y) \frac{(2\beta - 1)!!}{[2(a_i + a_j)]^{\beta}} \sum_{\gamma=0}^{[(l_z + r_i + r_j)/2]} f_{2\gamma}(l_z, r_i, r_j, P1_z, PA1_z, PB1_z) \frac{(2\gamma - 1)!!}{[2(a_i + a_j)]^{\gamma}}. \quad (46)
\end{aligned}$$

Note that Eq. (32) is finite because it is limited by the coefficient B_{ijk}^{lm} in Eq. (34). Thus, the electron repulsion tail integral is given by summations over the product of Eqs. (34) and (46).

VII. ACCURACY OF ANALYTICAL INTEGRATIONS

The closed-form expressions in Eqs. (15), (17), (23), (25), (34), and (46) are the main objectives of this work. Using these analytical expressions, one can incorporate **R**-matrix methods in existing electronic structure calculations on diatomic and polyatomic molecules. Since the com-

putation of the two-electron repulsion tail integrals is the most difficult, a numerical evaluation of the two-electron repulsion tail integrals provides a good test of the accuracy of our analytical expressions. As a validating example, we calculate several electron repulsion tail integrals for a CaF^+ molecular ion with the equilibrium internuclear distance of $3.54a_0$.⁴ In future work, these molecular integrals will be used in a multielectron generalization of our previous **R**-matrix treatment of CaF , which used a single electron effective potential.⁶ In all the numerical and analytical calculations, the CaF^+ ion is oriented along the z axis, and the CGOs used in the tail integral of Eq. (27) are given by

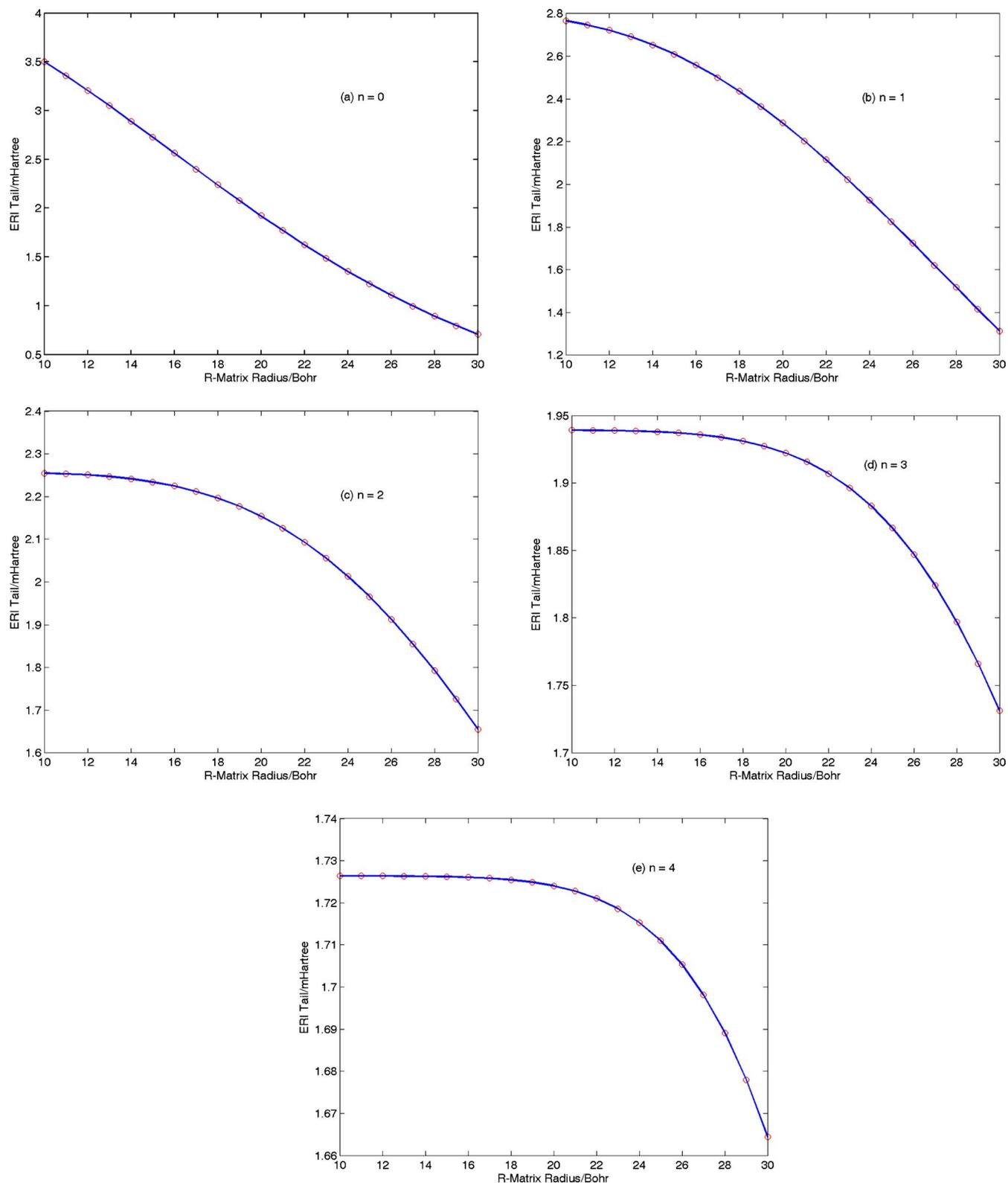


FIG. 2. [(a)–(e)] Electron repulsion tail integrals as a function of the \mathbf{R} -matrix radius for s -, p -, d -, f -, and g -type continuum orbitals. All of the numerical parameters for each of the plots were taken from Eqs. (47) and (48). The open circles correspond to a full six-dimensional numerical integration of the tail integrals, and solid lines are the result of the analytical summations over the product of Eqs. (34) and (46). The analytical expressions are in excellent agreement with the multidimensional numerical integrations.

$$\begin{aligned}\chi_{i,A1} &= 0.046\,168e^{-0.026\,016\,199\,96r_{A1}^2}, \\ \chi_{j,B1} &= 0.345\,60(z_1 + 2.4)e^{-0.321\,892r_{B1}^2}, \\ \chi_{k,O2} = \chi_{l,O2} &= \sqrt{\left(\frac{0.002}{\pi}\right)^{3/2} \frac{0.004^n}{(2n-1)!!}} z_2^n e^{-0.001r_2^2},\end{aligned}\quad (47)$$

where

$$\begin{aligned}\mathbf{r}_{A1} &= \mathbf{r}_1 - (0, 0, 1.14), \\ \mathbf{r}_{B1} &= \mathbf{r}_1 - (0, 0, -2.4),\end{aligned}\quad (48)$$

and $n=0, 1, 2, 3$, or 4 . The numerical parameters used in Eqs. (47) and (48) were taken from Pople's 6-311G(*d*) normalized basis set where $\chi_{i,A1}$ is an *s*-type calcium CGO, and $\chi_{j,B1}$ is a *p*-type fluorine CGO. In our numerical comparisons, we have allowed both $\chi_{k,O2}$, and $\chi_{l,O2}$ to occupy identical *s*-, *p*-, *d*-, *f*-, and *g*-type continuum orbitals ($n=0, 1, 2, 3$, or 4) with a very diffuse exponent. We compare the analytical results of the electron repulsion tail integral given by summations over the product of Eqs. (34) and (46) against a full six-dimensional numerical integration of the tail region of Eq. (27). Due to the high dimensionality of the electron repulsion tail integrals, we performed the numerical computations using a Monte Carlo integration algorithm in the MATHEMATICA 5.2 software package with 5×10^7 independent sample points throughout the integration region. This number of sample points was chosen to ensure the integration results remained accurate in the first two digits after the decimal point. The plots in Figs. 2(a)–2(e) demonstrate the quality of our analytic expressions for the *s*-, *p*-, *d*-, *f*-, and *g*-type continuum orbitals with **R**-matrix radii ranging from $20a_0$ to $30a_0$. For each of the **R**-matrix radius values, our analytic expressions are numerically within 1% of the full six-dimensional integration; similar accuracy is seen in the tail integrals for the higher angular-momentum continuum orbitals. It is clear that the computation of the two-electron repulsion tail integrals is not efficient using multidimensional Monte Carlo algorithms or even any other numerical integration method. The number of unique two-electron tail integrals, which must be evaluated in an *ab initio* calculation scales approximately as $N^4/8$, where N is the number of basis functions. For example, a multielectron calculation with a modest basis size of $N=100$ produces 1.25×10^7 two-electron tail integrals. The calculation of a single tail integral with the Monte Carlo scheme used here takes on the order of 5 min of computation time. Therefore, the calculation of this enormous number of integrals using six-dimensional numerical quadrature would result in very poor efficiency. The numerical examples presented merely demonstrate the adequacy of our method and validate the approximations in **R**-matrix integral evaluation.

VIII. CONCLUSIONS

All of the necessary molecular integral expressions for multielectron **R**-matrix methods are presented here in closed form. The **R**-matrix method requires specialized evaluations of molecular integrals since they are defined only within a

finite spherical volume. In this paper we have presented practical expressions for the evaluation of all of these nonstandard integrals. The proposed scheme for calculating molecular tail integrals fits conveniently within the framework of existing electronic structure programs. Rather than modify highly efficient codes for molecular integral evaluation, subtracting the outer or tail regions permits the evaluation of Hamiltonian matrix elements within the required finite spherical volume. Thus, the implementation of our approach, exploiting current bound-state software packages, is straightforward and practical. Furthermore, the required one- and two-electron tail integrals are expressed analytically without resorting to any type of numerical quadrature. Our detailed numerical analysis of the electron repulsion tail integrals for various angular momenta and **R**-matrix radii constitutes a test of the accuracy of our approximations and expressions.

To our knowledge, this is the first time that the analytical closed forms for the one- and two-electron integrals for **R**-matrix CGOs have been presented in the literature. Our treatment of the **R**-matrix molecular integrals is especially useful since the analytical forms allow the evaluation of these integrals to arbitrarily high accuracy for a given set of exponents and **R**-matrix radii. This analytical approach is expected to be more efficient and accurate for calculations on large polyatomics than the numerical approach used in version 6 of the MOLCAS software package.²⁰ It is important to mention that all of the molecular integrals given in this work are finite summations and can be applied to CGOs with any arbitrary angular momentum.

Future work will utilize the results derived here in a multielectron generalization of our previous treatment of CaF. This generalization allows for the inclusion of electronic configuration interaction, which becomes important in CaF at large internuclear distances. The repulsive state in the $\text{Ca}(4s^2)+\text{F}2p\sigma^{-1}$ hole $^2\Sigma^+$ configuration, goes through numerous avoided crossings with the Rydberg states of the type $n^* \ ^2\Sigma^+ \text{Ca}^2\text{F}^-$ at various internuclear distances. These avoided crossings with the repulsive state can only be calculated in the framework of multielectron **R**-matrix theory built upon a configuration-interaction (CI) treatment of the ion core.

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