Analytic evaluation of two-center molecular integrals

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By using the Fourier-transform technique, the explicit expressions for the one-electron—two-center overlap integrals of Slater-type atomic orbitals up to $3d$ are derived. The final expressions are analytic, simple, and independent of local coordinates. Furthermore, they do not contain the non-closed-form of exponential integrals which were presented in expressions given in earlier work. It is shown that the two-electron—two-center Coulomb integrals, as well as the hybrid integrals, can simply be expressed in terms of these integrals. The numerical instability arising from the situation in which the exponents of the two orbitals are almost equal is discussed, and a solution for this problem based on a Taylor-series expansion of the integral is suggested.

I. INTRODUCTION

Reliable and rapid methods of evaluating molecular integrals are essential to the understanding of physical properties of molecules and solids. Many articles have addressed this subject for Slater orbitals.[1–4] Explicit formulas and numerical tables have been prolific in the literature.[5–7] However, it has been a common practice that the early derivations are based on the approach that the prolate spheroidal coordinate is employed in which the quantization axes have to be pointing along the bond. This practice is favorable in the evaluation of diatomic integrals because some of them vanish due to symmetry relationships. However, in the evaluation of two-center integrals in a polyatomic molecule, this advantage is completely offset by the fact that for each pair of centers, new quantization axes have to be established. As a result, rotational operations have to be carried out in order to have a correct physical interpretation which can be very undesirable in practice. Another approach, which is based on the Fourier convolution property was first suggested by Prosser and Blanchard[8] for the evaluation of the one-electron—two-center integrals. Subsequently, Geller[9] has applied the same technique to the two-electron—two-center integrals, Epstein[10] has evaluated the two-center integrals involving momentum operators, and Avery and Cook[11] have tackled the one-electron—two-center integrals associated with molecular optical properties. Those approaches essentially transform the orbitals to momentum space, and after some manipulations, the quantity must be recast back to the configuration space. The radial part of the last step is not always easily carried out analytically except for the most elementary orbitals involved. An alternative approach is to integrate by numerical quadrature. This approach was found to be relatively inefficient because of the oscillation of the spherical Bessel functions appearing in the integrand. Geller[12] instead evaluated these integrals by a procedure using a recursion relation which is straightforward, but quite tedious.

Recent work[13–17] has rekindled the Fourier-transform approach and certain progress has been made. These approaches were carried out for the general Slater-type orbitals (STO) and the use of the Gaunt coefficient made the angular part of the integral tractable; however, to get the radial part, the use of the so-called "Bessel operator" in practice produces equally complicated expressions. Instead of dealing with the STO, the so-called "B function" was introduced,[15–17] of which the STO can be expressed as a linear combination. But the overlap integral over B functions with different scaling parameters is of similar complexity.[18]

Recently, the present author,[19] using the integral-transform method suggested by Shakeshaft, presented the formulas for the multicenter molecular integrals in which the final expressions are expressed in terms of multiple numerical integration whose integrands contain the complicated geometrical arrangement of the centers. However, for the two-center integral, it was noticed that, by setting the two vector constants $\mathbf{a}$ and $\mathbf{b}$ to zero, the final expression can be readily reduced to a closed, analytic form in which no parameters are introduced; above all, no special coordinate system is required, i.e., the quantization axis chosen can be totally independent of the bond direction. An analytic expression is always preferred, not only because it reduces the cost of obtaining the numerical value but also because it provides an invaluable insight to the problem studied. For example, the tasks of obtaining the derivative of the integral with respect to its bond distance, to variation with respect to the exponents, etc., are simplified with an analytic expression.

II. BASIC INTEGRALS AND PROCEDURE

Recently, Shakeshaft[20] has shown that an exchange integral of the form

$$\hat{I}(n_1,l_1;n_2,l_2)=\int r_A^{n_1-2} r_B^{n_2-2}(\mathbf{p}_1\cdot\mathbf{r}_A)(\mathbf{p}_2\cdot\mathbf{r}_A)\cdots(\mathbf{p}_{l_1}\cdot\mathbf{r}_A)(\mathbf{q}_1\cdot\mathbf{r}_B)(\mathbf{q}_2\cdot\mathbf{r}_B)\cdots(\mathbf{q}_{l_2}\cdot\mathbf{r}_B)e^{i\mathbf{a}\cdot\mathbf{r}_A+i\mathbf{b}\cdot\mathbf{r}_B-cr_A-dr_B}dr \quad (1)$$

can be reduced to a simple one-dimensional integral, where **a**,**b** are two real vectors, the constants c and d are real and positive, integers $n_1, n_2 > 1$, and $\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_{l_1}, \mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_{l_2}$ are arbitrary constant vectors. For example, it is shown that

$$\hat{I}(1,0;1,0) = \int_0^1 \frac{e^{i\boldsymbol{\beta}\cdot\mathbf{R}-\lambda R}}{\lambda} dy \tag{2}$$

where

$$\begin{aligned} &\lambda^2 = y(1-y)\,|\,\mathbf{a}+\mathbf{b}\,|^2 + yc^2 + (1-y)d^2\,, \\ &\boldsymbol{\beta} = y\mathbf{a} - (1-y)\mathbf{b}, \quad \mathbf{R} = \mathbf{r}_A - \mathbf{r}_B\,. \end{aligned} \tag{3}$$

In principle, the general integral $\hat{I}(n_1,l_1,;n_2,l_2)$ can be obtained by the following differential operation:

$$\begin{aligned} \hat{I}(n_1,l_1;n_2,l_2) = (-i)^{l_1+l_2}&(\mathbf{p}_1\cdot\nabla_a)(\mathbf{p}_2\cdot\nabla_a)\cdots(\mathbf{p}_{l_1}\cdot\nabla_a)(\mathbf{q}_1\cdot\nabla_b)(\mathbf{q}_2\cdot\nabla_b)\cdots(\mathbf{q}_{l_2}\cdot\nabla_b) \\ &\times(-\partial/\partial c)^{n_1-1}(-\partial/\partial d)^{n_2-1}\hat{I}(1,0;1,0)\,. \end{aligned} \tag{4}$$

The differentiation is straightforward, nevertheless, the procedure can be quite lengthy. Shakeshaft and Tai have given the expressions up to $\hat{I}(2,1;2,1)$. For practical purposes, higher $\hat{I}(n_1,l_1;n_2,l_2)$ are still needed. Once the expression of $\hat{I}(n_1,l_1;n_2,l_2)$ in terms of one-dimensional numerical integration such as Eq. (2) is obtained, we then let $\mathbf{p}_1\cdots\mathbf{p}_{l_1}$, $\mathbf{q}_1\cdots\mathbf{q}_{l_2}$, in particular, be a set of orthogonal unit vectors along the coordinate system, say, $\hat{\mathbf{e}}_x, \hat{\mathbf{e}}_y, \hat{\mathbf{e}}_z$, and simultaneously set the two vectors **a** and **b** to zero. Hereafter, the integral is denoted as I for the special case of $\hat{I}$ in which the two constant vectors **a** and **b** are set to zero. Then it is obvious that aside from a normalization factor the I's, or the linear combination of I's, are nothing but the two-center integrals of Slater-type atomic orbitals. Once the **a** and **b** are set to zero, the one-dimensional integration becomes trivial and analytic expressions can be obtained. For example, we can write

$$\begin{aligned} I(2,1;2,1) = 2\pi cd \int_0^1 &\{K_3\mathbf{p}_1\cdot\mathbf{q}_1 - K_2\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1\} \\ &\times y^2(1-y)^2 e^{-\lambda R} dy \end{aligned} \tag{5}$$

where K's are defined as before,[19]

$$\begin{aligned} &K_0(\lambda) = 1/\lambda\,, \\ &K_1(\lambda) = R/\lambda^2 + 1/\lambda^3\,, \\ &K_2(\lambda) = R^2/\lambda^3 + 3R/\lambda^4 + 3/\lambda^5\,, \end{aligned} \tag{6}$$

and so on. By inspection, K_n satisfies the following recursion relation:

$$K_n = \frac{RK_{n-1}}{\lambda} - K'_{n-1}/\lambda\,. \tag{7}$$

Furthermore, it can be shown that the K_n is related to the modified Bessel function of the third kind,[21] k_n, in a manner such as

$$K_n = e^{\lambda R}\frac{R^{n+1}}{\lambda^n} k_n(\lambda R)\,. \tag{8}$$

Using Eqs. (3) and (8), Eq. (5) becomes

$$I(2,1;2,1) = \frac{4\pi cd}{(c^2-d^2)^5}\int_d^c \left[k_3(\lambda R)\frac{R^4}{\lambda^3}(\mathbf{p}_1\cdot\mathbf{q}_1) - k_2(\lambda R)\frac{R^3}{\lambda^2}\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1\right](\lambda^2-d^2)^2(c^2-\lambda^2)^2\lambda\, d\lambda\,. \tag{9}$$

Equation (9) consists of the finite sum of the following form:

$$G_n^m = \int_d^c \frac{R^{n+1}}{\lambda^n} k_n(\lambda R)\lambda^m d\lambda, \quad m \text{ odd}$$

which can be expressed as

$$\begin{aligned} G_n^m &= R^{2n-m}\int_{dR}^{cR} x^{m-n} k_n(x)dx, \quad x = \lambda R \\ &= R^{2n-m}\sum_{j=0}^{n} 2^{-j}\frac{(n+j)!}{j!(n-j)!}\int_{dR}^{cR} x^{m-n-1-j}e^{-x}dx \\ &= R^{2n-m}\sum_{j=0}^{n}\frac{(n+j)!}{2^j(n-j)!j!}\left[-e^{-x}\left[x^{m-n-1-j} + \sum_{k=1}^{m-n-1-j}(m-n-1-j)\cdots(m-n-1-j-k+1)x^{m-n-1-j-k}\right]\right]_{dR}^{cR}, \end{aligned}$$

$$m > n+1+j \tag{10a}$$

or

$$G_n^m = R^{2n-m}\sum_{j=0}^{n}\frac{(n+j)!}{2^j j!(n-j)!}\left[-e^{-x}\sum_{k=1}^{n+j-m}\frac{(-1)^{k-1}}{(n+j-m)(n+j-m-1)\cdots(n+j+1-m-k)x^{n+j+1-m-k}} + \frac{(-1)^{n+j-m}}{(n+j-m)!}\mathrm{Ei}(-x)\right]_{dR}^{cR}, \quad m<n+1+j \tag{10b}$$

where the exponential integral

$$\mathrm{Ei}(ax)=\int e^{ax}x^{-1}dx$$

can only be expressed in terms of a series. Although this would not present any formal difficulties, it is helpful to know that all terms containing $\mathrm{Ei}(-R\lambda)$ do cancel out. It can be easily verified by examining the coefficient

$$S_{n,m}=\sum_{j=0}^{n}2^{-j}\frac{(n+j)!(-1)^{n+j-m}}{j!(n-j)!(n+j-m)!}\,. \tag{11}$$

Indeed, $S_{n,m}=0$ for m odd as in our case. The proof is given in Appendix A. Therefore, using the short-hand notation G_n^m, Eq. (9) can be written as

$$I(2,1;2,1)=4\pi cd/(c^2-d^2)^5\{\mathbf{p}_1\cdot\mathbf{q}_1[G_3^9-2(c^2+d^2)G_3^7+(c^4+d^4+4c^2d^2)G_3^5-2c^2d^2(c^2+d^2)G_3^3+c^4d^4G_3^1] - \mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1[G_2^9-2(c^2+d^2)G_2^7+(c^4+d^4+4c^2d^2)G_2^5-2c^2d^2(c^2+d^2)G_2^3+c^4d^4G_2^1]\}\,. \tag{12}$$

Aside from a normalization factor, Eq. (12) is just the general form of the two-center overlap integral for $2p$ orbitals. For example, letting $\mathbf{p}_1=\hat{\mathbf{e}}_x,\mathbf{q}_1=\hat{\mathbf{e}}_y$, Eq. (12) is just $(2p_{xA},2p_{yB})$; letting $\mathbf{p}_1=\hat{\mathbf{e}}_z$, $\mathbf{q}_1=\hat{\mathbf{e}}_z$, Eq. (12) is just $(2p_{zA},2p_{zB})$. Of course, in the conventional way, i.e., the two-handed coordinate system, in which Z axes are pointing toward each other, and $\mathbf{R}$ aligns along the Z axis, we would have $\mathbf{p}_1=\hat{\mathbf{e}}_z,\mathbf{q}_1=-\hat{\mathbf{e}}_z$.

If the condition $c=d$ is invoked in Eq. (5), then we obtain

$$I(2,1;2,1)=\pi c^2/15[K_3(c)\mathbf{p}_1\cdot\mathbf{q}_1 - K_2(c)\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1]e^{-cR} \tag{13}$$

as the analytic expression for two-center overlap integral in which the two exponents are exactly equal.

III. ONE-ELECTRON–TWO-CENTER OVERLAP INTEGRAL

If our normalized Slater atomic orbitals are chosen in Cartesian form,[22] then the one-electron–two-center overlap integrals can simply be written in terms of the I's listed in Appendixes B and C. Of course, expressions listed in Appendixes B and C are not meant to be exhaustive. In the following, we give a few examples for illustration, and the rest can be written down without difficulties. Let us change the notation by inserting the dependence of $\mathbf{p}_1,\mathbf{p}_2,\ldots,\mathbf{p}_{l_1}$, $\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_{l_2}$ and the exponents c and d in I, i.e., $I_{n_1,l_1;n_2,l_2}(\mathbf{p}_1,\ldots,\mathbf{p}_{l_1},c;\mathbf{q}_1,\ldots,\mathbf{q}_{l_2},d)$. As standard,[22] the normalization constants for the orbitals of interest are

$$C_n(c)=(2c)^{(2n+1)/2}/\sqrt{(2n)!},\quad N_s=1/(2\sqrt{\pi})\,, \qquad N_p=\sqrt{3/\pi}/2,\quad N_d=\sqrt{5/\pi}/2\,. \tag{14}$$

Then the overlap integrals, for example, can be expressed as

$$[\psi_{3p_y}(\mathbf{r}_A,c),\psi_{2p_z}(\mathbf{r}_B,d)]=C_3(c)C_2(d)N_p^2I_{3,1;2,1}(\hat{\mathbf{e}}_y,c;\hat{\mathbf{e}}_z,d)\,,$$
$$[\psi_{3d_{zz}}(\mathbf{r}_A,c),\psi_{3d_{xy}}(\mathbf{r}_B,d)]=C_3(c)C_3(d)N_d^2[(3\sqrt{3}/2)I_{2,2;2,2}(\hat{\mathbf{e}}_z,\hat{\mathbf{e}}_z,c;\hat{\mathbf{e}}_x,\hat{\mathbf{e}}_y,d)-(\sqrt{3}/2)I_{4,0;2,2}(c;\hat{\mathbf{e}}_x,\hat{\mathbf{e}}_y,d)]\,, \tag{15}$$

where the I's are listed in Appendix B.

In this way, other types of one-electron–two-center molecular integrals, such as the kinetic energy integrals, the nuclear attraction integrals, etc., can also be expressed in term of I's.

IV. TWO-ELECTRON–TWO-CENTER COULOMB AND HYBRID INTEGRALS

The two-electron–two-center Coulomb and hybrid integrals are defined, respectively, as follows:

$$J=\int\int\psi_i^2(\mathbf{r}_{1A},c)\frac{1}{r_{12}}\psi_j^2(\mathbf{r}_{2B},d)d\mathbf{r}_1\,d\mathbf{r}_2\,, \tag{16}$$

$$L=\int\int \psi_i^2(\mathbf{r}_{1A},c)\frac{1}{r_{12}}\psi_j(\mathbf{r}_{2A},d)\psi_k(\mathbf{r}_{2B},f)d\mathbf{r}_1 d\mathbf{r}_2 \ . \tag{17}$$

There are different ways to approach these (e.g., Szondy[23] and Harris[24]). A conceptually new approach is suggested here. For Eq. (17), we proceed first with the single-charge distribution, here electron number 1. Instead of expanding the term $1/r_{12}$ as is normally done, we could simply consider the coordinate of electron number 2 as the second center for electron number 1 and facilitate the two-center integration as described before (see Fig. 1). Of course, what would emerge is a function of radius vector $\mathbf{r}_{2A}$. With $\mathbf{r}_{2B}$, the two-center integration can be performed again. For example

$$\begin{aligned}
L_1&=\int\int \psi_{1s}^2(\mathbf{r}_{1A},c)\frac{1}{r_{12}}\psi_{3d_{xy}}(\mathbf{r}_{2A},d)\psi_{2p_z}(\mathbf{r}_{2B},f)d\mathbf{r}_1 d\mathbf{r}_2\\
&=N_s^2C_1^2(c)\int I_{2,0;1,0}(2c;0)\psi_{3d_{xy}}(\mathbf{r}_{2A},d)\psi_{2p_z}(\mathbf{r}_{2B},f)d\mathbf{r}_2\\
&=N_s^2C_1^2(c)\pi/c^3\int [1/r_{2A}-e^{-2cr_{2A}}(c+1/r_{2A})]\psi_{3d_{xy}}(\mathbf{r}_{2A},d)\psi_{2p_z}(\mathbf{r}_{2B},f)d\mathbf{r}_2\\
&=N_s^2C_1^2(c)\pi/c^3N_dN_pC_3(d)C_2(f)\sqrt{3}[I_{1,2;2,1}(\hat{\mathbf{e}}_x,\hat{\mathbf{e}}_y d;\hat{\mathbf{e}}_z,f)-cI_{2,2;2,1}(\hat{\mathbf{e}}_x,\hat{\mathbf{e}}_y,d+2c;\hat{\mathbf{e}}_z,f)\\
&\qquad -I_{1,2;2,1}(\hat{\mathbf{e}}_x,\hat{\mathbf{e}}_y,d+2c;\hat{\mathbf{e}}_z,f)] \ .
\end{aligned} \tag{18}$$

Likewise, the Coulomb integral can be written out in the same fashion.

V. NUMERICAL INSTABILITY

It is well known that in the evaluation of the molecular integral when the exponents of the two orbitals approach each other, i.e., $d\simeq c$, the results tend to become unstable and unpredictable answers can occur. This becomes obvious in our expressions. If we examine Eq. (12) closely as $d\simeq c$ we find a number of removable zeros appearing both in the numerator and denominator. If the expression is tested numerically by deliberately setting d very close to c, e.g., $|d-c|\simeq 10^{-3}$, some of the single-precision results begin to become unreliable while double precision still gives very accurate values until $|d-c|\simeq 10^{-6}$. By applying L'Hospital's rule to Eq. (12), we obtain definite and numerically stable expressions for $c\simeq d$, which is identical to what was obtained earlier [Eq. (13)]. This really confirms that the integrals are continuous functions of the variables c and d in the whole domain, for $c,d\geq 0$. Consequently, by considering c as a parameter, then the integral value $f(c,d)$ in the neighborhood of $d\simeq c$ can be written by the Taylor series as

$$f(c,d)=g(c)+g'(c)(d-c)+g''(c)(d-c)^2/2!+\cdots \ , \tag{19}$$

where g is the integral value for $c=d$. Expressions for the g's are listed in Appendix C. Therefore, we obtain the integral values in the neighborhood $d\simeq c$ as accurate as we required, by obtaining g',g'' and as many higher derivatives as needed for accuracy by simply differentiating g with respect to c.

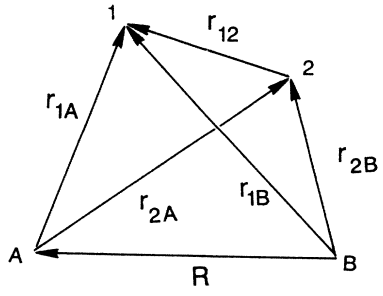

FIG. 1. Coordinate system for two-electron—two-center integrals.

VI. CONCLUSIONS

We have shown how a one-electron—two-center overlap integral can be expressed in a simple form. The orientation as well as the magnitude of the internuclear distance are manifested properly in the final expressions. The expressions are obtained through a series of parametric differentiations, which are quite lengthy processes. However, with the help of the recurrence relationship, Eq. (7), the effort of bookkeeping can be reduced to a minimum. Explicit expressions for integrals involving s, p, and d orbitals of principal quantum number $n=3$ are given, and with some extra effort the expressions involving f orbitals can also be obtained, but beyond that, this procedure becomes very tedious and unwieldy. Simple procedures for obtaining two-electron—two-center Coulomb and hybrid integrals are also described. The origin of the numerical instability of the integrals when the two exponents are nearly equal has been pointed out and a simple solution has been suggested. Contrary to what was believed earlier,[13,14] the term containing the exponential integral has been proven nonexistent. The present technique can be readily extended to the evaluation of other molecular integrals, both mentioned above, and those such as the matrix elements involving various momentum operators and moment operators arising from the calculation of molecular optical properties. With a different charge distribution of lower orbitals and geometrical configuration, conceivably, using this method, most of the physical quantities of a diatomic molecule can be expressed analytically.

APPENDIX A

Proof of $S_{n,m}=0$ for m odd

We rewrite Eq. (11) in a different form

$$S_{n,m}=\frac{(-1)^{n-m}}{n!}\sum_{j=0}^{n}(-\tfrac{1}{2})^j\begin{bmatrix}n\\j\end{bmatrix}\frac{(n+j)!}{(n+j-m)!}\ . \quad \text{(A1)}$$

This suggests that $S_{n,m}$ can be expressed as a function of variable x, $S_{n,m}(x)$. Of course, we are only interested in $S_{n,m}(-1/2)$,

$$\begin{aligned}S_{n,m}(x)&=\frac{(-1)^{n-m}}{n!}\sum_{j=0}^{n}\begin{bmatrix}n\\j\end{bmatrix}x^{j-n-j+m}\frac{d^m}{dx^m}x^{n+j}\\&=\frac{(-1)^{n-m}}{n!}x^{-n+m}\frac{d^m}{dx^m}x^n\sum_{j=0}^{n}\begin{bmatrix}n\\j\end{bmatrix}x^j\\&=\frac{(-1)^{n-m}}{n!}x^{-n+m}\frac{d^m}{dx^m}(x+x^2)^n\\&=\frac{(-1)^{n-m}}{n!}x^{-n+m}\frac{d^m}{dx^m}g_n\ ,\end{aligned} \quad \text{(A2)}$$

where the following relations have been used:

$$\begin{aligned}&\frac{d^m x^k}{dx^m}=\frac{k!}{(k-m)!}x^{k-m}\ ,\\&(1+x)^n=\sum_{j=0}^{n}\begin{bmatrix}n\\j\end{bmatrix}x^j\ ,\end{aligned} \quad \text{(A3)}$$

$g_n=(x+x^2)^n$, and its first few derivatives are

$$\begin{aligned}g_n'&=n(1+2x)g_{n-1}\ ,\\g_n''&=2ng_{n-1}+n(n-1)(1+2x)^2g_{n-2}\ ,\\g_n'''&=6n(n-1)(1+2x)g_{n-2}\\&\quad+n(n-1)(n-2)(1+2x)^3g_{n-3}\ ,\end{aligned} \quad \text{(A4)}$$

and so on. It is obvious that the odd derivatives of g_n have $(1+2x)$ as a factor. Therefore, $S_{n,m}(-\frac{1}{2})=0$, for m odd. Furthermore, $S_{n,m}(-1)=0$ for $m<n$, and $S_{n,m}(x)=0$ for any value of x if $m>2n$. To prove $S_{n,m}(-\frac{1}{2})$ for m even, let us take the pth derivative of g_n':

$$\begin{aligned}\frac{d^p}{dx^p}g_n'=g_n^{p+1}&=\frac{d^p}{dx^p}n(1+2x)g_{n-1}\\&=n\sum_{k=0}^{p}\begin{bmatrix}p\\k\end{bmatrix}\frac{d^k}{dx^k}(1+2x)\frac{d^{p-k}}{dx^{p-k}}g_{n-1}\ .\end{aligned} \quad \text{(A5)}$$

Recognizing that $k=0,1$ are the only terms not vanishing, the following recurrence relation is obtained:

$$g_n^{p+1}=n(2x+1)g_{n-1}^p+2np\,g_{n-1}^{p-1}\ . \quad \text{(A6)}$$

Since we are only interested at $x=-\frac{1}{2}$, let $p+1=m$ even:

$$\begin{aligned}g_n^m(-\tfrac{1}{2})&=2\times n\times(m-1)g_{n-1}^{m-2}(-\tfrac{1}{2})\\&=2^{m/2}\times n\times(n-1)\times\cdots\times(n-m/2+1)\times(m-1)\times(m-3)\times\cdots\times3\times1\,g_{n-m/2}(-1/2)\\&=2^{m/2}\frac{n!}{(n-m/2)!}\frac{m!}{(m/2)!2^{m/2}}g_{n-m/2}(-1/2)\ .\end{aligned} \quad \text{(A7)}$$

Substituting Eq. (A7) in Eq. (A2) and evaluating at $x=-\frac{1}{2}$, we have

$$S_{n,m}(-\tfrac{1}{2})=\frac{(-1)^{n-m}m!}{2^n(m/2)!(n-m/2)!},\quad m \text{ even}\ . \quad \text{(A8)}$$

APPENDIX B

Analytic expressions of I in which the exponents, $c\neq d$, include the following:

$G_n^m=R^{n+1}\int_d^c k_n(\lambda R)\lambda^{m-n}d\lambda$, m odd

[see Eq. 10(a) and 10(b) for explicit expressions of G_n^m]

$$I(1,0;1,0)=[4\pi/(c^2-d^2)]G_0^1 \quad \text{(B1)}$$

$$I(2,0;1,0)=[4\pi c/(c^2-d^2)^2](G_1^3-G_1^1)\ , \quad \text{(B2)}$$

$$I(2,0;2,0)=[4\pi cd/(c^2-d^2)^3][-G_2^5+(c^2+d^2)G_2^3-c^2d^2G_2^1]\ , \quad \text{(B3)}$$

$$I(1,1;1,0)=[4\pi\mathbf{R}\cdot\mathbf{p}_1/(c^2-d^2)^2][G_0^3-d^2G_0^1]\ , \quad \text{(B4)}$$

$$I(1,1;1,1)=[4\pi/(c^2-d^2)^3]\{\mathbf{p}_1\cdot\mathbf{q}_1[-G_1^5+(c^2+d^2)G_1^3-d^2c^2G_1^1]-\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1[-G_0^5+(c^2+d^2)G_0^3-c^2d^2G_0^1]\}\ , \quad \text{(B5)}$$

$$I(1,0;2,0)=[4\pi d/(c^2-d^2)^2][-G_1^3+c^2G_1^1]\ , \quad \text{(B6)}$$

$$I(2,1;1,0)=[4\pi c/(c^2-d^2)^3]\mathbf{R}\cdot\mathbf{p}_1[G_1^5-2d^2G_1^3+d^4G_1^1]\ , \tag{B7}$$

$$I(1,0;2,1)=-[4\pi d\mathbf{R}\cdot\mathbf{q}_1/(c^2-d^2)^3][G_1^5-2c^2G_1^3+c^4G_1^1]\ , \tag{B8}$$

$$I(2,1;2,0)=[4\pi cd\mathbf{R}\cdot\mathbf{p}_1/(c^2-d^2)^4][-G_2^7+(c^2+2d^2)G_2^5-(2d^2c^2+d^4)G_2^3+d^4c^2G_2^1]\ , \tag{B9}$$

$$\begin{aligned}I(2,1;2,1)=[4\pi cd/(c^2-d^2)^5]\{&\mathbf{p}_1\cdot\mathbf{q}_1[G_3^9-2(c^2+d^2)G_3^7+(c^4+d^4+4c^2d^2)G_3^5-2c^2d^2(c^2+d^2)G_3^3+c^4d^4G_3^1]\\&-\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1[G_2^9-2(c^2+d^2)G_2^7+(c^4+d^4+4c^2d^2)G_2^5-2c^2d^2(c^2+d^2)G_2^3+c^4d^4G_2^1]\}\ ,\end{aligned} \tag{B10}$$

$$\begin{aligned}I(2,2;2,0)=[4\pi cd/(c^2-d^2)^5]\{&\mathbf{p}_1\cdot\mathbf{p}_2[G_3^9-2(c^2+d^2)G_3^7+(c^4+d^4+4c^2d^2)G_3^5-2c^2d^2(c^2+d^2)G_3^3+c^4d^4G_3^1]\\&+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2[-G_2^9+(c^2+3d^2)G_2^7-3d^2(c^2+d^2)G_2^5+d^4(d^2+3c^2)G_2^3-d^6c^2G_2^1]\}\ ,\end{aligned} \tag{B11}$$

$$\begin{aligned}I(2,2;2,1)=[4\pi cd/(c^2-d^2)^6]\{&(\mathbf{R}\cdot\mathbf{p}_1\mathbf{p}_2\cdot\mathbf{q}_1+\mathbf{R}\cdot\mathbf{p}_2\mathbf{p}_1\cdot\mathbf{q}_1)[G_3^{11}-(2c^2+3d^2)G_3^9+(c^4+6c^2d^2+3d^4)G_3^7\\&-(3d^2c^4+6c^2d^4+d^6)G_3^5+(3d^4c^4+2c^2d^6)G_3^3-c^4d^6G_3^1]\\&-\mathbf{R}\cdot\mathbf{q}_1\mathbf{p}_1\cdot\mathbf{p}_2[-G_3^{11}+(3c^2+2d^2)G_3^9-(d^4+6c^2d^2+3c^4)G_3^7\\&+(3c^2d^4+6d^2c^4+c^6)G_3^5-(2d^2c^6+3c^4d^4)G_3^3+d^4c^6G_3^1]\\&-R\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_1[G_2^{11}-(2c^2+3d^2)G_2^9+(c^4+6c^2d^2+3d^4)G_2^7\\&-(3d^2c^4+6c^2d^4+d^6)G_2^5+(3d^4c^4+2c^2d^6)G_2^3-c^4d^6G_2^1]\}\ ,\end{aligned} \tag{B12}$$

$$\begin{aligned}I(2,2;2,2)=&[4\pi cd/(c^2-d^2)^7]\\&\times\{(\mathbf{p}_1\cdot\mathbf{q}_1\mathbf{p}_2\cdot\mathbf{q}_2+\mathbf{p}_1\cdot\mathbf{p}_2\mathbf{q}_1\cdot\mathbf{q}_2+\mathbf{p}_1\cdot\mathbf{q}_2\mathbf{p}_2\cdot\mathbf{q}_1)\\&\times[-G_4^{13}+3(c^2+d^2)G_4^{11}-3(c^4+d^4+3c^2d^2)G_4^9+(c^6+9c^4d^2+9c^2d^4+d^6)G_4^7\\&-3c^2d^2(d^4+c^4+3c^2d^2)G_4^5+3c^4d^4(c^2+d^2)G_4^3-c^6d^6G_4^1]\\&-(\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1\mathbf{p}_2\cdot\mathbf{q}_2+\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_1\mathbf{R}\cdot\mathbf{q}_2+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_2\mathbf{p}_2\cdot\mathbf{q}_1+\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_2\mathbf{p}_1\cdot\mathbf{q}_1)\\&\times[-G_3^{13}+3(c^2+d^2)G_3^{11}-3(c^4+d^4+3c^2d^2)G_3^9+(c^6+9c^4d^2+9c^2d^4+d^6)G_3^7\\&-3c^2d^2(d^4+3c^2d^2+d^4)G_3^5+3c^4d^4(c^2+d^2)G_3^3-c^6d^6G_3^1]\\&+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_1\mathbf{R}\cdot\mathbf{q}_2[-G_2^{13}+3(c^2+d^2)G_2^{11}-3(c^4+3c^2d^2+d^4)G_2^9+(c^69c^4d^2+9c^2d^4+d^6)G_2^7\\&-3c^2d^2(c^4+3c^2d^2+d^4)G_2^5+3c^4d^4(c^2+d^2)G_2^3-c^6d^6G_2^1]\\&+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\mathbf{q}_1\cdot\mathbf{q}_2[G_3^{13}-(4d^2+2c^2)G_3^{11}+(c^4+6d^4+8c^2d^2)G_3^9-4d^2(c^4+d^4+3c^2d^2)G_3^7\\&+(6c^4d^4+d^8+8c^2d^6)G_3^5-(4c^4d^6+2c^2d^8)G_3^3+c^4d^8G_3^1]\\&+\mathbf{R}\cdot\mathbf{q}_1\mathbf{R}\cdot\mathbf{q}_2\mathbf{p}_1\cdot\mathbf{p}_2[G_3^{13}-(4c^2+2d^2)G_3^{11}+(d^4+6c^4+8c^2d^2)G_3^9-4c^2(c^4+d^4+3c^2d^2)G_3^7\\&+(6c^4d^4+c^8+8c^6d^2)G_3^5-(4c^6d^4+2c^8d^2)G_3^3+d^4c^8G_3^1]\}\ ,\end{aligned} \tag{B13}$$

$$\begin{aligned}I(3,0;2,0)=4\pi\{&[c^2d/(c^2-d^2)^4][-G_3^7+(c^2+2d^2)G_3^5-(d^4+2c^2d^2)G_3^3+d^4c^2G_3^1]\\&-[d/(c^2-d^2)^3][-G_2^5+(c^2+d^2)G_2^3-c^2d^2G_2^1]\}\ ,\end{aligned} \tag{B14}$$

$$\begin{aligned}I(3,0;3,0)=4\pi\{&[c^2d^2/(c^2-d^2)^5][G_4^9-2(c^2+d^2)G_4^7+(c^4+4c^2d^2+d^4)G_4^5-2d^2c^2(c^2+d^2)G_4^3+c^4d^4G_4^1]\\&+[1/(c^2-d^2)^3][-G_2^5+(c^2+d^2)G_2^3-c^2d^2G_2^1]\\&-[c^2/(c^2-d^2)^4][-G_3^7+(2d^2+c^2)G_3^5-(d^4+2c^2d^2)G_3^3+d^4c^2G_3^1]\\&-[d^2/(c^2-d^2)^4][G_3^7-(2c^2+d^2)G_3^5+(c^4+2c^2d^2)G_3^3-d^2c^4G_3^1]\}\ ,\end{aligned} \tag{B15}$$

$$\begin{aligned}I(4,0;3,0)=4\pi\{&[c^3d^2/(c^2-d^2)^6][G_5^{11}-(2c^2+3d^2)G_5^9+(c^4+6c^2d^2+3d^4)G_5^7-(3d^2c^4+6c^2d^4+d^6)G_5^5\\&+(3c^4d^4+2c^2d^6)G_5^3-c^4d^6G_5^1]\\&-[3cd^2/(c^2-d^2)^5][G_4^9-2(c^2+d^2)G_4^7+(c^4+4c^2d^2+d^4)G_4^5-2c^2d^2(c^2+d^2)G_4^3+c^4d^4G_4^1]\\&-[c^3/(c^2-d^2)^5][-G_4^9+(c^2+3d^2)G_4^7-3d^2(c^2+d^2)G_4^5+d^4(d^2+3c^2)G_4^3-d^6c^2G_4^1]\\&+[3c/(c^2-d^2)^4][-G_3^7+(c^2+2d^2)G_3^5-(d^4+2c^2d^2)G_3^3+c^2d^4G_3^1]\}\ ,\end{aligned} \tag{B16}$$

$$
\begin{aligned}
I(4,0;4,0)=4\pi\{\,&[c^3d^3/(c^2-d^2)^7][-G_6^{13}+3(c^2+d^2)G_6^{11}-3(c^4+3c^2d^2+d^4)G_6^9+(c^6+9c^4d^2+9c^2d^4+d^6)G_6^7\\
&-3c^2d^2(c^4+3c^2d^2+d^4)G_6^5+3c^4d^4(c^2+d^2)G_6^3-c^6d^6G_6^1]\\
&-[3cd^3/(c^2-d^2)^6][-G_5^{11}+(3c^2+2d^2)G_5^9-(d^4+6c^2d^2+3c^4)G_5^7+(3c^2d^4+6d^2c^4+c^6)G_5^5\\
&-(2d^2c^6+3c^4d^4)G_5^3+d^4c^6G_5^1]\\
&-[3c^3d/(c^2-d^2)^6][G_5^{11}-(2c^2+3d^2)G_5^9+(c^4+6c^2d^2+3d^4)G_5^7-(3d^2c^4+6c^2d^4+d^6)G_5^5\\
&+(3d^4c^4+2c^2d^6)G_5^3-c^4d^6G_5^1]\\
&+[9cd/(c^2-d^2)^5][G_4^9-2(c^2+d^2)G_4^7+(c^4+4c^2d^2+d^4)G_4^5-2c^2d^2(c^2+d^2)G_4^3+c^4d^4G_4^1]\}\,,
\end{aligned}
\tag{B17}
$$

$$
\begin{aligned}
I(4,0;2,0)=4\pi\{\,&[c^3d/(c^2-d^2)^5][-G_4^9+(c^2+3d^2)G_4^7-3d^2(c^2+d^2)G_4^5+(d^6+3d^4c^2)G_4^3-d^6c^2G_4^1]\\
&-[3cd/(c^2-d^2)^4][-G_3^7+(c^2+2d^2)G_3^5-(2c^2d^2+d^4)G_3^3+d^4c^2G_3^1]\}\,,
\end{aligned}
\tag{B18}
$$

$$
\begin{aligned}
I(3,1;2,0)=4\pi\mathbf{R}\cdot\mathbf{p}_1\{\,&[c^2d/(c^2-d^2)^5][-G_3^9+(c^2+3d^2)G_3^7-3d^2(c^2+d^2)G_3^5+(d^6+3d^4c^2)G_3^3-d^6c^2G_3^1]\\
&-[1d/(c^2-d^2)^4][-G_2^7+(c^2+2d^2)G_2^5-(2c^2d^2+d^4)G_2^3+d^4c^2G_2^1]\}\,,
\end{aligned}
\tag{B19}
$$

$$
\begin{aligned}
I(3,1;2,1)=4\pi\{\,&[c^2d/(c^2-d^2)^6]\mathbf{p}_1\cdot\mathbf{q}_1[G_4^{11}-(2c^2+3d^2)G_4^9+(c^4+6c^2d^2+3d^4)G_4^7-d^2(3c^4+6c^2d^2+d^4)G_4^5\\
&+(3c^4d^4+2c^2d^6)G_4^3-c^4d^6G_4^1]\\
&-[dc^2/(c^2-d^2)^6]\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1[G_3^{11}-(2c^2+3d^2)G_3^9+(c^4+6c^2d^2+3d^4)G_3^7\\
&-(3c^4d^2+6c^2d^4+d^6)G_3^5+(3c^4d^4+2c^2d^6)G_3^3-c^4d^6G_3^1]\\
&-[d\mathbf{p}_1\cdot\mathbf{q}_1/(c^2-d^2)^5][G_3^9-2(c^2+d^2)G_3^7+(c^4+d^4+4c^2d^2)G_3^5-2c^2d^2(c^2+d^2)G_3^3+c^4d^4G_3^1]\\
&+[d/(c^2-d^2)^5]\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1[G_2^9-2(c^2+d^2)G_2^7+(c^4+d^4+4c^2d^2)G_2^5-2c^2d^2(c^2+d^2)G_2^3+c^4d^4G_2^1]\}\,,
\end{aligned}
\tag{B20}
$$

$$
\begin{aligned}
I(3,1;3,1)=4\pi(\,&\mathbf{p}_1\cdot\mathbf{q}_1\{[c^2d^2/(c^2-d^2)^7][-G_5^{13}+3(c^2+d^2)G_5^{11}-3(c^4+3c^2d^2+d^4)G_5^9\\
&+(c^6+9c^4d^2+9c^2d^4+d^6)G_5^7-3c^2d^2(c^4+3c^2d^2+d^4)G_5^5\\
&+3c^4d^4(c^2+d^2)G_5^3-c^6d^6G_5^1]\\
&-[c^2/(c^2-d^2)^6][G_4^{11}-(2c^2+3d^2)G_4^9+(c^4+6c^2d^2+3d^4)G_4^7-(3c^4d^2+6c^2d^4+d^6)G_4^5\\
&+(3c^4d^4+2c^2d^6)G_4^3-c^4d^6G_4^1]\\
&-[d^2/(c^2-d^2)^6][-G_4^{11}+(3c^2+2d^2)G_4^9-(3c^4+6c^2d^2+d^4)G_4^7\\
&+(c^6+6c^4d^2+3c^2d^4)G_4^5-(2d^2c^6+3c^4d^4)G_4^3+d^4c^6G_4^1]\\
&+[1/(c^2-d^2)^5][G_3^9-2(c^2+d^2)G_3^7+(c^4+4c^2d^2+d^4)G_3^5-2c^2d^2(c^2+d^2)G_3^3+c^4d^4G_3^1]\}\\
&+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1\{[-c^2d^2/(c^2-d^2)^7][-G_4^{13}+3(c^2+d^2)G_4^{11}-3(c^4+3c^2d^2+d^4)G_4^9\\
&+(c^6+9c^4d^2+9c^2d^4+d^6)G_4^7-3c^2d^2(c^4+d^4+3c^2d^2)G_4^5\\
&+3c^4d^4(c^2+d^2)G_4^3-c^6d^6G_4^1]\\
&+[c^2/(c^2-d^2)^6][G_3^{11}-(2c^2+3d^2)G_3^9+(c^4+6c^2d^2+3d^4)G_3^7\\
&-(3c^4d^2+6c^2d^4+d^6)G_3^5+(3d^4c^4+2c^2d^6)G_3^3-c^4d^6G_3^1]\\
&+[d^2/(c^2-d^2)^6][-G_3^{11}+(3c^2+2d^2)G_3^9-(3c^4+6c^2d^2+d^4)G_3^7\\
&+(c^6+6c^4d^2+3c^2d^4)G_3^5-(2d^2c^6+3c^4d^4)G_3^3+d^4c^6G_3^1]\\
&-[1/(c^2-d^2)^5][G_2^9-2(c^2+d^2)G_2^7+(c^4+4c^2d^2+d^4)G_2^5-2c^2d^2(c^2+d^2)G_2^3+c^4d^4G_2^1]\}\,)\,,
\end{aligned}
\tag{B21}
$$

$$
\begin{aligned}
I(2,2;3,0)=4\pi(\,&\mathbf{p}_1\cdot\mathbf{p}_1\{[cd^2/(c^2-d^2)^6][-G_4^{11}+(3c^2+2d^2)G_4^9-(3c^4+6c^2d^2+d^4)G_4^7\\
&+(c^6+6c^4d^2+3c^2d^4)G_4^5-(2c^6d^2+3c^4d^4)G_4^3+c^6d^4G_4^1]\\
&-[c/(c^2-d^2)^5][G_3^9-2(c^2+d^2)G_3^7+(c^4+4c^2d^2+d^4)G_3^5-2c^2d^2(c^2+d^2)G_3^3+c^4d^4G_3^1]\}\\
&+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\{[cd^2/(c^2-d^2)^6][G_3^{11}-(2c^2+d^2)G_3^9+(c^4+6c^2d^2+d^4)G_3^7\\
&-(3c^4d^2+6c^2d^4+d^6)G_3^5+(3c^4d^4+2c^2d^6)G_3^3-c^4d^6G_3^1]\\
&-[c/(c^2-d^2)^5][-G_2^9+(c^2+3d^2)G_2^7-3d^2(c^2+d^2)G_2^5+(d^6+3d^4c^2)G_2^3-d^6c^2G_2^1]\}),
\end{aligned}
\tag{B22}
$$

$$
\begin{aligned}
I(2,2;4,0)=4\pi(\,&\mathbf{p}_1\cdot\mathbf{p}_2\{[cd^3/(c^2-d^2)^7][G_5^{13}-(4c^2+2d^2)G_5^{11}+(6c^4+8c^2d^2+d^4)G_5^9-4c^2(d^4+3c^2d^2+c^4)G_5^7\\
&+c^4(c^4+8c^2d^2+6d^4)G_5^5-(4c^6d^4+2c^8d^2)G_5^3+c^8d^4G_5^1]\\
&-[3cd/(c^2-d^2)^6][-G_4^{11}+(3c^2+2d^2)G_4^9-(3c^4+6c^2d^2+d^4)G_4^7\\
&+(c^6+6c^4d^2+3c^2d^4)G_4^5-(2c^6d^2+3c^4d^4)G_4^3+c^6d^4G_4^1]\}\\
&+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\{[cd^3/(c^2-d^2)^6][-G_4^{11}+(3c^2+2d^2)G_4^9-(3c^4+6c^2d^2+d^4)G_4^7\\
&+(c^6+6c^4d^2+3c^2d^4)G_4^5-(3c^4d^4+2c^6d^2)G_4^3+c^6d^4G_4^1]\\
&-[3cd/(c^2-d^2)^6][G_3^{11}-(2c^2+3d^2)G_3^9+(c^4+6c^2d^2+3d^4)G_3^7\\
&+(3c^4d^2+6c^2d^4+d^6)G_3^5+(3c^4d^4+2c^2d^6)G_3^3-c^4d^6G_3^1]\}),
\end{aligned}
\tag{B23}
$$

$$
\begin{aligned}
I(2,2;3,1)=\,&4\pi((\mathbf{R}\cdot\mathbf{p}_1\mathbf{p}_2\cdot\mathbf{q}_1+\mathbf{R}\cdot\mathbf{p}_2\mathbf{p}_1\cdot\mathbf{q}_1)\\
&\times\{[cd^2/(c^2-d^2)^7][-G_4^{13}+3(c^2+d^2)G_4^{11}-3(c^4+3c^2d^2+d^4)G_4^9\\
&+(c^6+9c^4d^2+9c^2d^4+d^6)G_4^7-3c^2d^2(c^4+3c^2d^2+d^2)G_4^5\\
&+3c^4d^4(c^2+d^2)G_4^3-c^6d^6G_4^1]\\
&-[c/(c^2-d^2)^6][G_3^{11}-(2c^2+3d^2)G_3^9+(c^4+6c^2d^2+3d^4)G_3^7-(3c^4d^2+6c^2d^4+d^6)G_3^5\\
&+(2c^2d^6+3c^4d^4)G_3^3-c^4d^6G_3^1]\}\\
&+\mathbf{R}\cdot\mathbf{q}_1\mathbf{p}_1\cdot\mathbf{p}_2\{[-cd^2/(c^2-d^2)^7][G_4^{13}-2(2c^2+d^2)G_4^{11}+(6c^4+8c^2d^2+d^4)G_4^9\\
&-4c^2(c^4+3c^2d^2+d^4)G_4^7+(c^8+8c^6d^2+6c^4d^4)G_4^5\\
&-(2c^8d^2+4c^6d^4)G_4^3+c^8d^4G_4^1]\\
&+[c/(c^2-d^2)^6][-G_3^{11}+(3c^2+2d^2)G_3^9-(3c^4+6c^2d^2+d^4)G_3^7+(c^6+6c^4d^2+3c^2d^4)G_3^5\\
&-(2c^6d^2+3c^4d^4)G_3^3+c^6d^4G_3^1]\}\\
&+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_1\{[-cd^2/(c^2-d^2)^7][-G_3^{13}+3(c^2+d^2)G_3^{11}-3(c^4+3c^2d^2+d^4)G_3^9\\
&+(c^6+9c^4d^2+9c^2d^4+d^6)G_3^7-3c^2d^2(c^4+3c^2d^2+d^4)G_3^5\\
&+3c^4d^4(c^2+d^2)G_3^3-c^6d^6G_3^1]\\
&+[c/(c^2-d^2)^6][G_2^{11}-(2c^2+3d^2)G_2^9+(c^4+6c^2d^2+3d^4)G_2^7\\
&-(3c^4d^2+6c^2d^4+d^6)G_2^5+(3c^4d^4+2c^2d^6)G_2^3-c^4d^6G_2^1]\}),
\end{aligned}
\tag{B24}
$$

$$
\begin{aligned}
I(2,0;3,1)=-4\pi\mathbf{R}\cdot\mathbf{q}_1\{\,&[cd^2/(c^2-d^2)^5][-G_3^9+(d^2+3c^2)G_3^7-3c^2(c^2+d^2)G_3^5+(c^6+3c^4d^2)G_3^3-d^2c^6G_3^1]\\
&-[c/(c^2-d^2)^4][G_2^7-(2c^2+d^2)G_2^5+(c^4+2c^2d^2)G_2^3-d^2c^4G_2^1]\},
\end{aligned}
\tag{B25}
$$

$$
\begin{aligned}
I(3,0;3,1)=-4\pi\mathbf{R}\cdot\mathbf{q}_1\{\,&[c^2d^2/(c^2-d^2)^6][-G_4^{11}+(3c^2+2d^2)G_4^9-(3c^4+6c^2d^2+d^4)G_4^7\\
&+(c^6+6c^4d^2+3c^2d^4)G_4^5-(2d^2c^6+3c^4d^4)G_4^3+c^6d^4G_4^1]\\
&-[d^2/(c^2-d^2)^5][-G_3^9+(d^2+3c^2)G_3^7-3c^2(c^2+d^2)G_3^5+(c^6+3c^4d^2)G_3^3-d^2c^6G_3^1]\\
&-[c^2/(c^2-d^2)^5][G_3^9-2(c^2+d^2)G_3^7+(c^4+4c^2d^2+d^4)G_3^5-2c^2d^2(c^2+d^2)G_3^3+c^4d^4G_3^1]\\
&+[1/(c^2-d^2)^4][G_2^7-(2c^2+d^2)G_2^5+(c^4+2c^2d^2)G_2^3-c^4d^2G_2^1]\},
\end{aligned}
\tag{B26}
$$

$$I(4,0;3,1)=-4\pi\mathbf{R}\cdot\mathbf{q}_1\{[c^3d^2/(c^2-d^2)^7][-G_5^{13}+3(c^2+d^2)G_5^{11}-3(c^4+3c^2d^2+d^4)G_5^9 +(c^6+9c^4d^2+9c^2d^4+d^6)G_5^7-3c^2d^2(c^4+3c^2d^2+d^4)G_5^5 +3c^4d^4(c^2+d^2)G_5^3-c^6d^6G_5^1]$$
$$-[3cd^2/(c^2-d^2)^6][-G_4^{11}+(3c^2+2d^2)G_4^9-(3c^4+6c^2d^2+d^4)G_4^7 +(c^6+6c^4d^2+3c^2d^4)G_4^5-(2c^6d^2+3c^4d^4)G_4^3+c^6d^4G_4^1]$$
$$+[c^3/(c^2-d^2)^6][G_4^{11}-(2c^2+3d^2)G_4^9+(c^4+6c^2d^2+d^4)G_4^7-(c^6+6c^4d^2+3c^2d^4)G_4^5 +(3c^4d^4+2c^6d^2)G_4^3-c^4d^6G_4^1]$$
$$-[3c/(c^2-d^2)^5][G_3^9-2(c^2+d^2)G_3^7+(c^4+4c^2d^2+d^4)G_3^5-2c^2d^2(c^2+d^2)G_3^3+c^4d^4G_3^1]\}\ . \tag{B27}$$

APPENDIX C

Analytic expressions for I in which $c=d$ where K_n defined by Eq. (6) and Eq. (7) is a function of c,

$$I(1,0;1,0)=2\pi e^{-cR}/c\ , \tag{C1}$$
$$I(2,0;1,0)=\pi cK_1e^{-cR}=I(1,0;2,0)\ , \tag{C2}$$
$$I(2,0;2,0)=\pi c^2K_2e^{-cR}/3\ , \tag{C3}$$
$$I(1,1;1,0)=\pi\mathbf{R}\cdot\mathbf{p}_1e^{-cR}/c\ , \tag{C4}$$
$$I(1,1;1,1)=(\pi/3)(\mathbf{p}_1\cdot\mathbf{q}_1K_1-\mathbf{R}\cdot\mathbf{q}_1\mathbf{R}\cdot\mathbf{p}_1)e^{-cR}\ , \tag{C5}$$
$$I(2,1;1,0)=(2\pi/3)cK_1\mathbf{R}\cdot\mathbf{p}_1e^{-cR}\ , \tag{C6}$$
$$I(1,0;2,1)=-(2\pi/3)cK_1\mathbf{R}\cdot\mathbf{q}_1e^{-cR}\ , \tag{C7}$$
$$I(2,1;2,0)=(\pi/6)c^2K_2\mathbf{R}\cdot\mathbf{p}_1e^{-cR}\ , \tag{C8}$$
$$I(2,0;2,1)=-(\pi/6)c^2K_2\mathbf{R}\cdot\mathbf{q}_1e^{-cR}\ , \tag{C9}$$
$$I(2,1;2,1)=(\pi c^2/15)(K_3\mathbf{p}_1\cdot\mathbf{q}_1-K_2\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1)e^{-cR}\ , \tag{C10}$$
$$I(2,2;2,0)=\pi c^2(\mathbf{p}_1\cdot\mathbf{p}_2K_3/15+K_2\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2/10)e^{-cR}\ , \tag{C11}$$
$$I(2,2;2,1)=(\pi/30)[(\mathbf{R}\cdot\mathbf{p}_1\mathbf{p}_2\cdot\mathbf{q}_1+\mathbf{R}\cdot\mathbf{p}_2\mathbf{p}_1\cdot\mathbf{q}_1-\mathbf{R}\cdot\mathbf{q}_1\mathbf{p}_1\cdot\mathbf{p}_2)c^2K_3-\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_1c^2K_2]e^{-cR}\ , \tag{C12}$$
$$I(2,2;2,2)=\pi c^2\{[(\mathbf{p}_1\cdot\mathbf{q}_1\mathbf{p}_2\cdot\mathbf{q}_2+\mathbf{p}_1\cdot\mathbf{p}_2\mathbf{q}_1\cdot\mathbf{q}_2+\mathbf{p}_1\cdot\mathbf{q}_2\mathbf{p}_2\cdot\mathbf{q}_1)K_4-(\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1\mathbf{p}_2\cdot\mathbf{q}_2+\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_2\mathbf{p}_1\cdot\mathbf{q}_1+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_2\mathbf{p}_2\cdot\mathbf{q}_1 +\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_1\mathbf{p}_1\cdot\mathbf{q}_2)K_3+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_1\mathbf{R}\cdot\mathbf{q}_2K_2]/70$$
$$+2/105(\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\mathbf{q}_1\cdot\mathbf{q}_2+\mathbf{R}\cdot\mathbf{q}_1\mathbf{R}\cdot\mathbf{q}_2\mathbf{p}_1\cdot\mathbf{p}_2)K_3\}e^{-cR}\ , \tag{C13}$$
$$I(3,0;2,0)=\pi[c^3K_3/6-cK_2/3]e^{-cR}\ , \tag{C14}$$
$$I(3,0;3,0)=(\pi/3)[c^4K_4/5-c^2K_3+K_2]e^{-cR}\ , \tag{C15}$$
$$I(4,0;3,0)=\pi[c^5K_5/30-3c^3K_4/10+cK_3/2]e^{-cR}\ , \tag{C16}$$
$$I(4,0;4,0)=\pi[c^6K_6/70-c^4K_5/5+9c^2K_4/15]e^{-cR}\ , \tag{C17}$$
$$I(4,0;2,0)=\pi[c^4K_4/10-c^2K_3/2]e^{-cR}\ , \tag{C18}$$
$$I(3,1;2,0)=\pi\mathbf{R}\cdot\mathbf{p}_1[c^3K_3/10-cK_2/6]e^{-cR}\ , \tag{C19}$$
$$I(3,1;2,1)=\pi[\mathbf{p}_1\cdot\mathbf{q}_1(c^3K_4/30-cK_3/15)+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1(cK_2/15-c^3K_3/30)]e^{-cR}\ , \tag{C20}$$
$$I(3,1;3,1)=\pi[\mathbf{p}_1\cdot\mathbf{q}_1(c^4K_5/70-c^2K_4/15+K_3/15)+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{q}_1(c^2K_3/15-c^4K_4/70-K_2/15)]e^{-cR}\ , \tag{C21}$$
$$I(2,2;3,0)=\pi[\mathbf{p}_1\cdot\mathbf{p}_2(c^3K_4/30-cK_3/15)+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2(c^3K_3/30-cK_2/10)]e^{-cR}\ , \tag{C22}$$
$$I(2,2;4,0)=\pi[\mathbf{p}_1\cdot\mathbf{p}_2(2c^4K_5/105-c^2K_4/10)+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2(c^3K_4/70-cK_3/10)]e^{-cR}\ , \tag{C23}$$
$$I(2,2;3,1)=\pi[(\mathbf{R}\cdot\mathbf{p}_1\mathbf{p}_2\cdot\mathbf{q}_1+\mathbf{R}\cdot\mathbf{p}_2\mathbf{p}_1\cdot\mathbf{q}_1)(c^3K_4/70-cK_3/30)+\mathbf{R}\cdot\mathbf{q}_1\mathbf{p}_1\cdot\mathbf{p}_2(cK_3/30-2c^3K_4/105)$$
$$+\mathbf{R}\cdot\mathbf{p}_1\mathbf{R}\cdot\mathbf{p}_2\mathbf{R}\cdot\mathbf{q}_1(cK_2/30-c^3K_3/70)]e^{-cR}\ , \tag{C24}$$

$$I(2,0;3,1)=-\pi\mathbf{R}\cdot\mathbf{q}_1(c^3K_3/10-cK_2/6)e^{-cR}\ , \tag{C25}$$

$$I(3,0;3,1)=-\pi\mathbf{R}\cdot\mathbf{q}_1(c^4K_4/30-c^2K_3/6+K_2/6)e^{-cR}\ , \tag{C26}$$

$$I(4,0;3,1)=-\pi\mathbf{R}\cdot\mathbf{q}_1(c^5K_5/70-2c^3K_4/15+cK_3/5)e^{-cR}\ . \tag{C27}$$

[1]F. E. Harris and H. H. Michels, Adv. Chem. Phys. **13**, 205 (1967).

[2]D. M. Silver and K. Ruedenberg, J. Chem. Phys. **49**, 4301 (1968).

[3]K. Ruedenberg, K. O-Ohata, and D. G. Wilson, J. Math. Phys. **7**, 539 (1966).

[4]I. I. Guselnov, J. Phys. B **3**, 1399 (1970).

[5]R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. **17**, 1248 (1949).

[6]J. L. Roberts and H. H. Jaffe, J. Chem. Soc. **27**, 883 (1957).

[7]D. A. Brown and N. J. Fitzpatrick, J. Chem. Phys. **46**, 2005 (1966).

[8]F. P. Prosser and H. Blanchard, J. Chem. Phys. **36**, 1112 (1962).

[9]M. Geller, J. Chem. Phys. **39**, 853 (1963).

[10]I. R. Epstein, Chem. Phys. Lett. **9**, 9 (1971).

[11]J. Avery and M. Cook, Theor. Chim. Acta. **35**, 99 (1974).

[12]M. Geller, Jet Propulsion Laboratory, Pasadena, Technical Report No. 32-673.

[13]H. D. Todd, K. G. Kay, and H. J. Silverstone, J. Chem. Phys. **53**, 3951 (1970).

[14]S. A. Edwards, H. P. W. Gottlieb, and D. M. Dodrell, Mol. Phys. **38**, 1147 (1979).

[15]E. O. Steinborn and E. Filter, Theor. Chim. Acta. **52**, 189 (1979).

[16]H. P. Trivedi and E. O. Steinborn, Phys. Rev. A **25**, 113 (1982).

[17]H. P. Trivedi and E. O. Steinborn, Phys. Rev. A **27**, 670 (1982).

[18]E. O. Steinborn, *Method in Computational Molecular Physics,* edited by G. H. F. Dierksen and S. D. Wilson (Reidel, Dordrecht, 1983).

[19]H. Tai, J. Phys. B **12**, 177 (1979).

[20]R. Shakeshaft, J. Phys. B **8**, L134 (1975).

[21]G. Arfken, *Mathematical Methods for Physicists,* 2nd ed. (Academic, New York, 1973).

[22]R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (Academic, New York, 1969).

[23]T. Szondy, Acta. Phys. Acad. Sci. Hung. **18**, 381 (1965).

[24]F. E. Harris, J. Chem. Phys. **51**, 4770 (1969).