Generation of a two-center overlap integral over Slater orbitals of higher principal quantum numbers

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The expressions for two-center overlap integrals between angular s, p, and d Slater orbitals of arbitrary, higher principal quantum number are explicitly listed. The expressions obtained are extremely compact and independent of the coordinate system. It is further shown that the numerical values of the integrals obtained in this way are free from any numerical instability.

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I. INTRODUCTION

It is well known that in any *ab initio* molecular-orbital (MO) calculation, the major task involves the computation of molecular integrals, among which the computations of overlap integrals between two atomic orbitals (AO's) is the most frequently encountered. Although Gaussian-type functions (GTF's) are frequently used as AO's in many MO calculations, Slater-type orbitals (STO's) are preferred because they possess a better description of electronic distribution. However, it is more difficult to evaluate a STO molecular integral, especially in the multicentered case. Historically, the development of molecular-integral programs has played a major role in the development of theoretical chemistry and molecular physics. Consequently, there has been a great deal of discussion in the literature [1]; numerical tables and computer programs are also readily available [2]. Parameters associated with STO's and generated by the self-consistent-field (SCF) Hartree-Fock procedure are available for many atoms and ions [3]. By close examination, however, we have found that the majority of past work was patterned after the research pioneered by Mulliken *et al.*, whose approach formulated the calculation in the spheroidal coordinates, thereby requiring the quantization axis to be along the two nuclear centers. For polyatomic calculations, using this approach is often awkward. Nevertheless, to our knowledge, there are no general formulas for higher, arbitrary principal-quantum-number STO's. Another approach is to use the Fourier-transform technique [4] or an equivalent technique on the so called B function [5];. The B function belongs to a special class of exponential-type functions which is related to the reduced Bessel function. Recently, the B function received wide attention from its use as a basis function in a molecular *ab initio* calculation because of the simplicity of its Fourier transform. Consequently, a great deal of work has been done. A simple transformation between STO's and the B function has been obtained [5(b)]. In other words, a general STO can be expressed as the finite sum of a linear combination of the B functions or vice versa. By examining the transformation relation in Ref. [5(b)], we point out that a B function of a given principal quantum number and angular momentum quantum number is the sum of all STO's of the same angular momentum quantum number, but with different principal quantum number, from $n=1$ to the given principal quantum number. For example, a $5s$ B function is a linear combination of all $1s, 2s, \ldots$ up to $5s$ STO's. Therefore, a $\langle 5s|5s\rangle$ B-function overlap would consist of a sum of 25 terms of STO overlap integrals with different coefficients. For inverse transformation, i.e., the expression of a STO in terms of B functions, the number of terms is considerably less, in general, from 2 to 4 terms; i.e., one has to compute from 4 to 16 B-function integrals to obtain one STO integral. A general expression of overlap integrals between the B functions has been worked out. Therefore, a general expression of overlap integrals between STO's via the B function is obtainable; however, a summation operation is still required, especially when high principal quantum numbers are involved, which may increase its computing time by a big factor. There are also general expressions for STO overlap integrals; for example, the expression by Silverstone [6(a)] and others [6(b)] contains differentiation operations which often cannot be used efficiently in numerical calculation. Bhattacharya and Dhabal [7] also gave general expressions of overlap two-center molecular integrals between the STO's. Their expressions involve finite sums of one-dimensional numerical integration of infinite domain and, like many other procedures (including one of our two procedures), exhibit unreliable characteristics for some ranges of values of the orbital scaling parameters (or orbital exponents). A brief discussion of numerical aspects was also given by Weniger and Steinborn [8]. The present author recently gave explicit expressions for the one-electron–two-center overlap integrals, essentially up to $3d$ states [9(a)]. A closed, analytical expression can be obtained in the final form. More recently, the author also presented an article [9(b)] in which the expressions of multicenter molecular integrals involving higher-principal-quantum-number STO's are derived. The intent of this paper is to apply the same technique to generalize the expressions for one-electron–two-center overlap integrals coupling all ns, np, and nd states, n being any principal quantum number. Even though the present expressions are not general in the sense of arbitrary angular quantum number, for different angular quantum number, a specific expression has to be worked out. On the other hand, this approach offers a way to generate the

value of the integrals in a very speedy and reliable fashion that, in our opinion, exceeds the previously known methods.

II. PROCEDURES AND DERIVATIONS

The general, real, normalized STO is denoted as

$$\begin{aligned}\psi_{n,l,m}(\xi,\mathbf{r}) &= (2\xi)^{(2n+1)/2}/\sqrt{(2n)!}\,r^{n-1} \\ &\quad \times e^{-\xi r} Z^i_{l,m}(\hat{\mathbf{r}}) \\ &= C_n(\xi) r^{n-1} e^{-\xi r} Z^i_{lm}(\hat{\mathbf{r}}) \ , \end{aligned} \tag{1}$$

where the angular orbitals $Z^i_{lm}(\hat{\mathbf{r}})$, commonly referred as tesseral harmonics, are real and can be expressed as a linear combination of spherical harmonics Y_{lm} such as

$$\begin{aligned} Z^0_{l0} &= Y_{l0} \ , \\ Z^c_{lm} &= (1/\sqrt{2})[Y_{l-m} + (-1)^m Y_{lm}] \ , \quad m>0 \\ Z^s_{lm} &= (i/\sqrt{2})[Y_{l-m} - (-1)^m Y_{lm}] \ , \quad m>0 \ . \end{aligned} \tag{2}$$

In particular, some of the low-lying angular momentum states [10] and their commonly adopted notations (in parentheses) are listed in the following:

$$\begin{aligned} s &= \sqrt{1/4\pi} = Y_{00}(\hat{\mathbf{r}}) \ , \\ p_x &= p\pi = \sqrt{3/4\pi}\frac{x}{r} = \sqrt{1/2}[Y_{1-1}(\hat{\mathbf{r}}) - Y_{11}(\hat{\mathbf{r}})] \ , \\ p_y &= p\pi' = \sqrt{3/4\pi}\frac{y}{r} = \sqrt{1/2}i[Y_{1-1}(\hat{\mathbf{r}}) + Y_{11}(\hat{\mathbf{r}})] \ , \\ p_z &= p\sigma = \sqrt{3/4\pi}\frac{z}{r} = Y_{10}(\hat{\mathbf{r}}) \ , \\ d_{z^2} &= d\sigma = \sqrt{5/4\pi}\frac{1}{2}\frac{3z^2-r^2}{r^2} = Y_{20}(\hat{\mathbf{r}}) \ , \\ d_{x^2-y^2} &= d\delta = \sqrt{5/4\pi}\frac{1}{2}\sqrt{3}\frac{x^2-y^2}{r^2} \\ &= \sqrt{1/2}[Y_{22}(\hat{\mathbf{r}}) + Y_{2-2}(\hat{\mathbf{r}})] \ , \\ d_{xy} &= d\delta' = \sqrt{5/4\pi}\sqrt{3}\frac{xy}{r^2} \\ &= \sqrt{1/2}i[-Y_{22}(\hat{\mathbf{r}}) + Y_{2-2}(\hat{\mathbf{r}})] \ , \\ d_{yz} &= d\pi' = \sqrt{5/4\pi}\sqrt{3}\frac{yz}{r^2} \\ &= \sqrt{1/2}i[Y_{21}(\hat{\mathbf{r}}) + Y_{2-1}(\hat{\mathbf{r}})] \ , \\ d_{zx} &= d\pi = \sqrt{5/4\pi}\sqrt{3}\frac{zx}{r^2} \\ &= \sqrt{1/2}[-Y_{21}(\hat{\mathbf{r}}) + Y_{2-1}(\hat{\mathbf{r}})] \ . \end{aligned} \tag{3}$$

In the following, part of the derivation is parallel to Ref. [9(b)], which is repeated here for convenience. In Ref. [9(a)] we have given the two-center overlap-integral coupling two $1s$ atomic orbitals with exponents c and d, located at centers A and B whose coordinates are denoted as $\mathbf{R}_A$ and $\mathbf{R}_B$, respectively:

$$\begin{aligned} L &= \langle 1sA \,|\, 1sB \rangle \\ &= [C_1(c)C_1(d)/2]\int_0^1 cd[\kappa_2(\lambda R)R^3 u(1-u)/\lambda^2]du \ . \end{aligned} \tag{4}$$

In the above equation, κ_n is the spherical modified Bessel function [11], $\mathbf{R}=\mathbf{R}_B-\mathbf{R}_A$ is the intercenter radius vector, and λ is the positive root of $\lambda^2 = uc^2 + (1-u)d^2$.

Likewise, the integral coupling $2s$ and $1s$ orbitals can be written as

$$\begin{aligned} L_2 &= \langle 2sA \,|\, 1sB \rangle \\ &= [C_2(c)C_1(d)/2] \\ &\quad \times \int_0^1 d[R^4 u^2(1-u)c^2\kappa_3/\lambda^3 - R^3 u(1-u)\kappa_2/\lambda^2]du \ . \end{aligned} \tag{5}$$

If the integrand in Eq. (4) is denoted as

$$I = cd[\kappa_2(\lambda R)R^3 u(1-u)/\lambda^2] \ , \tag{6a}$$

then the integrand of Eq. (5), I_2, can be obtained according to Ref. [9(a)] by the following simple differentiation operation:

$$I_2 = \left[\frac{-\partial}{\partial c}\right] I \ . \tag{6b}$$

We point out that the normalization constant $C_n(\xi)$ is also a function of ξ, but was never involved in the parametric differentiation process.

Now we will generalize the process in the following way: A new variable $x = R\lambda$ is introduced, and Eq. (6a) can be written as

$$\begin{aligned} I &= cd[\kappa_l(x)/x^l]R^{2l+1}u(1-u) \\ &= cdf_l \ , \quad l=2 \end{aligned} \tag{7}$$

where

$$f_l = (\kappa_l/x^l)R^{2l+1}u(1-u) \ . \tag{8}$$

Considering I as a function of c and d, its mth and nth derivative with respect to c and d, respectively, can simply be expressed as

$$\begin{aligned} I^{mn} &= \left[\frac{\partial}{\partial c}\right]^m \left[\frac{\partial}{\partial d}\right]^n I \\ &= cd\left[\frac{\partial^m}{\partial c^m}\right]\left[\frac{\partial^n}{\partial d^n}\right] f_l + nc\left[\frac{\partial^m}{\partial c^m}\right]\left[\frac{\partial^{n-1}}{\partial d^{n-1}}\right] f_l \\ &\quad + md\left[\frac{\partial^{m-1}}{\partial c^{m-1}}\right]\left[\frac{\partial^n}{\partial d^n}\right] f_l \\ &\quad + mn\left[\frac{\partial^{m-1}}{\partial c^{m-1}}\right]\left[\frac{\partial^{n-1}}{\partial d^{n-1}}\right] f_l \ . \end{aligned} \tag{9}$$

Now the derivative of f_l requires more attention:

$$\frac{\partial f_l}{\partial c}=\frac{\partial x}{\partial c}\frac{df_l}{dx}=-c(\kappa_{l+1}/x^{l+1})R^{2(l+1)+1}u^2(1-u)\ , \tag{10}$$

where the differential formula for κ_n has been used [11]:

$$\frac{d(x^n\kappa_n)}{xdx}=-(x^{-(n+1)}\kappa_{n+1}) \tag{11}$$

and

$$\frac{\partial x}{\partial c}=R^2uc/x\ . \tag{12}$$

Define the quantity

$$F_l^{p,q,t}(m,n)=(-1)^{m+n}\frac{\kappa_{l+m+n}}{x^{l+m+n}} \times R^{2(l+m+n)+t}u^{m+p}(1-u)^{n+q}\ . \tag{13}$$

The introduction of constant parameters p,q,t is needed for accommodating different angular functions later. In the present case, $p=q=t=1$. Thus we have the following successive derivatives:

$$\frac{\partial f_l}{\partial c}=cF_l^{1,1,1}(1,0)\ ,$$

$$\frac{\partial^2 f_l}{\partial c^2}=c^2F_l^{1,1,1}(2,0)+F_l^{1,1,1}(1,0)\ ,$$

$$\frac{\partial^3 f_l}{\partial c^3}=c^3F_l^{1,1,1}(3,0)+3cF_l^{1,1,1}(2,0)\ , \tag{14}$$

$$\frac{\partial^4 f_l}{\partial c^4}=c^4F_l^{1,1,1}(4,0)+6c^2F_l^{1,1,1}(3,0)+3F_l^{1,1,1}(2,0)\ ,$$

$$\frac{\partial^5 f_l}{\partial c^5}=c^5F_l^{1,1,1}(5,0)+10c^3F_l^{1,1,1}(4,0)+15cF_l^{1,1,1}(3,0)\ ,\ \text{etc.}$$

By inspection, we can write the general derivative as

$$f_l^m=\frac{\partial^m f_l}{\partial c^m}=\sum_{j=0}^{[m/2]}(2j-1)!!\begin{bmatrix}m\\2j\end{bmatrix}c^{m-2j}F_l^{1,1,1}(m-j,0)\ . \tag{15}$$

In Eq. (15) each quantity is well defined; $[m/2]$ is understood as an integral part of $m/2$; $(-1)!!=1$, and $\binom{m}{2j}$ is the standard binomial coefficient. Likewise,

$$f_l^{m,n}=\frac{\partial^m}{\partial c^m}\frac{\partial^n}{\partial d^n}f_l =\sum_{j=0}^{[m/2]}\sum_{i=0}^{[n/2]}(2j-1)!!(2i-1)!!\begin{bmatrix}m\\2j\end{bmatrix}\begin{bmatrix}n\\2i\end{bmatrix}c^{m-2j}d^{n-2i}F_l^{1,1,1}(m-j,n-i)\ . \tag{16}$$

In order to show the dependence of $f_l^{m,n}$ on the parameters p, q, and t, we write instead $f_{l,p,q,t}^{m,n}$; i.e., we define

$$f_{l,p,q,t}^{m,n}=\sum_{j=0}^{[m/2]}\sum_{i=0}^{[n/2]}(2j-1)!!(2i-1)!!\begin{bmatrix}m\\2j\end{bmatrix}\begin{bmatrix}n\\2i\end{bmatrix}c^{m-2j}d^{n-2i}F_l^{p,q,t}(m-j,n-i)\ . \tag{17}$$

Therefore, a two-center overlap integral between an *ms* orbital and an *ns* orbital can be expressed as

$$\langle msA|nsB\rangle=(-1)^{m+n-2}[C_m(c)C_n(d)/2][cdf_{2,1,1,1}^{m-1,n-1}+(n-1)cf_{2,1,1,1}^{m-1,n-2} +(m-1)df_{2,1,1,1}^{m-2,n-1}+(m-1)(n-1)f_{2,1,1,1}^{m-2,n-2}]\ ,\quad m\geq 1\ ,\quad n\geq 1\ . \tag{18}$$

In Ref. [9(a)] it was shown that Eq. (4) can be integrated numerically rather simply and sometimes faster than the analytical expression which essentially performed a summation; however, at times, it is more desirable to achieve an analytical solution for elucidating its functional behavior. We will give the general expression for the following integral, from Eq. (13):

$$J=\int_0^1(-1)^{m+n}\frac{\kappa_{1+m+n}(\lambda R)}{\lambda^{l+m+n}}R^{(l+m+n)+t}u^{m+p}(1-u)^{n+q}du \tag{19}$$

$$=\sum_{j=0}^{[m+p]}\sum_{i=0}^{[n+q]}\int_d^c 2(-1)^{m+n+j+i}\frac{\kappa_{l+m+n}(\lambda R)}{\lambda^{l+m+n}}R^{l+m+n+t}\begin{bmatrix}m+p\\j\end{bmatrix}\begin{bmatrix}n+q\\i\end{bmatrix}\frac{c^{2(n+q-i)}d^{2j}\lambda^{2m+2p-2j+2i+1}}{(c^2-d^2)^{m+n+p+q+1}}d\lambda$$

$$=2\sum_{j=0}^{[m+p]}\sum_{i=0}^{[n+q]}(-1)^{m+n+j+i}\frac{c^{2(n+q-i)}d^{2j}G_{l+m+n,t}^{2m+2p-2j+2i+1}}{(c^2-d^2)^{m+n+p+q+1}}\ , \tag{20}$$

where the integration variable u has been replaced by λ. $G_{n,t}^m=G_{n,t}^m(R,c,d)$ is defined as

$$G^m_{n,t}=\int_d^c \frac{R^{n+t}}{\lambda^n}\kappa_n(\lambda R)\lambda^m d\lambda \ , \quad m=\text{odd} \ , \tag{21}$$

which can be expressed as

$$\begin{aligned}
G^m_{n,t}&=R^{2n-m+t-1}\int_{dR}^{cR} x^{m-n}\kappa_n(x)dx \ , \quad x=\lambda R \\
&=R^{2n-m+t-1}\sum_{j=0}^{n}\frac{(n+j)!}{2^j(n-j)!}\int_{dR}^{cR}x^{m-n-1-j}e^{-x}dx \\
&=R^{2n-m+t-1}\sum_{j=0}^{n}\frac{(n+j)!}{2^j(n-j)!} \\
&\quad\times\left[-e^{-x}\left[x^{m-n-1-j}+\sum_{k=1}^{m-n-1-j}(m-n-1-j)\cdots(m-n-1-j-k+1)x^{m-n-1-j-k}\right]\right]_{dR}^{cR}, \\
&\qquad\qquad m>n+1+j \\
&=R^{2n-m+t-1}\sum_{j=0}^{n}\frac{(n+j)!}{2^j(n-j)!}\left[-e^{-x}\sum_{k=1}^{n+j-m}\frac{(-1)^{k-1}}{(n+j-m)(n+j-m-1)\cdots(n+j+1-m-k)x^{n+j+1-m-k}}\right. \\
&\quad\left.+\frac{(-1)^{n+j-m+1}}{(n+j-m)!}\mathrm{Ei}(-x)\right]_{dR}^{cR}, \quad m<n+1+j \ ,
\end{aligned} \tag{22}$$

where the exponential integral $\mathrm{Ei}(-y)=-\int_y^\infty e^{-x}x^{-1}dx$ can only be expressed in terms of a series. However, in Ref. [9(a)] it is proved that the coefficient of the exponential integral is identical to zero for $m=$odd, which is this case, i.e.,

$$S_{n,m}=\sum_{j=0}^{n}\frac{(n+j)!(-1)^{n+j-m+1}}{2^j(n-j)!(n+j-m)!}=0 \quad \text{for } m=\text{odd} \ . \tag{23}$$

Therefore, the exponential integral never appears in the calculation.

In the Appendix we give the explicit expressions for two-center overlap integrals for arbitrary principal quantum numbers of angular quantum number ≤ 2. They are quite compact and easy to use.

III. LIMITING CASES

The case has been presented where the two orbitals' exponents are different, i.e., $c\neq d$. The condition for $c=d$ has to be properly invoked as pointed out in Ref. [9(a)]. For example, it is apparent that in our case the condition has to be invoked in Eq. (19); $\lambda\rightarrow c$, $\kappa_{l+m+n}(\lambda R)\rightarrow\kappa_{l+m+n}(cR)$, is independent of u. Equation (19) can be expressed as

$$\begin{aligned}
J&=(-1)^{m+n}\frac{\kappa_{l+m+n}(cR)}{c^{l+m+n}}R^{(l+m+n)+t}\int_0^1 u^{m+p}(1-u)^{n+q}du \\
&=(-1)^{m+n}\frac{\kappa_{l+m+n}(cR)}{c^{l+m+n}}R^{(l+m+n)+t}B(m+p+1,n+q+1) \\
&=(-1)^{m+n}\frac{\kappa_{l+m+n}(cR)}{c^{l+m+n}}R^{(l+m+n)+t}\frac{(m+p)!(n+q)!}{(m+p+n+q+1)!} \ ,
\end{aligned} \tag{24}$$

where, in Eq. (24), $B(p,q)$ denotes the beta function. As for the case where the component c is almost equal to d, Ref. [9(a)] has recommended the evaluation by a Taylor-series expansion, namely, by expanding the integral about the point where the two exponents are identically equal. However, by close examination, numerical integration, e.g., Eq. (19), gives a very stable solution, totally disregarding the values of the exponents. A comparison study will be shown in Sec. IV. Next we will show that the present formulation can transit to the one-center case. As $R\rightarrow 0$, the orthogonality property of the angular orbital will take effect, as is clearly borne out by our expressions. For example, it was pointed out [12] that by examining the series representation of κ_n, with j,n integers, we have

$$\lim_{R\rightarrow 0}R^j\kappa_n(\lambda R)=0 \ , \quad j>n+1 \tag{25}$$

$$=\frac{(2n)!}{2^n\lambda^{n+1}n!} \ , \quad j=n+1 \ . \tag{26}$$

We point out that Eqs. (25) and (26) immediately bear an interesting consequence; i.e., as $R\rightarrow 0$, the overlap integral between two orbitals of different angular quantum number would approach zero. This is clearly borne out in our expressions [see Eqs. (13) and (A1)–(A19)]. The

TABLE I. Comparison of overlap integrals computed by this method [Eq. (19)] (second row) and previously published values (first row).

	$p=1$	$p=2$	$p=7$	$p=10$	Reference
			$t=0.5$		
$\langle 5s\|5s\rangle$	0.977	0.915	0.417	0.166	[1(a)]
	0.981 869	0.931 732	0.521 937	0.280 178	
$\langle 5s\|5p\sigma\rangle$	0.142	0.273	0.445	0.218	[1(a)]
	0.114 206	0.221 257	0.485 406	0.345 197	
$\langle 1s\|5p\sigma\rangle$	0.238	0.431	0.227	0.052	[1(a)]
	0.154 869	0.304 344	0.295 094	0.090 297	
$\langle 5p\sigma\|5p\sigma\rangle$	−0.917	−0.693	0.413	0.281	[1(a)]
	0.941 272	0.779 014	−0.334 816	−0.409 893	
$\langle 5p\pi\|5p\pi\rangle$	0.972	0.893	0.277	0.084	[1(a)]
	0.980 256	0.923 901	0.392 312	0.150 328	
$\langle 2p\pi\|5p\pi\rangle$	0.707	0.635	0.119	0.023	[1(a)]
	0.531 951	0.504 042	0.150 366	0.037 266	
$\langle 3p\pi\|3d\pi\rangle$	0.289	0.487	0.199	0.043	[1(d)]
	0.281 513	0.474 199	0.193 291	0.041 645	
$\langle 2p\sigma\|5d\sigma\rangle$	−0.334	−0.452	0.241	0.118	[1(c)]
	0.258 236	0.401 807	−0.218 250	−0.165 058	
$\langle 2s\|5d\sigma\rangle$	0.055	0.191	0.327	0.106	[1(c)]
	0.047 804	0.169 960	0.420 788	0.175 113	
$\langle 3p\pi\|5d\pi\rangle$	0.285	0.497	0.287	0.076	[1(d)
	0.255 456	0.460 179	0.368 861	0.120 878	
$\langle 3d\pi\|5p\pi\rangle$	0.175	0.321	0.232	0.066	[1(d)]
	0.088 896	0.178 124	0.235 806	0.088 493	
$\langle 5p\pi\|5d\pi\rangle$	0.217	0.395	0.342	0.114	[1(d)]
	0.175 369	0.330 403	0.452 280	0.219 345	
$\langle 3d\sigma\|3d\sigma\rangle$	0.891	0.659	0.097	0.034	[1(b)]
	0.767 291	0.321 797	0.154 959	0.101 028	
$\langle 3d\pi\|5d\pi\rangle$	−0.799	−0.465	0.304	0.107	[1(d)]
	0.706 549	0.486 823	−0.311 709	−0.149 141	
$\langle 3d\sigma\|5d\sigma\rangle$	0.7728	0.4110	0.1244	0.1388	[1(c)]
	0.689 580	0.440 163	0.055 878	0.153 925	
$\langle 3d\delta\|5d\delta\rangle$	0.889	0.772	0.115	0.020	[1(d)]
	0.761 089	0.683 354	0.148 155	0.032 799	
$\langle 5d\pi\|5d\pi\rangle$	−0.882	−0.580	0.373	0.169	[1(d)]
	0.920 998	0.705 946	−0.400 779	−0.299 784	
$\langle 5d\sigma\|5d\sigma\rangle$	0.8587	0.5225	0.0854	0.1810	[1(c)]
	0.904 549	−0.656 643	−0.039 067	0.192 548	
$\langle 5d\delta\|5d\delta\rangle$	0.960	0.851	0.170	0.039	[1(d)]
	0.973 408	0.898 123	0.282 865	0.084 713	
			$t=-0.4$		
$\langle 1s\|5p\sigma\rangle$	0.293	0.493	0.192	0.046	[1(a)]
	0.265 119	0.474 816	0.272 320	0.074 107 1	
			$t=0.1$		
$\langle 2p\pi\|5p\pi\rangle$	0.563	0.515	0.114	0.023	[1(a)]
	0.381 706	0.370 903	0.135 864	0.038 476	
			$t=-0.5$		
$\langle 3d\pi\|5p\pi\rangle$	0.205	0.368	0.322	0.138	[1(d)]
	0.211 458	0.388 342	0.410 794	0.191 359	
			$t=0.5$		
$\langle 3p\pi\|3d\pi\rangle$	0.169	0.324	0.234	0.093	[1(d)]
	−0.181 535	−0.315 229	−0.227 523	−0.090 999	
$\langle 2p\sigma\|5d\sigma\rangle$	−0.066	−0.114	0.012	0.064	[1(c)]
	−0.025 815	−0.052 233	−0.035 751	0.029 884	
$\langle 2s\|5d\sigma\rangle$	0.021	0.078	0.329	0.246	[1(c)]
	0.008 425	0.033 625	0.250 791	0.251 877	
$\langle 3p\pi\|5d\pi\rangle$	0.091	0.169	0.213	0.115	[1(d)]
	−0.040 369	−0.079 669	−0.166 637	−0.119 547	
$\langle 3d\sigma\|3d\sigma\rangle$	0.335	0.265	0.052	0.024	[1(b)]
	0.300 534	0.166 752	0.031 402	0.046 932	

TABLE I. (*Continued*).

	$t=0.5$				
	$p=1$	$p=2$	$p=7$	$p=10$	Reference
$\langle 3d\pi \vert 5d\pi \rangle$	−0.159	−0.126	0.059	0.053	[1(d)]
	0.072 059	0.069 131	−0.014 212	−0.036 014	
$\langle 3d\sigma \vert 5d\sigma \rangle$	0.1565	0.1170	−0.0039	0.0235	[1(c)]
	0.071 879	0.067 046	−0.010 826	0.000 362	
$\langle 3d\delta \vert 5d\delta \rangle$	0.167	0.156	0.055	0.021	[1(d)]
	0.072 250	0.071 619	0.043 117	0.021 549	
$\langle 5d\sigma \vert 5d\sigma \rangle$	0.2515	0.1914	0.0107	0.003 47	[1(c)]
	0.197 990	0.175 979	−0.020 218	−0.005 861	

overlap integrals in these cases contain only the quantities $f^{m,n}_{l,p,q,t}$ with $t\neq 1$ [corresponding to $j>n+1$ in Eq. (25)], which approach zero because of Eqs. (17), (25), and (26) as $R\rightarrow 0$. Integrals coupling two orbitals with the same angular quantum number do contain additional quantities $f^{m,n}_{l,p,q,t}$ with $t=1$ [corresponding to $j=n+1$ in Eq. (26)] and approach a constant (not zero) as $R\rightarrow 0$. Next, we will show the normality condition between two atomic orbitals for a simple case. For example, by letting $R\rightarrow 0$ and setting $c=d$ in the expression of the integral $\langle 2p_i|2p_j\rangle$ [Eq. (A3)], we have

$$\begin{aligned}\langle 2p_i|2p_j\rangle &= \lim_{R\rightarrow 0} 2\pi\frac{(2c)^5}{4!}c^2\frac{\kappa_3 R^4}{\lambda^3} \\ &\quad\times\int_0^1 u^2(1-u)^2du\frac{3}{4\pi}\delta_{ij} \\ &= 2\pi\frac{(2c)^5}{4!}c^2\frac{6!}{2^3c^7 3!}\frac{2!2!}{5!}\frac{3}{4\pi}\delta_{ij}=\delta_{ij}\ .\end{aligned} \tag{27}$$

Therefore, the orthonormality condition of two orbitals is restored when $R\rightarrow 0$.

IV. NUMERICAL STABILITY STUDY AND COMPARISON OF RESULTS

In this section we demonstrate that by using the method mentioned above, accurate numerical values can be easily obtained which are free from any numerical instability problems. Comparison was done with values [1(a)–1(d), 2(a)] that were published some 40 years ago to make sure that our expressions are correct and also to reveal if some of the old results may have suffered from the instability. Since the expressions (Appendix) are fairly straightforward, we decided to code with RM/FORTRAN [13] on a PC using double-precision arithmetic. Both Eqs. (19) and (20) were coded so that we can compare their results as a function of the exponents as well the principal quantum numbers. By comparing our results against some of the published results, we also found some misprints and inaccuracies associated with those reports. Since all of those results were generated by using spheroidal coordinates in which the quantization axes are pointing to each other, therefore, an overall sign difference may be possible, but of no concern for the purpose of comparison. Most of the earlier results were listed as a function of two parameters p and t, which are defined as

$$p=(c+d)R/2\ ,\quad t=(c-d)/(c+d)\ . \tag{28}$$

We computed our results as a function of the exponents c and d and as a function of the intercenter distance R. However, a direct comparison can be obtained quite easily. We have done quite an extensive comparison, and we found the numerical values listed in Ref. [2(a)] to agree with ours quite well, up to the d states, since we do not have any values for f states. The comparison to the Ref. [1(a)] is also fairly good in most cases; however, we did find some misprints in this 40 year old report which might not be known to some workers in this field. Their Table IX labeled the overlap integral $S(1s,5s)$, which should be labeled $S(1s,4s)$ and also their Table XXI labeled $S(2p\pi,2p\pi)$, which should read $S(2p\pi,3p\pi)$. The comparison between our results to the results listed in Refs. [1(b)–1(d)] are mixed; some values show good agreement, and some do not. For example, we found excellent agreement in the values of $S(3d\sigma,3d\sigma)$ in Ref. [1(b)] and $S(3d\pi,3d\pi)$ and $S(3d\delta,3d\delta)$ in Ref. [1(c)] but not other values. In Table I we listed only those which show discrepancy, ranging from 1% to a factor of 2, and we believe these discrepancies are solely due to the numerical instability associated with the higher principal quantum numbers, rather than by mistakes possibly contained in the expressions themselves. Of course, the tables are by no means exhaustive, we merely point out that there are some discrepancies between the values obtained this way and some of the values published in the open literature. Our expression is quite general. In this case the center B is placed at distance R from center A along the z axis in order to have a viable comparison. Tables I–III are generated using Eq. (19) by a 12-point Gauss-Legendre quadrature integration routine, while Table IV is generated by a 40-point routine because quadrature routine using more points is needed especially when the orbitals have largely differing exponents, whereas in Tables I–III, in general, we can get by with a quadrature routine using fewer points, especially when the two exponents are not largely differing (corresponding small $|t|$). The previously published values are listed in the first row along with the reference and our computed values are listed in the second row for each entry. In Table II we compare the overlap-integral values generat-

TABLE II. Comparison of integral values evaluated by the analytic method [Eq. (20)] and by numerical integration [Eq. (19)] as a function of the exponents c and d at $R=1$.

	$c=1.5,\ d=0.5$		$c=1.5,\ d=1.4$	
	Eq. (20)	Eq. (19)	Eq. (20)	Eq. (19)
$\langle 1s\|1s\rangle$	0.579 709	0.579 713	0.738 054	0.738 054
$\langle 2s\|2s\rangle$	0.480 678	0.480 392	0.894 073	0.894 073
$\langle 4s\|4s\rangle$	0.278 761	0.276 016	bad	0.948 151
$\langle 5s\|5s\rangle$	0.210 167	0.148 093	bad	0.956 843
$\langle 3d\sigma\|2s\rangle$	−0.010 237	−0.010 237	0.098 029	0.098 029
$\langle 5d\sigma\|3s\rangle$	−0.011 158	−0.011 159	0.051 052	0.051 944
$\langle 3d\delta\|3d\delta\rangle$	0.346 583	0.346 621	0.860 599	0.860 605
$\langle 5d\delta\|5d\delta\rangle$	0.203 622	0.203 093	bad	0.938 978

ed by these two methods: one by the analytic method, essentially summing up all the finite alternating terms [Eqs. (20) and (22)], and second, by the numerical method [Eq. (19)] as a function of the orbitals' exponents. We confirm that if the two exponents are close enough, the analytic method simply cannot give a numerically stable solution for an orbital with higher principal quantum number. In Table III the numerical procedure definitely demonstrates that it can provide a stable solution no matter how close the two exponents are. In Table IV we try to repeat the same calculation shown in Ref. [7] (Table V); however, only 12 digits are retained in the results, and they do agree quite well. Table IV seems to suggest that when the two exponents are largely differing, the analytical method is more capable of giving better results than the numerical integration based on the comparison to the results of Ref. [7]. Of course, we cannot use the analytical expressions when the two exponents of the orbitals are close or identical.

V. CONCLUSION

We have derived the explicit expressions for two-center overlap molecular integrals coupling any arbitrary higher principal quantum number with angular s, p, and d orbitals. The final expression is compact and quite easily adopted for automatic numerical application. Since the radial and angular dependences are completely separated, the angular dependence, independent of the coordinate system, is manifested in the radius vector connecting the two centers. The separation of radial and angular dependences offers great computational advantage; i.e., the radial part is identical for integrals having identical angular quantum number orbitals, e.g., $\langle d_{xy}|d_{xy}\rangle$ and $\langle d_{x^2-y^2}|d_{x^2-y^2}\rangle$ and only needs to be generated once. A simple computer code can be written, in essence, just to perform a summation and not involve any numerical integration at all. Preliminary tests of the numerical stability study have shown, however, that this claim is true only for n and m not too large, for example, ≤ 3 (of course, this also depends on the values of the exponents c and d). For a value greater than 3, the numerical integration [Eq. (19)] definitely offers a more stable solution. Closer observation reveals the reason. The finite-sum solution [Eqs. (20)–(22)] may involve large numbers with alternate signs, and in the subtraction of two large numbers, the relative errors may soar to a point that makes the result worthless. This is especially true when c is not very different from d, since the power of (c^2-d^2) appears in the denominator. When we compared the numerical results generated by our method and the previously published results [1,2], we did find good agreement when the principal quantum numbers involved are not high, say, ≤ 3; however, when the principal quantum numbers are higher, >3, quite a discrepancy is found. The earlier treatments which exclusively employ spheroidal coordinates also exhibit such alternating finite-sum behavior [1(a)–1(c)] and subsequently encounter the numerical instability problem. We believe this is exactly the reason for such a discrepancy. The approach here is to derive the simplest form coupling the specific angular momentum of the lowest-principal-quantum-number orbitals and then use the parametric differential process to step up in the direction of reaching a higher principal quantum number. Also, we may add that caution has to be exercised if a highly accurate integral value is desired for integrals involving two largely differing exponents, large intercenter distance, and higher principal quantum numbers. The reason is quite simple and purely a numerical one. Higher principal quantum numbers, in this formulation, means more terms in the integrand and therefore more cancellations, larger R, and largely differing exponents, higher quantum numbers meaning bigger numbers with higher power. For example, as is indicated by the integral $\langle 2p\sigma|5d\sigma\rangle$ in Table IV with largely differing exponents 2.0 and 0.3, a Gauss-Legendre quad-

TABLE III. Test of numerical stability of overlap integrals when the two exponents are approaching to each other at $R=1$.

	$c=1.5,$ $d=1.499$	$c=1.5,$ $d=1.4999$	$c=1.5,$ $d=1.5$
$\langle 1s\|1s\rangle$	0.725 312	0.725 187	0.725 173
$\langle 2s\|2s\rangle$	0.889 799	0.889 738	0.889 731
$\langle 4s\|4s\rangle$	0.949 785	0.949 757	0.949 754
$\langle 5s\|5s\rangle$	0.960 266	0.960 244	0.960 241
$\langle 3d\sigma\|2s\rangle$	0.114 273	0.114 419	0.114 435
$\langle 5d\sigma\|3s\rangle$	0.061 949	0.062 038	0.062 048
$\langle 3d\delta\|3d\delta\rangle$	0.855 551	0.855 474	0.855 465
$\langle 5d\delta\|5d\delta\rangle$	0.941 278	0.941 245	0.941 242

TABLE IV. Comparison of STO overlap integrals computed in Ref. [7] (Table V) and this method.

	$A=(0,0,0)$		$B=(0,0,1.4)$ This method		
	Exponents		Bhattacharya and Dhabal [7]	Numerical [Eq. (19)]	Analytical [Eqs. (20)–(22)]
$\langle 1s\|1s\rangle$	10	10	6.679 947 376 8(−5)	6.679 947 258 4(−5)	
$\langle 5s\|5s\rangle$	0.1	0.1	9.996 371 894 1(−1)	9.996 372 192 6(−1)	
$\langle 1s\|2p\sigma\rangle$	10	2.0	−1.174 137 896 9(−1)	−1.174 137 959 2(−1)	−1.174 137 896 9(−1)
$\langle 4s\|4p\sigma\rangle$	0.5	0.4	−1.230 350 868 9(−1)	−1.230 350 883 4(−1)	−1.230 280 911 4(−1)
$\langle 2p\sigma\|2p\sigma\rangle$	2.0	2.0	−1.007 403 821 5(−1)	−1.007 403 806 6(−1)	
$\langle 2p\sigma\|5d\sigma\rangle$	2.0	0.3	−2.332 300 817 2(−3)	−2.332 253 640 4(−3)	−2.332 300 817 2(−3)
$\langle 3d\sigma\|5d\sigma\rangle$	1.5	0.3	1.228 363 596 4(−2)	1.228 364 352 2(−2)	1.228 363 596 4(−2)

rature with a rather large number of 40 points seems not adequate for higher accuracy. In this case the finite-sum solution is able to produce more accurate results, as may be seen by comparison with the results of Bhattacharya and Dhabal. In the other case of similar exponents, the situation is reversed. Here the numerical quadrature method is much more accurate than the inherently unstable sum solution of Eqs. (20)–(22). Therefore, we have established the criterion of choice depending upon the two exponents; we use the numerical integration method for the cases that the two exponents are identical or similar; we use the finite-sum expressions for the cases that the two exponents are largely differing; in the middle ground, either method can be employed. For the numerical integration method, the following options might improve the accuracy of the integral values: (1) better numerical integration scheme [14], (2) further subdivision of the region of integration, (3) employment of uneven points of integration, (4) use of a computer with larger word length, and (5) possibly use of a certain scaling scheme—e.g., Eq. (28), indeed, suggested at the scaling may be possible. Of course, this approach is not limited to the molecular-overlap integrals just studied. Other types of integrals [1(e)] can be formulated in a similar fashion.

APPENDIX

In the following the integers m and n assume the values ≥ 1 for the s state, ≥ 2, for the p state, and ≥ 3 for the d state. For the overlap integral between different combinations within the set of angular orbitals that was prescribed earlier, we have the following list:

$$\langle msA|nsB\rangle=(-1)^{m+n-2}[C_m(c)C_n(d)/2]$$
$$\times[cdf^{m-1,n-1}_{2,1,1,1}+(n-1)cf^{m-1,n-2}_{2,1,1,1}+(m-1)df^{m-2,n-1}_{2,1,1,1}+(m-1)(n-1)f^{m-2,n-2}_{2,1,1,1}]\,, \tag{A1}$$

$$\langle mp_i|ns\rangle=(-1)^{m+n-1}\sqrt{\pi}p_i(\hat{\mathbf{R}})C_m(c)C_n(d)$$
$$\times[cdf^{m-2,n-1}_{2,2,1,2}+(n-1)cf^{m-2,n-2}_{2,2,1,2}+(m-2)df^{m-3,n-1}_{2,2,1,2}+(m-2)(n-1)f^{m-3,n-2}_{2,2,1,2}]$$
$$(i=x,\ y\ ,\text{ or } z)\,, \tag{A2}$$

$$\langle mp_i|np_j\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-2,n-2}_{3,2,2,1}+(n-2)cf^{m-2,n-3}_{3,2,2,1}+(m-2)df^{m-3,n-2}_{3,2,2,1}+(m-2)(n-2)f^{m-3,n-3}_{3,2,2,1}]3\delta_{ij}/4\pi$$
$$-[cdf^{m-2,n-2}_{2,2,2,3}+(n-2)cf^{m-2,n-3}_{2,2,2,3}+(m-2)df^{m-3,n-2}_{2,2,2,3}+(m-2)(n-2)f^{m-3,n-3}_{2,2,2,3}]p_i(\hat{\mathbf{R}})p_j(\hat{\mathbf{R}})\}\,, \tag{A3}$$

where δ_{ij} is the usual Kronecker symbol:

$$\langle md_{ij}|ns\rangle=(-1)^{m+n}\sqrt{\pi}C_m(c)C_n(d)d_{ij}(\hat{\mathbf{R}})$$
$$\times[cdf^{m-3,n-1}_{2,3,1,3}+c(n-1)f^{m-3,n-2}_{2,3,1,3}+d(m-3)f^{m-4,n-1}_{2,3,1,3}+(m-3)(n-1)f^{m-4,n-2}_{2,3,1,3}]\,, \tag{A4}$$

$$\langle md_{z^2}|ns\rangle=(-1)^{m+n}\sqrt{\pi}C_m(c)C_n(d)d_{z^2}(\hat{\mathbf{R}})$$
$$\times[cdf^{m-3,n-1}_{2,3,1,3}+c(n-1)f^{m-3,n-2}_{2,3,1,3}+d(m-3)f^{m-4,n-1}_{2,3,1,3}+(m-3)(n-1)f^{m-4,n-2}_{2,3,1,3}]\,, \tag{A5}$$

$$\langle md_{x^2-y^2}|ns\rangle=(-1)^{m+n}\sqrt{\pi}C_m(c)C_n(d)d_{x^2-y^2}(\hat{\mathbf{R}})$$
$$\times[cdf^{m-3,n-1}_{2,3,1,3}+c(n-1)f^{m-3,n-2}_{2,3,1,3}+d(m-3)f^{m-4,n-1}_{2,3,1,3}+(m-3)(n-1)f^{m-4,n-2}_{2,3,1,3}]\,, \tag{A6}$$

$$\langle md_{ij}|np_k\rangle=(-1)^{m+n-1}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-2}_{3,3,2,2,}+(n-2)cf^{m-3,n-3}_{3,3,2,2}+(m-3)df^{m-4,n-2}_{3,3,2,2}+(m-3)(n-2)f^{m-4,n-3}_{3,3,2,2}]$$
$$\times(p_j(\hat{\mathbf{R}})\delta_{ik}+p_i(\hat{\mathbf{R}})\delta_{jk})(15/4\pi)^{1/2}$$
$$-[cdf^{m-3,n-2}_{2,3,2,4}+(n-2)cf^{m-3,n-3}_{2,3,2,4}+(m-3)df^{m-4,n-3}_{2,3,2,4}+(m-3)(n-2)f^{m-4,n-3}_{2,3,2,4}]d_{ij}(\hat{\mathbf{R}})p_k(\hat{\mathbf{R}})\}\ , \tag{A7}$$

$$\langle md_{z^2}|np_i\rangle=(-1)^{m+n-1}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-2}_{3,3,2,2}+(n-2)cf^{m-3,n-3}_{3,3,2,2}+(m-3)df^{m-4,n-2}_{3,3,2,2}+(m-3)(n-2)f^{m-4,n-3}_{3,3,2,2}]$$
$$\times(2p_z(\hat{\mathbf{R}})\delta_{iz}-p_y(\hat{\mathbf{R}})\delta_{iy}-p_x(\hat{\mathbf{R}})\delta_{ix})(5/4\pi)^{1/2}$$
$$-[cdf^{m-3,n-2}_{2,3,2,4}+(n-2)cf^{m-3,n-3}_{2,3,2,4}+(m-3)df^{m-4,n-2}_{2,3,2,4}+(m-3)(n-2)f^{m-4,n-3}_{2,3,2,4}]d_{z^2}(\hat{\mathbf{R}})p_i(\hat{\mathbf{R}})\}\ , \tag{A8}$$

$$\langle md_{x^2-y^2}|np_i\rangle=(-1)^{m+n-1}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-2}_{3,3,2,2}+(n-2)cf^{m-3,n-3}_{3,3,2,2}+(m-3)df^{m-4,n-2}_{3,3,2,2}+(m-3)(n-2)f^{m-4,n-3}_{3,3,2,2}]$$
$$\times[p_x(\hat{\mathbf{R}})\delta_{ix}-p_y(\hat{\mathbf{R}})\delta_{iy}](15/4\pi)^{1/2}$$
$$-[cdf^{m-3,n-2}_{2,3,2,4}+(n-2)cf^{m-3,n-3}_{2,3,2,4}+(m-3)df^{m-4,n-2}_{2,3,2,4}+(m-3)(n-2)f^{m-4,n-3}_{2,3,2,4}]$$
$$\times d_{x^2-y^2}(\hat{\mathbf{R}})p_i(\hat{\mathbf{R}})\}\quad(i=x\ ,\ y,\ \text{or}\ z)\ , \tag{A9}$$

$$\langle md_{ij}|nd_{ij}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-3}_{4,3,3,1}+(n-3)cf^{m-3,n-4}_{4,3,3,1}+(m-3)df^{m-4,n-3}_{4,3,3,1}+(m-3)(n-3)f^{m-4,n-3}_{4,3,3,1}](15/4\pi)$$
$$-[cdf^{m-3,n-3}_{3,3,3,3}+(n-3)cf^{m-3,n-4}_{3,3,3,3}+(m-3)df^{m-4,n-3}_{3,3,3,3}+(m-3)(n-3)f^{m-4,n-4}_{3,3,3,3}]$$
$$\times 5[p_i(\hat{\mathbf{R}})p_i(\hat{\mathbf{R}})+p_j(\hat{\mathbf{R}})p_j(\hat{\mathbf{R}})]+[cdf^{m-3,n-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-3}_{2,3,3,5}$$
$$+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]d_{ij}(\hat{\mathbf{R}})d_{ij}(\hat{\mathbf{R}})\}\ , \tag{A10}$$

$$\langle md_{z^2}|nd_{xy}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-3}_{3,3,3,3}+(n-3)cf^{m-3,n-4}_{3,3,3,3}+(m-3)df^{m-4,n-3}_{3,3,3,3}+(m-3)(n-3)f^{m-4,n-4}_{3,3,3,3}]$$
$$\times(10/\sqrt{3})p_x(\hat{\mathbf{R}})p_y(\hat{\mathbf{R}})$$
$$+[cdf^{m-3,m-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-3}_{2,3,3,5}+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]$$
$$\times d_{z^2}(\hat{\mathbf{R}})d_{xy}(\hat{\mathbf{R}})\}\ , \tag{A11}$$

$$\langle md_{z^2}|nd_{xz}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-3}_{3,3,3,3}+(n-3)cf^{m-3,n-4}_{3,3,3,3}+(m-3)df^{m-4,n-3}_{3,3,3,3}+(m-3)(n-3)f^{m-4,n-4}_{3,3,3,3}]$$
$$\times(-5/\sqrt{3})p_x(\hat{\mathbf{R}})p_z(\hat{\mathbf{R}})$$
$$+[cdf^{m-3,n-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-3}_{2,3,3,5}+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]$$
$$\times d_{z^2}(\hat{\mathbf{R}})d_{xz}(\hat{\mathbf{R}})\}\ , \tag{A12}$$

$\langle md_{z^2}|nd_{yz}\rangle=$(same as above except replace x,z by y,z) ,

$$\langle md_{ij}|nd_{ik}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-3}_{3,3,3,3}+(n-3)cf^{m-3,n-4}_{3,3,3,3}+(m-3)df^{m-4,n-3}_{3,3,3,3}+(m-3)(n-3)f^{m-4,n-4}_{3,3,3,3}]$$
$$\times(-5)p_j(\hat{\mathbf{R}})p_k(\hat{\mathbf{r}})$$
$$+[cdf^{m-3,n-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-3}_{2,3,3,5}+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]$$
$$\times d_{ij}(\hat{\mathbf{R}})d_{ik}(\hat{\mathbf{R}})\}\ , \tag{A13}$$

$$\langle md_{x^2-y^2}|nd_{xz}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-3}_{3,3,3,3}+(n-3)cf^{m-3,n-4}_{3,3,3,3}+(m-3)df^{m-4,n-3}_{3,3,3,3}+(m-3)(n-3)f^{m-4,n-4}_{3,3,3,3}$$
$$\times(-5)p_x(\hat{\mathbf{R}})p_z(\hat{\mathbf{R}})$$
$$+[cdf^{m-3,n-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-3}_{2,3,3,5}+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]$$
$$\times d_{x^2-y^2}(\hat{\mathbf{R}})d_{xz}(\hat{\mathbf{R}})\}\ , \tag{A14}$$

$$\langle md_{x^2-y^2}|nd_{yz}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-3}_{3,3,3,3}+(n-3)cf^{m-3,n-4}_{3,3,3,3}+(m-3)df^{m-4,n-3}_{3,3,3,3}+(m-3)(n-3)f^{m-4,n-4}_{3,3,3,3}]5p_y(\hat{\mathbf{R}})p_z(\hat{\mathbf{R}})$$
$$+[cdf^{m-3,n-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-3}_{2,3,3,5}+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]$$
$$\times d_{x^2-y^2}(\hat{\mathbf{R}})d_{yz}(\hat{\mathbf{R}})\}\ , \tag{A15}$$

$$\langle md_{x^2-y^2}|nd_{xy}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-3}_{2,3,3,5}+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]$$
$$\times d_{x^2-y^2}(\hat{\mathbf{R}})d_{xy}(\hat{\mathbf{R}})\}\ , \tag{A16}$$

$$\langle md_{z^2}|nd_{z^2}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-3}_{4,3,3,1}+(n-3)cf^{m-3,n-4}_{4,3,3,1}+(m-3)df^{m-4,n-3}_{4,3,3,1}+(m-3)(n-3)f^{m-4,n-4}_{4,3,3,1}](15/4\pi)$$
$$-[cdf^{m-3,n-3}_{3,3,3,3}+(n-3)cf^{m-3,n-4}_{3,3,3,3}+(m-3)df^{m-4,n-3}_{3,3,3,3}+(m-3)(n-3)f^{m-4,n-4}_{3,3,3,3}]$$
$$\times\tfrac{5}{3}[p_x(\hat{\mathbf{R}})p_x(\hat{\mathbf{R}})+p_y(\hat{\mathbf{R}})p_y(\hat{\mathbf{R}})+4p_z(\hat{\mathbf{R}})p_z(\hat{\mathbf{R}})]$$
$$+[cdf^{m-3,n-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-3}_{2,3,3,5}+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]$$
$$\times d_{z^2}(\hat{\mathbf{R}})d_{z^2}(\hat{\mathbf{R}})\}\ , \tag{A17}$$

$$\langle md_{z^2}|nd_{x^2-y^2}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times\{[cdf^{m-3,n-3}_{3,3,3,3}+(n-3)cf^{m-3,n-4}_{3,3,3,3}+(m-3)df^{m-4,n-3}_{3,3,3,3}+(m-3)(n-3)f^{m-4,n-4}_{3,3,3,3}]$$
$$\times(5/\pi)^{1/2}d_{x^2-y^2}(\hat{\mathbf{R}})$$
$$+[cdf^{m-3,n-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-3}_{2,3,3,5}+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]$$
$$\times d_{z^2}(\hat{\mathbf{R}})d_{x^2-y^2}(\hat{\mathbf{R}})\}\ , \tag{A18}$$

$$\langle md_{x^2-y^2}|nd_{x^2-y^2}\rangle=(-1)^{m+n}2\pi C_m(c)C_n(d)$$
$$\times[cdf^{m-3,n-3}_{4,3,3,1}+(n-3)cf^{m-3,n-4}_{4,3,3,1}+(m-3)df^{m-4,n-3}_{4,3,3,1}+(m-3)(n-3)f^{m-4,n-4}_{4,3,3,1}](15/4\pi)$$
$$-[cdf^{m-3,n-3}_{3,3,3,3}+(n-3)cf^{m-3,n-4}_{3,3,3,3}+(m-3)df^{m-4,n-3}_{3,3,3,3}+(m-3)(n-3)f^{m-4,n-4}_{3,3,3,3}]$$
$$\times 5[p_x(\hat{\mathbf{R}})p_x(\hat{\mathbf{R}})+p_y(\hat{\mathbf{R}})p_y(\hat{\mathbf{R}})]$$
$$+[cdf^{m-3,n-3}_{2,3,3,5}+(n-3)cf^{m-3,n-4}_{2,3,3,5}+(m-3)df^{m-4,n-4}_{2,3,3,5}+(m-3)(n-3)f^{m-4,n-4}_{2,3,3,5}]$$
$$\times d_{x^2-y^2}(\hat{\mathbf{R}})d_{x^2-y^2}(\hat{\mathbf{R}})\}\ . \tag{A19}$$

Of course, we have the simple relation

$$\langle\Psi_{n,l,m}(c,\mathbf{r}_A)|\psi_{n',l',m'}(d,\mathbf{r}_B)\rangle=(-1)^{l+l'}\langle\Psi_{n',l',m'}(d,\mathbf{r}_A)|\psi_{n,l,m}(c,\mathbf{r}_B)\ , \tag{A20}$$

to obtain the numerical value of the rest of the other integrals.

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