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Bipolar Expansion for $r_{12}^n Y_l^m(\theta_{12}, \phi_{12})$*

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Explicit formulas for the radial functions $V^{(n)}{}_{l_1l_2l_3l}(r_1, r_2, R)$ in the bipolar expansion for $r_{12}^n Y_l^m(\theta_{12}, \phi_{12})$,

$$r_{12}^n Y_l^m(\theta_{12}, \phi_{12}) = \Sigma(2\lambda+1)^{1/2}(2l_3+1)^{1/2} c^\lambda(lm; l_1m_1) c^{l_3}(\lambda, m-m_1; l_2m_2) \times Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2) Y_{l_3}^{m-m_1-m_2}(\theta_R, \phi_R) V^{(n)}{}_{l_1l_2l_3l}(r_1, r_2, R),$$

where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 - \boldsymbol{R}$, are derived with the use of the theory of generalized functions and Fourier transforms. When $n \le -4$ and $n-l$ is odd, there are delta-function terms. In this approach the delta-function terms and the four-region form of the expansion are obtained from a single, unified formula valid in all regions. Recurrence formulas for the $V^{(n)}{}_{l_1l_2l_3l}$ are given.

I. INTRODUCTION

Recently there has been a revival of interest in the bipolar expansion for evaluating two-electron multicenter integrals. The bipolar expansion for r_{12}^{-1} is well known from the work of Carlson and Rushbrooke,[1] Buehler and Hirschfelder,[2] and Rose,[3] and has the general form,

$$r_{12}^{-1} = \sum_{l_1=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{m_2=-l_2}^{l_2} \sum_{l_3=|l_1-l_2|}^{l_1+l_2} B_{l_1l_2l_3m_1m_2}(r_1, r_2, R) \times Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2) Y_{l_3}^{-m_1-m_2}(\theta_R, \phi_R). \quad (1)$$

Here $\mathbf{r}_1$ is measured from point A, $\mathbf{r}_2$ from point B, and $\mathbf{R}$ runs from A to B (see Fig. 1). The vector $\mathbf{r}_{12}$ is

$$\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 - \mathbf{R}. \quad (2)$$

Several attempts have been made to generalize Eq. (1) for $r_{12}^n Y_l^m(\theta_{12}, \phi_{12})$. Chiu[4] and Nozawa[5] suggested obtaining a bipolar-type expansion for $r_{12}^{-l-1} Y_l^m(\theta_{12}, \phi_{12})$ by performing two successive Laplace-type expansions, but Sack[6] has pointed out that their formulas do not completely separate angular and radial variables, thus negating the very purpose of the bipolar expansion. Sack[7] derived the bipolar expansion of r_{12}^n, for n an integer ≥ -1, in terms of Appell functions, but was unable to treat completely $n = -2$ or n not an integer. In a later paper,[6] Sack attacked the general $f(r) Y_l^m$ problem, obtaining a multiple integral for the radial functions [analogous to B in Eq. (1)] in which the integrand involved the solution of an integral equation. But the method is very cumbersome, and Sack obtained no new *explicit* formulas for the bipolar expansion. Ruedenberg[8] has reformulated the bipolar expansion by means of the Fourier transform inversion theorem, obtaining an expression for the radial functions as an integral of the product of three spherical Bessel functions and the radial Fourier transform of the function being expanded. Salmon, Birss, and Ruedenberg[9] later discussed the r_{12}^{-1} expansion in a novel way, but they have not treated explicitly any other function of $\mathbf{r}_{12}$.

In this paper we derive the bipolar expansion for $r_{12}^n Y_l^m(\theta_{12}, \phi_{12})$. The formulation is essentially the one outlined by Ruedenberg.[8] In addition, the theory of generalized functions is used to define the Fourier transforms of the $r^n Y_l^m$, which do not exist in the ordinary function sense. The derivation closely resembles the derivation of Laplace-type expansions given in the preceding paper[10] (hereafter referred to as I). The well-known four-region form for the formulas arises naturally in this formulation. In addition, there are Dirac delta-function terms when $n \le -4$ and $n-l$ is odd. Some recurrence relations are also derived to aid in applications.

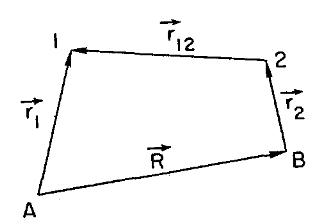

FIG. 1. Definition of the vectors $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_{12}$, and $\boldsymbol{R}$.

II. NOTATION AND CONVENTIONS

As discussed in I, we require

$$n + l + 2 > -1. \quad (3)$$

We refer extensively to Eqs. (4)–(12) of I, which define Condon–Shortley coefficients, the partial-wave expansion of $\exp(i\mathbf{k}\cdot\mathbf{r})$, spherical Bessel functions, double factorials, the sgn function, and $\delta^{(n)}(x)$. The main difference in notation between I and here is that $\mathbf{r}_1$ and $\mathbf{r}_2$ are measured from different origins, and $\mathbf{r}_{12}$ is defined by Eq. (2).

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III. DERIVATION

Write $r_{12}^nY_l^m(\theta_{12},\phi_{12})$ as an inverse Fourier-transform (cf. Ruedenberg[8]),

$$r_{12}^nY_l^m(\theta_{12},\phi_{12})=(2\pi)^{-3}\int d^3\mathbf{k}\exp[-i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2-\mathbf{R})]\,\text{F.T.}\{r^nY_l^m\},\tag{4}$$

where F.T. $\{r^nY_l^m\}$ denotes the Fourier transform of $r^nY_l^m(\theta,\phi)$. Using Eqs (4), (5), and (14)–(16) of I, one obtains

$$r_{12}^nY_l^m(\theta_{12},\phi_{12})=\sum_{l_1=0}^{\infty}\sum_{m_1=-l_1}^{l_1}\sum_{\lambda=|l-l_1|}^{l+l_1}\sum_{l_2=0}^{\infty}\sum_{m_2=-l_2}^{l_2}\sum_{l_3=|l_2-\lambda|}^{l_2+\lambda}(2\lambda+1)^{1/2}(2l_3+1)^{1/2}c^{\lambda}(lm;l_1m_1)c^{l_3}(\lambda,m-m_1;l_2m_2)$$
$$\times Y_{l_1}^{m_1}(\theta_1,\phi_1)Y_{l_2}^{m_2}(\theta_2,\phi_2)Y_{l_3}^{m-m_1-m_2}(\theta_R,\phi_R)V_{l_1l_2l_3l}^{(n)}(r_1,r_2,R),\tag{5}$$

where

$$V_{l_1l_2l_3l}^{(n)}(r_1,r_2,R)\equiv4(-1)^{(l-l_1+l_2+l_3)/2}\int_{-\infty}^{\infty}dk\,k^2j_{l_1}(kr_1)j_{l_2}(kr_2)j_{l_3}(kR)\mathfrak{F}_{nl}(k),\tag{6}$$

and is analogous to $v_{l_1l_2l}^{(n)}(r_1,r_2)$ in the Laplace expansion [Eq. (17) of I]. The $\mathfrak{F}_{nl}(k)$ is the radial part of F.T. $\{r^nY_l^m\}$ and is given by Eqs. (23)–(25) and (23′) of I. If one notes that

$$j_{l_1}(kr_1)j_{l_2}(kr_2)j_{l_3}(kR)=-\tfrac{1}{4}(-1)^{l_1+l_2+l_3}r_1^{l_1}(r_1^{-1}d/dr_1)^{l_1}r_1^{-1}r_2^{l_2}(r_2^{-1}d/dr_2)^{l_2}r_2^{-1}R^{l_3}(R^{-1}d/dR)^{l_3}R^{-1}k^{-l_1-l_2-l_3-3}$$
$$\times\{\sin[k(R+r_1+r_2)]+\sin[k(R-r_1-r_2)]-\sin[k(R+r_1-r_2)]-\sin[k(R-r_1+r_2)]\},\tag{7}$$

the integration of Eq. (6) is almost identical with the integration of Eq. (17) of I, and the result is

$$V_{l_1l_2l_3l}^{(n)}(r_1,r_2,R)=4\pi(-1)^{l-l_1}(n+l+1)!!(n-l)!!\sum_{\substack{\mu_1\geq0,\mu_2\geq0,\mu_3\geq0\\ [\mu_1+\mu_2+\mu_3=(n-l_1-l_2-l_3)/2]}}r_1^{l_1+2\mu_1}r_2^{l_2+2\mu_2}R^{l_3+2\mu_3}$$
$$\times[(2l_1+2\mu_1+1)!!(2\mu_1)!!(2l_2+2\mu_2+1)!!(2\mu_2)!!(2l_3+2\mu_3+1)!!(2\mu_3)!!]^{-1},$$
$$(n-l\geq0\text{ and even. N.B., }V=0\text{ when }n<l_1+l_2+l_3),\tag{8}$$

$$=\pi(-1)^{l_1+1+(n+l)/2}(n+l+1)!![(l-n-2)!!(n+l_1+l_2+l_3+3)!]^{-1}r_1^{l_1}(r_1^{-1}d/dr_1)^{l_1}r_1^{-1}$$
$$\times r_2^{l_2}(r_2^{-1}d/dr_2)^{l_2}r_2^{-1}R^{l_3}(R^{-1}d/dR)^{l_3}R^{-1}[(R+r_1+r_2)^{n+l_1+l_2+l_3+3}\log|R+r_1+r_2|+(R-r_1-r_2)^{n+l_1+l_2+l_3+3}$$
$$\times\log|R-r_1-r_2|-(R+r_1-r_2)^{n+l_1+l_2+l_3+3}\log|R+r_1-r_2|-(R-r_1+r_2)^{n+l_1+l_2+l_3+3}\log|R-r_1+r_2|],$$
$$(n-l\leq-2\text{ and even}),\tag{9}$$

$$=\pi(-1)^{l_1+(n+l+1)/2}(n+l+1)!![(l-n-2)!!(n+l_1+l_2+l_3+3)!]^{-1}r_1^{l_1}(r_1^{-1}d/dr_1)^{l_1}r_1^{-1}$$
$$\times r_2^{l_2}(r_2^{-1}d/dr_2)^{l_2}r_2^{-1}R^{l_3}(R^{-1}d/dR)^{l_3}R^{-1}[(R+r_1+r_2)^{n+l_1+l_2+l_3+3}\operatorname{sgn}(R+r_1+r_2)$$
$$+(R-r_1-r_2)^{n+l_1+l_2+l_3+3}\operatorname{sgn}(R-r_1-r_2)-(R+r_1-r_2)^{n+l_1+l_2+l_3+3}\operatorname{sgn}(R+r_1-r_2)$$
$$-(R-r_1+r_2)^{n+l_1+l_2+l_3+3}\operatorname{sgn}(R-r_1+r_2)],\qquad(n-l\text{ odd}),\tag{10}$$

$$=\pi(-1)^{l_1}(l-n-3)!![(-l-n-3)!!]^{-1}\Gamma(n-l+2)[\Gamma(n+l_1+l_2+l_3+4)]^{-1}$$
$$\times r_1^{l_1}(r_1^{-1}d/dr_1)^{l_1}r_1^{-1}r_2^{l_2}(r_2^{-1}d/dr_2)^{l_2}r_2^{-1}R^{l_3}(R^{-1}d/dR)^{l_3}R^{-1}[|R+r_1+r_2|^{n+l_1+l_2+l_3+3}\operatorname{sgn}(R+r_1+r_2)$$
$$+|R-r_1-r_2|^{n+l_1+l_2+l_3+3}\operatorname{sgn}(R-r_1-r_2)-|R+r_1-r_2|^{n+l_1+l_2+l_3+3}\operatorname{sgn}(R+r_1-r_2)$$
$$-|R-r_1+r_2|^{n+l_1+l_2+l_3+3}\operatorname{sgn}(R-r_1+r_2)],\qquad(n\text{ not an integer}).\tag{11}$$

IV. REMARKS

When $n-l\geq0$ and is even, the series (5) terminates [Eq. (8)], because $r_{12}^nY_l^m(\theta_{12},\phi_{12})$ is just a homogeneous polynomial of degree n in x_{12}, y_{12}, and z_{12}. When $n-l$ is even and negative, there are logarithmic terms [Eq. (9)]. We have not carried out the differentiations in Eq. (9) because for $n\leq-4$, the derivatives generate poles. In this case, one must interpret integrals [such as Eq. (2) of I] over the bipolar expansion in the generalized function sense, and either integrate by parts or take the derivatives (by manipulating them into derivatives with respect to R) after integration. Note that in Eqs. (9)–(11), the use of absolute value and sgn functions gives a single formula valid for all (positive) values of r_1 and r_2. The $n-l$ odd and $n\leq-4$ case, Eq. (10), contains Dirac delta functions. In the next section we separate off the delta-function terms and also write the remainder in the familiar (at least for r_{12}^{-1}) four-region form.

We note that Eqs. (8)–(10) can be obtained from Eq. (11) by letting n approach an integer and using l'Hospital's rule, when necessary. We also note that the structure of the solutions for $V_{l_1l_2l_3l}{}^{(n)}(r_1, r_2, R)$ is that postulated by Sack.[11]

V. DELTA-FUNCTION TERMS

When $n \leq -4$, and $n-l$ is odd, Eq. (10) contains delta functions. Write

$$V_{l_1l_2l_3l}{}^{(n)} = V_{l_1l_2l_3l}{}^{(n)(\text{no }\delta)} + V_{l_1l_2l_3l}{}^{(n)(\delta)},$$

$$(n-l \text{ odd}, n \leq -4). \quad (12)$$

The $\text{sgn}(R \pm r_1 \pm r_2)$ change sign along the lines, $r_1+r_2=R$, $r_1-r_2=R$, and $r_2-r_1=R$, thus dividing r_1r_2 space into four regions (see Fig. 2). One can obtain formulas for each region by expanding

$$(R \pm r_1 \pm r_2)^{n+l_1+l_2+l_3+3}$$

as a polynomial and then taking the derivatives in Eq. (10). The results are

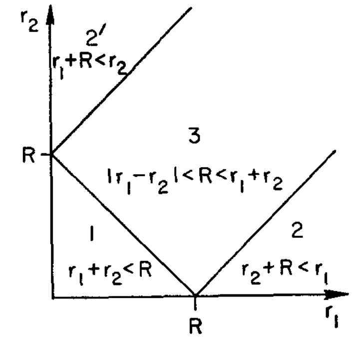

FIG. 2. The four regions of applicability for bipolar expansion formulas.

$$V_{l_1l_2l_3l}{}^{(n)(\text{no }\delta)}(r_1, r_2, R) = 4\pi(-1)^{l_1+(n+l+1)/2}(n+l+1)!![(l-n-2)!!]^{-1}$$
$$\times\left[\sum_{\substack{\mu_1\geq 0,\mu_2\geq 0,\mu_3\geq 0\\ [\mu_1+\mu_2+\mu_3=(n-l_1-l_2+l_3+1)/2]}} \frac{r_1{}^{l_1+2\mu_1} r_2{}^{l_2+2\mu_2} R^{2\mu_3-l_3-1}}{(2l_1+2\mu_1+1)!!(2\mu_1)!!(2l_2+2\mu_2+1)!!(2\mu_2)!!(2\mu_3-2l_3-1)!!(2\mu_3)!!}\right],$$
$$(\text{Region 1, } r_1+r_2<R. \text{ N.B., } V^{(\text{no }\delta)}=0, \text{ when } n-l_1-l_2+l_3+1<0), \quad (13)$$

$V_{l_1l_2l_3l}{}^{(n)(\text{no }\delta)}(r_1, r_2, R) =$ [same as Eq. (13), except that r_1, l_1, μ_1 and R, l_3, μ_3 are interchanged in the expression enclosed by brackets], (Region 2, $r_2+R<r_1$. N.B., $V^{(\text{no }\delta)}=0$, when $n+l_1-l_2-l_3+1<0$), (14)

$V_{l_1l_2l_3l}{}^{(n)(\text{no }\delta)}(r_1, r_2, R) =$ [same as Eq. (13), except that r_2, l_2, μ_2 and R, l_3, μ_3 are interchanged in the expression enclosed by brackets], (Region 2′, $r_1+R<r_2$. N.B., $V^{(\text{no }\delta)}=0$, when $n_1-l_1+l_2-l_3+1<0$), (15)

$$V_{l_1l_2l_3l}{}^{(n)(\text{no }\delta)}(r_1, r_2, R) = \pi(-1)^{l_1+(n+l+1)/2}(n+l+1)!![(l-n-2)!!]^{-1} \sum_{\substack{\mu_1\geq 0,\mu_2\geq 0,\mu_3\geq 0\\ (\mu_1+\mu_2+\mu_3=n+l_1+l_2+l_3+3)}} [1-(-1)^{\mu_1}-(-1)^{\mu_2}$$
$$-(-1)^{\mu_3}] r_1{}^{\mu_1-l_1-1} r_2{}^{\mu_2-l_2-1} R^{\mu_3-l_3-1} [\mu_1!!(\mu_1-2l_1-1)!!\mu_2!!(\mu_2-2l_2-1)!!\mu_3!!(\mu_3-2l_3-1)!!]^{-1},$$
$$(\text{Region 3, } |r_1-r_2|<R<r_1+r_2). \quad (16)$$

In the Region 3 formula [Eq. (16)], $[(-2N)!!]^{-1}$ is to be interpreted as zero, when $N>0$.

The delta-function terms, arising from derivatives of the sgn functions, are readily seen to be

$$V_{l_1l_2l_3l}{}^{(n)(\delta)}(r_1, r_2, R) = (2\pi)(-1)^{l_1+(n+l+1)/2}(n+l+1)!![(l-n-2)!!]^{-1}$$
$$\times \sum_{\mu_1\geq 0}^{l_1} \sum_{\mu_2\geq 0}^{l_2} \sum_{\substack{\mu_3\geq 0\\ (-n-4-\mu_1-\mu_2-\mu_3\geq 0)}}^{l_3} \frac{(l_1+\mu_1)!}{(l_1-\mu_1)!(2\mu_1)!!} \frac{(l_2+\mu_2)!}{(l_2-\mu_2)!(2\mu_2)!!} \frac{(l_3+\mu_3)!}{(l_3-\mu_3)!(2\mu_3)!!} (-1)^{\mu_3} r_1{}^{-\mu_1-1} r_2{}^{-\mu_2-1} R^{-\mu_3-1} (d/dR)^{-n-4-\mu_1-\mu_2-\mu_3}$$
$$\times[(-1)^{l_1+l_2}\delta(R-r_1-r_2) - (-1)^{\mu_1+l_2}\delta(R+r_1-r_2) - (-1)^{l_1+\mu_2}\delta(R-r_1+r_2)]. \quad (17)$$

The total δ-function contribution can be simplified by plugging Eq. (17) into Eq. (5) and then summing over l_3 and λ. One makes use of Eq. (35) of I and the relation

$$\sum_{l_1=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{m_2=-l_2}^{l_2} \sum_{\lambda=|l-l_1|}^{l+l_1} \sum_{l_3=|l_2-\lambda|}^{l_2+\lambda} (-1)^{(l_1\pm l_1)/2}(-1)^{(l_2\pm l_2)/2}(2\lambda+1)^{1/2}$$
$$\times(2l_3+1)^{1/2}(4\pi)^{-1} c^{\lambda}(lm; l_1m_1)\, c^{l_3}(\lambda m-m_1; l_2m_2)\, Y_{l_3}{}^{m-m_1-m_2}(\theta_R, \phi_R)\, Y_{l_1}{}^{m_1}(\theta_1, \phi_1)\, Y_{l_2}{}^{m_2}(\theta_2, \phi_2)$$
$$= \sum_{l_1=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{m_2=-l_2}^{l_2} (-1)^{(l_1\pm l_1)/2}(-1)^{(l_2\pm l_2)/2} Y_l{}^m(\theta_R, \phi_R)\, Y_{l_1}{}^{m_1*}(\theta_R, \phi_R)\, Y_{l_1}{}^{m_1}(\theta_1, \phi_1)\, Y_{l_2}{}^{m_2*}(\theta_R, \phi_R)\, Y_{l_2}{}^{m_2}(\theta_2, \phi_2), \quad (18)$$

$$= Y_l{}^m(\theta_R, \phi_R)\,\delta(\Omega_1 \pm \Omega_R)\,\delta(\Omega_2 \pm \Omega_R), \quad (19)$$

[11] See Ref. 6, p. 1776, question (b).

where $\delta(\Omega)$ is the delta function of solid angle, to obtain,

$$[r_{12}^n Y_l^m(\theta_{12},\phi_{12})]^{(\delta)} \equiv [\text{Eq. (5) with } V^{(n)(\delta)} \text{ substituted for } V^{(n)}], \tag{20}$$

$$= 8\pi^2(-1)^{(n+l+1)/2}(n+l+1)!![(l-n-2)!!]^{-1} \sum_{\substack{\mu_1\geq 0\\(-n-4-\mu_1-\mu_2-\mu_3\geq 0)}} \sum_{\mu_2\geq 0} \sum_{\mu_3\geq 0} (-1)^{\mu_3}$$
$$\times[(2\mu_1)!!(2\mu_2)!!(2\mu_3)!!]^{-1} r_1^{-\mu_1-1} r_2^{-\mu_2-1} R^{-\mu_3-1}(d/dR)^{-n-4-\mu_1-\mu_2-\mu_3}$$
$$\times\{\prod_{\nu_1=1}^{\mu_1}[\hat{\mathbf{l}}_1^2-\nu_1(\nu_1-1)]\}\{\prod_{\nu_2=1}^{\mu_2}[\hat{\mathbf{l}}_2^2-\nu_2(\nu_2-1)]\}\{\prod_{\nu_3=1}^{\mu_3}[\hat{\mathbf{l}}_R^2-\nu_3(\nu_3-1)]\}$$
$$\times Y_l^m(\theta_R,\phi_R)[\delta(R-r_1-r_2)\delta(\Omega_1-\Omega_R)\delta(\Omega_2+\Omega_R)-(-1)^{\mu_1}\delta(R+r_1-r_2)\delta(\Omega_1+\Omega_R)\delta(\Omega_2+\Omega_R)$$
$$-(-1)^{\mu_2}\delta(R-r_1+r_2)\delta(\Omega_1-\Omega_R)\delta(\Omega_2-\Omega_R)], \qquad (n-l \text{ odd}, n\leq -4). \tag{21}$$

Note that the double integral

$$\int dV_1 \int dV_2$$

of Eq. (21) reduces to a line integral along the internal boundaries of the four regions [see, e.g., Fig. 2]. By use of relations like

$$\delta(R-r_1-r_2)\delta(\Omega_1-\Omega_R)\delta(\Omega_2+\Omega_R) = R\int_0^1 dt\delta(\mathbf{r}_1-t\mathbf{R})\delta(\mathbf{r}_2+\mathbf{R}-t\mathbf{R})r_1^2r_2^2, \tag{22}$$

the result can be cast in terms of one-dimensional integrals over the products of two three-dimensional δ functions,

$$[r_{12}^n Y_l^m(\theta_{12},\phi_{12})]^{(\delta)} = 8\pi^2(-1)^{(n+l+1)/2}(n+l+1)!![(l-n-2)!!]^{-1} \sum_{\substack{\mu_1\geq 0\\(-n-4-\mu_1-\mu_2-\mu_3\geq 0)}} \sum_{\mu_2\geq 0} \sum_{\mu_3\geq 0} (-1)^{\mu_3}$$
$$\times[(2\mu_1)!!(2\mu_2)!!(2\mu_3)!!]^{-1} r_1^{-\mu_1+1} r_2^{-\mu_2+1} R^{-\mu_3-1}(d/dR)^{-n-4-\mu_1-\mu_2-\mu_3} R$$
$$\times\{\prod_{\nu_1=1}^{\mu_1}[\hat{\mathbf{l}}_1^2-\nu_1(\nu_1-1)]\}\{\prod_{\nu_2=1}^{\mu_2}[\hat{\mathbf{l}}_2^2-\nu_2(\nu_2-1)]\}\{\prod_{\nu_3=1}^{\mu_3}[\hat{\mathbf{l}}_R^2-\nu_3(\nu_3-1)]\}$$
$$\times Y_l^m(\theta_R,\phi_R)\left(\int_0^1 dt\delta(\mathbf{r}_1-t\mathbf{R})\delta(\mathbf{r}_2+\mathbf{R}-t\mathbf{R}) - \int_0^\infty dt[(-1)^{\mu_1}\delta(\mathbf{r}_1+t\mathbf{R})\delta(\mathbf{r}_2+\mathbf{R}+t\mathbf{R})\right.$$
$$\left.+(-1)^{\mu_2}\delta(\mathbf{r}_1-\mathbf{R}-t\mathbf{R})\delta(\mathbf{r}_2-t\mathbf{R})]\right), \qquad (n-l \text{ odd}, n\leq -4). \tag{23}$$

The simplest example is $n=-4$, $l=3$,

$$[r_{12}^{-4}Y_3^m(\theta_{12},\phi_{12})]^{(\delta)} = (8\pi^2/15)r_1r_2Y_3^m(\theta_R,\phi_R)\left(\int_0^1 dt\delta(\mathbf{r}_1-t\mathbf{R})\delta(\mathbf{r}_2+\mathbf{R}-t\mathbf{R}) - \int_0^\infty dt\delta(\mathbf{r}_1+t\mathbf{R})\delta(\mathbf{r}_2+\mathbf{R}+t\mathbf{R})\right.$$
$$\left.-\int_0^\infty dt\delta(\mathbf{r}_1-\mathbf{R}-t\mathbf{R})\delta(\mathbf{r}_2-t\mathbf{R})\right). \tag{24}$$

VI. RECURRENCE FORMULAS

Of the five indices on which the $V_{l_1l_2l_3l}^{(n)}$ depend, the dependence on l is particularly simple, involving only a multiplicative constant

$$V_{l_1l_2l_3l+2}^{(n)} = [(n+l+3)/(n-l)]V_{l_1l_2l_3l}^{(n)}. \tag{25}$$

Four more independent recurrence formulas can be derived directly from Eq. (6) along with Eqs. (23)–(25) and (23′) of I, and via the well-known recurrence formulas for spherical Bessel functions,

$$x^{-1}j_l(x) = [j_{l+1}(x)+j_{l-1}(x)]/(2l+1), \tag{26}$$

$$j_{l-1}(x) = x^{-l-1}(d/dx)x^{l+1}j_l(x). \tag{27}$$

These are

$$(n-l+2)^{-1}V_{l_1l_2l_3l-1}^{(n+1)}(r_1,r_2,R) = [r_1/(2l_1+1)][V_{l_1-1,l_2l_3l}^{(n)}(r_1,r_2,R)-V_{l_1+1,l_2l_3l}^{(n)}(r_1,r_2,R)], \tag{28}$$

$$= -[r_2/(2l_2+1)][V_{l_1l_2-1,l_3l}^{(n)}-V_{l_1l_2+1,l_3l}^{(n)}] \tag{29}$$

$$= -[R/(2l_3+1)][V_{l_1l_2l_3-1,l}^{(n)}-V_{l_1l_2l_3+1,l}^{(n)}] \tag{30}$$

and

$$[(n+l_1+l_2+l_3+4)/(n-l+2)]V_{l_1l_2l_3l-1}{}^{(n+1)}=r_1V_{l_1-1,l_2l_3l}{}^{(n)}-r_2V_{l_1l_2-1,l_3l}{}^{(n)}-RV_{l_1l_2l_3-1,l}{}^{(n)}. \tag{31}$$

VII. SUMMARY

The bipolar expansion for $r_{12}{}^{n}Y_{l}{}^{m}(\theta_{12}, \phi_{12})$ is derived via the theory of generalized functions and Fourier transforms. The results are contained in Eqs. (5) and (8)–(11). The four-region form of the expansion is implicit in the formulas through the occurrence of the absolute value and sgn functions. When $n-l$ is odd and $n\leq-4$, there are delta-function terms, which have been separated from the ordinary terms in Eqs. (12)–(17). The delta-function part of the expansion is summed explicitly in Eq. (23). Some recurrence formulas for the radial functions $V_{l_1l_2l_3l}{}^{(n)}(r_1, r_2, R)$ are given—Eqs. (25) and (28)–(31).

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Threshold Electron-Impact Excitation and Negative-Ion Formation in XeF_6 and XeF_4*

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Electronic excitation and dissociative electron attachment in XeF_6 and XeF_4 were investigated by studying the products of low-energy electron–molecule collisions in the gas phase. The relative abundances of the major negative ions produced were recorded as a function of the electron-beam energy. Both molecules attached electrons at ~0 and ~5 eV and dissociated into a number of negative-ion products. The similar energy dependence of the various ion currents suggested that the fragment ions were competing for the electron attached to XeF_6 or XeF_4. The threshold electron-impact excitation spectra were determined by means of the "SF_6-electron-scavenger" technique. No evidence for low-lying electronic states was found.

INTRODUCTION

Xenon hexafluoride was first prepared in 1963.[1,2] Since that time, the compound has been the subject of numerous experimental studies as well as considerable theoretical speculation. Despite this concentration of activity, the nature of gaseous XeF_6 is still a puzzle. Vapor-density determinations[3] show no association in the gas phase. The infrared and Raman spectra[3–6] have not been explained satisfactorily. Electron-diffraction experiments[7–9] indicate that the vapor molecules do not have octahedral symmetry. Molecular-beam experiments[10,11] show that the dipole moment of XeF_6 is very close to zero and that the gaseous substance is not paramagnetic. Mass-spectral studies of the positive ions produced by electron impact[12] showed the ions XeF_6^+, XeF_5^+, XeF_4^+, XeF_3^+, XeF_2^+, XeF^+, and Xe^+, with the XeF_6^+ ion current being very weak. We felt that the negative-ion spectrum and the threshold electron-impact excitation spectrum of XeF_6 might give information about dissociation of the molecule and about its electronic energy levels. Since the optical selection rules do not hold for low-energy electron-impact excitation, it is possible to observe states in the electron-impact spectrum which are optically forbidden. Studies of the fluorine–xenon system[3] showed that the low-pressure thermodynamic equilibrium favors the dissociation of XeF_6 into XeF_4 and F_2. For this reason, we also examined XeF_4 briefly in the same manner as XeF_6 to ascertain if we were actually observing XeF_6 in the mass spectrometer. The marked differences between the ion-abundance curves and the threshold excitation spectra for XeF_6 and XeF_4 showed clearly that XeF_6 does not dissociate rapidly at low pressures to XeF_4 and F_2.

EXPERIMENTAL

Xenon hexafluoride was prepared by heating an excess of F_2 with Xe in a prefluorinated Ni reaction vessel containing NaF pellets. The vessel was heated for several days at 250°C and the excess F_2 and other

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