Two-Center Calculations for X-Ray Scattering

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An analytical procedure for the evaluation of two-center integrals in x-ray scattering calculations has been developed. The scattering potential is represented in prolate spheroidal coordinates. The plane wave operator is expanded in spheroidal wave-functions. All integrals are evaluated analytically with the aid of stable recursion relations. It is found that the several infinite sums involved are rapidly convergent, so that a practical computational method is at hand. The method is illustrated with a calculation of the molecular scattering factor for C–H from a near Hartree–Fock wavefunction comprised of an extended basis set of Slater-type orbitals. The coherent x-ray scattering intensity of H_2 has been computed from a natural spin orbital expansion of the exact electronic wavefunction for the $^1\Sigma_g^+$ state of H_2.

INTRODUCTION

The interpretation of x-ray scattering experiments in terms of N-electron wavefunctions requires an evaluation of Fourier transforms. For example, the coherent x-ray scattering intensity is given by

$$I_c = f^*(\mathbf{S}) f(\mathbf{S}) \tag{1}$$

in which $f(\mathbf{S}) = \int \rho(\mathbf{r}) \exp(i\mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r}$.

The one-electron density function is

$$\rho(\mathbf{r}) = \int | \psi(\tau_1, \tau_2, \ldots, \tau_N)|^2 \, d\sigma_1 \, d\tau_2 \cdots d\tau_N, \tag{2}$$

in which τ_i is a vector of the space and spin coordinates of electron i, and $d\sigma_1$ represents integration over the spin coordinate of electron 1. ψ in (2) is the N-electron wavefunction for the molecule or atom in the ground state. The variable $\mathbf{S}$, the scattering vector, is the difference between the incident and scattered momenta of the x-rays. Expressions similar to (1) are found for incoherent and total x-ray scattering [e.g., 1–2].

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If the wavefunction can be expanded in single-particle basis functions, then all such scattered x-ray intensities can be evaluated from the Fourier transforms of products of the several basis functions. (The scattering in this case is within the first Born approximation.) Basis functions are often centered on the several nuclei of the molecule, so that the calculations of the integrals

$$I_1 = \int \phi_1(\mathbf{r}_a) \exp(i\mathbf{S} \cdot \mathbf{r}) \, \phi_2(\mathbf{r}_a) \, d\mathbf{r}$$

and

$$I_2 = \int \phi_1(\mathbf{r}_a) \exp(i\mathbf{S} \cdot \mathbf{r}) \, \phi_2(\mathbf{r}_b) \, d\mathbf{r} \tag{3}$$

are required. The vectors $\mathbf{r}_a$ and $\mathbf{r}_b$ in (3) have origins at centers a and b, respectively; the origin of $\mathbf{r}$ is a matter of convenience. Analytical expressions for these integrals depend explicitly on the form of the basis functions ϕ_i; several expressions (e.g., Refs. [3–6]) have been given for I_1 and I_2 in the most common bases, exponential (usually Slater) orbitals and Gaussian orbitals. We wish to present an analytical scheme for evaluation of I_2 which is general for exponential basis functions and capable of arbitrary accuracy.

MATHEMATICAL FORMALISM

The coordinate system to be employed is the prolate spheroidal system, defined in terms of centers a and b separated by a distance R by $\xi = (r_a + r_b)/R$, $\eta = (r_a - r_b)/R$, and ϕ, the coordinate of rotation about the a–b axis. In this system [7],

$$r_a = (\xi + \eta) \, R/2,$$

$$r_b = (\xi - \eta) \, R/2,$$

$$\begin{Bmatrix} x \\ y \end{Bmatrix} = (R/2)[(\xi^2 - 1)(1 - \eta^2)]^{1/2} \begin{Bmatrix} \cos \phi \\ \sin \phi \end{Bmatrix}, \tag{4}$$

$$z = \xi \eta R/2.$$

In these coordinates, the plane wave may be expanded in spheroidal wavefunctions [9]

$$\exp(i\mathbf{S} \cdot \mathbf{r}) = 2 \sum_{m=0}^{\infty} \sum_{n=m}^{\infty} i^n (2 - \delta_{0m}) \, N_{m,n}^{-1}(c) \, S_{m,n}(c, \eta') \, S_{m,n}(c, \eta) \, R_{m,n}^{(1)}(c, \xi)$$

$$\times \cos m(\phi - \phi_0). \tag{5}$$

The components of $\mathbf{S}$ are S, η' ($= \cos \theta_0$), and ϕ_0 (spherical polar coordinates); $c = SR/2$ and $|\mathbf{S}| = 4\pi \sin \theta/\lambda$, where 2θ is the scattering angle. The spheroidal wavefunctions are defined by [8]

$$S_{m,n}(c, \eta) = \sum_{r=0,1}^{\infty}{}' d_r^{m,n}(c) P_{r+m}^m(\eta),$$ (6)

$$R_{m,n}^{(1)}(c, \xi) = [(\xi^2 - 1)/\xi^2]^{m/2} \sum_{r=0,1}^{\infty}{}' a_r^{m,n}(c) j_{r+m}(c\xi),$$ (7)

and

$$\int_{-1}^{1} S_{m,n}(c, \eta) S_{m,n'}(c, \eta) \, d\eta = N_{m,n}(c) \delta_{n,n'}.$$ (8)

Primed summations indicate that the summation index r only takes values of the same parity as $n - m$. $P_l^m(\eta)$ and $j_l(c\xi)$ denote the lth-order associated Legendre and spherical Bessel functions, respectively. The expansion coefficients $d_r^{m,n}(c)$ are determined by the scalar Helmholtz differential equation and the Legendre recursion relations [10]. The coefficients $a_r^{m,n}(c)$ are simply related to the d's by $a_r^{m,n} = (-1)^{(n-m-r)/2} (r + 2m)!/r! \times (n - m)!/(n + m)! \, d_r^{m,n}$.

In the prolate spheroidal representation, a normalized Slater-type atomic orbital (STO) may be expressed as follows:

$$\phi_{nlm}^{\text{STO}}(\mathbf{r}) = N_{nl} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi) \propto e^{-\alpha\xi} e^{\beta\eta} e^{im\phi} [(\xi^2 - 1)(1 - \eta^2)]^{m/2} \sum_i b_i \xi^{k_i} \eta^{l_i}.$$ (9)

This transformation follows from Eqs. (4) and closely follows the presentation of Ruedenberg [11]. Application of Eqs. (5) and (9) puts I_2 into the form

$$I_2 = \int \phi_{n'l'm'} \phi_{n''l''m''} \exp(i\mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r}$$

$$= 2N_{n'l'} N_{n''l''} (R/2)^{n'+n''+1} \sum_{n=M}^{\infty} i^n S_{M,n}(c, \eta') e^{iM\phi_0} N_{M,n}^{-1}(c) \sum_j w_j \mathscr{R}_{M,n}^{(j)}(c) \mathscr{S}_{M,n}^{(j)}(c),$$ (10)

where $M = |m' - m''|$,

$$\mathscr{R}_{M,n}^{(j)}(c) = \sum_{r=0,1}^{\infty}{}' a_r^{M,n}(c) I_{r,k_j}^M(c, \alpha),$$ (11)

$$\mathscr{S}_{M,n}^{(j)}(c) = \sum_{r=0,1}^{\infty}{}' d_r^{M,n}(c) B_{r,l_j}^M(\beta).$$ (12)

The factor $(\xi^2 - \eta^2)$ due to the volume of integration has been collected into polynomials in ξ and η which are incorporated into the $\mathscr{R}_{M,n}^{(j)}$ and $\mathscr{S}_{M,n}^{(j)}$ functions. w_j is the appropriate coefficient for each term in the polynomial. The functions in (11) and (12) are the integrals

$$I_{r,k}^m(c, \alpha) = \int_1^\infty \xi^{k-m}(\xi^2 - 1)^m j_{r+m}(c\xi) \, e^{-\alpha\xi} \, d\xi \tag{13}$$

and

$$B_{r,l}^m(\beta) = \int_{-1}^1 \eta^l(1 - \eta^2)^{m/2} P_{r+m}^m(\eta) \, e^{\beta\eta} \, d\eta. \tag{14}$$

Thus, (10) is the formal solution to the problem. One needs to evaluate (13) and (14) and also the expansion coefficients $a_r^{m,n}(c)$ and $d_r^{m,n}(c)$. The convergence properties of $\mathscr{R}_{m,n}^{(j)}(c)$ and $\mathscr{S}_{m,n}^{(j)}(c)$, defined in (11) and (12), need to be studied. Finally, the sum over j and rate of convergence for the sum over n in (10) must be determined in order to appraise the computational utility of (10).

COMPUTATIONAL PROCEDURES

The integral (13) has, in previous studies (e.g., [12, 13]), been evaluated numerically. In the present work, we employ a generalized version of an analytical procedure given by Stewart, Davidson, and Simpson [4]. Details are given in Appendix I.

Treatments of the integral (14) have been published previously. The tables given by Kotani, Amemiya, Ishiguro and Kimura [14], for example, were prepared by constructing tables of $B_{0,l}^0(\beta)$ by means of a recursion resulting from integration by parts, then extending to general r and M by means of recursions derived from the properties of associated Legendre functions. Harris [15] has presented a procedure wherein recursion is performed on the ratios $x_r = B_{r+1}/B_r$ in order to obtain the $B_{r,0}^0$'s which are then generalized as above. In practice, we used a routine written by Stephen Rothenberg [16] which is similar to the procedure of Harris. Calculated integrals were compared to those of Kotani $et\,al.$, and agreement was reached to the limit of the machine word.

Associated Legendre functions, used in the evaluation of $S_{m,n}(c, \eta')$ in (10), were calculated by the procedure of Belousov [17].

The expansion coefficients of (6) and (7) are discussed at length in texts on spheroidal wavefunctions [8, 18]. Our computational procedure follows that of Little and Corbató [19]. In brief, application of the Helmholtz equation and a recursion expression for associated Legendre functions leads to a recursion expression for the $d_r^{M,n}$'s (or the $a_r^{M,n}$'s) of the form

$$A d_{r+2} + B(t) \, d_r + C d_{r-2} = 0, \tag{15}$$

in which t is a separation constant from the Helmholtz equation and is usually unknown. In practice, (15) is recast as a continued fraction of the ratios d_{r+2}/d_r or d_{r-2}/d_r, an initial estimate of t is made and then refined by an iterative procedure. When t has converged and accurate values of the ratios are on hand, the expansion coefficients are determined by the normalization condition of Stratton, Morse, Chu, Little and Corbató [18].

Given the procedure outlined above (and described in detail by Little and Corbató [19]), the problem is to insure that reasonable estimates of the separation constant t are input. This saves computational labor and insures that the iteration for t will converge. For parameters in the ranges $0 \leqslant M \leqslant 8$, $M \leqslant n \leqslant 8$, and $0 \leqslant c \leqslant 8.0$, values for $t_{M,n}(c)$ can be taken (or interpolated) from the tables of Little and Corbató [19]. Tables of $t_{M,n}(c)$ can then be extended by means of quadratic extrapolation. We have found this procedure satisfactory for $c \leqslant 25.0$ and $n \leqslant 50$.

CONVERGENCE PROPERTIES

In order to assess the utility and limitations of the method, we must examine the convergence behavior of $\mathscr{R}_{M,n}^{(j)}$ and $\mathscr{S}_{M,n}^{(j)}$, and the summation over n. In all cases in which extent of convergence must be assessed, our procedure is as follows: The most recent increment to a particular sum is compared to the value of that sum. If their ratio is smaller than a specified convergence criterion, the summation is terminated.

The behavior of $\mathscr{R}_{M,n}^{(j)}$ and $\mathscr{S}_{M,n}^{(j)}$ is governed to a large extent by that of the $a_r^{M,n}$ and $d_r^{M,n}$, respectively, since the functions $I_{r,k}^M$ and $B_{r,l}^M$ generally vary more slowly with r than their coefficients. As functions of r, these spheroidal expansion coefficients attain maximum values at or near $r = n - M$ and decline smoothly in absolute value thereafter. We do not consider it worthwhile to check for convergence of $\mathscr{R}$ or $\mathscr{S}$ until the summation has extended beyond $r = n - M$. Thereafter, one may derive from the asymptotic behavior of $a_r^{M,n}(c)$ as a function of r an approximate expression for the depth to which r should be taken to achieve arbitrary convergence of $\sum_{r=0,1}^{\prime \infty} a_r^{M,n}(c)$. Let r_t be the value of r for which $\sum_r^{\prime} a_r^{M,n}(c)$ has converged to one part in 10^q; then $r_t = n - M + p$, and p is given by

$$p \approx -q \ln 10/\ln\{c/(2n - 2M + p)\}. \tag{16}$$

A derivation is presented in Appendix II. For example, with $q = 10$, $c = 25$, $n = 8$, and $M = 8$, (16) yields $p = 43$ which predicts that 22 terms beyond $r = n - M = 0$ are needed for convergence to 10^{-10}. A comparable expression may be obtained for the $d_r^{M,n}$'s. The only circumstance which should cause $\mathscr{R}$ or $\mathscr{S}$ to require more than r_t terms is monotonic increase of the functions $I_{r,k}^M$ or

$B_{r,l}^M$ in the region $r = n - M$. The $I_{r,k}^m(c, \alpha)$ integrals exhibit this behavior to an increasing extent with increasing c. The worst case studied was $c = 25.0$, at which value the $a_r^{M,n}$'s decrease most slowly and the $I_{r,k}^M$'s increase most rapidly. In the case of the parameters given above, 13 terms beyond r_t were required for convergence to one part in 10^{10}. When $c = 25$, $M = 0$ and $n = 10$ or higher, the satisfactory calculation of $\mathscr{R}_{M,n}^{(j)}(c, \alpha)$ required 6 or fewer terms beyond r_t. For large r, the function $I_{r,k}^M$ has the asymptotic expansion

$$I_{r,k}^M \sim (\sqrt{\pi/2} \ c^{r+M}/(\alpha + \gamma)^{r+M+1/2} \ \gamma^{k-M+1/2}) \ r^{k+M-1/2}, \qquad (17)$$

where γ, a function of α and c, is defined by (A13) of Appendix I. The relation (17) follows from (A13) and (A14) when r is allowed to increase without bound. At large r [20],

$$a_{r+2}^{M,n}/a_r^{M,n} \sim (c/2r)^2. \qquad (18)$$

Thus convergence of $\mathscr{R}_{M,n}^{(j)}(c)$ is guaranteed since, in the limit of large r,

$$(a_{r+2}^{M,n} I_{r+2,k}^M)/(a_r^{M,n} I_{r,k}^M) \rightarrow c^4/(4(\alpha + \gamma)^2 r^2). \qquad (19)$$

For c bounded, (19) becomes less than one at sufficiently large r. The rapid fall-off of the $a_r^{M,n}(c)$ with increasing r makes $\mathscr{R}_{M,n}^{(j)}$ a computationally useful function.

An additional problem is created by the $I_{r,k}^M$'s due to their oscillatory behavior at small r: if a particular value of $I_{r,k}^M$ lies near a node, it could result in premature truncation of the summation. The oscillations do not extend beyond $r \sim c$, however, so this difficulty can be avoided by deferring the convergence test until r is greater than c or $n - M$, whichever is larger. $B_{r,l}^M(\beta)$ is free of the difficulties associated with $I_{r,k}^M(c, \alpha)$, so that the convergence for $\mathscr{S}_{M,n}^{(j)}$ is easily achieved. For example, Eq. (16) suggests that it would require 24 terms to calculate $\mathscr{S}_{0,0}^{(j)}$ ($c = 25$, $\beta = 15$) to an accuracy of one part in 10^{10}. Actually, only 16 terms are necessary.

The behavior of the summation over n in (10) is more difficult to analyze, since it depends, in principle, upon the exponential parameters α and β, the powers of ξ and η (denoted by k and l, respectively), and the values of c and M. A test function

$$T(k, l, M, \alpha, \beta, c) = \sum_n N_{M,n}^{-1}(c) \ \mathscr{R}_{M,n}^{(k)}(c, \alpha) \ \mathscr{S}_{M,n}^{(l)}(c, \beta) \qquad (20)$$

was evaluated at representative values of its arguments, and the truncation value $n_{\max}$ was related to those arguments. In all cases convergence to one part in 10^{10} was observed; a reasonable upper limit for the necessary number of terms in the summation is given by $n_{\max} = 16 + 1.2c + M/2$. Convergence length was prac-

tically independent of k and decreased (erratically) with increasing l, namely, $\Delta n_{max}/\Delta l$ varied from $-.4$ to 0. Variation of α and β yielded only one significant trend: combinations of large α and small β (e.g., $\alpha = 20$, $\beta \leqslant 5$) converged in two or three fewer terms than most other combinations. The parameters were varied over the ranges $0 \leqslant k$ or $l \leqslant 12$, $0 \leqslant M \leqslant 10$, $2 \leqslant \alpha \leqslant 20$, $0 \leqslant \beta \leqslant 20$ and $0 \leqslant c \leqslant 25$. The ranges of k, l, M, α and β correspond to the ranges of values that are encountered in wavefunctions of diatomic molecules with Z_A, $Z_B < 10$ (e.g., the diatomic hydrides of Cade and Huo [21]). The maximum value of c corresponds to $\sin\theta/\lambda$ slightly greater than 2 Å^{-1} for the case of $R = 2$ Å; thus it extends far enough to include the range of x-ray scattering by silver $K\bar{\alpha}$ radiation.

ACCURACY: ONE-CENTER TESTS

The assembled program was checked by using it to calculate scattering factors for one-center orbital products, which can be readily evaluated by independent methods [6]. If the orbital product is displaced from the origin by a distance $\mathbf{R}/2$ and its scattering factor, $f_2(\mathbf{S})$, is calculated in the two-center frame with a unit function on center b it will be related to the scattering factor $f_1(\mathbf{S})$ calculated in the one-center frame by

$$f_1(\mathbf{S}) = \exp(i\mathbf{S} \cdot \mathbf{R}/2) f_2(\mathbf{S}). \tag{21}$$

The scattering factor of an orbital product will be real or imaginary if the total orbital angular momentum is even or odd, respectively [6]. If we calculate the terms of Eq. (21) with a specified convergence criterion of 10^{-n}, the ideal outcome would be as follows: the nonvanishing component on the right-hand side of Eq. (21) should agree with the corresponding component on the left-hand side through the first n digits. The other component, which is formally zero, should be at least n orders of magnitude smaller than the nonzero component. When these conditions are not fulfilled, a loss of accuracy has occurred.

In Tables I–III we present typical calculations of the scattering factors of one-center orbital products $f_1(\mathbf{S})$, calculated (i) by the one-center method of Stewart [6], and (ii) by the present two-center method. The orbital products $(1s)^2$, $1s4f_0$, and $(4f_0)^2$ are, respectively, 2-, 12-, and 30-term polynomials in ξ and η. In each case the displacement $|\mathbf{R}/2| = 1$ atomic unit (0.529167 Å), the orbital exponents $\zeta = 1.0$, the convergence criterion was one part in 10^{10}, and the Bragg vector $\mathbf{S}$ was fixed in the direction $\eta' = 1$ (i.e., parallel to $\mathbf{R}$). These calculations were done in double precision (72 bits) on a UNIVAC 1108. Two trends are evident in Tables I–III. The agreement between $f_1(\mathbf{S})$ and $\exp(i\mathbf{S} \cdot \mathbf{R}/2) f_2(\mathbf{S})$ becomes worse with increasing S. In addition, it becomes worse with increasing polynomial

TABLE I

One-Center Orbital Product Test[a]: $(1s)^2$

c	$\sin\theta/\lambda$, Å^{-1}	Procedure (i)[b]	Procedure (ii)	
		Re $f_1(S)$	Re $f_1(S)$	Im $f_1(S)$
0	0	0.1000000000(+1)[c]	0.1000000000(+1)	0
0.5	0.075	0.8858131488(+0)	0.8858131488(+0)	0.54(−14)
1.0	0.150	0.6400000000(+0)	0.6400000000(+0)	−0.75(−14)
2.0	0.301	0.2500000000(+0)	0.2500000000(+0)	0.75(−13)
3.0	0.451	0.9467455621(−1)	0.9467455621(−1)	0.59(−12)
4.0	0.602	0.4000000000(−1)	0.4000000000(−1)	−0.69(−13)
5.0	0.752	0.1902497027(−1)	0.1902497027(−1)	0.20(−13)
7.0	1.053	0.5695977216(−2)	0.5695977216(−2)	−0.12(−12)
10.0	1.504	0.1476289941(−2)	0.1476289941(−2)	0.11(−12)
15.0	2.256	0.3051047844(−3)	0.3051047844(−3)	0.36(−13)
20.0	3.008	0.9802960494(−4)	0.9802960496(−4)	−0.46(−14)
25.0	3.760	0.4044070256(−4)	0.4044070252(−4)	0.23(−13)

[a] The vector S is taken parallel to R, that is, $\eta' = 1$. The orbital exponent $\zeta = 1$, and $R = 2$ bohrs.

[b] Procedures (i) and (ii) are described in the text in connection with Eq. (21).

[c] The notation 0.10(+1) indicates $0.10 \times 10^{+1}$.

TABLE II

One-Center Orbital Product Test[a]: $(1s\,4f_0)$

c	$\sin\theta/\lambda$, Å^{-1}	Procedure (i)	Procedure (ii)	
		Im $f_1(S)$	Im $f_1(S)$	Re $f_1(S)$
0	0	0	0	−0.34(−17)
0.5	0.075	−0.8256772392(−1)	−0.8256772392(−1)	−0.11(−14)
1.0	0.150	−0.2930859019(+0)	−0.2930859019(+0)	0.37(−14)
2.0	0.301	−0.2236067978(+0)	−0.2236067978(+0)	−0.49(−13)
3.0	0.451	−0.6660271801(−1)	−0.6660271801(−1)	0.91(−13)
4.0	0.602	−0.1831786887(−1)	−0.1831786887(−1)	−0.88(−13)
5.0	0.752	−0.5581680502(−2)	−0.5581680502(−2)	−0.74(−13)
7.0	1.053	−0.7512071661(−3)	−0.7512071660(−3)	−0.46(−13)
10.0	1.504	−0.7527976482(−4)	−0.7527976489(−4)	−0.15(−13)
15.0	2.256	−0.4908415463(−5)	−0.4908415401(−5)	−0.45(−13)
20.0	3.008	−0.6808134259(−6)	−0.6808134022(−6)	−0.47(−13)
25.0	3.760	−0.1453488999(−6)	−0.1453489112(−6)	−0.95(−14)

[a] See Table I for details.

TABLE III

One-Center Orbital Product Test[a]: $(4f_0)^2$

c	$\sin\theta/\lambda$, Å^{-1}	Procedure (i)	Procedure (ii)	
		$\mathrm{Re}\,f_1(S)$	$\mathrm{Re}\,f_1(S)$	$\mathrm{Im}\,f_1(S)$
0	0	0.1000000000(+1)	0.1000000000(+1)	0
0.5	0.075	0.1237110171(+0)	0.1237110171(+0)	−0.82(−14)
1.0	0.150	−0.2018508800(+0)	−0.2018508800(+0)	0.29(−13)
2.0	0.301	−0.1250000000(+0)	−0.1250000000(+0)	0.84(−13)
3.0	0.451	−0.3893112173(−1)	−0.3893112173(−1)	0.13(−12)
4.0	0.602	−0.7892480000(−2)	−0.7892480000(−2)	−0.26(−13)
5.0	0.752	−0.1635670827(−2)	−0.1635670827(−2)	−0.44(−13)
7.0	1.053	−0.1043270236(−3)	−0.1043270236(−3)	−0.13(−13)
10.0	1.504	−0.4149960168(−5)	−0.4149960161(−5)	−0.27(−13)
15.0	2.256	−0.8684803383(−7)	−0.8684804299(−7)	−0.70(−14)
20.0	3.008	−0.5227976953(−8)	−0.5227958253(−8)	−0.32(−13)
25.0	3.760	−0.5790398748(−9)	−0.5790333719(−9)	0.93(−14)

[a] See Table I for details.

length of the function being transformed. Polynomial length, in turn, increases with increasing orbital quantum numbers n and l.

The loss of accuracy observed in Tables I–III is a result of the oscillatory nature of the functions involved in the various summations. At small S (corresponding to $c < 7$) the summations over n and r in Eqs. (10)–(12) are usually dominated by one term. As S increases, this peaking character is lost, especially for the function $\mathscr{R}^{(j)}_{M,n}$, and one must sum over terms of comparable magnitude but varying sign. When the final magnitude of such a summation is less than that of its largest term, the difference in magnitude corresponds to the number of digits of accuracy lost through numerical differencing. The manner in which this situation comes about is best illustrated by considering specific examples.

At $c = 1$, for instance, the spheroidal expansion coefficients $a_r^{M,n}(c)$ attain their maximum value for a given n, M at $r_{\max} = n - M$, for which $a_{n-M}^{M,n} \simeq 1$. For all other r, $|a_r^{M,n}|$ is less than 1, usually more than an order of magnitude smaller. Likewise, the functions $I_{r,k}^M(c = 1, \alpha)$ attain their maximum value for a given M, k at $r \sim k/2$, although they do not peak as sharply as the $a_r^{M,n}$'s. Thus $\mathscr{R}^{(j)}_{M,n}(c = 1, \alpha)$ is usually dominated by the term containing the largest coefficient $a_{n-M}^{M,n}$, and loss of accuracy seldom occurs, although both $I_{r,k}^M$ and $a_r^{M,n}$ oscillate before reaching their respective maxima.

At $c = 25$, the coefficients still peak at $r_{\max} \sim n - M$; however, the maximum is now on the order of 10^{10} for $n = 0$, falling to $|a_{r_{\max}}^{M,n}| \sim 1$ by $n \sim 15$. They

decline rapidly after $r > r_{max}$, but are not particularly small in the oscillatory region $r < r_{max}$. Meanwhile, the corresponding functions $I_{r,k}^M(c = 25, \alpha)$ oscillate in the region $r \lesssim c$, above which they increase to a maximum whose position depends on k and α. The $I_{r,k}^M$ increase so gradually that $\mathscr{R}_{M,n}^{(j)}$ may have converged to the required accuracy before this maximum is reached. In this case, the sum $\mathscr{R}_{M,n}^{(j)}(c = 25, \alpha)$ contains a rather large number of terms which are of comparable magnitude but varying sign; thus, the opportunities for differencing are abundant. Detailed numerical studies indicate that this is precisely what happens. $\mathscr{R}_{0,0}^{(j)}(c = 25, \alpha)$ is about 14 orders of magnitude smaller than its largest term, $\mathscr{R}_{0,7}^{(j)}$ is about 7 orders smaller and $\mathscr{R}_{0,14}^{(j)}$ is of the same order of magnitude as its largest term. Thus, if the $a_r^{0,n}(c = 25)$ are computed subject to a convergence criterion of 10^{-10}, $\mathscr{R}_{0,n}^{(j)}(c = 25, \alpha)$ with low n ($\lesssim 5$) are completely untrustworthy. When $n \gtrsim 14$, $\mathscr{R}_{0,n}^{(j)}$ is given to the ten significant figures specified by the convergence criterion. (Evidently one can attempt to suppress this problem by computing $a_r^{M,n}(c)$ and $I_{r,k}^M(c, \alpha)$ to a greater accuracy than the rest of the calculation, but this merely postpones the inevitable and is already impractical at $c = 25$.) At $c = 25$, the terms near $n = 0$ are usually not the dominant ones in the summation (10), although they may be large enough to deprive the scattering factor of most of its significant figures. Obviously, if the present method is to be at all useful at $c = 25$, the totally inaccurate $\mathscr{R}_{0,n}^{(j)}$'s must be discounted or weighted lightly. The functions $\mathscr{S}_{0,n}^{(j)}(c, \beta)$, $S_{0,n}(c, \eta')$ and $N_{0,n}^{-1}(c)$, which multiply $\mathscr{R}_{0,n}^{(j)}$, will, under certain circumstances, provide relatively small weights for the $\mathscr{R}_{0,n}^{(j)}$ with small n. In general, $\mathscr{S}_{0,n}^{(j)}(c = 25, \beta)$ and $S_{0,n}(c = 25, \eta')$ are of the same order of magnitude as the largest $a_r^{0,n}$ for that value of n, and $N_{0,n}(c)$ is of the same order as the square of the largest $a_r^{0,n}(c)$. Thus the $\mathscr{R}_{0,n}^{(j)}$'s are given comparable weights and the resulting scattering factor is quite inaccurate. However, when $\eta' = 1$, then $P_r(\eta') = 1$, and $S_{0,n}(c, \eta') = \sum_r' d_r^{0,n}(c) = 1$, which is the normalization condition for the $d_r^{0,n}$. In this case, the relative weights given to the $\mathscr{R}_{0,n}^{(j)}$ are proportional to the inverse of the largest $a_r^{0,n}$ for each n. Since $[a_r^{0,0}(c = 25)]_{max} \sim 10^{10}$ and $[a_r^{0,14}(c = 25)]_{max} \sim 1$, the function $S_{0,n}(c, \eta' = 1)$ will minimize the contributions of the most inaccurate $\mathscr{R}_{0,n}^{(j)}$'s. This is illustrated by f_{1s1s} at $c = 25$. From Table I, the accurate one-center calculation yields $f = 0.4044070256 \times 10^{-4}$, while the two-center expansion, evaluated at $\eta' = 1$, yields a real component of $0.4044070252 \times 10^{-4}$, in excellent agreement. However, when f_{1s1s} is evaluated with the two-center expansion and $\eta' = 0$, the result is $0.4041615822 \times 10^{-4}$, a considerable loss of accuracy which is completely due to the effect of $S_{0,n}(c, \eta')$.

Another case in which it is possible to maintain substantial accuracy at $c = 25$ is the calculation of scattered intensities. In this case one performs an integration of the sort

$$I(S) \propto \int f^*(\mathbf{S}) f(\mathbf{S}) \, d\hat{\mathbf{S}}, \tag{22}$$

in which $d\hat{S}$ represents integration over the angular coordinates of S. The integration over ϕ_0 is trivial; the integration over η' is performed using Eq. (8), the orthogonality condition for $S_{M,n}(c, \eta')$. The resulting equation is

$$I(c) \propto \sum_{n}^{\infty} \left[\sum_{j} \mathscr{R}_{M,n}^{(j)}(c, \alpha) \, \mathscr{S}_{M,n}^{(j)}(c, \beta) \right]^2 \Big/ N_{M,n}(c),$$

which gives a weight to $(\mathscr{R}_{M,n}^{(j)})^2$ proportional to the inverse square of the largest $a_r^{M,n}$ for that M and n.

We note in passing that the functions $\mathscr{S}_{M,n}^{(j)}(c, \beta)$ present none of the difficulties of the $\mathscr{R}_{M,n}^{(j)}$, chiefly because the functions $B_{r,i}^{M}(\beta)$ decline monotonically as a function of r over most of the range of r. A further simplification occurs when $\beta = 0$: the infinite series (12) becomes a finite series of length $l/2 + 1$, in which l is the power of η.

The remaining important cause of loss of accuracy is the summation over the density function polynomial

$$\sum_{j} w_j \mathscr{R}_{M,n}^{(j)}(c, \alpha) \, \mathscr{S}_{M,n}^{(j)}(c, \beta)$$

in which the terms often have comparable magnitudes but varying signs. This effect appears in Tables I–III as a loss of four significant figures of $f_{4f_0 4f_0}(c = 25, \eta' = 1)$ relative to $f_{1s1s}(c = 25, \eta' = 1)$.

The tests and examples discussed here enable us to estimate accuracy requirements for the present method. In the range $0 \leqslant c < 10$, a convergence criterion of 10^{-n} will usually provide an accuracy of n digits. In the range $10 \leqslant c \leqslant 20$, a convergence criterion of 10^{-n-4} will usually provide an accuracy of n digits. At $c = 25$, the present method is inapplicable, except in the particular instances noted above, namely, the calculation of intensities, for which the integration over orientation of S is performed, and the case $M = 0$, $\eta' = 1$. In addition, it appears that single-precision calculations will suffice when $c < 10$ (as long as $n < 8$), but double precision is required when $c \geqslant 10$.

FURTHER RESULTS AND CONCLUSIONS

In Table IV we present the molecular scattering factor for the CH radical. The density function $\rho(\mathbf{r})$ was obtained from the near-Hartree–Fock wavefunction of Cade and Huo [21]. The Bragg vector is fixed at $\eta' = 1$, which corresponds to setting S parallel to $\mathbf{R}$, the internuclear vector. The convergence criterion is 10^{-6}; no more accuracy is needed in the range of c employed since the wavefunction is only specified to five digits. The wavefunction places 12 sigma and 6 pi atomic

TABLE IV

Molecular Scattering Factors for CH Radical[a]

c	$\sin\theta/\lambda$, Å^{-1}	Procedure (i)[b]		Procedure (ii)	
		Re Component	Im Component	Re Component	Im Component
0	0	0.69999597(+1)[c]	0	0.69999591(+1)	0
0.5	0.071	0.55434074(+1)	−0.24026690(+1)	0.55434057(+1)	−0.24026689(+1)
1.0	0.142	0.25745624(+1)	−0.31770937(+1)	0.25745620(+1)	−0.31770938(+1)
2.0	0.283	−0.12094642(+1)	−0.16455484(+1)	−0.12094637(+1)	−0.16455482(+1)
3.0	0.425	−0.17823923(+1)	0.88346996(−2)	−0.17823921(+1)	0.88348681(−2)
4.0	0.566	−0.96852174(+0)	0.11390798(+1)	−0.96852162(+0)	0.11390788(+1)
5.0	0.708	0.40099820(+0)	0.12690749(+1)	0.40099795(+0)	0.12690753(+1)
7.5	1.062	0.37002344(+0)	−0.96005455(+0)	0.37002354(+0)	−0.96005520(+0)
10.0	1.416	−0.60657926(+0)	0.38290796(+0)	−0.60657886(+0)	0.33290774(+0)

[a] The Bragg vector S is parallel to the molecular axis. The convergence criterion is 10^{-6}.

[b] Procedures (i) and (ii) are described in the text.

[c] The notation follows Table I. Normalization of the scattering factors is such that $f(\mathbf{0}) = N$, the number of electrons in the system. The difference between $f(\mathbf{0})$ and its formal value of 7.0 is due to the fact that the molecular wavefunction is only specified to 5 digits.

orbitals (including $3d$ and $4f$ orbitals) on the carbon atom, and 4 sigma and 2 pi atomic orbitals (including $2p$ and $3d$ orbitals) on the hydrogen atom. $f(\mathbf{S})$ was calculated in two ways: (i) all two-center orbital products were done by the present method, but all one-center products were done by Stewart's method [6], and (ii) both one- and two-center orbital products were done by the present method. Since the greater part of the molecular electron density is on the carbon atom, the largest contribution of $f(\mathbf{S})$ will be from orbital products on the carbon atom, and comparison of the two scattering factors should be a good test of the present method.

As may be seen in Table IV, the factors agree to the six digits specified by the convergence criterion. The single exception is $\mathrm{Im}\,f(\mathbf{S})$ at $c = 3$, at which point the imaginary component of the molecular scattering factor lies close to a node. Since the individual orbital product scattering factors do not, in general, have their own nodes here, accuracy is lost in summing over the orbitals in the basis function (this loss will occur regardless of the method employed to calculate the orbital product scattering factors).

Finally, Table V gives the coherent x-ray scattering intensity for the hydrogen molecule. This has been calculated using Davidson and Jones' [22] natural spin-orbital expansion of the essentially exact ground state wavefunction of Kolos and Roothaan [23].

TABLE V

Coherent Intensity for Hydrogen Molecule

c	$\sin\theta/\lambda$, Å^{-1}	$I_{coh}(S)/I_{cl}$
0	0.0000	3.99985
0.1	0.0215	3.93080
0.2	0.0429	3.73360
0.3	0.0644	3.43069
0.4	0.0859	3.05464
0.5	0.1073	2.64117
0.6	0.1288	2.22314
0.7	0.1503	1.82656
0.8	0.1718	1.46890
0.9	0.1932	1.15934
1.0	0.2147	0.90036
1.2	0.2576	0.52227
1.4	0.3006	0.29169
1.6	0.3435	0.15919
1.8	0.3864	0.08607
2.0	0.4294	0.04672
3.0	0.6441	0.00360
4.0	0.8588	0.00064
5.0	1.0735	0.00011
7.5	1.6102	0.00001
10.0	2.1469	0.00000

Intensities can be calculated by means of the formula [2]

$$I_{coherent}(S)/I_{cl} = \int\int |f(\mathbf{S})|^2 \, d\eta' \, d\phi_0 \,. \tag{23}$$

As in Eq. (22), the integration over η' in (23) is performed using the orthogonality of $S_{M,n}(c, \eta')$ (8). I_{cl} is the classical expression for the total intensity of radiation scattered by a free electron [24]. One can check the results of (23) by means of the sum-rule procedure [25, 26]

$$\rho(\mathbf{0}) = (2\pi)^{-3} \int f(\mathbf{S}) \, d\mathbf{S}. \tag{24}$$

$\rho(\mathbf{0})$ is the electron density at the midpoint of the bond. Application of (24) to the molecular scattering factor of H_2 yielded $\rho(\mathbf{0}) = 0.13608$ electrons per cubic bohr. Direct calculation using Davidson and Jones' wavefunction [4] gave $\rho(\mathbf{0}) = 0.13614$ electrons per cubic bohr. The integration over S was performed using Simpson's rule with an upper limit of $S_{max} = 28.55$ bohr^{-1} rather than

infinity. This corresponds to a c of 20 and is near the limit of reliability for scattering factors, as discussed above. Truncation at $c = 20$ allows us to account for 99.96 % of the electron density at the bond center.

We are presently engaged in further studies utilizing this method, such as the projection of accurate diatomic wavefunctions into approximate scattering models. Some preliminary results have been reported [27]. In addition, our algorithm can be applied to the study of molecular scattering of electrons (see, e.g., Ref. [28]).

In conclusion, we would like to point out that all of the basic functions and integrals used in our program are produced with an accuracy limited by the size of the computer word; the loss of accuracy involved in assembling them into a scattering factor is due to computational differencing and not to any instability in the recursion relations. Therefore, greater accuracy can be achieved at any time by imposing a more stringent convergence criterion and increasing the size of the computer word, for instance, by converting the program from single to double precision (36 and 72 bits, respectively, on the UNIVAC 1108). On this basis, we claim that the method presented here is capable of arbitrary accuracy.

APPENDIX I: Evaluation of the Integral

$$\int_1^\infty (\xi^2 - 1)^m \, \xi^{k-m} e^{-\alpha\xi} j_{r+m}(c\xi) \, d\xi$$

Let $I_{R,K}^M(c, \alpha) = \int_1^\infty (\xi^2 - 1)^M \xi^K e^{-\alpha\xi} j_R(c\xi) \, d\xi$, where $\alpha > 0$, $K = k - M$, $R = r + M$. The integers k, M, and r are all nonnegative. From the following two recursion relations for spherical Bessel functions,

$$j_{r-1}(x) + j_{r+1}(x) = (2r + 1) \, j_r(x)/x, \tag{A1}$$

$$\partial j_r(x)/\partial x = j_{r-1}(x) - (r + 1) \, j_r(x)/x, \tag{A2}$$

a useful recursion for $I_{R,K}^M$ can be derived. Let $z = \alpha/c$, $A_R = (R - K + 1)/(2R + 1)$, $B_R = z$, and $C_R = -(R + K)/(2R + 1)$. Then,

$$A_R I_{R+1,K}^M + B_R I_{R,K}^M + C_R I_{R-1,K}^M = (2M I_{R,K+1}^{M-1} + \delta_{0M} e^{-\alpha} j_R(c))/c, \tag{A3}$$

where δ_{0M} is the Kronecker delta. (A3) is an inhomogeneous finite difference equation. At large R, (A3) has a homogeneous solution of the type

$$I_{R,K}^M = \beta^R, \tag{A4}$$

where β has the two roots

$$\beta_\pm = -z \pm (1 + z^2)^{1/2}. \tag{A4'}$$

For $0 < z < \infty$, (A4') has the ranges, $0 < \beta_+ < 1$ and $-1 > \beta_- \geqslant -\infty$, so that for forward recursion on R, β_- introduces a homogeneous solution to $I_{R,K}^M$ and for backward recursion on R, β_+ introduces a similar error. Thus (A3) is unstable for recursion on R in either direction.

For the case, $R = -K$, we note that $C_{-K} = 0$, so that (A3) is a two term finite difference equation. Let y_R be the inhomogeneous term

$$y_R = [2MI_{R,K+1}^{M-1} + \delta_{0M}e^{-\alpha}j_R(c)]/c. \qquad (A5)$$

Then by Gaussian elimination, starting at $R = M$, i.e., $k = 0$ so that zeros are avoided in the generation of coefficients, (A3) becomes a useful two-term recursion relation

$$A_R I_{R+1,-M}^M + \bar{B}_R I_{R,-M}^M = \bar{y}_R, \qquad (A6)$$

where

$$\bar{B}_R = B_R - C_R A_{R-1}/\bar{B}_{R-1}, \qquad \bar{B}_M = B_M, \qquad (A6')$$

and

$$\bar{y}_R = y_R - C_R \bar{y}_{R-1}/\bar{B}_{R-1}, \qquad \bar{y}_M = y_M. $$

At large R,

$$\bar{B}_R \to [z \pm (1 + z^2)^{1/2}]/2 = \gamma, \qquad (A7)$$

and we take the positive root of $\bar{B}_R$ which is always true for $K = -M$. A homogeneous solution for (A6) is β^R, where

$$\beta = -2\gamma. \qquad (A8)$$

For $0 < z \leqslant \infty$, the range for (A8) is $-1 < \beta \leqslant \infty$. A downward recursion in R for (A6) is therefore stable. By starting (A6) at large R, an error introduced into $I_{R+1,K}^M$ will decrease exponentially. The task, then, is to evaluate $I_{R,K}^M$ at large R. The function $I_{R,K}^0(M = 0)$ may be represented by the power series,

$$I_{R,K}^0(\alpha, c) = \sqrt{\pi} \sum_{l=0}^{\infty} \frac{(-1)^l (c)^{R+2l}(R + K + 2l)!\, e^{-\alpha}}{l!\, 2^{R+1+2l}\Gamma(R + l + 3/2)\, \alpha^{R+K+1+2l}} \sum_{p=0}^{R+K+2l} \frac{\alpha^p}{p!}. \qquad (A9)$$

For large R the product $e^{-\alpha} \sum_{p=0}^{R+K+2l} \alpha^p/p!$ approaches unity. One then has the power series representation of the integral from zero to infinity so that

$$I_{R,K}^0 \approx \int_0^{\infty} \xi^K e^{-\alpha\xi} j_R(c\xi)\, d\xi. \qquad (A10)$$

The absolute value of the ratio of (A9) to (A10) will be less than $\alpha^{R+1}/(R+1)!$. For example at $\alpha = 2$ and $R = 30$ the relative error in (A10) is at most 1.9×10^{-24}. At $\alpha = 25$ and $R = 100$, the corresponding error is less than 1.7×10^{-16}.

The integral (A10) may be represented by a hypergeometric function [29]:

$$I^0_{R,K} \approx \frac{\sqrt{\pi}\, c^R \Gamma(R+K+1)}{2^{R+1}\alpha^{R+K+1}\Gamma(R+3/2)}\, {}_2F_1\left(\frac{R+K+1}{2}, \frac{R+K+2}{2}; R+3/2; -(c/\alpha)^2\right).$$

$$(A11)$$

The circle of convergence for (A11) only holds for $c \leqslant \alpha$, and, moreover, the series is divergent for $K > 0$ and only conditionally convergent for $K = 0$. By analytic continuation we can get (A11) into a unit circle for all c. Since the difference of the numerator terms in ${}_2F_1$ of (A11) is $1/2$, we may use one of Kummer's quadratic transformations. From the relation [30]

$$(1+x)^{2a}\, {}_2F_1(2a, 2a+1-c; c; x) = {}_2F_1(a, a+1/2; c; 4x(1+x)^{-2}),$$

(A11) becomes

$$I^0_{R,K} \approx \frac{\sqrt{\pi}\, c^R \Gamma(R+K+1)\, 2^K}{\beta^{R+K+1}\Gamma(R+3/2)}\, {}_2F_1(R+K+1, K+1/2; R+3/2; -(c/\beta)^2),$$

$$(A12)$$

where $\beta = \alpha + \sqrt{\alpha^2 + c^2}$. The circle of convergence for (A12) holds for all c, but ${}_2F_1$ is divergent for $K > 0$. Again, by analytic continuation we transform (A12) by the linear transformation [30]

$${}_2F_1(a, b; c; x) = (1-x)^{-b}\, {}_2F_1(b, c-a; c; x(x-1)^{-1})$$

to the computationally useful relation

$$I^0_{R,K} \approx \frac{\sqrt{\pi/2}\, c^R \Gamma(R+K+1)}{\beta^{R+1/2}\gamma^{K+1/2}\Gamma(R+3/2)}\, {}_2F_1(K+1/2, -K+1/2; R+3/2; c^2/(2\beta\gamma)),$$

$$(A13)$$

where β is defined in (A12) and $\gamma = \sqrt{\alpha^2 + c^2}$.

The argument in ${}_2F_1$ of (A13) is between 0 and $1/2$ for $0 \leqslant c \leqslant \infty$. The series is now absolutely convergent for all $K \geqslant 0$. Recall that (A11)–(A13) are approximations to $I^0_{R,K}$ at large R. In practice we choose R such that the relative error is at least less than 1×10^{-10}. Typically five to seven terms in ${}_2F_1$ of (A13) are needed for convergence to ten place accuracy. For $M \neq 0$ and R large, the binomial expansion,

$$I^M_{R,K} = \sum_{P=0}^{M} (-1)^P \binom{M}{P} I^0_{R,K+2(M-P)}$$

$$(A14)$$

may be used for constructing a border array in K at constant M and R, where (A13) is used to evaluate $I^0_{R,K+2(M-P)}$. Roundoff in (A14) is not severe provided M is not too large. In practice, M is less than 10. Once a border array in K at large R has been constructed by (A13) or (A14), then (A6) and (A6′) give a second border in R at $K = -M$. The rest of the table is filled in for constant M by

$$I^M_{R-1,K} = (\alpha/c)\, I^M_{R,K} + (R - K + 1)\, I^M_{R,K-1}/c - y_R \tag{A15}$$

and

$$I^M_{R,K} = (\alpha/c)^{-1}(y_R - I^M_{R+1,K}) + (R + K)\, I^M_{R,K-1}/\alpha. \tag{A16}$$

y_R is defined in (A5) above. (A15) applies when $\alpha/c < 1$ and (A16) is stable for $\alpha/c > 1$, whereby a downward recursion on R, with K stepped up one each time, is executed. A suitable table of y_R entries is retrieved from a previous calculation of $I^{M-1}_{R,K}$ except at $M = 0$, where a vector of elements $e^{-x}j_R(c)/c$ is first computed. Thus one must start the table of integrals at $M = 0$ and work up to the desired value of M. For the two-center Fourier transforms of interest M varies least, so that one loses very little time with this procedure.

Tables of $I^M_{R,K}(\alpha, c)$ have been computed for $2 < \alpha < 25$, $0 \leqslant c \leqslant 25$, $0 \leqslant k \leqslant 14$, $0 \leqslant r \leqslant 100$, and $0 \leqslant M \leqslant 10$ by means of (A13), (A14), (A15) and (A16). The entries were spot-checked by both three-term recursion relations (A3) and

$$I^M_{R-1,K} + I^M_{R+1,K} = (2R + 1)\, I^M_{R,K-1}, \tag{A17}$$

where (A17) follows from (A1). Agreement was always within two integers in the least significant decimal place of the machine word (about 8 decimal places for the Univac 1108). A third relation

$$I^M_{R,K} + I^{M-1}_{R,K} = I^{M-1}_{R,K+2} \tag{A18}$$

was used to check the entries among the M levels. The agreement in this case was comparable to the other checks. Also, certain elementary integrals, such as $I^0_{0,1}(\alpha, c)$, were explicitly evaluated and found to agree with the tables to within the accuracy of the machine word.

APPENDIX II: ESTIMATE OF TERMS FOR CONVERGENCE OF $\sum'^\infty_{r=0,1} a^{m,n}_r(c)$

We desire a value of p such that $|a_{n-m+p}/a_{n-m}| \leqslant 10^{-q}$. The ratio a_{n-m+p}/a_{n-m} may be expanded

$$\frac{a_{n-m+p}}{a_{n-m}} = \frac{a_{n-m+p}}{a_{n-m+p-2}} \cdot \frac{a_{n-m+p-2}}{a_{n-m+p-4}} \cdots \frac{a_{n-m+2}}{a_{n-m}} = \gamma_{n-m+p}\; {}_2\gamma_{n-m+p-4} \cdots \gamma_{n-m}\,.$$

The asymptotic behavior of γ_r is given by [20]

$$\lim_{r\to\infty} \gamma_r = (c/2r)^2$$

If we apply this relationship to the nonasymptotic region around $r = n - m$, we get

$$a_{n-m+p}/a_{n-m} \approx (c/2)^p [(n - m + p - 2)^2 (n - m + p - 4)^2 \cdots (n - m)^2]^{-1}.$$

We may approximate the term in square brackets by $(n - m + p/2)^p$ and write

$$(c/(2n - 2m + p))^p \sim 10^{-q},$$

the logarithm of which is Eq. (16) of the text. It is noted that this expression is more useful for determining computer program storage requirements and reasonable input parameters than for actual computation. Because of the application of the asymptotic relationship to the nonasymptotic region, $p \leqslant r_t - (n - M)$. The inequality seldom amounts to more than 10, that is, 5 additional terms in the summation.

ACKNOWLEDGMENTS

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