Gaussian Wave Functions for Polyatomic Molecules

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I. INTRODUCTION

GAUSSIAN wave functions have been suggested by several workers[1-6] as an alternative to the more usual Slater-type orbitals in polyatomic molecules, where the latter lead to extremely tedious integral computations. The Gaussian functions possess the distinct advantage that all the integrals needed for the usual nonrelativistic, spin-free approximate molecular Hamiltonian can be evaluated in closed form, including the three- and four-center integrals which for Slater orbitals have proved exceedingly difficult. For atoms, it is possible that Gaussian orbitals, which possess the wrong radial dependence at large distances from the nucleus, will provide too poor an electronic description to be of great value. However, in molecules, the electron distribution will differ more radically from that of hydrogenic or Slater orbitals, and Gaussian functions may be fairly satisfactory over the more important spatial regions. Moreover, the increased ease of computation with Gaussians makes possible the free use of linear combinations of functions for each orbital, and it is distinctly possible that a combination giving better results than a Slater type orbital can be handled more easily.

In addition to the possibility of using Gaussian functions for orbitals, there also exists the alternative of using Slater orbitals and evaluating the multicenter integrals by an integral transform method first proposed by Kikuchi.[7] The transform converts the integrals involving exponential functions into forms identical to those appearing in the Gaussian orbital formulation. Use of the transform method, then, involves integration of Gaussian integrals followed by the numerical application of the inverse transform. Shavitt[8] was the first to point out the applicability of this transform to the evaluation of molecular integrals.

If Gaussian functions are to be most useful, it is necessary to be able to compute integrals among functions centered at arbitrary spatial points, with a general angular dependence and a radial dependence analogous to various values of the "principal quantum number" of atomic problems. A suitable angular dependence is provided by the spherical harmonics, provided we permit the axes for each orbital to be independently oriented. This enables us to describe p, d, or higher orbitals directed, for example, along the bond directions of the molecule.

Previous work with Gaussian functions, particularly by Boys,[1] has led to formulas for the simplest integrals of each type. While it is formally possible to differentiate these formulas in various ways to produce all the integrals we describe, this process is tedious and leads through work which is more complicated than necessary. It is also desirable, if machine computations are contemplated, to have algebraic, rather than operator formulas. The present paper is designed to contribute in this direction, by providing a workable collection of formulas for the application of a general set of Gaussian functions to molecular problems. We have managed to reduce to explicit closed algebraic form all dependence of the integrals upon the locations, angular dependence, and orientation of the various orbitals. We have left in operator form, however, the extension of the formulas to integrals for which the principal quantum number exceeds the azimuthal quantum number. The resultant differential forms are easy to evaluate for specific cases, but appear to be difficult to specify algebraically.

We considered two forms for the pre-exponential radial dependence of the Gaussian wave functions, namely, simple powers of the radial distance, and the Laguerre polynomials which accompany the Gaussian exponential in the eigenfunctions of the three-dimensional harmonic oscillator. We did not find sufficient benefit from the special properties of the Laguerre polynomials to make their use lead to simpler formulas in many-center systems, so that we used the simple powers in the work which follows.

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II. DEFINITIONS

The wave functions used are of the form

$$\psi^A_{nlm}(\mathbf{r}) = r_A^{2n+l} P_l^m(\cos\theta_A) e^{im\varphi_A - ar^2_A}, \quad (1)$$

where (r_A,θ_A,φ_A) are spherical polar coordinates with origin at point **A**, and with axes $\theta_A = 0$, $\varphi_A = 0$ in directions specified by Eulerian angles $(\alpha_A,\beta_A,\gamma_A)$ relative to a fixed axial frame which is the same for all orbitals. To avoid ambiguity, the definition of Eulerian angles used here is described fully in Appendix 1. We also use circular cylindrical coordinates (ρ_A,z_A,φ_A), with

$$\rho_A = r_A \sin\theta_A, \quad (2a)$$

$$z_A = r_A \cos\theta_A. \quad (2b)$$

Subscripts and arguments are suppressed throughout the paper wherever possible without ambiguity. Additional orbitals, ψ^B, ψ^C, ψ^D will be of the form of Eq. (1), with a replaced by b,c,d, respectively. If coordinates of two electrons appear in the same expression, they will be distinguished by additional subscripts 1,2, as in r_{A1}, θ_{A2}, $\psi^A(\mathbf{r}_1)$, etc. Note that the foregoing definition permits orbitals at arbitrary positions, with arbitrary orientation. The powers of r in excess of l must be even to partake of the advantages of the Gaussian formulation.

The integrals with which we are concerned are the overlap integral

$$(Anlm|Bn'l'm') = \int d\mathbf{r}\psi^{A*}_{nlm}(\mathbf{r})\psi^B_{n'l'm'}(\mathbf{r}), \quad (3)$$

the kinetic-energy integral

$$(Anlm|-\tfrac{1}{2}\nabla^2|Bn'l'm') = -\tfrac{1}{2}\int d\mathbf{r}\psi^{A*}_{nlm}(\mathbf{r})\nabla^2\psi^B_{n'l'm'}(\mathbf{r}), \quad (4)$$

the nuclear-attraction integral

$$(Anlm|\frac{1}{r_C}|Bn'l'm') = \int d\mathbf{r}\psi^{A*}_{nlm}(\mathbf{r})\frac{1}{r_C}\psi^B_{n'l'm'}(\mathbf{r}), \quad (5)$$

and the electron-repulsion integral

$$(AnlmBn'l'm'|Cn''l''m''Dn'''l'''m''') = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi^{A*}_{nlm}(\mathbf{r}_1)\psi^{C*}_{n''l''m''}(\mathbf{r}_2)\frac{1}{r_{12}}\psi^B_{n'l'm'}(\mathbf{r}_1) \times \psi^D_{n'''l'''m'''}(\mathbf{r}_2). \quad (6)$$

Here ∇^2 is the Laplace operator, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and $r_C = |\mathbf{r} - \mathbf{C}|$. The integrations are over all space. Notice that in Eq. (6) $(AB|CD)$ refers to ψ^{A*} and ψ^B for one electron, ψ^{C*} and ψ^D for the other. This notation differs from that usual in some branches of physics but it is common in this context.

The associated Legendre functions appearing in Eq. (1) are defined as

$$P_l^m(t) = \frac{(-1)^m(1-t^2)^{\frac{1}{2}|m|}}{2^l l!}\frac{d^{l+|m|}}{dt^{l+|m|}}(t^2-1)^l. \quad (7)$$

With the definition of Eq. (7), the representation of a spherical harmonic originally in coordinates θ,φ when expressed in coordinates θ',φ' about an axial system derived from the original system by rotation of the axes through Eulerian angles (α,β,γ), is[9]

$$P_l^m(\cos\theta)e^{im\varphi} = \sum_{\sigma=-l}^{l} D_l^{m\sigma}(\alpha,\beta,\gamma)P_l^\sigma(\cos\theta')e^{i\sigma\varphi'} \quad (8)$$

with representation coefficients

$$D_l^{m\sigma}(\alpha,\beta,\gamma) = e^{im\alpha+i\sigma\gamma}d^l(\cos\beta)_{m\sigma}, \quad (9a)$$

where

$$d^l(t)_{m\sigma} = (l+m)!(l-\sigma)! \times \sum_s \frac{(-1)^s\left(\frac{1-t}{2}\right)^{s-m/2+\sigma/2}\left(\frac{1+t}{2}\right)^{l+m/2-\sigma/2-s}}{s!(l-\sigma-s)!(s+\sigma-m)!(l+m-s)!}, \quad m,\sigma \geqslant 0. \quad (9b)$$

Negative m and σ are reached through the relations

$$d^l(t)_{m\sigma} = d^l(t)_{-m,-\sigma} = (-1)^{l+m+\sigma}d^l(-t)_{-m,\sigma} = (-1)^{l+m+\sigma}d^l(-t)_{m,-\sigma}. \quad (9c)$$

The functions $d^l(t)_{m\sigma}$ can be written in terms of Jacobi polynomials, leading to recurrence relations among $d^l(t)_{m\sigma}$ with different indices. Since $d^l(t)_{m\sigma}$ is real, Eq. (9a) implies $D_l^{m\sigma*} = D_l^{-m-\sigma}$. Properties of the Jacobi polynomials, Legendre functions, and representation coefficients are collected in Appendix 2.

In discussing the integrals of Eqs. (3)–(6), the following definitions will be employed:

$$R_1 = |\mathbf{A} - \mathbf{B}|, \quad (10a)$$

$$R_2 = |\mathbf{C} - \mathbf{D}|, \quad (10b)$$

$$x_1 = \frac{abR_1^2}{a+b}, \quad (11a)$$

$$x_2 = \frac{cdR_2^2}{c+d}, \quad (11b)$$

$$\mathbf{P} = \frac{a\mathbf{A} + b\mathbf{B}}{a+b}, \quad (12a)$$

$$\mathbf{Q} = \frac{c\mathbf{C} + d\mathbf{D}}{c+d}, \quad (12b)$$

[9] A general reference on transformations of spherical harmonics is A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), particularly Chap. 4.

$$u = a + b\,, \tag{13a}$$

$$v = c + d\,, \tag{13b}$$

$$R = |\mathbf{P} - \mathbf{Q}|\,, \tag{14}$$

$$x = \frac{uvR^2}{u+v}\,. \tag{15}$$

The point **P** is on the line between **A** and **B** at a point which is optimum for expansion of $\psi_A^*\psi_B$. It will prove to be convenient to discuss a coordinate system centered at **P**, with polar axis $\theta = 0$ along the directed line **B** − **A**. Such an axial system, which we shall characterize by Eulerian angles $(\alpha_P,\beta_P,\gamma_P)$, defines the coordinates (r_P,θ_P,φ_P). In terms of **A** and **B**, the Eulerian angles are

$$\cos\alpha_p = \frac{B_x - A_x}{R_1 \sin\beta_p}\,, \qquad \sin\alpha_p = \frac{B_y - A_y}{R_1\sin\beta_p}\,, \tag{16a}$$

$$\cos\beta_p = \frac{B_Z - A_Z}{R_1}\,, \tag{16b}$$

$$\gamma_p = 0\,. \tag{16c}$$

Similar remarks define coordinates (r_Q,θ_Q,φ_Q) centered at **Q** with axes defined by Eulerian angles $(\alpha_Q,\beta_Q,\gamma_Q)$ specified in terms of **C** and **D**.

In discussion of the nuclear attraction integral, Eq. (5), it will turn out that the natural parameter is the specification of **C** in the coordinate system about **P** introduced in the preceding paragraph. We let the coordinates of **C** in that system be (R_C,Θ_C,Φ_C) and indicate them collectively by $\mathbf{R}_C$. The quantity in Eq. (5) playing the role of x in the evaluation of Eq. (6) we denote by y, defined as

$$y = (a+b)R_C^2\,. \tag{17}$$

When discussing rotations of the axial systems appearing on the problem so as to bring them to convenient orientations, it will be necessary to refer to the Eulerian angles of a system of axes relative to some other system which is not the single fixed axial frame of the problem. We introduce the notation $(\alpha_{PA},\beta_{PA},\gamma_{PA})$ to refer to the Eulerian angles which carry the axial system A into the system P, with analogous definitions for other subscript combinations. In Appendix 1 we discuss the calculation of $(\alpha_{PA},\beta_{PA},\gamma_{PA})$ when $(\alpha_A,\beta_A,\gamma_A)$ and $(\alpha_P,\beta_P,\gamma_P)$ are known.

Our most complicated orientation problems occur in the evaluation of Eq. (6). There we shall find it convenient to introduce two axial systems not previously discussed, which we denote by P' and Q', centered at **P** and at **Q**, respectively. These systems have a common orientation, with polar axis $\theta = 0$ along the directed line **Q** − **P**, and with $(\alpha_{P'},\beta_{P'},\gamma_{P'}) = (\alpha_{Q'},\beta_{Q'},\gamma_{Q'})$ given by the equivalent of Eqs. (16), with **P** and **Q** in place of **A** and **B**. The coordinate systems defined by these axial systems we denote by $(r'_P,\theta'_P,\varphi'_P)$ and $(r'_Q,\theta'_Q,\varphi'_Q)$.

Finally, two special functions enter our work,

$$A_n(t) = \int_1^\infty s^n e^{-ts}\,ds\,, \tag{18}$$

$$F_n(t) = \int_0^1 s^{2n} e^{-ts^2}\,ds\,. \tag{19}$$

A_n is an elementary function occurring also in the integrations of conventional atomic orbitals.[10] F_n is nonelementary, but may be reduced to an expression involving the error function. Both A_n and F_n are discussed in Appendix 3.

III. OVERLAP INTEGRALS

The evaluation of the integrals $(A|B)$ is conveniently performed by rotating the axes of A and B to a common orientation, namely, that of the coordinate system centered at P and described in the preceding section. This means that ψ^A and ψ^B are to be expressed in coordinates reached from the A and B systems by rotations $(\alpha_{PA},\beta_{PA},\gamma_{PA})$ and $(\alpha_{PB},\beta_{PB},\gamma_{PB})$, respectively. Representing such coordinates by primes, we find

$$\psi^A_{nlm} = \sum_{\sigma=-l}^{l} D_l^{m\sigma}(PA) r_A^{l+2n} P_l^\sigma(\cos\theta'_A) e^{i\sigma\varphi' - ar_A^2} \tag{20}$$

with a similar expression for ψ^B with σ' in place of σ. When the expressions of the form of Eq. (20) are substituted into $(A|B)$, the φ' integration causes all terms to vanish except those for which $\sigma' = \sigma$, leading to the result

$$(Anlm|Bn'l'm') = \sum_{\sigma=-l_-}^{l_-} D_l^{m\sigma *}(PA) D_{l'}^{m'\sigma}(PB) \times S^\sigma_{nln'l'}(a,b,R_1)\,, \tag{21}$$

where l_- is the smaller of l and l', and

$$S^\sigma_{nln'l'}(a,b,R_1) = \int dr r_A^{l+2n} P_l^\sigma(\cos\theta'_A) r_B^{l'+2n'} \times P_{l'}^\sigma(\cos\theta'_B)\exp[-ar_A^2 - br_B^2]\,. \tag{22}$$

The integrals $S^\sigma_{nln'l'}$ depend, as indicated, only upon the screening constants a and b, and upon the distance R_1 between centers **A** and **B**, the angular contributions having been separated in Eq. (21).

The integral of Eq. (22) can be readily evaluated for $n = n' = 0$, as shown in Appendix 4. The result is

[10] M. Kotani *et al.*, *Molecular Integrals* (Maruzen Company, Ltd., Tokyo, 1955).

$$S^{\sigma}_{ll'}(a,b,R_1) = \left(\frac{\pi}{a+b}\right)^{\frac{3}{2}} e^{-x_1}\left(\frac{bR_1}{a+b}\right)^{l-l'}\left(\frac{1}{a+b}\right)^{l'} \times \sum_{k=0}^{l'-|\sigma|} A^{\sigma}_{ll'k} x_1^k, \quad l' \leqslant l \tag{23}$$

with

$$A^{\sigma}_{ll'k} = \frac{(-1)^k (l+|\sigma|)!(l'+|\sigma|)!(2l'-2k-1)!!}{k!(l'-k+\sigma)!(l'-k-\sigma)!2^{l'-k}(l-l'+k)!} \tag{24}$$

Values for $l' > l$ are reached through the identity

$$S^{\sigma}_{ll'}(a,b,R_1) = (-1)^{l'-l} S^{\sigma}_{l'l}(b,a,R_1) . \tag{25}$$

For nonzero n and n', we leave the result in terms of the indicated differentiations:

$$S^{\sigma}_{nln'l'}(a,b,R_1) = \left(-\frac{\partial}{\partial a}\right)^n \left(-\frac{\partial}{\partial b}\right)^{n'} S^{\sigma}_{ll'}(a,b,R_1) . \tag{26}$$

IV. KINETIC ENERGY INTEGRALS

The kinetic-energy integrals can be transformed into linear combinations of overlap integrals. A convenient way of so doing is to employ the vector identity[11]

$$\nabla^2 fg = f\nabla^2 g + g\nabla^2 f + 2\nabla f \cdot \nabla g .$$

Setting

$$f = r_B^{l'+2n'} e^{-br_B^2}, \qquad g = P_{l'}^{m'}(\cos\theta_B) e^{im'\varphi_B},$$

$$\nabla^2 f = \left[\frac{(2n'+l')(2n'+l'+1)}{r_B^2} - 2b(4n'+2l'+3) + 4b^2 r_B^2\right] f ,$$

$$\nabla^2 g = -\frac{l'(l'+1)}{r_B^2} g ,$$

$$\nabla f \cdot \nabla g = 0 ,$$

and

$$-\tfrac{1}{2}\nabla^2 \psi^B_{n'l'm'} = -n'(2n'+2l'+1)\psi^B_{n'-1l'm'} + b(4n'+2l'+3)\psi^B_{n'l'm'} - 2b^2 \psi^B_{n'+1l'm'} . \tag{27}$$

Thus,

$$(Anlm|-\tfrac{1}{2}\nabla^2|Bn'l'm') = -n'(2n'+2l'+1) \times (Anlm|Bn'-1l'm') + b(4n'+2l'+3) \times (Anlm|Bn'l'm') - 2b^2(Anlm|Bn'+1l'm') . \tag{28}$$

[11] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953). The result used here may be obtained from those given on p. 114.

V. NUCLEAR ATTRACTION INTEGRALS

The nuclear attraction integrals may be evaluated by transforming them to axes of common orientation, just as for the overlap integrals. Thus, the corresponding formula is

$$(Anlm\left|\frac{1}{r_C}\right|Bn'l'm') = \sum_{\sigma=-l}^{l}\sum_{\sigma'=-l'}^{l'} D_l^{m\sigma *}(PA) D_{l'}^{m'\sigma'}(PB) \times J^{\sigma\sigma'}_{nln'l'}(a,b,R_1,\mathbf{R}_C) , \tag{29}$$

where

$$J^{\sigma\sigma'}_{nln'l'}(a,b,R_1,\mathbf{R}_C) = \int d\mathbf{r}\left(\frac{1}{r_C}\right) r_A^{l+2n} P_l^{\sigma}(\cos\theta'_A) r_B^{l'+2n'} P_{l'}^{\sigma'} \times (\cos\theta'_B)\exp[i(\sigma'-\sigma)\varphi' - ar_A^2 - br_B^2] . \tag{30}$$

The special case $n = n' = 0$ is discussed in Appendix 4, where it is shown that $J^{\sigma\sigma'}_{ll'}$ can be written in the two alternative forms

$$J^{\sigma\sigma'}_{ll'}(a,b,R_1,\mathbf{R}_C) = 2\pi e^{-x_1} \sum_{j=|\sigma|}^{l}\sum_{j'=|\sigma'|}^{l'} \binom{l+|\sigma|}{j+|\sigma|} \times \binom{l'+|\sigma'|}{j'+|\sigma'|}\left(\frac{bR_1}{a+b}\right)^{l-j}\left(\frac{-aR_1}{a+b}\right)^{l'-j'} \times \sum_k C^{\sigma\sigma'}_{kjj'} R_C^{j+j'+2} P_k^{\sigma'-\sigma}(\cos\Theta_C) e^{i(\sigma'-\sigma)\Phi_C}\left(\frac{2}{2k+1}\right) \times \left[F_{\frac{1}{2}(j+j'+k+2)}(y) + \tfrac{1}{2} A_{\frac{1}{2}(j+j'-k)}(y)\right], \tag{31a}$$

$$= \left(\frac{2\pi}{a+b}\right) e^{-x_1} \sum_{j=|\sigma|}^{l}\sum_{j'=|\sigma'|}^{l'} \binom{l+|\sigma|}{j+|\sigma|}\binom{l'+|\sigma'|}{j'+|\sigma'|} \times \left(\frac{bR_1}{a+b}\right)^{l-j}\left(\frac{-aR_1}{a+b}\right)^{l'-j'} \sum_k C^{\sigma\sigma'}_{kjj'} R_C^k \times P_k^{\sigma'-\sigma}(\cos\Theta_C) e^{i(\sigma'-\sigma)\Phi_C}\left(\frac{1}{a+b}\right)^{\frac{1}{2}(j+j'-k)} \times \sum_{i=0}^{\frac{1}{2}(j+j'-k)} \frac{[\frac{1}{2}(j+j'-k)]!}{i!} y^i F_{k+i}(y) . \tag{31b}$$

Note that the dependence of the integral upon the location of point C enters conveniently as a result of the use of coordinates $\mathbf{R}_C = (R_C, \Theta_C, \Phi_C)$ centered about the point **P**. The coefficients $C^{\sigma\sigma'}_{kjj'}$ arise as a result of the integrations of the Legendre functions and are defined in Eq. (52) of Appendix 2. The sum over k is for all values such that $C^{\sigma\sigma'}_{kjj'}$ does not vanish.

Substitution of either of Eqs. (31) may now be made into Eq. (29) and the summations may be rearranged to place the σ and σ' sums within the sums over j, j', and k. Equation (29) then becomes

$$\left(Alm\left|\frac{1}{r_C}\right|Bl'm'\right) = \left(\frac{2\pi}{a+b}\right) e^{-x_1} \sum_{j=0}^{l}\sum_{j'=0}^{l'}\sum_k$$

$$\times \left(\frac{bR_1}{a+b}\right)^{l-j}\left(\frac{-aR_1}{a+b}\right)^{l'-j'} W_{kjj'}^{lml'm'0}(PA,PB,CP)$$
$$\times \left(\frac{1}{a+b}\right)^{\frac{1}{2}(j+j')} Y_{\frac{1}{2}(j+j'-k),k}(y) \tag{32}$$

where

$$W_{kjj'}^{lml'm'M}(PA,PB,P'P) = \sum_{\sigma=-j}^{j}\sum_{\sigma'=-j'}^{j'} D_l^{m\sigma*}(PA) \times D_{l'}^{m'\sigma'}(PB) D_k^{(\sigma'-\sigma)M}(P'P) C_{kjj'}^{\sigma\sigma'} \times \binom{l+|\sigma|}{j+|\sigma|}\binom{l'+|\sigma'|}{j'+|\sigma'|} \tag{33}$$

and

$$Y_{qk}(y) = \sum_{i=0}^{q} \frac{q!}{i!}\, y^{i+(k/2)} F_{k+i}(y) \tag{34a}$$

$$= \left(\frac{2}{2k+1}\right) y^{q+(k/2)+1}[F_{k+q+1}(y) + \tfrac{1}{2} A_q(y)] . \tag{34b}$$

The formula for W depends only on the relative orientations A, B, P, and P', and is thus essentially a geometrical factor. We introduce the definition of W for arbitrary M with an eye to its usefulness in the discussion of the 2-electron integrals. For $M = 0$

$$D_k^{(\sigma'-\sigma)0}(CP) = P_k^{\sigma'-\sigma}(\cos\beta_{CP}) e^{i(\sigma'-\sigma)\alpha_{CP}} ,$$

so that placing $\beta_{CP} = \Theta_C$, $\alpha_{CP} = \Phi_C$, Eq. (32) may be reconciled with Eqs. (29) and (31).

A bit more simplification results if we further rearrange the summations, by introducing $q = \frac{1}{2}(j + j' - k)$ and doing the k sum outside. The result is

$$\left(Alm\left|\frac{1}{r_C}\right|Bl'm'\right) = \left(\frac{2\pi}{a+b}\right) e^{-x_1} \sum_{k=0}^{l+l'} \sum_{q=0}^{\frac{1}{2}(l+l'-k)} \times \left(\frac{1}{a+b}\right)^{q+(k/2)} V_{kq}^{lml'm'0}(PA,PB,CP,a,b,R_1) Y_{qk}(y) , \tag{35}$$

with

$$V_{kq}^{lml'm'M}(PA,PB,P'P,a,b,R_1) = \left(\frac{-x_1}{a+b}\right)^{-q} \times \left(\frac{bR_1}{a+b}\right)^{l}\left(\frac{-aR_1}{a+b}\right)^{l'-k} \sum_j \left(-\frac{a}{b}\right)^j \times W_{k,j+q,k+q-j}^{lml'm'M}(PA,PB,P'P) . \tag{36}$$

This formulation is useful in connection with the 2-electron integrals.

Extension of Eqs. (31) to nonzero n and n' is provided by

$$J_{nln'l'}^{\sigma\sigma'}(a,b,R_1,\mathbf{R}_C) = \left(-\frac{\partial}{\partial a}\right)^n \left(-\frac{\partial}{\partial b}\right)^{n'} J_{ll'}^{\sigma\sigma'}(a,b,R_1,\mathbf{R}_C) , \tag{37}$$

where the dependence of $\mathbf{R}_C$ upon a and b must be included in the differentiation. $\mathbf{R}_C$ depends on a and b only through its dependence upon $\mathbf{P}$. Let dP_0 refer to a differential of $\mathbf{P}$ in the polar direction of the P coordinates; this is the direction in which $\mathbf{P}$ moves as a result of changes in a or b. In particular,

$$\frac{\partial P_0}{\partial a} = -\frac{bR_1}{(a+b)^2} , \qquad \frac{\partial P_0}{\partial b} = \frac{aR_1}{(a+b)^2} .$$

Now, derivatives of the form

$$(\partial/\partial P_0)[R_C^k P_k^{\sigma'-\sigma}(\cos\Theta_C)]$$

are discussed in Appendix 5, in connection with the evaluation of the two integrals. Using the techniques there described, we find

$$\frac{\partial}{\partial a}\left[R_C^k P_k^{\sigma'-\sigma}(\cos\Theta_C) e^{i(\sigma'-\sigma)\Phi_C}\right] = \left(\frac{k+|\sigma'-\sigma|}{a+b}\right)\left(\frac{bR_1}{a+b}\right) R_C^{k-1} \times P_{k-1}^{\sigma'-\sigma}(\cos\Theta_C) e^{i(\sigma'-\sigma)\Phi_C}, \tag{38a}$$

$$\frac{\partial}{\partial b}\left[R_C^k P_k^{\sigma'-\sigma}(\cos\Theta_C) e^{i(\sigma'-\sigma)\Phi_C}\right] = \left(\frac{k+|\sigma'-\sigma|}{a+b}\right)\left(-\frac{aR_1}{a+b}\right) R_C^{k-1} \times P_{k-1}^{\sigma'-\sigma}(\cos\Theta_C) e^{i(\sigma'-\sigma)\Phi_C} , \tag{38b}$$

with

$$\frac{\partial}{\partial a}\left[R_C^k P_{|\sigma'-\sigma|}^{\sigma'-\sigma}(\cos\Theta_C) e^{i(\sigma'-\sigma)\Phi_C}\right] = \frac{\partial}{\partial b}\left[R_C^k P_{|\sigma'-\sigma|}^{\sigma'-\sigma}(\cos\Theta_C) e^{i(\sigma'-\sigma)\Phi_C}\right] = 0 .$$

Equations (38a) and (38b) facilitate the carrying out of the operations of Eq. (37), particularly if Eq. (31b) is used for $J_{ll'}^{\sigma\sigma'}$. If Eq. (37) need not be applied, i.e., if $n = n' = 0$, it is possible that Eq. (31a) will be the more convenient.

VI. TWO-ELECTRON INTEGRALS

As for the one-electron integrals, we remove some of the angular contributions to the problem by aligning the coordinate axes of A and B to the P orientation, and by aligning the C and D axes to the Q orientation. We then reduce the integral to a two-center problem by expanding $\psi^A(\mathbf{r}_1)$ and $\psi^B(\mathbf{r}_1)$ about P, and $\psi^C(\mathbf{r}_2)$ and $\psi^D(\mathbf{r}_2)$ about Q. Proceeding as for the one-electron integrals discussed in Appendix 4, one obtains for the special case $n = n' = 0$

$$\psi^{A^*}_{lm}(\mathbf{r}_1)\psi^{B}_{l'm'}(\mathbf{r}_1) = e^{-x_1}\sum_{\sigma=-l}^{l}\sum_{\sigma'=-l'}^{l'} D_l^{m\sigma^*}(PA)$$
$$\times D_{l'}^{m'\sigma'}(PB)\sum_{j=|\sigma|}^{l}\sum_{j'=|\sigma'|}^{l'}\left(\frac{bR_1}{a+b}\right)^{l-j}\left(\frac{-aR_1}{a+b}\right)^{l'-j'}$$
$$\times\binom{l+|\sigma|}{j+|\sigma|}\binom{l'+|\sigma'|}{j'+|\sigma'|}\sum_k C^{\sigma\sigma'}_{kjj'}\psi^{P}_{\frac{1}{2}(j+j'-k),k,\sigma'-\sigma}(\mathbf{r}_1). \tag{39}$$

A corresponding expression may be written for the second electron.

We next transform the expression of Eq. (39) to the P' coordinate system, and transform the corresponding expression for the second electron to the Q' system. This set of transformations leads to the standard form in which we shall express the two-electron integrals. We may write the result of the transformations just described in the form

$$(AlmBl'm'|Cl''m''Dl'''m''') = e^{-x_1-x_2}$$
$$\times\sum_{\sigma=-l}^{l}\sum_{\sigma'=-l'}^{l'}\sum_{\sigma''=-l''}^{l''}\sum_{\sigma'''=-l'''}^{l'''} D_l^{m\sigma^*}(PA)D_{l'}^{m'\sigma'}(PB)$$
$$\times D_{l''}^{m''\sigma''*}(QC)D_{l'''}^{m'''\sigma'''}(QD)\sum_{j=|\sigma|}^{l}\sum_{j'=|\sigma'|}^{l'}\sum_{j''=|\sigma''|}^{l''}$$
$$\times\sum_{j'''=|\sigma'''|}^{l'''}\left(\frac{bR_1}{a+b}\right)^{l-j}\left(\frac{-aR_1}{a+b}\right)^{l'-j'}\left(\frac{dR_2}{c+d}\right)^{l''-j''}$$
$$\times\left(\frac{-cR_2}{c+d}\right)^{l'''-j'''}\binom{l+|\sigma|}{j+|\sigma|}\binom{l'+|\sigma'|}{j'+|\sigma'|}$$
$$\times\binom{l''+|\sigma''|}{j''+|\sigma''|}\binom{l'''+|\sigma'''|}{j'''+|\sigma'''|}\sum_k\sum_{k'} C^{\sigma\sigma'}_{kjj'}C^{\sigma''\sigma'''}_{k'j''j'''}$$
$$\times\sum_{M=-k_-}^{k_-} D_k^{(\sigma'-\sigma),-M}(P'P)D_{k'}^{(\sigma'''-\sigma''),M}(Q'Q)$$
$$\times X^{M}_{\frac{1}{2}(j+j'-k),k,\frac{1}{2}(j''+j'''-k'),k'}(u,v,R), \tag{40}$$

where k_- is the smaller of k and k' and

$$X^{M}_{NLN'L'}(u,v,R)$$
$$= \int d\mathbf{r}'_{P1}d\mathbf{r}'_{Q2}\frac{1}{r_{12}}r'^{2N+L}_{P1}P^M_L(\cos\theta'_{P1})r'^{2N'+L'}_{Q2}$$
$$\times P^M_{L'}(\cos\theta'_{Q2})e^{-ur'^2_{P1}-vr'^2_{Q2}+iM(\varphi'_{Q_2}-\varphi'_{P_1})}. \tag{41}$$

We have used the symmetry of the integral in the P', Q' coordinates to reduce the transformation so that only one new summation, over M, is introduced. The corresponding summation which would have permitted independent variation of the φ' dependence of the two electrons leads to vanishing contributions in the terms not explicitly shown in Eqs. (40) and (41).

The sums appearing in Eq. (40) may be rearranged as for the nuclear attraction integrals. The result of so doing can be cast in the form

$$(AlmBl'm'|Cl''m''Dl'''m''') = e^{-x_1-x_2}$$
$$\times\sum_{k=0}^{l+l'}\sum_{k'=0}^{l''+l'''}\sum_{m=+k_-}^{k_-}\sum_{q=0}^{\leq\frac{1}{2}(l+l'-k)}\sum_{q'=0}^{\leq\frac{1}{2}(l''+l'''-k')}$$
$$\times V^{lml'm'M}_{kq}(PA,PB,P'P,a,b,R_1)$$
$$V^{l''m''l'''m'''-M}_{k'q'}$$
$$\times(QC,QD,Q'Q,c,d,R_2)\times X^{M}_{q,k,q',k'}(u,v,R). \tag{42}$$

We have been able to obtain a general explicit formula for $X^{M}_{NLN'L'}$ when $N = N' = 0$. Then, as shown in Appendix 5,

$$X^{M}_{LL'}(u,v,R) = \frac{2\pi^{\frac{5}{2}}}{uv(u+v)^{\frac{1}{2}}}\left(\frac{vR}{u+v}\right)^{L-L'}\left(\frac{1}{u+v}\right)^{L'}$$
$$\times\sum_{j=0}^{L'-|M|} A^{M}_{LL'j}x^jF_{L+j}(x), \qquad L\geqslant L' \tag{43}$$

where $A^{M}_{LL'j}$ is given by the same expression as for the overlap integral, namely, Eq. (24). For $L'\geqslant L$,

$$X^{M}_{LL'}(u,v,R) = (-1)^{L'-L}X^{M}_{L'L}(v,u,R). \tag{44}$$

Nonzero N and N' values are obtained from

$$X^{M}_{NLN'L'}(u,v,R) = \left(-\frac{\partial}{\partial u}\right)^N\left(-\frac{\partial}{\partial v}\right)^{N'}X^{M}_{LL'}(u,v,R), \tag{45}$$

thus, completing the specification of the two-electron integrals for $n = n' = n'' = n''' = 0$. The most general case is reached by the formula

$$(AnlmBn'l'm'|Cn''l''m''Dn'''l'''m''')$$
$$= \left(-\frac{\partial}{\partial a}\right)^n\left(-\frac{\partial}{\partial b}\right)^{n'}\left(-\frac{\partial}{\partial c}\right)^{n''}\left(-\frac{\partial}{\partial d}\right)^{n'''}$$
$$\times(AlmBl'm'|Cl''m''Dl'''m'''). \tag{46}$$

VII. ACKNOWLEDGMENTS

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APPENDIX 1. EULERIAN ANGLES

We use a right-handed coordinate system, such that a counterclockwise rotation by an angle $\pi/2$

about the z axis[12] carries the positive x axis into the position originally occupied by the positive y axis. Then the Eulerian angles (α,β,γ) describe the following ordered operations on a set of coordinate axes: (1) rotation by an angle α counterclockwise about the new z axis, (2) rotation by an angle β, $0 \leqslant \beta \leqslant \pi$ counterclockwise about the new y axis, (3) rotation by an angle γ counterclockwise about the new z axis.

In the text we have introduced the notation $(\alpha_{PA},\beta_{PA},\gamma_{PA})$ to signify the rotation which carries axes denoted by $(\alpha_A,\beta_A,\gamma_A)$ into the system denoted by $(\alpha_P,\beta_P,\gamma_P)$. By straightforward trigonometric manipulations, one finds

$$\cos\beta_{PA} = \cos\beta_A\cos\beta_P + \sin\beta_A\sin\beta_P\cos(\alpha_P - \alpha_A), \tag{47a}$$

$$\alpha_{PA} = -\gamma_A + \theta, \tag{47b}$$

where

$$\sin\theta = \frac{\sin\beta_P\sin(\alpha_P - \alpha_A)}{\sin\beta_{PA}}, \tag{47c}$$

$$\cos\theta = \frac{-\cos\beta_P + \cos\beta_A\cos\beta_{PA}}{\sin\beta_A\sin\beta_{PA}}, \tag{47d}$$

$$\gamma_{PA} = \gamma_P - \chi, \tag{47e}$$

where

$$\sin\chi = \frac{\sin\beta_A\sin(\alpha_P - \alpha_A)}{\sin\beta_{PA}}, \tag{47f}$$

$$\cos\chi = \frac{\cos\beta_A - \cos\beta_P\cos\beta_{PA}}{\sin\beta_P\sin\beta_{PA}}. \tag{47g}$$

Specification of the range $0 \leqslant \beta_{PA} \leqslant \pi$ insures that Eq. (47a) is single valued in β_{PA}.

Equations (47) are not properly defined for certain values of the angles. If $\beta_{PA} = 0$ or π, one may use in place of Eqs. (47b) and (47e):

$$\alpha_{PA} = \alpha_P - \alpha_A, \tag{48a}$$

$$\gamma_{PA} = \gamma_P - \gamma_A. \tag{48b}$$

If $\beta_{PA} \neq 0$ or π, but $\sin\beta_A$ or $\sin\beta_P = 0$, Eqs. (47d) and (47g) may be modified by substitution of Eq. (47a) which in this special case becomes

$$\cos\beta_{PA} = \cos\beta_A\cos\beta_P.$$

The result is

$$\cos\theta = -\frac{\sin\beta_A\cos\beta_P}{\sin\beta_{PA}}, \tag{47d'}$$

$$\cos\chi = \frac{\cos\beta_A\sin\beta_P}{\sin\beta_{PA}}. \tag{47g'}$$

It should be noted that $(\alpha_{PA},\beta_{PA},\gamma_{PA}) \neq (\alpha_{AP},\beta_{AP},\gamma_{AP})$, but that

$$\alpha_{AP} = \pi - \gamma_{PA}, \tag{49a}$$

$$\beta_{AP} = \beta_{PA}, \tag{49b}$$

$$\gamma_{AP} = \pi - \alpha_{PA}. \tag{49c}$$

APPENDIX 2. SPHERICAL HARMONICS, JACOBI POLYNOMIALS, AND ROTATION REPRESENTATIONS

The associated Legendre functions defined in Eq. (7) of the main text are orthogonal, and normalized so that

$$\int_{-1}' P_l^m(t)P_{l'}^m(t)dt = \delta_{ll'}\left(\frac{2}{2l+1}\right)\frac{(l+|m|)!}{(l-|m|)!}. \tag{50}$$

Expansion of the product of two Legendre functions leads to the formula[13]

$$P_l^m(t)P_{l'}^{m'}(t) = \sum_j C_{jll'}^{mm'}P_j^{m'-m}(t), \tag{51}$$

where the coefficient $C_{jll'}^{mm'}$ is specified by

$$C_{jll'}^{mm'} = \frac{(2j+1)(l+m)!(-1)^{g-j-m}(2g-2l)!g!}{(g-j)!(g-l)!(g-l')!(2g+1)!}$$

$$\times\sum_s \frac{(-1)^s(l'+m'+s)!(j+l-m'-s)!}{(l'-m'-s)!(j-l+m'+s)!(l-m-s)!s!}$$

$$m' \geqslant m \geqslant 0. \tag{52}$$

The sum over s in Eq. (52) is to be over all values such that the factorials are well defined, and $g = \frac{1}{2}(l+l'+j)$. These coefficients vanish unless g is an integer or zero, and j satisfies the relations $|m-m'| \leqslant j$ and $|l-l'| \leqslant j \leqslant |l+l'|$. As indicated, Eq. (52) only applies for values $m' \geqslant m \geqslant 0$. Extension of the definition to other values of m and m' are provided by the following formulas, derivable from the definition of Eq. (7) and consideration of the integral relation to be cited below.

$$C_{jll'}^{mm'} = C_{jl'l}^{m'm} = C_{jl'l}^{-m-m'}, \qquad m' \geqslant m \geqslant 0 \tag{53}$$

$$C_{jll'}^{m-m'} = \left(\frac{2j+1}{2l'+1}\right)\frac{(l'+|m'|)!(j-|m'+m|)!}{(l'-|m'|)!(j+|m'+m|)!}$$

$$\times C_{l'lj}^{m(m+m')} \qquad m' \geqslant m \geqslant 0. \tag{54}$$

Equation (51), when applied to the integration of products of three associated Legendre functions, leads to

$$\int_{-1}^{1} P_j^{m'-m}(t)P_l^m(t)P_{l'}^{m'}(t)dt$$

[12] The sense of all rotations described here is to be determined while looking toward the origin of the axial system from a point in the positive direction along the axis of rotation.

[13] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 176.

$$= \frac{(j + |m - m'|)!}{(j - |m - m'|)!} \left(\frac{2}{2j + 1}\right) C^{mm'}_{jll'} . \quad (55)$$

The associated Legendre functions satisfy various recursion formulas, which prove to be extremely useful in the developments of the later Appendices. In a form consistent with the definition, Eq. (7), the formulas we used are[14]

$$(1 - t^2) \frac{d}{dt} P^m_l(t) = -ltP^m_l(t) + (l + |m|)P^m_{l-1}(t) , \quad (56)$$

$$(l - |m| + 1)P^m_{l+1}(t) - (2l + 1)tP^m_l(t) + (l + |m|)P^m_{l-1}(t) = 0 , \quad (57)$$

$$P^m_{|m|+1}(t) = (2|m| + 1)tP^m_{|m|}(t) . \quad (58)$$

For initiating the use of the above formulas, it is convenient to use the result

$$P^m_{|m|}(t) = (-1)^m(2|m| - 1)!!(1 - t^2)^{|m|/2} . \quad (59)$$

Upon rotation of the coordinate system, spherical harmonics transform as indicated in Eqs. (8) and (9). The representation coefficients of Eq. (9b) can also be written in terms of Jacobi polynomials,[15] a form which facilitates study of the relations among coefficients of different indices.

$$d^l(t)_{m\sigma} = \frac{(-1)^{m+\sigma}(l + m)!}{2^m(l + \sigma)!} (1 - t)^{(m-\sigma)/2} \times (1 + t)^{(m+\sigma)/2} P^{(m-\sigma, m+\sigma)}_{l-m}(t) , \quad m,\sigma \geqslant 0 . \quad (60)$$

The Jacobi polynomial $P^{(\alpha,\beta)}_n(t)$ is defined as

$$P^{(\alpha,\beta)}_n(t) = \frac{(-1)^n}{2^n n!} (1 - t)^{-\alpha}(1 + t)^{-\beta} \times \frac{d^n}{dt^n} [(1 - t)^{n+\alpha}(1 + t)^{n+\beta}] . \quad (61)$$

The Jacobi polynomials and the associated Legendre functions are related by the formula

$$P^m_l(t) = \frac{(-1)^m(l + m)!}{2^m l!} (1 - t^2)^{m/2} P^{(m,m)}_{l-m}(t) , \quad m \geqslant 0 . \quad (62)$$

Many formulas relating to the $d^l_{m\sigma}$ can be derived from Eq. (60). Some of these formulas are

$$d^\sigma(t)_{m\sigma} = \frac{(1 - t)^{(\sigma-m)/2}(1 + t)^{(\sigma+m)/2}}{2^\sigma(\sigma - m)!} , \quad \sigma \geqslant m \geqslant 0 \quad (63)$$

$$d^m(t)_{m\sigma} = \frac{(-1)^{m-\sigma}(2m)!}{2^m(m + \sigma)!} (1 - t)^{(m-\sigma)/2}(1 + t)^{(m+\sigma)/2} , \quad m \geqslant \sigma \geqslant 0 \quad (64)$$

$$\frac{(l + \sigma + 1)(l - m + 1)}{(l + 1)} d^{l+1}(t)_{m\sigma} - (2l + 1) \times \left(t - \frac{m\sigma}{l(l + 1)}\right) d^l(t)_{m\sigma} + \frac{(l - \sigma)(l + m)}{l} \times d^{l-1}(t)_{m\sigma} = 0 , \quad l - 1 \geqslant m,\sigma \geqslant 0 . \quad (65)$$

Starting from either Eq. (63) or (64), repeated application of Eq. (65) enables generation of all $d^l_{m\sigma}$, for $m, \sigma \geqslant 0$. For the special cases $l = m$ or $l = \sigma$, Eq. (65) can be used if $d^{m-1}_{m\sigma}$ and $d^{\sigma-1}_{m\sigma}$ are defined as zero. Values of $d^l_{m\sigma}$ for negative m and σ can be related to values for positive m and σ by considering the effect of changing variables in Eq. (8) from φ to $-\varphi$, or from φ' to $-\varphi'$, with corresponding changes in α, β, and γ so as to maintain the same physical content. The results of these considerations are expressed in Eq. (9c).

In addition to discussing the transformation of spherical harmonics upon axial rotations, one may consider the effect of translation of the origin of a spherical harmonic expansion. In particular, a solid spherical harmonic in coordinates (r,θ,φ) may be expressed in coordinates (r',θ',φ') about an axial system translated without rotation a distance t from the unprimed system along the polar direction $\theta = 0$[16]:

$$r^l P^m_l(\cos\theta)e^{im\varphi} = \sum_{j=|m|}^{l} \binom{l + |m|}{j + |m|} t^{l-j} r'^j \times P^m_j(\cos\theta')e^{im\varphi} . \quad (66)$$

Equation (66) which is apparently not as widely known as the corresponding formulas for rotations, proves to be most useful in the work described in the later Appendices.

Finally, we make the observation useful in the later Appendices, that the Green's function expansion in spherical coordinates takes the form, consistent with the associated Legendre function definitions of Eq. (7),[17]

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{(l - |m|)!}{(l + |m|)!} P^m_l(\cos\theta_1)P^m_l(\cos\theta_2) \times e^{im(\varphi_2-\varphi_1)} \frac{r_-^l}{r_+^{l+1}} . \quad (67)$$

[14] W. Magnus and F. Oberhettinger, *Special Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1949), Chap. 4.

[15] For a general discussion of Jacobi polynomials see Bateman Manuscript Project, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 2, pp. 168 ff.

[16] E. W. Hobson, *The Theory of Spherical and Ellipsoidal Harmonics* (Cambridge University Press, New York, 1931), pp. 139 ff.

[17] P. M. Morse and H. Feshbach, reference 11, p. 1274.

APPENDIX 3. SPECIAL FUNCTIONS

The function $A_n(t)$ defined in Eq. (18) of the main text is most conveniently generated by the recursion formula[10]

$$A_n(t) = (n/t)A_{n-1}(t) + A_0(t) \tag{68}$$

together with the initial value $A_0(t) = e^{-t}/t$. The function $F_n(t)$ is closely related to $A_{n-\frac{1}{2}}(t)$, as may be seen by making the substitution $u = s^2$ in the formula of Eq. (19), giving an expression differing from $A_{n-\frac{1}{2}}$ only in the limits of integration. By a partial integration, it is possible to show that $F_n(t)$ satisfies a recursion formula quite similar to Eq. (68),

$$F_n(t) = [(n - \tfrac{1}{2})/t]F_{n-1}(t) - \tfrac{1}{2}A_0(t) . \tag{69}$$

Equation (69) may be conveniently applied to proceed to F_n from values of F_0. F_0 is the function introduced by Boys[1] in the form

$$F_0(t) = t^{-\frac{1}{2}}\int_0^{t^{\frac{1}{2}}} e^{-y^2}dy \tag{70}$$

which may be evaluated from tables or by methods of computation suitable for the error function.

By differentiation of the formulas Eqs. (18) and (19), one sees that advancement of the index corresponds to derivatives in the sense that

$$\left(\frac{d}{dt}\right)^n A_0(t) = (-1)^n A_n(t) , \tag{71}$$

$$\left(\frac{d}{dt}\right)^n F_0(t) = (-1)^n F_n(t) . \tag{72}$$

APPENDIX 4. ONE-ELECTRON INTEGRALS

The integration of $S^{\sigma}_{ll'}$ of Eq. (22) is conveniently performed in a coordinate system centered at the point **P** of Eq. (12a), with the axial orientation given by Eqs. (16). Using the expansion of Eq. (66), we write $r_A^l P_l^{\sigma}(\cos\theta_{A'})$ in terms of solid spherical harmonics about **P**, which is a distance $|\mathbf{P} - \mathbf{A}| = bR_1/(a+b)$ along the polar axis of the A' axial system. In a similar manner, we write $r_B^{l'}P_{l'}^{\sigma}(\cos\theta'_{\beta})$ in terms of solid spherical harmonics about **P**, which is a distance $-|\mathbf{P} - \mathbf{B}| = -aR_1/(a+b)$ along the polar axis of the B' system. The result of these substitutions, for $n + n' = 0$ is

$$S^{\sigma}_{ll'}(a,b,R_1) = e^{-x_1}\sum_{j=|\sigma|}^{l}\sum_{j'=|\sigma|}^{l'}\binom{l+|\sigma|}{j+|\sigma|}\binom{l'+|\sigma|}{j'+|\sigma|}$$
$$\times\left(\frac{bR_1}{a+b}\right)^{l-j}\left(\frac{-aR_1}{a+b}\right)^{l'-j'}\int_0^{2\pi}d\varphi_P\int_0^{\pi}d\theta_P\sin\theta_P$$
$$\times P_j^{\sigma}(\cos\theta_P)P_{j'}^{\sigma}(\cos\theta_P)\int_0^{\infty}dr_P r_P^{j+j'+2}\exp[-(a+b)r_P^2], \tag{73}$$

where we have used in the exponent the relation

$$\begin{aligned} ar_A^2 + br_B^2 &= (a+b)\rho_P^2 + az_A'^2 + bz_B'^2 , \\ &= (a+b)\rho_P^2 + a\left(z_P + \frac{bR_1}{a+b}\right)^2 \\ &\quad + b\left(z_P - \frac{aR_1}{a+b}\right)^2 , \\ &= (a+b)(\rho_P^2 + z_P^2) + \frac{abR_1^2}{a+b} , \\ &= (a+b)r_P^2 + x_1 . \end{aligned}$$

The integral over the associated Legendre functions vanishes unless $j = j'$, in which case it has the value given in Eq. (50). Identifying[18]

$$\int_0^{\infty} dr_P r_P^{2j+2}e^{-(a+b)r_P^2} = \frac{(2j+1)!!}{2^{j+2}}\pi^{\frac{1}{2}}(a+b)^{-j-\frac{3}{2}}, \tag{74}$$

we obtain

$$S^{\sigma}_{ll'}(a,b,R_1) = \left(\frac{\pi}{a+b}\right)^{\frac{3}{2}}e^{-x_1}$$
$$\times\sum_{j=|\sigma|}^{l_-}\frac{(-1)^{l'-j}(l+|\sigma|)!(l'+|\sigma|)!(2j-1)!!}{(l'-j)!(j+\sigma)!(j-\sigma)!2^j(l-j)!}$$
$$\times\left(\frac{bR_1}{a+b}\right)^{l-j}\left(\frac{aR_1}{a+b}\right)^{l'-j}\left(\frac{1}{a+b}\right)^{j}, \tag{75}$$

which, upon setting $k = l' - j$, can be converted to the form of Eqs. (23) and (24). The upper limit l_- of the sum over j is the lesser of l and l', and enters the problem through the orthogonality condition on the associated Legendre functions.

The integral $J^{\sigma\sigma'}_{ll'}$ of Eq. (30) may be evaluated by methods quite similar to those just employed for $S^{\sigma}_{ll'}$. Writing the solid spherical harmonics in coordinates centered at **P**, using Eq. (66), and introducing the Green's function expansion, Eq. (67), for the quantity $1/r_C$, it is possible to bring Eq. (30) to the form

$$J^{\sigma\sigma'}_{ll'}(a,b,R_1,\mathbf{R}_C) = e^{-x_1}\sum_{j=|\sigma|}^{l}\sum_{j'=|\sigma'|}^{l'}\binom{l+|\sigma|}{j+|\sigma|}$$
$$\times\binom{l'+|\sigma'|}{j'+|\sigma'|}\left(\frac{bR_1}{a+b}\right)^{l-j}\left(\frac{-aR_1}{a+b}\right)^{l'-j'}$$
$$\times\sum_k C^{\sigma\sigma'}_{kjj'}P_k^{\sigma'-\sigma}(\cos\Theta_C)e^{i(\sigma'-\sigma)\Phi_C}\left(\frac{4\pi}{2k+1}\right)$$
$$\times\int_0^{\infty}dr_P r_P^{j+j'+2}\frac{r_-^k}{r_+^{k+1}}\exp[-(a+b)r_P^2] , \tag{76}$$

where $C^{\sigma\sigma'}_{kjj'}$, defined in Eq. (52), enters through the integration of the product of three associated Legendre functions. The sum over k in Eq. (76) is to include all values for which $C^{\sigma\sigma'}_{kjj'}$ does not vanish, and

[18] W. Magnus and F. Oberhettinger, reference 14, Chap. 1.

r_-, r_+, are the lesser and greater, respectively, of r_P and R_C.

To more completely evaluate the integral over r_P, we change to the dimensionless variable $s = r_P/R_C$, and introduce y as given in Eq. (17). These substitutions lead to

$$\int_0^\infty dr_P r_P^{j+j'+2} \frac{r_-^k}{r_+^{k+1}} \exp[-(a+b)r_p^2]$$
$$= R_C^{j+j'+2}\left[\int_0^1 e^{-ys^2} s^{j+j'+k+2} ds + \int_1^\infty e^{-ys^2} s^{j+j'-k+1} ds\right],$$
$$= R_C^{j+j'+2}\left[F_{\frac{1}{2}(j+j'+k+2)}(y) + \tfrac{1}{2} A_{\frac{1}{2}(j+j'-k)}(y)\right], \quad (77)$$

where the last of Eqs. (77) was obtained by introducing the definitions of Eqs. (18) and (19). The A_n term may be verified by changing the variable of integration from s to s^2. The subscripts of A_n and F_n are integral by virtue of the conditions under which $C_{kjj'}^{\sigma\sigma'}$ is nonvanishing. Application of Eq. (77) leads, with Eq. (76) to Eq. (31a) of the main text. To obtain Eq. (31b), it is necessary to apply the recursion formulas, Eqs. (68) and (69) to F_n and A_n so as to reduce the subscript magnitudes. Operating in this way on the entire A_n contribution at each step, and operating on the amount of the F_n contribution necessary to cancel out the A_0 term, one may after sufficient steps arrive at

$$\int_0^\infty dr_P r_P^{j+j'+2} \frac{r_-^k}{r_+^{k+1}} \exp[-(a+b)r_p^2]$$
$$= (k+\tfrac{1}{2}) R_C^k \left(\frac{1}{a+b}\right)^{\frac{1}{2}(j+j'-k+2)}$$
$$\times \sum_{i=0}^{\frac{1}{2}(j+j'-k)} \frac{\left(\frac{j+j'-k}{2}\right)!}{i!} y^i F_{k+i}(y). \quad (78)$$

The use of Eq. (78) with Eq. (76) leads to Eq. (31b).

APPENDIX 5. TWO-ELECTRON INTEGRALS

The main object of this Appendix is the evaluation of the integral $X_{LL'}^M$ of Eq. (41) of the main text. A subsidiary goal is the evaluation of derivatives of the sort $(\partial/\partial P_0)[r_P^k P_k^\sigma(\cos\theta_P)]$, where dP_0 refers to a differential of P in the polar direction of the P coordinates.

We shall proceed toward the evaluation of $X_{LL'}^M$, by the method of mathematical induction. Since $X_{LL'}^M = X_{LL'}^{-M}$, we shall restrict explicit discussion to the case $M \geqslant 0$. We begin by evaluating X_{MM}^M. Using Eq. (59) for P_M^M, and writing $r^2 = \rho^2 + z^2$, we have the expression in cylindrical coordinates

$$X_{MM}^M = [(2M-1)!!]^2 \int d\rho_1 dz_{P1} d\rho_2 dz_{Q2} d\varphi_1 d\varphi_2$$
$$\times \frac{\rho_1^{M+1}\rho_2^{M+1}}{r_{12}} e^{-u\rho_1^2 - v\rho_2^2 - uz_{P_1}^2 - vz_{Q_2}^2 + iM(\varphi_2-\varphi_1)}. \quad (79)$$

We have dropped the primes and subscripts P and Q where no confusion can result. We now introduce the Green's function expansion for $1/r_{12}$ in clyindrical coordinates,[19]

$$\frac{1}{r_{12}} = \sum_{m=-\infty}^{\infty} \int_0^\infty dk e^{-k|z_1-z_2|} J_{|m|}(k\rho_1) J_{|m|}(k\rho_2) e^{im(\varphi_2-\varphi_1)} \quad (80)$$

in which J_m is the Bessel function of the first kind, of order m. The sum over m reduces to the single term for which $m = -M$, as a result of the integrations, and then contributes the factor $4\pi^2$. Thus,

$$X_{MM}^M = 4\pi^2[(2M-1)!!]^2$$
$$\times \int_0^\infty dk \Big[\int dz_1 dz_2 e^{-k|z_1-z_2| - uz_{P_1}^2 - vz_{Q_2}^2}$$
$$\times \int_0^\infty d\rho_1 \rho_1^{M+1} e^{-u\rho_1^2} J_M(k\rho_1) \cdot \int_0^\infty d\rho_2 \rho_2^{M+1} e^{-v\rho_2^2} J_M(k\rho_2)\Big]. \quad (81)$$

The ρ_1 integral has the value[20] $(k/2u)^M(e^{-k^2/4u}/2u)$, while that over ρ_2 is equal to $(k/2v)^M(e^{-k^2/4v}/2v)$.

The integrals over z_1 and z_2 present more difficulty on account of the absolute value in the exponent. Using coordinates z_{P1} and z_{P2}, introducing $t = |z_1 - z_2|$ in place of z_2, and denoting the z_1 and z_2 integral by Z,

$$Z = \int dz_1 dz_2 e^{-k|z_1-z_2| - uz_{P_1}^2 - vz_{Q_2}^2}$$
$$= \int_0^\infty dt \int_{-\infty}^\infty dz_{P1} e^{-kt - uz_{P_1}^2}\left(e^{-v(z_{P_1}-R-t)^2} + e^{-v(z_{P_1}-R+t)^2}\right). \quad (82)$$

Completing the square in the exponent, the z_{P1} integral may now be evaluated,

$$Z = \left(\frac{\pi}{u+v}\right)^{\frac{1}{2}}$$
$$\times \int_0^\infty dt e^{-kt}\left[e^{-[uv/(u+v)](R+t)^2} + e^{-[uv/(u+v)](R-t)^2}\right]. \quad (83)$$

Substituting the work thus far done into Eq. (81),

$$X_{MM}^M = \frac{\pi^{\frac{5}{2}}}{uv(u+v)^{\frac{1}{2}}}[(2M-1)!!]^2$$
$$\times \int_0^\infty dk \left(\frac{k^2}{4uv}\right)^M e^{-k^2(u+v)/4uv}$$

[19] P. M. Morse and H. Feshbach, reference 11, p. 1263.

[20] Bateman Manuscript Project, *Tables of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. 1, p. 185, formula 30.

$$\times \int_0^\infty dt e^{-kt}(e^{-[uv/(u+v)](R+t)^2} + e^{-[uv/(u+v)](R-t)^2}) . \quad (84)$$

Changing variables to $p = \frac{1}{2} k[(u + v)/uv]^{\frac{1}{2}}$, $q = t[uv/(u + v)]^{\frac{1}{2}} + (k/2)[(u + v)/uv]^{\frac{1}{2}}$, and introducing $x = uvR^2/(u + v)$,

$$X^M_{MM} = \frac{2\pi^{\frac{5}{2}}[(2M-1)!!]^2}{uv(u+v)^{M+\frac{1}{2}}} \chi_M , \quad (85)$$

where

$$\chi_M = \int_0^\infty dq \int_0^q dp p^{2M}[e^{2px^{\frac{1}{2}}-(q+x^{\frac{1}{2}})^2} + e^{-2px^{\frac{1}{2}}-(q-x^{\frac{1}{2}})^2}] . \quad (86)$$

Integrating χ_M by parts twice with respect to p, one obtains the recursion formula

$$\chi_M = -\frac{M}{x}\int_0^\infty dq e^{-q^2-x} q^{2M-1} + \frac{(2M)(2M-1)}{4x}\chi_{M-1}$$
$$= -\frac{M! e^{-x}}{2x} + \left(\frac{2M-1}{2x}\right) M\chi_{M-1} . \quad (87)$$

By comparison with Eq. (69), we see that $\chi_M/M!$ satisfies the same recursion formula as does $F_M(x)$. Since

$$\chi_0 = \frac{1}{2x^{\frac{1}{2}}}\int_0^\infty dq(e^{-(q-x^{\frac{1}{2}})^2} - e^{-(q+x^{\frac{1}{2}})^2}) = F_0 , \quad (88)$$

we have in general $\chi_M(x) = M!\, F_M(x)$, and

$$A^M_{MM} = \frac{2\pi^{\frac{5}{2}}}{uv(u+v)^{\frac{1}{2}}}\left(\frac{1}{u+v}\right)^M A^M_{MM0} F_M(x) ,$$
$$A^M_{MM0} = \frac{(2M)!(2M-1)!!}{2^M} \quad (89)$$

in accord with Eq. (43).

The next step in the inductive demonstration of the formula for $X^M_{LL'}$ is the application of recursion formulas to advance the lower indices from M to L and L'. The subsequent work can be expressed more concisely if we introduce a symbolic notation

$$X^M_{LL'}\{f(\mathbf{r}_1,\mathbf{r}_2)\}$$
$$\equiv \int d\mathbf{r}_1 d\mathbf{r}_2 f(\mathbf{r}_1,\mathbf{r}_2)\frac{1}{r_{12}} r_1^L P_L^M(\cos\theta_1) r_2^{L'} P_{L'}^M(\cos\theta_2)$$
$$\times e^{-ur_1^2-vr_2^2+iM(\varphi_2-\varphi_1)} , \quad (90)$$

where $f(\mathbf{r}_1,\mathbf{r}_2)$ may be any function of the indicated variables.

Substituting the recursion formula, Eq. (57), for $P_L^M(\cos\theta_1)$, Eq. (41) for $X^M_{LL'}$ leads to

$$(L-M+1)X^M_{L+1,L'} = (2L+1)X^M_{LL'}\{z_{P1}\} - (L+M)X^M_{L-1,L'}\{r_1^2\} , \quad L-1 \geqslant M \quad (91)$$

where the z_{P1} and r_1^2 factors in the integrals arise from the excess powers of r_1 after use of Eq. (57).

Differentiation of $X^M_{LL'}$ with respect to u leads to

$$-\frac{\partial}{\partial u} X^M_{LL'} = X^M_{LL'}\{r_1^2\} , \quad (92)$$

while differentiation with respect to P_z (in the P' axial system) leads to an expression for $X^M_{LL'}\{z_{P1}\}$. In passing, we observe that this differentiation with respect to P_z is the same process as that needed to pass from Eq. (37) to Eqs. (38) in the discussion of the nuclear attraction integrals. To carry out the differentiation, we use the relations $\partial r_1/\partial P_z = -z_{P1}/r_1$, $\partial \cos\theta_1/\partial P_z = (\cos^2\theta_1 - 1)/r_1$, and Eq. (56). These considerations lead to

$$\partial X^M_{LL'}/\partial P_z = 2uX^M_{LL'}\{z_{P1}\} - (L+M)X^M_{L-1,L'} , \quad L-1 \geqslant M . \quad (93)$$

Introducing Eqs. (92) and (93) into Eq. (91),

$$(L-M+1)X^M_{L+1,L'} = \left(\frac{2L+1}{2u}\right)\left[\frac{\partial X^M_{LL'}}{\partial P_z} + (L+M)X^M_{L-1,L'}\right] + (L+M)\frac{\partial X^M_{L-1,L'}}{\partial u} , \quad L-1 \geqslant M . \quad (94)$$

Equation (94) does not hold for $L = M$. Using Eq. (58) and the methods employed immediately above, one may show

$$X^M_{M+1,L'} = \frac{2M+1}{2u}\frac{\partial X^M_{ML'}}{\partial P_z} . \quad (95)$$

The corresponding formulas for advancement of the second index are obtainable by similar methods. They are

$$(L'-M+1)X^M_{L,L'-1} = \left(\frac{2L'+1}{2v}\right)\left[\frac{\partial X^M_{LL'}}{\partial Q_z} + (L'+M)X^M_{L,L'-1}\right] + (L'+M)\frac{\partial X^M_{L,L'-1}}{\partial v} , \quad L'-1 \geqslant M \quad (96)$$

$$X^M_{L,M+1} = \frac{2M+1}{2v}\frac{\partial X^M_{LM}}{\partial Q_z} . \quad (97)$$

We now carry out the inductive process by substituting Eq. (43) into Eqs. (94)–(97), confirming its validity for arbitrary values of L and L'. With Eq. (89) for X^M_{MM}, these steps complete a proof of Eq. (43).

In using Eqs. (94)–(97), it is found that the desired verification is by no means immediate. We begin by remarking that $\partial/\partial Q_z = -\partial/\partial P_z = \partial/\partial R$,

and $F_l'(x) = -F_{l+1}(x)$. It is, in addition, necessary to make rearrangements involving the functions $F_k(x)$ so as to cause them to appear multiplied by suitable powers of x. The basic technique involved is the multiple application of Eq. (69), to lead to identities such as

$$2x^{j+1}F_{l+j}(x) - (2l + 2j - 1)x^jF_{l+j-1}(x) = 2x^{j+1}F_{l+j+1}(x) - (2l + 2j + 1)x^jF_{l+j}(x) . \quad (98)$$

The actual work, though tedious, is straightforward if the above considerations are kept in mind.

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Polynomial Orthogonality and Integration Quadratures

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1. INTRODUCTION

QUADRATURE integration formulas, when used with polynomials, link together two kinds of orthogonal properties: orthogonality in the sense of integration on the one hand, and orthogonality in the sense of summation on the other. The interrelationships can be exploited towards the solution of eigenvalue problems in quantum theory.

Polynomials $\varphi_k(x)$ and $\varphi_m(x)$, of degrees k and m, respectively, are orthogonal in the sense of integration (or briefly integration-orthogonal) over (a,b) for the weight function $w(x)$, if

$$\int_a^b w(x)\varphi_k(x)\varphi_m(x)dx = A_k\delta_{km}; A_k > 0 . \quad (1)$$

We restrict ourselves in the choices of (a,b) and $w(x)$ to the cases where a complete set of $\{\varphi_k(x)\}$ can be so defined.

The same polynomials would be termed orthogonal in the sense of summation (or briefly summation-orthogonal) over the n abscissas $\{x_i\}$ for the n weights $\{W_i\}$ if

$$\sum_{i=0}^{n-1} W_i\varphi_k(x_i)\varphi_m(x_i) = A_k\delta_{km}; A_k > 0 \quad (2)$$

holds. Many properties of the orthogonal polynomials are well established.[1] Of particular interest to numerical computation are

(a) the least-squares properties of orthogonal expansions of either kind;

(b) Gaussian quadrature integration formulas based on interpolation of the integrand at zeros of integration-orthogonal polynomials. The n-point quadrature formula has a degree of precision[2] of $p = 2n - 1$—twice as large as corresponding Newton–Cotes formulas.

2. SUMMATION-ORTHOGONALITY THROUGH QUADRATURES

We first observe that the Legendre polynomials $P_k(x)$, $P_m(x)$, which are characterized by integration-orthogonal relationships [over $(-1, +1)$ for $w(x) = 1$], are, for $k + m \leq 3$, nevertheless, summation-orthogonal over $\{x_i\} = -1, 0, +1$ for $\{W_i\} = 1/3, 4/3$, and $1/3$, respectively. These abscissas and weights are precisely those used in Simpson's rule, whose degree of precision is 3.

This is not surprising since quadrature integration formulas serve as a bridge between an integral and a finite sum.

Theorem. Given an n-point quadrature formula of degree of precision p over (a,b) for $w(x)$. If $\varphi_k(x)$ and $\varphi_m(x)$ are integration-orthogonal in the same sense and, further, $k + m \leq p$, then these polynomials are also summation-orthogonal over the abscissas and weights specified by the quadrature formula.

Proof. Clearly $\varphi_k(x)\varphi_m(x)$ is a polynomial of degree $k + m \leq p$. Hence,

$$A_k\delta_{km} = \int_a^b w(x)\varphi_k(x)\varphi_m(x)dx = \sum_{i=0}^{n-1} W_i\varphi_k(x_i)\varphi_m(x_i) . \quad \text{Q.E.D.}$$

[1] See, for example, G. Szegö, *Orthogonal Polynomials* (American Mathematical Society, New York, 1959); also A. Erdélyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Chap. X.

[2] The degree of precision of a formula is the maximum degree of an otherwise arbitrary polynomial integrand for which the formula is exact.