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Note

Gaussian Matrix Elements of the Free-Particle Green's Function*

1. Introduction

Recently we proposed a method for calculating electron-molecule scattering cross sections which requires the evaluation of matrix elements of the free-particle Green's function over Cartesian Gaussian basis function [1]. This arises when the scattering potential, V, is approximated by a sum of separable terms of the form

$$V(\mathbf{r}, \mathbf{r}') \simeq V^{t} = \sum_{\alpha,\beta=1}^{N} \varphi_\alpha(\mathbf{r})\, V_{\alpha\beta}\varphi_\beta^*(\mathbf{r}'), \tag{1}$$

where

$$V_{\alpha\beta} = \int \varphi_\alpha^*(\mathbf{r})\, V(\mathbf{r})\, \varphi_\beta(\mathbf{r})\, d^3r, \tag{2}$$

and the basis functions $\varphi_\alpha(\mathbf{r})$ are Cartesian Gaussian functions. If the truncated potential, Eq. (1), is inserted, the Lippmann–Schwinger equation for the transition operator

$$T^{t} = U^{t} + U^{t}G_0{}^{+}T^{t} \tag{3}$$

becomes a matrix equation with elements

$$T_{\alpha\beta}^{t} = U_{\alpha\beta}^{t} + \sum_{\gamma,\delta} U_{\alpha\gamma}^{t}(G_0{}^{+})_{\gamma\delta}\, T_{\delta\beta}^{t}, \tag{4}$$

where $U = 2V$ and $G_0{}^{+}$ is the free-particle Green's function. Equation (3) is then solved by a simple matrix inversion. This procedure requires the evaluation of the matrix elements of $G_0{}^{+}$ over the basis functions $\varphi_\alpha(\mathbf{r})$. For molecular systems a convenient choice of functions for the expansion of the potential, Eq. (1), is Cartesian Gaussian basis functions. A large number of such Gaussian functions can be required to adequately represent a scattering potential, and hence it is important to have an efficient procedure for the evaluation of the matrix elements $(G_0{}^{+})_{\alpha\beta}$.

In this paper we present a method for generating analytic formulas for Gaussian matrix elements of the free-particle Green's function. The method is based on Ostlund's technique for evaluating scattering integrals involving Gaussian and plane wave functions [2], but it derives its simplicity from some recursive properties of the spherical Bessel functions.

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In Section 2 we present our technique for deriving formulas for Gaussian matrix elements of G_0^+. Our results are tabulated in Section 3 for matrix elements involving Cartesian Gaussian functions of up to f-type symmetry. The formulas given are valid for polyatomic systems, but only those combinations of Gaussian functions which contribute to the Σ, Π, and Δ symmetries of a linear molecule are listed.

2. Theory

The free-particle Green's function satisfies the equation

$$(\nabla^2 + k^2)\, G_0(k; \mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \tag{5}$$

The solution for the outgoing wave boundary condition is

$$G_0^+(k; \mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}, \tag{6a}$$

and the solution for the standing wave boundary condition is the principal-value Green's function

$$G^P(k; \mathbf{r}, \mathbf{r}') = \frac{1}{4\pi} \cdot \frac{\cos(k\,|\underset{\sim}{r} - \underset{\sim}{r}'|)}{|\mathbf{r} - \mathbf{r}'|}. \tag{6b}$$

We are interested in matrix elements of the form $\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^+ \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle$, where $\mu_{lmn}^{\alpha,\mathbf{A}}$ is a normalized Cartesian Gaussian function with center at $\mathbf{A}$,

$$\mu_{lmn}^{\alpha,\mathbf{A}} = N_{lmn}(x - A_x)^l\, (y - A_y)^m\, (z - A_z)^n\, e^{-\alpha|\mathbf{r}-\mathbf{A}|^2}, \tag{7}$$

where N_{lmn} is a normalization factor

$$N_{lmn}^{-1} = \frac{[(2l-1)!!\,(2m-1)!!\,(2n-1)!!]^{1/2}}{(2\alpha^{1/2})^{l+m+n}} \left(\frac{\pi}{2\alpha}\right)^{3/4} \tag{8}$$

and

$$n!! = n(n-2)(n-4) \cdots 1. \tag{9}$$

Taking Fourier transforms, we obtain the integral representation

$$\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^+(E) \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle = \lim_{\epsilon \to 0^+} \frac{1}{(2\pi)^3} \int d^3\mathbf{k}\, \langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid \mathbf{k} \rangle \frac{\langle \mathbf{k} \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle}{(k_0^2 - k^2 + i\epsilon)}, \tag{10}$$

where $E = k_0^2/2$. The Fourier transform of a Gaussian function may be evaluated by elementary methods and is given by

$$\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid \mathbf{k} \rangle = \left(\frac{2\pi}{\alpha}\right)^{3/4} \frac{i^{l+m+n}}{[(2l-1)!!\,(2m-1)!!\,(2n-1)!!]^{1/2}} \times e^{i\mathbf{k}\cdot\mathbf{A} - k^2/4\alpha} H_l\left(\frac{k_x}{2\alpha^{1/2}}\right) H_m\left(\frac{k_y}{2\alpha^{1/2}}\right) H_n\left(\frac{k_z}{2\alpha^{1/2}}\right), \tag{11}$$

where H_l is the Hermite polynomial of order l. Introducing the Cauchy principal value, Eq. (10) may be written in the form

$$\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^{+} \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle$$
$$= \frac{1}{(2\pi)^3} \left[P \int d^3k \, \frac{\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid \mathbf{k} \rangle \langle \mathbf{k} \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle}{k_0^2 - k^2} - i\pi \left(\frac{k_0}{2} \right) \langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid \mathbf{k}_0 \rangle \langle \mathbf{k}_0 \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle \right], \quad (12a)$$

where P denotes the Cauchy principal-value integral and the second term is the residue. The corresponding matrix element for the principal-value Green's function is

$$\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^{P} \mid \mu_{l'm'n'}^{\beta,\mathbf{P}} \rangle = \frac{1}{(2\pi)^3} \, P \int d^3k \, \frac{\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid \mathbf{k} \rangle \langle \mathbf{k} \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle}{k_0^2 - k^2}. \quad (12b)$$

Evaluation of the residue term on the r.h.s. of Eq. (12a) is straightforward. Evaluation of the first term, which is just the matrix element of G_0^P, is the subject of this paper. Substituting Eq. (11) into Eq. (12b) and using the expansion of the plane wave

$$e^{i\mathbf{k}\cdot\mathbf{R}} = 4\pi \sum_{LM} i^L j_L(kR) \, Y_{LM}(\hat{R}) \, Y_{LM}^*(\hat{k}), \quad (13)$$

where

$$\mathbf{R} = \mathbf{A} - \mathbf{B}, \quad (14)$$

leads to the expansion

$$\langle \mu_{lmn}^{\alpha,\mathbf{A}} \mid G_0^{(P)} \mid \mu_{l'm'n'}^{\beta,\mathbf{B}} \rangle = \sum_{LM} i^L C(lmn, l'm'n') \, f_{LM}(k_0, \alpha, \beta; lmn, l'm'n') \, Y_{LM}(\hat{R}), \quad (15)$$

where

$$C(lmn; l'm'n') = -\left(\frac{2}{\pi} \right)^{1/2} \frac{1}{(\alpha\beta)^{3/4}} \, [(2l-1)!!\,(2m-1)!!\,(2n-1)!!\,(2l'-1)!!$$
$$\times (2m'-1)!!\,(2n'-1)!!]^{1/2} \, i^{l-l'+m-m'+n-n'} \quad (16)$$

and

$$f_{LM}(k_0, \alpha, \beta; lmn, l'm'n')$$
$$= P \int_0^\infty dk \, \frac{k^2 e^{-ak^2} j_L(kR)}{k^2 - k_0^2} \int d\hat{k} \, Y_{LM}^*(\hat{k}) \, H_l\left(\frac{k_x}{2\alpha^{1/2}} \right) H_m\left(\frac{k_y}{2\alpha^{1/2}} \right)$$
$$\times H_n\left(\frac{k_z}{2\alpha^{1/2}} \right) H_{l'}\left(\frac{k_x}{2\beta^{1/2}} \right) H_{m'}\left(\frac{k_y}{2\beta^{1/2}} \right) H_{n'}\left(\frac{k_z}{2\beta^{1/2}} \right). \quad (17)$$

Evaluation of the coefficients, f_{LM}, leads to integrals of the form

$$I_L^p = P \int_0^\infty dk \, \frac{k^p e^{-ak^2} j_L(kR)}{k^2 - k_0^2}, \quad (18)$$

where

$$a = (\alpha + \beta)/4\alpha\beta, \tag{19a}$$

and

$$p \geqslant L + 2. \tag{19b}$$

The evaluation of matrix elements of G_0^P for all combinations of Cartesian Gaussian functions of up to *f*-type symmetry requires the integrals I_L^p for $0 \leqslant L \leqslant 6$, $2 \leqslant p \leqslant 8$. The straightforward way to obtain all these I_L^p is to differentiate the lower-order ones, i.e., in L and p, successively with respect to a and R. However, by using the recursive properties of the spherical Bessel functions, i.e.,

$$\frac{(2L+1)}{kR} j_L(kR) = j_{L-1}(kR) + j_{L+1}(kR), \tag{20}$$

we can establish the relation

$$I_L^p = \frac{R}{2L+1} [I_{L-1}^{p+1} + I_{L+1}^{p+1}]. \tag{21}$$

With the result, Eq. (21), we need only obtain I_0^p, $p = 4, 6, 8$ and I_1^p, $p = 5, 7$ by successive differentiations. To see this we start from the relation, pointed out by Ostlund [2], of I_0^2 to the error function of the complex argument

$$I_0^2 = \frac{\pi}{2R} e^{-aq^2} \operatorname{Re}\left[e^{iqR} \operatorname{erf}\left(\frac{R}{2a^{1/2}} + i(a)^{1/2} q\right)\right]; \qquad q = k_0. \tag{22}$$

The formula for I_1^3 is obtained by differentiating Eq. (22) with respect to R:

$$I_1^3 = \frac{\pi}{2} e^{-aq^2} \operatorname{Re}\left[\left(\frac{1}{R^2} - i\frac{q}{R}\right) e^{iqR} \operatorname{erf}\left(\frac{R}{2a^{1/2}} + i(a)^{1/2} q\right)\right] - \frac{\pi^{1/2}}{2} \frac{e^{-R^2/4a}}{R(a)^{1/2}}. \tag{23}$$

3. Results

We have used this approach to obtain explicit expressions for the matrix elements of the Green's function with Cartesian Gaussian functions of *s*, *p*, *d*, and *f*-type. For convenience we list the matrix elements appropriate for axially symmetric molecules, i.e., Σ, Π, and Δ cases. The matrix elements for the Σ, Π, and Δ symmetries are shown in Tables I, II, and III, respectively.

In Table IV we also give actual numerical values for matrix elements of the Green's function for several choices of Gaussian basis functions. In these calculations we used a program based on Gautschi's algorithm for evaluating the complex error function [3].

TABLE I

Matrix Elements of the Principal-Value Part of the Free-Particle Green's Function for Σ Cases[a,b,c]

$$S^{\mathbf{A}} - S^{\mathbf{B}} = AI_0^2$$

$$Z^{\mathbf{A}} - S^{\mathbf{B}} = -\frac{A}{\alpha^{1/2}} P_1 I_1^3$$

$$Z^{\mathbf{A}} - Z^{\mathbf{B}} = \frac{A}{(\alpha\beta)^{1/2}} \{-\tfrac{2}{3} P_2 I_2^4 + \tfrac{1}{3} I_0^4\}$$

$$ZZ^{\mathbf{A}} - S^{\mathbf{B}} = \frac{A}{3^{1/2}} \left\{\frac{2}{3\alpha} P_2 I_2^4 - \frac{1}{3\alpha} I_0^4 + 2I_0^2\right\}$$

$$ZZ^{\mathbf{A}} - Z^{\mathbf{B}} = \frac{A}{3^{1/2}} \left\{\frac{2}{5\alpha\beta^{1/2}} P_3 I_3^5 - \frac{3}{5\alpha\beta^{1/2}} P_1 I_1^5 + \frac{2}{\beta^{1/2}} P_1 I_1^3\right\}$$

$$\begin{aligned} ZZ^{\mathbf{A}} - ZZ^{\mathbf{B}} = \frac{A}{3} \Big\{&\frac{8}{35\alpha\beta} P_4 I_4^6 - \frac{4}{7\alpha\beta} P_2 I_2^6 + \frac{4}{3} BP_2 I_2^4 - \frac{1}{5\alpha\beta} I_0^6 \\ &- \tfrac{2}{3} BI_0^4 + 4I_0^2\Big\} \end{aligned}$$

$$ZZZ^{\mathbf{A}} - S^{\mathbf{B}} = \frac{A}{(15)^{1/2}} \left\{-\frac{2}{5\alpha^{3/2}} P_3 I_3^5 + \frac{3}{5\alpha^{3/2}} P_1 I_1^5 - \frac{6}{\alpha^{1/2}} P_1 I_1^3\right\}$$

$$\begin{aligned} ZZZ^{\mathbf{A}} - Z^{\mathbf{B}} = \frac{A}{(15)^{1/2}} \Big\{&-\frac{8}{35\alpha(\alpha\beta)^{1/2}} P_4 I_4^6 + \frac{4}{7\alpha(\alpha\beta)^{1/2}} P_2 I_2^6 - \frac{1}{5\alpha(\alpha\beta)^{1/2}} I_0^6 \\ &- \frac{4}{(\alpha\beta)^{1/2}} P_2 I_2^4 + \frac{2}{(\alpha\beta)^{1/2}} I_0^4\Big\} \end{aligned}$$

$$\begin{aligned} ZZZ^{\mathbf{A}} - ZZ^{\mathbf{B}} = \frac{A}{3(5^{1/2})} \Big\{&-\frac{8}{63\alpha^{3/2}\beta} P_4 I_4^6 + \frac{4}{9\alpha^{3/2}\beta} P_3 I_3^7 \\ &- \frac{3}{7\alpha^{3/2}\beta} P_1 I_1^7 - \frac{4B^*}{5\alpha^{1/2}} P_3 I_3^5 + \frac{6B^*}{5\alpha^{1/2}} P_1 I_1^5 - \frac{12}{\alpha^{1/2}} P_1 I_1^3\Big\} \end{aligned}$$

$$\begin{aligned} ZZZ^{\mathbf{A}} - ZZZ^{\mathbf{B}} = \frac{A}{15} \Big\{&-\frac{16}{231(\alpha\beta)^{3/2}} P_6 I_6^8 + \frac{24}{77(\alpha\beta)^{3/2}} P_4 I_4^8 \\ &- \frac{10}{21(\alpha\beta)^{3/2}} P_2 I_2^8 + \frac{1}{7(\alpha\beta)^{3/2}} I_0^8 - \frac{48}{35} \frac{B}{(\alpha\beta)^{1/2}} P_4 I_4^6 \\ &+ \frac{24}{7} \frac{B}{(\alpha\beta)^{1/2}} P_2 I_2^6 - \frac{6}{5(\alpha\beta)^{1/2}} I_0^6 - \frac{24}{(\alpha\beta)^{1/2}} P_2 I_2^4 + \frac{12}{(\alpha\beta)^{1/2}} I_0^4\Big\} \end{aligned}$$

[a] A, B, and B^* are defined as

$$A = -\left(\frac{2}{\pi}\right)^{1/2} \frac{1}{(\alpha\beta)^{3/4}}, \qquad B = \left(\frac{1}{\alpha} + \frac{1}{\beta}\right), \qquad B^* = \frac{1}{\alpha} + \frac{3}{\beta},$$

where α and β are the exponents of the Cartesian Gaussian function.

[b] The argument of all P_L is $\hat{R}$.

[c] $S^{\mathbf{A}}$, $Z^{\mathbf{A}}$, $ZZ^{\mathbf{A}}$ are related to $\mu_{lmn}^{\alpha,\mathbf{A}}$ of Eq. (7) as follows: $S^{\mathbf{A}} = \mu_{000}^{\alpha,\mathbf{A}}$, $Z^{\mathbf{A}} = \mu_{001}^{\alpha,\mathbf{A}}$, $ZZ^{\mathbf{A}} = \mu_{002}^{\alpha,\mathbf{A}}$. Higher orders follow analogously. $ZZZ^{\mathbf{A}} - ZZZ^{\mathbf{B}}$ is a shorthand notation for $\langle \mu_{003}^{\alpha,\mathbf{A}} | G_0^{+(p)} | \mu_{003}^{\beta,\mathbf{B}} \rangle$ of Eq. (15).

TABLE II

Matrix Elements of the Principal-Value Part of the Free-Particle Green's Function for Π Cases[a,b,c]

$$X^{A} - X^{B} = \frac{A}{(\alpha\beta)^{1/2}} \left\{ -\left(\frac{2\pi}{15}\right)^{1/2} Q_{22} I_2^{4} + \frac{1}{3} P_2 I_2^{4} + \frac{1}{3} I_0^{4} \right\}$$

$$XZ^{A} - XZ^{B} = \frac{A}{\alpha\beta} \left\{ \frac{1}{21}\left(\frac{8\pi}{5}\right)^{1/2} Q_{42} I_4^{6} - \frac{1}{7}\left(\frac{2\pi}{15}\right)^{1/2} Q_{22} I_2^{6} - \frac{4}{35} P_4 I_4^{6} - \frac{1}{21} P_2 I_2^{6} - \frac{1}{15} I_0^{6} \right\}$$

$$\begin{aligned} XZZ^{A} - XZZ^{B} = \frac{A}{(\alpha\beta)^{2/3}} \frac{1}{3} \Bigg\{ & -\frac{8}{3465}\left(\frac{420\pi}{13}\right)^{1/2} Q_{62} I_6^{8} + \frac{2}{77}\left(\frac{8\pi}{5}\right)^{1/2} Q_{42} I_4^{8} \\ & - \frac{1}{21}\left(\frac{2\pi}{15}\right)^{1/2} Q_{22} I_2^{8} + \frac{8}{231} P_6 I_6^{8} - \frac{16}{385} P_4 I_4^{8} - \frac{1}{21} P_2 I_2^{8} \\ & + \frac{1}{35} I_0^{8} - \frac{2B\alpha\beta}{21}\left(\frac{8\pi}{5}\right)^{1/2} Q_{42} I_4^{6} - \frac{2B\alpha\beta}{7}\left(\frac{2\pi}{15}\right)^{1/2} Q_{22} I_2^{6} \\ & + \frac{8B\alpha\beta}{35} P_4 I_4^{6} + \frac{2\alpha\beta B}{21} P_2 I_2^{6} + \frac{2B\alpha\beta}{15} I_0^{6} \\ & - 4\alpha\beta\left(\frac{2\pi}{15}\right)^{1/2} Q_{22} I_2^{4} + \frac{4\alpha\beta}{3} P_2 I_2^{4} + \frac{4\alpha\beta}{3} I_0^{4} \Bigg\} \end{aligned}$$

$$XZ^{A} - X^{B} = \frac{A}{\alpha\beta^{1/2}} \left\{ \left(\frac{2\pi}{105}\right)^{1/2} Q_{32} I_3^{5} - \frac{1}{5} P_3 I_3^{5} - \frac{1}{5} P_1 I_1^{5} \right)$$

$$\begin{aligned} XZZ^{A} - X^{B} = \frac{A}{(\alpha\beta)^{1/2} 3^{1/2}} \Bigg\{ & -\frac{1}{21\alpha} Q_{42} I_4^{6} + \frac{1}{7\alpha}\left(\frac{2\pi}{15}\right)^{2/1} Q_{22} I_2^{6} \\ & + \frac{4}{35\alpha} P_4 I_4^{6} + \frac{1}{21\alpha} P_2 I_2^{6} - \frac{1}{15\alpha} I_0^{6} - 2\left(\frac{2\pi}{15}\right)^{1/2} Q_{22} I_2^{4} \\ & + \frac{2}{3} P_2 I_2^{4} + \frac{2}{3} I_0^{4} \Bigg\} \end{aligned}$$

$$\begin{aligned} XZZ^{A} - XZ^{B} = \frac{A}{3^{1/2}} \frac{1}{(\alpha\beta)^{1/2}} \Bigg\{ & -\frac{2}{315\alpha}\left(\frac{210\pi}{11}\right)^{1/2} Q_{52} I_5^{7} + \frac{1}{3\alpha}\left(\frac{2\pi}{105}\right)^{1/2} Q_{32} I_3^{7} \\ & + \frac{4}{63\alpha} P_5 I_5^{7} - \frac{1}{45\alpha} P_3 I_3^{7} - \frac{3}{35\alpha} P_1 I_1^{7} \Bigg\} \end{aligned}$$

[a] See footnote *a* of Table I for the definitions of A, B, and B^*.

[b] We define $Q_{LM} = Y_{LM} + Y_{L-M}$.

[c] X^{A}, XZ^{A}, and XZZ^{A} are related to $\mu_{lmn}^{\alpha,\mathrm{A}}$ of Eq. (7) as follows: $X^{A} = \mu_{100}^{\alpha,\mathrm{A}}$, $XZ^{A} = \mu_{101}^{\alpha,\mathrm{A}}$, and $XZZ^{A} = \mu_{102}^{\alpha,\mathrm{A}}$. Also see footnote *c* of Table I.

TABLE III

Matrix Elements of the Principal-Value Part of the Free-Particle Green's Function for Δ Cases[a]

$$XY^{\underset{\sim}{A}} - XY^{\underset{\sim}{B}} = \frac{A}{\alpha\beta}\left\{-\frac{1}{6}\left(\frac{8\pi}{35}\right)^{1/2} Q_{44}I_4{}^6 + \frac{1}{35}P_4I_4{}^6 + \frac{2}{21}P_2I_2{}^6 + \frac{1}{15}I_0{}^6\right\}$$

$$XYZ^{\underset{\sim}{A}} - XYZ^{\underset{\sim}{B}} = \frac{A}{(\alpha\beta)^{3/2}}\left\{\frac{2}{35}\left(\frac{2\pi}{91}\right)^{1/2} Q_{64}I_6{}^8 - \frac{1}{66}\left(\frac{8\pi}{35}\right)^{1/2} Q_{44}I_4{}^8 - \frac{2}{231}P_6I_6{}^8 + \frac{1}{105}I_0{}^8\right\}$$

$$XYZ^{\underset{\sim}{A}} - XY^{\underset{\sim}{B}} = \frac{A}{\alpha^{3/2}\beta}\left\{\frac{2}{3}\left(\frac{\pi}{770}\right)^{1/2} Q_{54}I_5{}^7 - \frac{1}{63}P_5I_5{}^7 - \frac{2}{45}P_3I_3{}^7 - \frac{1}{35}P_1I_1{}^7\right\}$$

[a] See footnotes a, b, and c of Table II.

TABLE IV

Some Numerical Values for Matrix Elements of the Free-Particle Green's Function

A. Σ Symmetry cases

Basis functions	Matrix element[a]	
1–1	−0.16922(−3)	−0.10364(−6)
1–2	−0.35845(−3)	−0.42964(−6)
2–3	−0.40672(−2)	−0.306211(−4)
4–4	−0.12444(−1)	−0.59651(−8)
4–5	−0.98178(−2)	−0.34388(−5)
6–6	−0.88728	−0.46259(−1)
6–3	−0.10915	−0.49350(−2)
3–7	−0.23692	−0.23196(−1)
3–9	0.334011(−2)	−0.52021(−6)
3–8	0.182042	−0.19020(−1)
4–8	0.27396(−2)	−0.143465(−5)
6–8	−0.16438(1)	−0.17828

The exponents, symmetry type, and coordinates of basis functions 1 to 9 are

Basis function	Type	Exponent	Coordinates
1	S	5909.44	(0, 0, R)
2	S	887.451	(0, 0, R)
3	S	19.9981	(0, 0, R)
4	Z	26.786	(0, 0, R)
5	Z	0.1654	(0, 0, R)
6	ZZ	1.225	(0, 0, R)
7	S	0.128	(0, 0, 0)
8	ZZ	0.202	(0, 0, 0)
9	Z	5.9564	(0, 0, R)

$R = -1.034$ a.u., and (a, b, c) are the coordinates of the Cartesian Gaussian function.

[a] For $k_0 = 0.03756808$. The two columns are the real and imaginary parts of the matrix element, and the numbers in parentheses are the powers of ten by which the numbers are to be multiplied.

Table continued

TABLE IV—*Continued*

B. Π Symmetry cases

Basis functions	Matrix element[b]	
1–1	−0.166675(−2)	−0.7385(−9)
1–2	−0.73788(−3)	−0.96335(−5)
3–3	−0.200066(−1)	−0.26408(−9)
2–5	0.49331(−1)	0.14935(−4)
3–4	−0.106265(−1)	−0.497154(−7)
1–6	−0.255868(−6)	−0.73535(−9)
4–5	−0.96181(−1)	−0.27830(−5)

The exponents, symmetry type, and coordinates of basis functions 1 to 6 are

Basis function	Type	Exponent	Coordinates
1	X	200.	$(0, 0, R)$
2	X	0.1	$(0, 0, R)$
3	XZ	10.0	$(0, 0, R)$
4	XZ	0.5	$(0, 0, R)$
5	XZ	1.0	$(0, 0, 0)$
6	X	200.	$(0, 0, -R)$

$R = -1.034$ a.u.

[b] For $k_0 = 0.1$. See also footnote a.

4. Conclusions

We have described an efficient method for generating analytic formulas for Gaussian matrix elements of the free-particle Green's function. The method is based on Ostlund's technique for evaluating integrals involving Gaussian and plane wave functions, but it derives its simplifying features from some recursive properties of spherical Bessel functions. The procedure is straightforward and avoids a great deal of the successive differentiations previously involved in generating these matrix elements. The method is applicable to general polyatomic systems.

APPENDIX: The Basic Integrals I_L^p, Eq. (18), for $0 \leqslant L \leqslant 6$, $2 \leqslant p \leqslant 8$

The basic integrals I_L^p which define the matrix elements of the principal value of the Green's function through Eq. (17) are listed for the cases $0 \leqslant L \leqslant 6$, $2 \leqslant p \leqslant 8$. The I_L^p for $2 \leqslant L \leqslant 6$, $4 \leqslant p \leqslant 8$ are related to the first seven I_L^p below through Eq. (21).

$$I_0^2 = \frac{\pi}{2R}\, e^{-aq^2}\, \mathrm{Re}\left[e^{iqR}\, \mathrm{erf}\left(\frac{R}{2a^{1/2}} + i(a)^{1/2}\, q\right)\right],$$

$$I_0^4 = q^2 I_0^2 + \frac{\pi^{1/2}}{4}\, a^{-3/2} e^{-R^2/4a},$$

$$I_0^6 = q^2 I_0^4 - \frac{\pi^{1/2}}{4}\, e^{-k^2/4a}\left[\frac{R^2 a^{-7/2}}{4} - \frac{3}{2}\, a^{-5/2}\right],$$

$$I_0^8 = q^2 I_0^6 - \frac{\pi^{1/2}}{4}\, e^{-R^2/4a}\left[-\frac{R^4}{16}\, a^{-11/2} + \frac{5}{4}\, R^2 a^{-9/2} - \frac{15}{4}\, a^{-7/2}\right],$$

$$I_1^3 = \frac{\pi}{2}\, e^{-aq^2}\, \mathrm{Re}\left[\left(\frac{1}{R^2} - \frac{iq}{R}\right) e^{iqR}\, \mathrm{erf}\left(\frac{R}{2a^{1/2}} + i(a)^{1/2}\, q\right)\right] - \frac{\pi^{1/2}}{2}\, e^{-R^2/4a}\, \frac{a^{-1/2}}{R},$$

$$I_1^5 = q^2 I_1^3 + \frac{\pi^{1/2}}{8}\, e^{-R^2/4a} R a^{-5/2},$$

$$I_1^7 = q^2 I_1^5 + \frac{\pi^{1/2}}{8}\, e^{-R^2/4a}\left(\frac{5}{2}\, R a^{-7/2} - \frac{R^3}{4}\, a^{-9/2}\right),$$

$$I_2^4 = \frac{3}{R}\, I_1^3 - I_0^4,$$

$$I_2^6 = \frac{3}{R}\, I_1^5 - I_0^6,$$

$$I_2^8 = \frac{3}{R}\, I_1^7 - I_0^8,$$

$$I_3^5 = -I_1^5 + \frac{15}{R^2}\, I_1^3 - \frac{5}{R}\, I_0^4,$$

$$I_3^7 = -I_1^7 + \frac{15}{R^2}\, I_1^5 - \frac{5}{R}\, I_0^6,$$

$$I_4^6 = -\frac{10}{R}\, I_1^5 + \frac{105}{R^3}\, I_1^3 + I_0^6 - \frac{35}{R^2}\, I_0^4,$$

$$I_4^8 = -\frac{10}{R}\, I_1^7 + \frac{105}{R^3}\, I_1^5 + I_0^8 - \frac{35}{R^2}\, I_0^6,$$

$$I_5^7 = I_1^7 - \frac{105}{R^2}\, I_1^5 + \frac{945}{R^4}\, I_1^3 + \frac{14}{R}\, I_0^6 - \frac{315}{R^3}\, I_0^4,$$

$$I_6^8 = \frac{21}{R}\, I_1^7 - \frac{1260}{R^3}\, I_1^5 + \frac{10395}{R^5}\, I_1^3 - I_0^8 + \frac{189}{R^2}\, I_0^6 - \frac{3465}{R^4}\, I_0^4.$$

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