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Angular integrals and radial recurrence relations for two-electron matrix elements in Hylleraas coordinates

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General formulas are obtained for the reduction of a wide class of two-electron matrix elements in Hylleraas coordinates to finite sums of radial integrals for states of arbitrary angular momentum. Multipole transition integrals and the Breit interaction are treated as special cases. A number of recurrence relations are derived for radial integrals containing $P_L(\cos\theta)$ (where $\cos\theta = \hat{r}_1 \cdot \hat{r}_2$) in terms of radial integrals containing lower-order Legendre polynomials. The results are well suited to computer implementation.

I. INTRODUCTION

A large number of highly accurate variational calculations have now been done for the energies and other atomic properties of two-electron systems in terms of the well-known r_1, r_2, r ($r = |\vec{r}_1 - \vec{r}_2|$) Hylleraas coordinates. This work has dealt primarily with *S* and *P* states. However, for matrix elements involving states of high angular momentum, the evaluation of angular integrals and the reduction to radial integrals can become very laborious. The problem is complicated by the fact that if $r_1, r_2,$ and r are regarded as the independent variables in the radial integration, then only one of \hat{r}_1 and \hat{r}_2 may be treated as independent in the angular integration. Of the six independent variables, the three independent angles are the ones which determine the orientation in space of the triangle formed by $\vec{r}_1, \vec{r}_2,$ and \vec{r} .

The reduction of matrix elements to radial integrals over $r_1, r_2,$ and r has been studied by several authors^{1,2} for a number of special cases, but few results of a general nature have been published. The only previous work appears to be a general reduction to radial integrals for the overlap matrix element in terms of uncoupled angular momentum eigenfunctions by Calais and Löwdin.³ In this paper we collect together a number of general angular integration formulas for the reduction of the matrix elements of a wide class of operators to radial integrals. The wave functions are assumed to be vector coupled eigenfunctions of the total angular momentum operator $\vec{L} = \vec{L}_1 + \vec{L}_2$. Recurrence relations for the associated radial integrals are given to complete the efficient and automatic evaluation of matrix elements for states of arbitrary angular momentum. The recurrence relations derived by Sack⁴ for the coefficients in the Legendre polynomial expansion of functions of r emerge as a special case of the present analysis.

In particular, we consider the general problem

of evaluating integrals of the form

$$I = \int \int d\vec{r}_1 d\vec{r}_2 R Y_{l_1 l_2 L}^{M'}(\hat{r}_1, \hat{r}_2)^* \times T_{k_1 k_2 K}^Q Y_{l_1 l_2 L}^M(\hat{r}_1, \hat{r}_2) R, \quad (1)$$

where $Y_{l_1 l_2 L}^{M'}$, $T_{k_1 k_2 K}^Q$, and $Y_{l_1 l_2 L}^M$ all denote vector coupled products of spherical harmonics of the form

$$Y_{l_1 l_2 L}^M(\hat{r}_1, \hat{r}_2) = \sum_{m_1 m_2} \langle l_1 l_2 m_1 m_2 | LM \rangle \times Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2) \quad (2)$$

$$T_{k_1 k_2 K}^Q(\hat{r}_1, \hat{r}_2) = \sum_{\mu_1 \mu_2} \langle k_1 k_2 \mu_1 \mu_2 | KQ \rangle \times Y_{k_1}^{\mu_1}(\hat{r}_1) Y_{k_2}^{\mu_2}(\hat{r}_2), \quad (3)$$

and $R = R(r_1, r_2, r)$ denotes the correlated radial part of the function. We also consider integrals where T_K^Q is constructed from the components of \vec{p}_1 and/or \vec{p}_2 instead of the components of \vec{r}_1 and \vec{r}_2 . The results to follow apply whenever the integrals exist.

II. REDUCTION TO RADIAL INTEGRALS

Let us start by first evaluating the primitive integral

$$I(l_1 m_1, l_2 m_2; R'R) = \int \int d\vec{r}_1 d\vec{r}_2 R Y_{l_1}^{m_1}(\hat{r}_1)^* \times Y_{l_2}^{m_2}(\hat{r}_2) R. \quad (4)$$

The radial integrals are conveniently done by integrating explicitly over the r coordinate with the volume element⁵

$$d r_1 d r_2 = r_1 d r_1 r_2 d r_2 r d r \sin\theta_1 d\theta_1 d\varphi_1 d\chi, \quad (5)$$

where θ_1, φ_1 are the polar angles of the vector \vec{r}_1 , and χ is the angle of rotation of the rigid triangle formed by $\vec{r}_1, \vec{r}_2,$ and \vec{r} about the \vec{r}_1 direction. In this coordinate system, θ_2 and φ_2 are not indepen-

dent variables, but $Y_{l_2}^{m_2}(\theta_2, \varphi_2)$ in (4) can be expressed in terms of the independent variables by means of the rotation matrix relation⁶

$$Y_{l_2}^{m_2}(\theta_2, \varphi_2) = \sum_m \mathfrak{D}_{m_2, m}^{l_2}(\varphi_1, \theta_1, \chi) * Y_{l_2}^m(\theta, \varphi), \quad (6)$$

where θ, φ are the polar angles of \vec{r}_2 relative to \vec{r}_1 . Substitution of (6) into (4) and integration over θ_1, φ_1 , and χ then leads to the basic angular integral algorithm³

$$I(l_1 m_1, l_2 m_2; R'R) = 2\pi \delta_{m_1 m_2} \delta_{l_1 l_2} I_{l_1}(R'R), \quad (7)$$

where

$$I_{l_1}(R'R) = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \times \int_{|r_1 - r_2|}^{r_1 + r_2} r dr R' R P_l(\cos\theta). \quad (8)$$

$P_l(\cos\theta)$ is a Legendre polynomial and $\cos\theta$ is a radial function defined by

$$\cos\theta = (r_1^2 + r_2^2 - r^2)/2r_1 r_2. \quad (9)$$

We return to the evaluation of the radial integrals in Sec. IV.

Let us consider now the full integral (1). Using standard angular-momentum coupling techniques together with the basic integral algorithm (7), the integral can be written in the form

$$I = (-1)^{L'-M'} \begin{pmatrix} L' & K & L \\ -M' & Q & M \end{pmatrix} \sum_{\lambda_1, \lambda_2} X_{\lambda_1, \lambda_2, \Lambda} D_{\lambda_1, \lambda_2, \Lambda} I_{\Lambda}(R'R), \quad (10)$$

where $I_{\Lambda}(R'R)$ is the radial integral (8) involving $P_{\Lambda}(\cos\theta)$,

$$X_{\lambda_1, \lambda_2, \Lambda} = \frac{(-1)^{l_1' + l_2' + L' + \Lambda}}{8\pi} (\lambda_1, \lambda_2, \Lambda)(l_1, k_1, l_1', l_2, k_2, l_2', L, L', K)^{1/2} \times \begin{pmatrix} l_1 & k_1 & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & \lambda_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k_2 & \lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2' & \lambda_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix}, \quad (11)$$

and $D_{\lambda_1, \lambda_2, \Lambda}$ is represented by the angular-momentum coupling graph⁶ shown in Fig. 1. We have used the notation $(\alpha, \beta, \dots) = (2\alpha+1)(2\beta+1)\dots$. The graph for $D_{\lambda_1, \lambda_2, \Lambda}$ can be separated across the

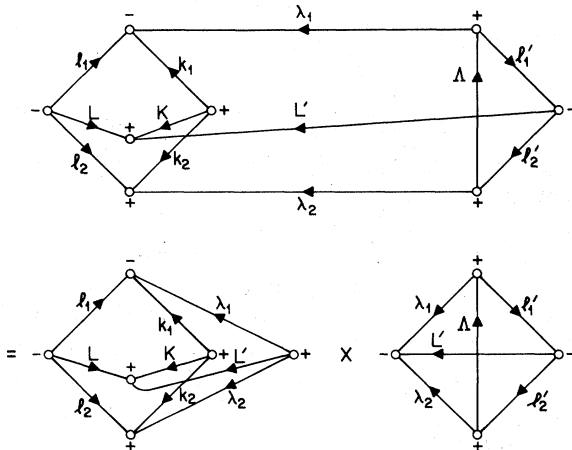


FIG. 1. Angular-momentum coupling graph from Eq. (10) showing the decomposition into the product of a 6- j and a 9- j symbol. All angular momenta are assumed to be integers. Also $X_{\lambda_1, \lambda_2, \Lambda}$ defined by Eq. (11) vanishes unless each of the sums $l_1 + k_1 + \lambda_1$, $l_1' + \lambda_1 + \Lambda$, $l_2 + k_2 + \lambda_2$, and $l_2' + \lambda_2 + \Lambda$ is even. Each vertex represents a 3- j symbol as in Ref. 6.

λ_1, λ_2, L' lines into the product of a 6- j and a 9- j symbol as shown with the result

$$D_{\lambda_1, \lambda_2, \Lambda} = \begin{Bmatrix} L' & l_2' & l_1' \\ \Lambda & \lambda_1 & \lambda_2 \end{Bmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ k_1 & k_2 & K \\ \lambda_1 & \lambda_2 & L' \end{Bmatrix}. \quad (12)$$

The 9- j symbol reduces to a 6- j symbol if any index is zero.⁶ The above formulas thus express the integral (1) in the form

$$I = \sum_{\Lambda} C_{\Lambda} I_{\Lambda}(R'R), \quad (13)$$

where the C_{Λ} are the angular coefficients

$$C_{\Lambda} = \sum_{\lambda_1, \lambda_2} C_{\lambda_1, \lambda_2, \Lambda} \quad (14)$$

and

$$C_{\lambda_1, \lambda_2, \Lambda} = (-1)^{L'-M'} \begin{pmatrix} L' & K & L \\ -M' & Q & M \end{pmatrix} X_{\lambda_1, \lambda_2, \Lambda} D_{\lambda_1, \lambda_2, \Lambda}. \quad (15)$$

Recurrence relations for the radial integrals $I_{\Lambda}(R'R)$ are given in Sec. IV.

III. SPECIAL CASES

A. Scalar operators

Consider matrix elements of operators of the form $T_{k,k,0}^0(\hat{r}_1, \hat{r}_2)$. Using the definition (3), the simplest example is

$$C_{\lambda_1, \lambda_2, \Lambda}(T_{k,k,0}^0) = \frac{(-1)^\Lambda}{8\pi} (\lambda_1, \lambda_2, \Lambda)(k, l_1, l'_1, l_2, l'_2)^{1/2} \begin{pmatrix} l_1 & k & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_1 & \lambda_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k & \lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_2 & \lambda_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{Bmatrix} L & \lambda_1 & \lambda_2 \\ \Lambda & l'_2 & l'_1 \end{Bmatrix} \begin{Bmatrix} L & \lambda_1 & \lambda_2 \\ k & l_2 & l_1 \end{Bmatrix} \delta_{L, L'} \delta_{M, M'} \quad (17)$$

The above form is useful in some applications because λ_1 and λ_2 label separately the various angular-momentum contributions which result when the operator is multiplied to the right into $Y_{l_1}^{m_1}(\hat{r}_1)$ and $Y_{l_2}^{m_2}(\hat{r}_2)$, respectively. For example, since

$$\hat{r}_i Y_i^m = -r \left(\frac{l+1}{2l+1} \right)^{1/2} \bar{Y}_{i, i+1}^m + r \left(\frac{l}{2l+1} \right)^{1/2} \bar{Y}_{i, i-1}^m \quad (18)$$

where $\bar{Y}_{l, \lambda}^m$ is a vector spherical harmonic,⁷ then $C_{\lambda_1, \lambda_2, \Lambda}(\hat{r}_1 \cdot \hat{r}_2)$ is the contribution to $P_\Lambda(\cos\theta)$ from the term [cf. Eq. (2)],

$$a_1 a_2 \sum_{m_1, m_2} \langle l_1 m_1 m_2 | LM \rangle r_1 r_2 \bar{Y}_{l_1 \lambda_1}^{m_1}(\hat{r}_1) \cdot \bar{Y}_{l_2 \lambda_2}^{m_2}(\hat{r}_2)$$

with

$$a_i = \begin{cases} -\left(\frac{l_i+1}{2l_i+1} \right)^{1/2} & \text{if } \lambda_i = l_i + 1 \\ \left(\frac{l_i}{2l_i+1} \right)^{1/2} & \text{if } \lambda_i = l_i - 1. \end{cases}$$

Similarly, $C_{\lambda_1, \lambda_2, \Lambda}(\hat{r}_1 \times \hat{r}_2)$ is the corresponding contribution from $\bar{Y}_{l_1 \lambda_1}^{m_1}(\hat{r}_1) \times \bar{Y}_{l_2 \lambda_2}^{m_2}(\hat{r}_2)$ except that the general equation (15) must be used for the $C_{\lambda_1, \lambda_2, \Lambda}$ since the operator is now a tensor of rank 1. These results will be applied in Sec. III B.

For computational purposes, (17) can be expressed in a simpler form. After application of the Biedenharn-Elliott sum rule⁸ and two contractions of products of a $6-j$ symbol with two $3-j$ symbols,⁹ the complete integral (13) can be written

$$I(T_{k,k,0}^0) = \frac{1}{4\pi} \sum_{\Lambda} C_{\Lambda}(1) I_{\Lambda}[R'RP_k(\cos\theta)], \quad (19)$$

where

$$C_{\Lambda}(1) = \frac{(-1)^{L+\Lambda}}{2} (2\Lambda+1)(l_1, l'_1, l_2, l'_2)^{1/2} \\ \times \begin{pmatrix} l'_1 & l_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_2 & l_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & l_1 & l_2 \\ \Lambda & l'_2 & l'_1 \end{Bmatrix} \quad (20)$$

$$\hat{r}_1 \cdot \hat{r}_2 = -(4\pi/\sqrt{3}) r_1 r_2 T_{1,1,0}^0(\hat{r}_1, \hat{r}_2). \quad (16)$$

Since the $9-j$ symbol in (12) reduces to a $6-j$ symbol, the coefficients $C_{\lambda_1, \lambda_2, \Lambda}$ in (14) for the operator $T_{k,k,0}^0(\hat{r}_1, \hat{r}_2)$ are

is the coefficient of $I_{\Lambda}(R'R)$ in the overlap integral containing $4\pi T_{0,0,0}^0(\hat{r}_1, \hat{r}_2) = 1$, i.e.,

$$I(1) = \sum_{\Lambda} C_{\Lambda}(1) I_{\Lambda}(R'R). \quad (21)$$

In (19), it is useful to use the rule for expanding products of Legendre polynomials as sums of Legendre polynomials so that

$$I_{\Lambda}[R'RP_k(\cos\theta)] = \sum_K (2K+1) \begin{pmatrix} \Lambda & k & K \\ 0 & 0 & 0 \end{pmatrix}^2 I_K(R'R). \quad (22)$$

B. Matrix elements involving the gradient operator and ∇^2

The Breit interaction¹⁰ contains operators such as $\hat{r}_1 \times \nabla_2$, $\hat{r}_1 \cdot \nabla_2$, and $\nabla_1 \cdot \nabla_2$. To reduce these operators to radial integrals, we separate the radial and angular parts of the gradient operators according to

$$\nabla_1 = \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\hat{r}_1 - \hat{r}_2)}{r} \frac{\partial}{\partial r} + \nabla_1^Y, \quad (23a)$$

$$\nabla_2 = \hat{r}_2 \frac{\partial}{\partial r_2} + \frac{(\hat{r}_2 - \hat{r}_1)}{r} \frac{\partial}{\partial r} + \nabla_2^Y, \quad (23b)$$

where ∇^Y is understood to act only on spherical harmonics. Since the angular integrations for the radial parts can be performed by the methods already given in Secs. I and II we consider first only the ∇^Y part. The coefficients $C_{\lambda_1, \lambda_2, \Lambda}$ can be obtained from those for the closely related operators

$$(\hat{r}_1 \times \hat{r}_2)_Q = -(i4\pi\sqrt{2}/3) T_{111}^Q(\hat{r}_1, \hat{r}_2) \quad (24)$$

$$\hat{r}_1 \cdot \hat{r}_2 = (-4\pi/\sqrt{3}) T_{110}^0(\hat{r}_1, \hat{r}_2) \quad (25)$$

by noting that

$$\nabla Y_i^m = -\left(\frac{l+1}{2l+1} \right)^{1/2} \left(\frac{-l}{r} \right) \bar{Y}_{i, i+1}^m \\ + \left(\frac{l}{2l+1} \right)^{1/2} \left(\frac{l+1}{r} \right) \bar{Y}_{i, i-1}^m \quad (26)$$

Comparing (26) with (18) shows that

$$C_{\lambda_1, \lambda_2, \Lambda}(\hat{r}_1, \nabla_2^Y) = \frac{b_{\lambda_2}}{r_2} C_{\lambda_1, \lambda_2, \Lambda}(\hat{r}_1, \hat{r}_2) \quad (27)$$

and

$$C_{\lambda_1, \lambda_2, \Lambda}(\nabla_1^Y, \nabla_2^Y) = \frac{b_{\lambda_1} b_{\lambda_2}}{r_1 r_2} C_{\lambda_1, \lambda_2, \Lambda}(\hat{r}_1, \hat{r}_2), \quad (28)$$

where

$$b_{\lambda_i} = \begin{cases} -l_i & \text{if } \lambda_i = l_i + 1 \\ l_i + 1 & \text{if } \lambda_i = l_i - 1 \end{cases} \quad (29)$$

for $i = 1, 2$. The above is valid for any vector-coupled product $(r_1, \nabla_2^Y)_Q^K$ or $(\nabla_1^Y, \nabla_2^Y)_Q^K$ with $K = 0, 1, 2$. The radial factors in (27) and (28) are to be included in the $I_\Lambda(R'R)$ radial integrals. As an example, the complete reduction to radial integrals for the operator $\hat{r}_1 \times \nabla_2$ is

$$I(\hat{r}_1 \times \nabla_2) = \sum_{\lambda_1, \lambda_2, \Lambda} C_{\lambda_1, \lambda_2, \Lambda}(\hat{r}_1 \times \hat{r}_2) I_\Lambda(R' \Omega_{\lambda_2} R), \quad (30)$$

with

$$C_\Lambda = \frac{(-1)^{L'-M'}}{2(4\pi)^{1/2}} \begin{pmatrix} L' & k & L \\ -M' & q & M \end{pmatrix} (-1)^{l_2'+L'+L+k} (l_1, l_1', l_2, l_2', L, L')^{1/2} \\ \times \sum_\lambda (\lambda, \Lambda, k) \begin{pmatrix} l_1 & k & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & \lambda & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & \lambda & l_2 \\ \Lambda & l_2' & l_1' \end{pmatrix} \begin{pmatrix} L' & \lambda & l_2 \\ l_1 & L & k \end{pmatrix} \quad (32)$$

The corresponding result for $Y_k^q(\hat{r}_2)$ is obtained by interchanging the subscripts 1 and 2 throughout and multiplying by $(-1)^{L+L'+k}$. For the dipole operator, the only nonvanishing contributions come from $\lambda = l_1 \pm 1$.

D. Breit interaction

The matrix elements of the Breit interaction¹⁰ are of considerable interest in atomic-structure calculations and have been worked out in detail

$$H_2 = \frac{\alpha^2}{2} \left\{ \frac{(2r^2 \cos\theta - r_1 r_2 \sin^2\theta)}{r^3} \frac{\partial^2}{\partial r_1 \partial r_2} - \frac{2}{r^2} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) + \frac{(r_2^2 - r_1^2 - r^2)}{r_1 r^2} \frac{\partial^2}{\partial r_1 \partial r} + \frac{(r_1^2 - r_2^2 - r^2)}{r_2 r^2} \frac{\partial^2}{\partial r_2 \partial r} \right. \\ \left. + (\vec{r}_1 \cdot \nabla_2^Y) \left[\frac{(r_1^2 - r_2^2 + 3r^2)}{2r_1 r^3} \frac{\partial}{\partial r_1} + \frac{2}{r^2} \frac{\partial}{\partial r} \right] + (\vec{r}_2 \cdot \nabla_1^Y) \left[\frac{(r_2^2 - r_1^2 + 3r^2)}{2r_2 r^3} \frac{\partial}{\partial r_2} + \frac{2}{r^2} \frac{\partial}{\partial r} \right] \right. \\ \left. + (\nabla_1^Y \cdot \nabla_2^Y) \frac{(r^2 - r_1 r_2 \cos\theta)}{r^3} - \frac{(L^2 - l_1^2 - l_2^2)}{2r^3} \right\} \quad (34)$$

As before, ∇_1^Y , ∇_2^Y , \vec{I}_1 , and \vec{I}_2 act only on the spherical harmonic part of the wave function. The parts of (34) not containing ∇^Y factors are the same as those given by Schiff *et al.*,¹ while the rest is a generalization of their results to arbitrary angular

$$\Omega_{\lambda_2} = \frac{\partial}{\partial r_2} + \frac{r_1}{r} \frac{\partial}{\partial r} + \frac{b_{\lambda_2}}{r_2}.$$

The Laplacian operator for particle 1 in our notation is

$$\nabla_1^2 = \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{(l_1^Y)^2}{r_1^2} \\ + \frac{2(r_1 - r_2 \cos\theta)}{r} \frac{\partial^2}{\partial r_1 \partial r} - 2(\nabla_1^Y \cdot \vec{r}_2) \frac{1}{r} \frac{\partial}{\partial r}, \quad (31)$$

where $(l_1^Y)^2$ acts only on the spherical harmonics. The corresponding result for ∇_2^2 is obtained by interchanging the subscripts 1 and 2.

C. Multipole transition integrals

Consider matrix elements of $Y_k^q(\hat{r}_1)$ $= \sqrt{4\pi} T_{k,0,k}^q(\hat{r}_1, \hat{r}_2)$. Since the C_Λ vanish unless $\lambda_2 = l_2$ in (14), we obtain

by Schiff *et al.*¹ for the special case of $1snp^{1,3}P$ states. Using the methods already developed here, the general reduction to radial integrals is straightforward for all the terms, except for the orbit-orbit interaction given by

$$H_2 = \alpha^2/2 [(1/r) \nabla_1 \cdot \nabla_2 + (1/r^3) \vec{r}_{12} (\vec{r}_{12} \cdot \nabla_1) \nabla_2] \quad (33)$$

in atomic units, where α is the fine-structure constant and $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$. This operator can also be reduced in general to radial integrals if (23a) and (23b) are first used to express H_2 in the form

momentum. The angular coefficients for the latter parts are given by (27) and (28), while the former parts require only the overlap coefficients (20). Factors of $\cos\theta$ do not affect the angular integration since these are purely radial functions given

by (9).

The spin-spin type interactions of the form

$$H_{ss} = \alpha^2/r^3 [\vec{s}_1 \cdot \vec{s}_2 - 3(\vec{s}_1 \cdot \vec{r}_{12})(\vec{s}_2 \cdot \vec{r}_{12})/r^2] \quad (35)$$

do not present any new difficulties if H_{ss} is first written in the scalar product form¹¹

$$H_{ss} = \underline{S}^{(2)} \cdot \underline{L}^{(2)}, \quad (36)$$

where $\underline{S}^{(2)}$ and $\underline{L}^{(2)}$ are irreducible tensors of rank 2 given by

$$S_m^{(2)} = (\frac{2}{5}\pi)^{1/2} (\vec{s}_1 \cdot \nabla)(\vec{s}_2 \cdot \nabla) r^2 Y_2^m(\hat{r}), \quad (37)$$

$$L_m^{(2)} = (\frac{3}{5}\pi)^{1/2} (\alpha^2/r^3) Y_2^m(\hat{r}_{12}). \quad (38)$$

The angular coefficients for the matrix elements of $L_m^{(2)}$ in the uncoupled (L, S, M_L, M_S) scheme can be found from the decomposition

$$Y_2^m(\hat{r}_{12}) = (r_1^2/r^2) Y_2^m(\hat{r}_1) + (r_2^2/r^2) Y_2^m(\hat{r}_2) - 2(\frac{10}{3}\pi)^{1/2} T_{112}^m(\hat{r}_1, \hat{r}_2). \quad (39)$$

The C_Λ for the first two terms are obtained either directly from (32) or from its interchange as discussed in Sec. III C. The C_Λ for the last term are obtained from (14) and (15). The final result for a particular matrix element of $L_m^{(2)}$ in the uncoupled representation is

$$\begin{aligned} \langle l_1 l_2 L' M' | L_m^{(2)} | l_1 l_2 L M \rangle \\ = (\frac{3}{5}\pi)^{1/2} \alpha^2 \sum_\Lambda \left\{ C_\Lambda [Y_2^m(\hat{r}_1)] \left(\frac{R' R r_1^2}{r^5} \right) \right. \\ \left. + C_\Lambda [Y_2^m(\hat{r}_2)] I_\Lambda \left(\frac{R' R r_2^2}{r^5} \right) \right. \\ \left. - 2(\frac{10}{3}\pi)^{1/2} C_\Lambda (T_{112}^m) I_\Lambda \left(\frac{R' R}{r^3} \right) \right\}. \quad (40) \end{aligned}$$

This determines the reduced matrix element of $L^{(2)}$ in

$$\begin{aligned} \langle \gamma' L' S' J' M' | \underline{L}^{(2)} \cdot \underline{S}^{(2)} | \gamma L S J M \rangle \\ = (-1)^{L+S'+J} \delta_{J', J} \delta_{M', M} \begin{Bmatrix} J & S' & L' \\ 2 & L & S \end{Bmatrix} \\ \times \langle \gamma' L' || L^{(2)} || \gamma L \rangle \langle S' || S^{(2)} || S \rangle. \quad (41) \end{aligned}$$

A similar reduction can be written down immediately for the spin-orbit and spin-other-orbit interactions.

IV. RADIAL INTEGRAL RECURRENCE RELATIONS

The results of Secs. I–III reduce the matrix elements for a wide variety of operators to sums of radial integrals (8), which we now write in the abbreviated form

$$I_l(g) = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 f(r_1, r_2) \times \int_{|r_1-r_2|}^{r_1+r_2} r dr g(r) P_l(\cos\theta), \quad (42)$$

where $f(r_1, r_2)$ and $g(r)$ are any functions for which the integral exists. A recurrence relation for the $I_l(g)$ is obtained by first considering the coefficients $R_l(g)$ in the Legendre polynomial expansion⁴

$$g(r) = \sum_{L=0}^{\infty} R_L(g) P_L(\cos\theta). \quad (43)$$

This is also an abbreviated notation since the $R_L(g)$ are functions of r_1 and r_2 . Multiplying (43) by $P_l(\cos\theta) d\cos\theta$ and integrating from -1 to $+1$ yields

$$R_l(g) = \frac{2l+1}{2r_1 r_2} J_l(g), \quad (44)$$

where

$$J_l(g) = \int_{|r_1-r_2|}^{r_1+r_2} r dr g(r) P_l(\cos\theta). \quad (45)$$

In (45), the variable of integration has been changed to $r = (r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta)^{1/2}$. A recurrence relation for the $J_l(g)$ is obtained by substituting

$$P_l(x) = [P'_{l+1}(x) - P'_{l-1}(x)] / (2l+1), \quad (46)$$

and integrating by parts with the result

$$J_{l+1}(g'/r) = \frac{2l+1}{r_1 r_2} J_l(g) + J_{l-1}(g'/r). \quad (47)$$

In each case, the prime means differentiation with respect to the argument. It is clear from the definitions (42) and (45) that the $I_l(g)$ satisfy the analogous recurrence relation

$$I_{l+1}(g'/r) = (2l+1) I_l(r_1^{-1} r_2^{-1} g) + I_{l-1}(g'/r). \quad (48)$$

Equation (48) generates a wide variety of integral recurrence relations depending on the choice made for the function $g(r)$. For integrals containing only powers of r , the choice $g(r) = r^{c+2}$ yields

$$I_{l+1}(r^c) = \frac{2l+1}{c+2} I_l(r_1^{-1} r_2^{-1} r^{c+2}) + I_{l-1}(r^c), \quad c \neq -2. \quad (49)$$

The special case with $l=1$ was employed in the calculations of Schwartz.¹² Except for the case $c=-2$, the relation is valid whenever the integrals exist. It allows the efficient and rapid computation of all $I_l(r^c)$ from a smaller table of values of $I_0(r_1^a r_2^b r^c)$ than would be required for the direct evaluation of (42). Using (42) and (9), the values of $I_1(r_1^a r_2^b r^c)$ needed to start the recurrence relation are

$$I_1(r_1^a r_2^b r^c) = \frac{1}{2} [I_0(r_1^{a+1} r_2^{b-1} r^c) + I_0(r_1^{a-1} r_2^{b+1} r^c) - I_0(r_1^{a-1} r_2^{b-1} r^{c+2})]. \quad (50)$$

Equation (49) is indeterminate for $c = -2$, but the choice $g(r) = \ln r$ yields the well-defined equation

$$I_{l+1}(r^{-2}) = (2l+1)I_l(r_1^{-1}r_2^{-1}\ln r) + I_{l-1}(r^{-2}) \quad (51)$$

to be used in place of (49) when $c = -2$. A recurrence relation for logarithmic integrals follows immediately from (48) with the choice $g(r) = r^{c+2} \ln r - r^{c+2}/(c+2)$, resulting in

$$I_{l+1}(r^c \ln r) = \frac{(2l+1)}{c+2} [I_l(r_1^{-1}r_2^{-1}r^{c+2} \ln r) - I_l(r_1^{-1}r_2^{-1}r^{c+2})/(c+2)] + I_{l-1}(r^c \ln r). \quad (52)$$

Using (9) to replace a factor of r^2 in the integrand of $I_l(r_1^{-1}r_2^{-1}r^{c+2} \ln r)$, along with the recurrence relation for the Legendre polynomials, (52) becomes

$$\begin{aligned} (c+2l+4)I_{l+1}(r^c \ln r) &= (2l+1) I_l[(r_1^2+r_2^2)r_1^{-1}r_2^{-1}r^c \ln r] \\ &\quad - \frac{1}{(c+2)} I_l(r_1^{-1}r_2^{-1}r^{c+2}) \\ &\quad + (c-2l+2)I_{l-1}(r^c \ln r). \end{aligned} \quad (53)$$

The same technique applied to the term $I_l(r_1^{-1}r_2^{-1}r^{c+2})$ in (50) yields the recurrence relation

$$\begin{aligned} (c+2l+4)I_{l+1}(r^c) &= (2l+1)I_l[(r_1^2+r_2^2)r_1^{-1}r_2^{-1}r^c] \\ &\quad + (c-2l+2)I_{l-1}(r^c). \end{aligned} \quad (54)$$

Many other integral relations can be derived in the same way. The choice $g(r) = \exp(-r^2)$ leads to the particularly simple result

$$-2I_{l+1}(e^{-r^2}) = (2l+1)I_l(r_1^{-1}r_2^{-1}e^{-r^2}) - 2I_{l-1}(e^{-r^2}). \quad (55)$$

The corresponding recurrence relations for the coefficients $R_l(g)$ in the Legendre polynomial expansion (43) can easily be derived. From (44) and (47), the general relation is

$$\frac{R_{l+1}(g'/r)}{(2l+3)} = \frac{R_l(g)}{r_1 r_2} + \frac{R_{l-1}(g'/r)}{(2l-1)}. \quad (56)$$

The choice $g(r) = r^{c+2}$ leads to the recurrence relation

$$\frac{R_{l+1}(r^c)}{(2l+3)} = \frac{R_l(r^{c+2})}{(c+2)r_1 r_2} + \frac{R_{l-1}(r^c)}{(2l-1)}, \quad (57)$$

which is equivalent to Eq. (31c) of Sack⁴ obtained by a more lengthy procedure.

Similarly, the analog of (54) is

$$\begin{aligned} \frac{(c+2l+4)}{(2l+3)} R_{l+1}(r^c) &= \frac{(r_1^2+r_2^2)}{r_1 r_2} R_l(r^c) \\ &\quad + \frac{(c-2l+2)}{(2l-1)} R_{l-1}(r^c), \end{aligned} \quad (58)$$

and the analog of (53) is

$$\begin{aligned} (c+2l+4)/(2l+3)R_{l+1}(r^c \ln r) &= 1/r_1 r_2 [(r_1^2+r_2^2)R_l(r^c \ln r) - \frac{1}{(c+2)} R_l(r^{c+2})] \\ &\quad + \frac{(c-2l+2)}{(2l-1)} R_{l-1}(r^c \ln r). \end{aligned} \quad (59)$$

Sack did not derive an expression equivalent to (59), but (59) reduces to his equation (39) for the case $c = 0$. The choice $g(r) = \exp(-\alpha r^2)$ yields

$$-\frac{2\alpha R_{l+1}(e^{-\alpha r^2})}{2l+3} = \frac{R_l(e^{-\alpha r^2})}{r_1 r_2} - \frac{2\alpha R_{l-1}(e^{-\alpha r^2})}{2l-1} \quad (60)$$

for the coefficients in the Legendre polynomial expansion of $\exp(-\alpha r^2)$. The above formula reproduces the first few terms given by Swiatecki.¹³ Other recurrence relations, including those given by Sack, can easily be obtained by using (9) to replace factors of r^2 in the integrand of (45), together with recurrence relations for the Legendre polynomials.

Most of the formulas in this paper have been checked for accuracy in a number of special cases. In particular, recurrence relations such as (48) and (51) have now been used in a large number of calculations with correlated variational wave functions,¹⁴ and have been found to be very stable against round-off error when used in the forward direction. Together with the angular integration formulas, the results make possible the construction of efficient general-purpose integration routines to handle most of the matrix elements encountered in two-electron problems.

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