

On Radial Weighting Effects in Gaussian Expansions of Self-Consistent Field Atomic Orbitals*

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Gaussian expansions of the SCF functions for the first row atoms, boron through fluorine, in ground and low-lying electronic states have been generated under a wide range of radial weighting conditions by a full least-squares procedure. Typical results are presented and the quality of the wavefunctions obtained are analyzed in terms of regional electron densities and a variety of expectation values including energies. A novel method for recursive evaluation of repeated integrals of the error function, $F_1(\alpha, \zeta)$, is adopted and analyzed. These integrals are central quantities in the least-squares procedure employed.

Engendrement de représentations gaussiennes des fonctions SCF pour les atomes de la première ligne, du bore au fluor, dans les états électroniques fondamentaux et faiblement excités, avec un large éventail de conditions de pondération radiale obtenues par une procédure de moindres carrés. Des résultats typiques sont présentés et les qualités des fonctions d'onde obtenues sont analysées en fonction des densités électroniques par régions et de différentes valeurs moyennes dont les énergies. Adoption et analyse d'une nouvelle méthode pour l'évaluation récursive d'intégrales répétées de la fonction d'erreur $F_1(\alpha, \zeta)$. Ces intégrales sont des quantités centrales dans les procédures de moindres carrés utilisées.

Entwicklungen nach Gaußfunktionen für SCF-Funktionen von Elementen der ersten Reihe (Bor bis Fluor) wurden für den Grundzustand und niedrige angeregte Zustände einer Methode der kleinsten Quadrate berechnet, wobei eine Reihe von radialen Gewichtungsfaktoren benutzt wurden. Einige typische Ergebnisse werden mitgeteilt und die Qualität der erhaltenen Wellenfunktion wird mit Hilfe von regionalen Elektronendichten und einer Reihe von Erwartungswerten sowie der Energie geprüft. Eine neue Methode für die rekursive Auswertung der mehrfachen Integrale der Fehlerfunktion $F_1(\alpha, \zeta)$ wird angewendet und analysiert. Diese Integrale sind von zentraler Bedeutung in der benutzten Methode der kleinsten Quadrate.

Introduction

Gaussian-type orbital (GTO) sets have recently supplanted minimal Slater-type atomic orbital (STO) sets as routine basis function choices in linear combination of atomic orbitals-molecular orbital (LCAO MO) calculations, principally because of differences in efficiency of calculation of two-electron integrals. Nevertheless, the extensive body of results obtained with the minimal STO bases have been, and continue to be of much use as benchmarks for calculations with GTO sets. Extrinsicly, comparisons of goodness, usually in the sense of energy, are made of the LCAO MO SCF functions constructed from the alternative atomic functions [1]. More directly, considerable effort has been spent in obtaining accurate analytical GTO expansions of the STO's and optimized SCF STO atom

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ground state functions, with the purpose of simultaneously realizing the advantages of both types of functions in future calculations [2].

In a recent paper [3], the optimization method of least-squares fitting of GTO sums to $1s$, $2s$ and $2p$ STO's was reexamined, and the conclusion was drawn that radial weighting in the fitting procedure was potentially useful, depending upon the intended application of the expansion function. In this paper further examination is made of the effects of weighting on AO representations. Specifically, modest size expansions of Clementi's SCF atomic functions [4] for first row atoms are generated under a wide range of radial weighting constraints, and various expectation values, regional electron densities and energies are computed. These are compared to those obtained from the SCF STO functions directly, and from GTO functions obtained by other expedients (i.e., direct energy minimization). Certain generalizations concerning these comparisons are discussed, as are their implications with regards to fitting of functions obtained from other sources, e.g., empirically, from experimental determination of electron densities by particle or photon scattering.

Expansion Methods

The least-squares error functions for the SCF STO AO expansions weighted by r^n and subject to explicit normalization are defined as,

$$\begin{aligned} \varepsilon_n &= \int (\psi - \psi'_n)^2 r^n d\tau + \lambda_n (1 - \int (\psi'_n)^2 d\tau) \\ &= \iiint (\psi - \psi'_n)^2 r^{n+2} dr \sin\theta d\theta d\phi + \lambda_n (1 - \iiint (\psi'_n)^2 r^2 dr \sin\theta d\theta d\phi), \end{aligned} \quad (1)$$

where,

$$\psi_k = \sum_j a_{jk} \phi_j, \quad (2)$$

and ϕ_k and a_{jk} are, here, respectively the STO's and combination coefficients for the ground state SCF AO's of the first row atoms [4]. The functions ψ'_n are,

$$\begin{aligned} \psi'_{ms,n} &= \sum_j d_{ms,n,k} \left(\frac{2\alpha_{ms,n,k}}{\pi} \right)^{3/4} \exp(-\alpha_{ms,n,k} \cdot r^2) \\ \psi'_{2p,n} &= \sum_j d_{2p,n,k} \left(\frac{128\alpha_{2p,n,k}^5}{\pi^3} \right)^{1/4} \cos\theta r \exp(-\alpha_{2p,n,k} \cdot r^2). \end{aligned} \quad (3)$$

Note, the $2s$ SCF AO's are expanded in terms of $1s$ -type GTO's and no interorbital constraints are placed on the exponents.

Eqs. (1-3) are identical in their origins and representation to those derived and used in Ref. [3], with the important exception that the functions to be expanded correspond closely to real atom states at or near the Hartree Fock level. Solution of these equations, i.e., minimization of ε_n at any expansion level as a function of the α and d parameters is accomplished in the same way as in Ref. [3] with the following noteworthy difference.

The STO- and GTO-containing integrals of the form,

$$\int_0^\infty r^l \exp(-\alpha r^2 - \zeta_{\text{STO}} r) dr, \quad (4)$$

lead in the course of evaluation to repeated integrals of the error function, $i^l \operatorname{erfc} Z$, where Z is $\zeta_{\text{STO}}/2\alpha^{1/2}$. Unlike the previous study, where unit exponent STO's limited the Z -range to less than 2.7, integrals with large Z are encountered here. Details of the novel method adopted for computation of these integrals, based on a recursive technique due to Gautschi [5], are presented in the Appendix. It is a matter of some interest that this technique, based on second-order difference equation solution methods, simultaneously generates all integrals (l , from zero to l_{max}) to controllable accuracy without recourse to Gauss-Laguerre quadrature procedures, an expedient followed by all other investigators of the least-squares GTO expansion problems cited.

Other procedural differences, as regards Ref. [3], of a more mechanical nature, include routine variation of initial choice of the Lagrangian multiplier, λ , to facilitate convergence of the least-squares method, and geometric mean extrapolation of parameters based on residuals of previous cycles when divergence in the iterative procedure is encountered. In many cases, especially for the $2s$ SCF expansions, initial guesses of λ (as well as of the α and d values) guided by converged results of neighboring weighted cases often speeded convergence. Where instability after several cycles led to divergence in the least-squares procedure, it was often found useful to adjust new initial guesses of the parameters by assuming proportionality of changes in these parameters with the changes in residuals, $\varepsilon'_{n,j}(P^0)$, see Ref. [3], Eq. (5), and then extrapolating by assuming a geometric mean relationship [6].

Expansion Results, Radial Densities and Simple Expectation Values

Tables 1–3 list the three-, four- and five-term GTO expansion coefficients and exponents for the $1s$, $2s$ and $2p$ SCF functions for $N(^4S)$, and, as well, various fitting measures, electron densities at arbitrarily chosen values of r and r -dependent expectation values. The results are typical for all the first row atoms in various electronic states examined; similar compilations for boron through fluorine and the unit-zeta STO functions are available from the author on request. The radial weighting factor range is from r^{-2} , stressing the region close to the nucleus, to r^3 , stressing regions rather far away. The fitting measures EPSBAR ($\bar{\varepsilon}_n$) and $1 - S_n$ are defined in the footnotes, and are as in Ref. [3]. In all cases, for the square matrix of second derivatives over the coefficient and exponent parameters, the eigenvalues were positive, indicating a minimum in ε_n .

Most of the effects of weighting upon parameter sizes, measures of fitting, etc., noted for STO functions [3] are also observed for the SCF atomic functions. Important new details and differences, beyond the obvious scaling effects to be expected, are as follows.

In general, the $\bar{\varepsilon}_n$ -values ($\varepsilon_n/\langle r^n \rangle$) at any level of expansion are larger for the SCF than the STO functions, being most noticeably so for the $2s$ functions and only somewhat less apparent for the $2p$ functions. The magnitude of the effect varies with the weighting constraint. It is also apparent when all the first row atomic state results are examined, that for the unweighted and positively weighted expansions, the fitting for all orbitals worsens proceeding from B to F. For the

TABLE 1. COEFFICIENTS AND EXPONENTS FOR THE WEIGHTED GAUSSIAN EXPANSIONS OF THE 1S SCF FUNCTION OF NITROGEN (4S)

N	<R**(N)>	3-TERM			4-TERM			5-TERM		
		EXPONENT	COEFFICIENT	EPSBAR 1-S	EXPONENT	COEFFICIENT	EPSBAR 1-S	EXPONENT	COEFFICIENT	EPSBAR 1-S
-2	8.98382(1)	7.88582(0)	7.72716(-1)	3.99(-4)	5.99862(0)	6.13645(-1)	7.21(-5)	4.86622(0)	4.77725(-1)	1.55(-5)
		4.97109(1)	3.23759(-1)	2.51(-3)	2.76279(1)	4.36106(-1)	5.62(-4)	1.85416(1)	4.75051(-1)	1.40(-4)
		6.04124(2)	2.89357(-2)		1.68421(2)	8.50804(-2)		8.25284(1)	1.50714(-1)	
					2.04385(3)	6.41456(-3)		5.00458(2)	2.30491(-2)	
								6.07618(3)	1.65101(-3)	
-1	6.65337(0)	5.69298(0)	5.87965(-1)	4.38(-4)	4.38314(0)	4.14577(-1)	6.92(-5)	3.56478(0)	2.87178(-1)	1.31(-5)
		2.64691(1)	4.67380(-1)	4.87(-4)	1.99546(1)	5.26375(-1)	7.75(-5)	1.11768(1)	5.22457(-1)	1.08(-5)
		1.97021(2)	8.70547(-2)		7.11096(1)	1.82518(-1)		3.90394(1)	2.66602(-1)	
					5.24366(2)	2.67542(-2)		1.71745(2)	6.76736(-2)	
								1.26394(3)	9.04879(-3)	
0	1.00001(0)	4.44010(0)	4.29160(-1)	4.29(-4)	3.42381(0)	2.67792(-1)	6.25(-5)	2.73840(0)	1.60076(-1)	1.13(-5)
		1.71175(1)	5.45580(-1)	2.08(-4)	1.07712(1)	5.35310(-1)	2.48(-5)	7.64880(0)	4.72913(-1)	-8.00(-7)
		2.64691(1)	4.67380(-1)	4.87(-4)	3.96101(1)	2.82570(-1)		2.29538(1)	3.60654(-1)	
		9.55731(1)	1.67753(-1)		2.17669(2)	6.48332(-2)		8.29242(1)	1.32797(-1)	
								4.53391(2)	2.67714(-2)	
1	2.28302(-1)	3.62787(0)	3.05414(-1)	4.38(-4)	2.74418(0)	1.63008(-1)	6.28(-5)	2.06450(0)	7.48492(-2)	1.20(-5)
		1.23350(1)	5.69958(-1)	4.25(-4)	7.85968(0)	4.93568(-1)	7.19(-5)	5.47042(0)	3.80382(-1)	1.12(-5)
		5.72238(1)	2.58308(-1)		2.53604(1)	3.68976(-1)		1.48118(1)	4.22452(-1)	
					1.14873(2)	1.20025(-1)		4.68277(1)	2.13515(-1)	
								2.10039(2)	5.92709(-2)	
2	7.02696(-2)	3.06638(0)	2.16289(-1)	5.29(-4)	2.19274(0)	9.03797(-2)	8.13(-5)	1.36495(0)	2.27194(-2)	1.68(-5)
		9.62828(0)	5.59630(-1)	1.04(-3)	5.99543(0)	4.24331(-1)	2.58(-4)	3.88416(0)	2.59165(-1)	8.13(-5)
		4.02135(1)	3.47131(-1)		1.77473(1)	4.33929(-1)		9.86467(0)	4.44237(-1)	
					7.16953(1)	1.89398(-1)		2.85506(1)	3.06079(-1)	
								1.13384(2)	1.12746(-1)	
3	2.73167(-2)	2.62394(0)	1.49869(-1)	7.64(-4)	1.64988(0)	3.99585(-2)	1.37(-4)	7.83121(-1)	5.42533(-3)	2.47(-5)
		7.83949(0)	5.30091(-1)	2.04(-3)	4.59961(0)	3.35609(-1)	6.93(-4)	2.87082(0)	1.50100(-1)	2.82(-4)
		3.08233(1)	4.32203(-1)		1.28887(1)	4.78411(-1)		7.01450(0)	4.12843(-1)	
					4.88465(1)	2.74635(-1)		1.91351(1)	3.85407(-1)	
								7.10199(1)	1.83708(-1)	

SIX SIGNIFICANT FIGURES ARE TABULATED FOR EACH GAUSSIAN PARAMETER. THE APPROPRIATE POWER OF 10 IS ENCLOSED IN PARENTHESES TO THE RIGHT OF EACH ENTRY. THE RADIAL WEIGHTING FACTOR IS N, AND <R**(N)> IS THE EXPECTATION VALUE FOR THE OPERATOR (R**(N)) COMPUTED WITH THE SCF ORBITAL. EPSBAR IS EPS/<R**(N)> AND S IS THE OVERLAP BETWEEN THE SCF AND GAUSSIAN ORBITALS.

R	EXP FUNCT	DENSITY ON A PER ELECTRON BASIS AT R (AU)					
		-2	-1	0	1	2	3
0.00000	1234.16339	1116.20669	949.91706	776.81486	629.21973	528.97967	455.37710
		1169.35479	1055.46889	917.99024	776.78562	664.78233	568.91688
		1196.37278	1117.45927	1009.77163	884.43033	760.68018	659.70878
.05000	615.69619	600.20278	643.25810	604.98855	527.53887	460.81327	406.15536
		618.58061	614.49711	630.60528	599.44470	546.42734	487.81260
		616.12451	612.02324	620.08299	622.82231	590.95123	540.99606
.25000	41.60249	39.65416	41.87042	42.57917	40.71671	41.13448	43.39296
		41.85654	41.75558	41.27466	42.09995	41.51158	41.08063
		42.05367	41.42338	41.73716	41.45921	41.88580	41.44905
.50000	1.61854	1.63681	1.78886	1.57158	1.56979	1.65133	1.67820
		1.79480	1.58080	1.60887	1.64153	1.60673	1.60882
		1.63823	1.60320	1.63042	1.60963	1.62718	1.61378
1.00000	.00316	.00001	.00034	.00153	.00291	.00354	.00349
		.00022	.00157	.00310	.00345	.00315	.00303
		.00093	.00285	.00340	.00311	.00315	.00321

N	EXP FUNCT	EXPECTATION VALUES OF R**(N)					
		-2	-1	0	1	2	3
-2	89.83820	89.87843	87.33057	81.80216	74.79007	68.83779	63.72851
		89.84806	88.87443	84.10030	81.50379	76.47529	71.26242
		89.84081	89.43328	87.98457	84.98210	80.71268	76.00664
-1	6.65337	6.67284	6.65061	6.57122	6.41663	6.25305	6.08820
		6.65753	6.65289	6.62807	6.55694	6.45384	6.32220
		6.65438	6.65324	6.64466	6.61053	6.54145	6.44335
0	1.00001	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
		1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
		1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
1	.22830	.22449	.22758	.22835	.22939	.23077	.23265
		.22724	.22815	.22830	.22858	.22910	.23004
		.22798	.22826	.22830	.22839	.22863	.22911
2	.07027	.06583	.06929	.07013	.07052	.07086	.07134
		.06880	.07004	.07024	.07033	.07044	.07064
		.06976	.07021	.07026	.07029	.07033	.07042
3	.02732	.02323	.02617	.02706	.02734	.02745	.02755
		.02571	.02700	.02726	.02732	.02735	.02739
		.02668	.02722	.02730	.02732	.02733	.02735
4	.01288	.00936	.01163	.01251	.01280	.01289	.01292
		.01124	.01246	.01278	.01286	.01288	.01289
		.01213	.01273	.01285	.01287	.01288	.01288

IN SUB-ROW ORDER, FOR THE 3-, 4- AND 5-TERM EXPANSIONS, OBTAINED WITH THE WEIGHTING SPECIFIED BY COLUMN HEADING.

negatively weighted expansions, $\bar{\epsilon}_n$ remains fairly constant across this span, and, in fact, decreases slightly for the $1s$ orbitals. These variations of $\bar{\epsilon}_n$ appear to reflect how the various STO contributions to the SCF functions modify smooth (single term) exponential behavior and produce nodes in the various regions of space stressed, above and beyond the normalization afforded by $\langle r^n \rangle$. (Contrast these expectation values for STO's and SCF AO's of $N(^4S)$, Tables 1–3).

The related phenomenon of distinct local minima observed for the $2s$ STO functions at or near the crossover point (in coefficient sign, as related to variation in weighting) is also encountered with the SCF expansions. The crossover points are of course different, see Table 2, here and in Ref. [3]: for the single STO expansions, the $1s$ GTO's must approximate a node at the nucleus, where for the SCF atom functions $1s$ and $2s$ STO contributions produce the node away from the nucleus and otherwise generate quite different looking AO functions.

Electron density at the nucleus comparisons with the STO functions previously reported may also be drawn. Table 4 of Ref. [3],¹ reveals the similarity of the $1s$ functions near the nucleus and how they are approximated by GTO's, and at the same time the gross differences between the STO and SCF $2s$ functions. Scaling by ζ^3 of the leading term, (for $N(^4S)$ ζ equals 6.46), reasonably matches the densities for the $1s$ AO exponential type functions. The GTO expansions for the STO and SCF functions both quite reasonably improve going from positive to negative power r -weighting, the SCF function expansion improving faster. For the $2s$ AO's, of course, the density at the nucleus is zero for the Slater function, and finite for the SCF function, due solely to the small but significant $1s$ contributions in the SCF function. Hence, the comparisons cannot be the same as for the $1s$ AO's, but once again the important effects of weighting can be noted. As with the STO expansions, appropriate weighting can do more at these expansion levels for matching of properties than the addition of extra terms. As well, around the coefficient crossover points, the expansions with more negative terms better approximate the density at the nucleus.

Electron densities computed for other regions and expectation values of r^n also indicate the utility of weighting in determining GTO expansions. In general, the best densities for a particular region and the best approximation to an expectation value stressing this region will be computed with expansions generated under heavy weighting of this region. For finite, non-zero r , however, the density effects are not as clear-cut, becoming less distinct at large distances, and particularly so for the non-monotonic functions, $2s$ and $2p$. Also, for $\langle r^n \rangle$, with large n , the distinctions among the variously weighted expansions fade.

Energy Comparisons

Perhaps of the most direct, although by no means exclusive interest in the context described, are the energies associated with the GTO expansions obtained under the various weighting constraints. Table 4 presents the total and kinetic energies for the $N(^4S)$ state expansions, along with the Hartree-Fock values and

¹ Angular variable θ and ϕ integrations have *not* been included in this table (multiply all values by 4π). This deficiency has been kindly pointed out by Dr. B. Tsapline of Karlsruhe University.

those obtained by direct energy optimization of GTO expansions of the same length [7].

The most immediate and striking observation, verified to be general for all the first row atoms in all states examined, is that *the r^{-1} -weighted expansions yield significantly better total energies than the unweighted expansions*. Functions generated under other weighting constraints are generally poorer. Of almost equal significance is the fact that the better 2s expansions (by $\bar{\epsilon}_n$ criteria) are often poorer as regards total energy. In general, over all cases examined and independent of the level of expansion, around the coefficient crossover points, the better energy is associated with the expansion having the greater number of subtractive, highly contracted GTO terms.

Both of these observations, pertinent to the general issue of function expansion may be further examined and rationalized as follows. Of the components of total energy, the potential energy term is expected, and found to be most satisfactorily represented by r^{-1} -weighted expansion because its integrals have forms resembling $\langle r^{-1} \rangle$. The kinetic energy components are more complicated, the requisite Laplacians on GTO's leading to multiple-term, internally cancelling expectation values of powers of (αr) . For the weighting variations considered, the potential energy dominates, and hence the best integral power for weighting is -1 . That the 2s function with the maximum of subtractive, contracted GTO

TABLE 2. COEFFICIENTS AND EXPONENTS FOR THE WEIGHTED GAUSSIAN EXPANSIONS OF THE 2S SCF FUNCTION OF NITROGEN (4S)

N	⟨R**⟨N⟩⟩	3-TERM			4-TERM			5-TERM		
		EXPONENT	COEFFICIENT	EPSBAR 1-S	EXPONENT	COEFFICIENT	EPSBAR 1-S	EXPONENT	COEFFICIENT	EPSBAR 1-S
-2	4.75310(0)	3.82754(-1)	1.01347(0)	2.37(-3)	4.02135(-1)	1.02211(0)	5.69(-4)C	1.65258(-1)	3.60548(-1)	2.80(-4)
		1.31110(1)	-2.64741(-1)	5.08(-3)	1.02697(1)	-2.50379(-1)	5.74(-3)	5.44351(-1)	7.24040(-1)	1.41(-4)
		1.62590(2)	-3.16940(-2)		6.50747(1)	-5.78860(-2)		9.21116(0)	-2.57518(-1)	
					7.92167(2)	-4.59717(-3)		5.72308(1)	-6.6496(-2)	
								6.95377(2)	-5.39844(-3)	
-1	1.07819(0)	3.89236(-1)	1.01859(0)	4.12(-3)A	1.79691(-1)	4.07253(-1)	8.05(-4)D	1.96147(-1)	4.73270(-1)	9.57(-5)
		1.11044(1)	-2.53651(-1)	5.15(-3)	5.71513(-1)	6.78572(-1)	1.38(-4)	6.29242(-1)	6.26294(-1)	4.13(-5)
		8.76997(1)	-5.09704(-2)		9.29198(0)	-2.66240(-1)		7.34492(1)	-2.36695(-1)	
					7.08530(1)	-6.46615(-2)		3.33869(1)	-9.5470(-2)	
								2.47509(2)	-1.48764(-2)	
0	1.00002(0)	1.73192(-1)	3.78854(-1)	2.13(-3)B	1.90151(-1)	4.50926(-1)	1.81(-4)	1.92816(-1)	4.62512(-1)	9.60(-5)G
		5.44760(-1)	6.96758(-1)	1.05(-3)	6.10295(-1)	6.45284(-1)	7.92(-5)	6.22840(-1)	6.37994(-1)	3.69(-5)
		1.18523(1)	-2.95026(-1)		7.89770(0)	-2.49889(-1)		7.03189(0)	-2.23924(-1)	
					4.52898(1)	-1.8.85441(-2)		2.75775(1)	-1.00831(-1)	
								1.54073(2)	-2.20602(-2)	
1	1.33225(0)	1.80833(-1)	4.13056(-1)	5.17(-4)	1.84215(-1)	4.28253(-1)	2.39(-4)E	1.21878(-1)	1.42540(-1)	1.81(-5)H
		5.76340(-1)	6.76175(-1)	1.35(-3)	5.92891(-1)	6.66147(-1)	9.49(-5)	2.92660(-1)	5.13280(-1)	8.51(-5)
		1.00594(1)	-2.90570(-1)		7.82239(0)	-2.40369(-1)		7.51186(-1)	4.58358(-1)	
					3.90451(1)	-9.29427(-2)		6.59701(0)	-2.32410(-1)	
								3.08203(1)	-1.15335(-1)	
2	2.14890(0)	1.74831(-1)	3.88736(-1)	5.41(-4)	1.15469(-1)	1.19247(-1)	8.39(-5)F	1.20256(-1)	1.37125(-1)	1.03(-5)
		5.58362(-1)	6.97405(-1)	1.29(-3)	2.72352(-1)	4.92297(-1)	1.97(-3)	2.88565(-1)	5.14626(-1)	1.25(-4)
		1.02800(1)	-2.89712(-1)		7.05962(-1)	4.96849(-1)		7.50395(-1)	4.63538(-1)	
					8.78069(0)	-2.91647(-1)		6.34569(0)	-2.21649(-1)	
								2.70469(1)	-1.25350(-1)	
3	4.09116(0)	1.64841(-1)	3.44442(-1)	9.09(-4)	1.14477(-1)	1.16288(-1)	3.83(-5)	1.15684(-1)	1.20736(-1)	1.92(-5)
		5.18324(-1)	7.21379(-1)	1.75(-3)	2.71001(-1)	4.94184(-1)	1.86(-3)	2.75324(-1)	5.01412(-1)	1.01(-4)
		1.25744(1)	-3.25956(-1)		7.07767(-1)	4.97966(-1)		7.21287(-1)	4.88333(-1)	
					8.83701(0)	-2.96521(-1)		6.65533(0)	-2.25594(-1)	
								2.90716(1)	-1.21417(-1)	

SIX SIGNIFICANT FIGURES ARE TABULATED FOR EACH GAUSSIAN PARAMETER. THE APPROPRIATE POWER OF 10 IS ENCLOSED IN PARENTHESES TO THE RIGHT OF EACH ENTRY. THE RADIAL WEIGHTING FACTOR IS N, AND <R**⟨N⟩⟩ IS THE EXPECTATION VALUE FOR THE OPERATOR (R**⟨N⟩) COMPUTED WITH THE SCF ORBITAL. EPSBAR IS EPS/<R**⟨N⟩⟩ AND 1-S IS THE OVERLAP BETWEEN THE SCF AND GAUSSIAN ORBITALS.

- A) THE 2 POSITIVE, 1 NEGATIVE COEFFICIENT SET HAS EPSBAR(-1)= 1.21(-2) AND 1-S(-1)= 2.03(-3).
 B) THE 1 POSITIVE, 2 NEGATIVE COEFFICIENT SET HAS EPSBAR(0)= 9.52(-3) AND 1-S(0)= 4.75(-3).
 C) THE 2 POSITIVE, 2 NEGATIVE COEFFICIENT SET HAS EPSBAR(-2)= 2.23(-3) AND 1-S(-2)= 1.18(-3).
 D) THE 1 POSITIVE, 3 NEGATIVE COEFFICIENT SET HAS EPSBAR(-1)= 3.73(-3) AND 1-S(-1)= 5.21(-3).
 E) THE 3 POSITIVE, 1 NEGATIVE COEFFICIENT SET HAS EPSBAR(1)= 3.64(-4) AND 1-S(1)= 1.46(-3).
 F) THE 2 POSITIVE, 2 NEGATIVE COEFFICIENT SET HAS EPSBAR(2)= 4.96(-4) AND 1-S(2)= 1.82(-4).
 G) THE 3 POSITIVE, 2 NEGATIVE COEFFICIENT SET HAS EPSBAR(0)= 1.16(-4) AND 1-S(0)= 4.70(-5).
 H) THE 2 POSITIVE, 3 NEGATIVE COEFFICIENT SET HAS EPSBAR(1)= 2.33(-4) AND 1-S(1)= 4.58(-5).

TABLE 2 (continued)

R	EXP FUNCT	DENSITY ON A PER ELECTRON BASIS AT R (AU)					
		GAUSS FUNCT (WTS)					
		-2	-1	0	1	2	3
0.00000	59.92522	49.11954	39.94979	11.47949	7.43765	7.83172	17.31054
		54.90787	37.93398	29.44905	25.67388	5.12195	5.48563
		48.97632	50.28875		6.88615	37.19627	193.59472
		54.57808	47.51670	41.93715	22.13934	19.96362	22.04056
				28.76381	41.85230		
.05000	29.16707	31.84731	30.12376	10.56742	6.89578	7.25550	15.93565
		28.31609	29.49361	24.52540	21.83365	4.76813	5.10893
		31.92486	29.38495		6.39460	30.40052	113.53231
		28.32680	30.20836	29.72264	19.23003	17.55119	19.26003
				24.09020	29.74827		
.25000	.47997	.66340	.52578	.87776	.69742	.71997	1.45275
			.77184	.52130			
		.48397	.46556	.40791	.44242	.52680	.58205
		.67007	.47336		.67676	.44653	.53057
			.48780	.46927	.92524	.52677	
			.40339	.47950			
.50000	.75919	.91870	.82408	.94910	.84573	.85083	.91568
			1.05982	.81377			
		.81154	.80567	.75044	.75507	.78839	.78545
		.92965	.79289		.83288	.78008	.82258
			.75150	.73735	.74835	.74756	
			.74158	.75847			
1.00000	.79109	.72204	.73826	.74556	.76802	.76383	.72917
			.69933	.70358			
		.76062	.76258	.77713	.77518	.78666	.78477
		.71810	.74346		.77304	.75964	.72609
			.78222	.78816	.78896	.78480	
			.78025	.77933			
		EXPECTATION VALUES OF R ⁿ n					
		GAUSS FUNCT (WTS)					
		-2	-1	0	1	2	3
-2	4.75310	4.74692	4.48141	2.58304	2.02957	2.08231	3.42481
			3.53947	4.32459			
		4.75633	4.43046	3.99005	3.73260	1.69745	1.75605
		4.74359	4.68636		1.95725	4.64620	13.19169
			4.50141	3.47836	3.31360	3.51512	
			3.95284	4.51182			
-1	1.07619	1.08166	1.07626	1.01436	.97117	.97442	1.07803
			1.06968	1.05996			
		1.08484	1.07762	1.06640	1.05692	.94559	.95088
		1.07682	1.07656		.96661	1.09859	1.37110
			1.07591	1.04782	1.04184	1.05293	
			1.07811	1.06566	1.07671		
0	1.00002	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
			1.00000	1.00000			
		1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
		1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
			1.00000	1.00000	1.00000	1.00000	
1	1.33225	1.30899	1.30597	1.33359	1.33951	1.33986	1.32748
			1.33852	1.33482			
		1.28999	1.33250	1.33231	1.33350	1.34175	1.34032
		1.34167	1.30906		1.33935	1.33135	1.31976
			1.33226	1.33325	1.33331	1.33235	
			1.33229	1.33288			
2	2.14890	2.00525	1.98898	2.15217	2.15881	2.15985	2.14689
			2.17615	2.08412			
		1.93630	2.14974	2.14779	2.15060	2.16024	2.15729
		2.17785	1.98425		2.15651	2.14983	2.14043
			2.14746	2.15024	2.15011	2.14901	
			2.14905	2.14976			
3	4.09116	3.45733	3.40386	4.09714	4.10313	4.10560	4.09454
			4.16855	3.66115			
		3.26248	4.08865	4.08013	4.08870	4.10639	4.10059
		4.18758	3.38829		4.10731	4.09218	4.08779
			4.07824	4.09327	4.09277	4.09146	
			4.09167	4.08729			
4	9.06490	6.57107	6.41748	9.05694	9.05553	9.06942	9.06755
			9.32518	7.08892			
		6.05312	9.02674	8.98462	9.02207	9.08936	9.07750
		9.54070	8.37251		9.09662	9.04747	9.05862
			9.05817	9.06702	9.06702	9.06528	
			8.97434	9.01904			
			9.06625				

 IN SUB-ROW ORDER, FOR THE 3-, 4- AND 5-TERM EXPANSIONS, OBTAINED WITH THE WEIGHTING SPECIFIED BY COLUMN HEADING. WHERE ENTRIES APPEAR IN THE EVEN NUMBERED SUB-ROWS, THEY ARE FOR THE ALTERNATIVE, POORER FITTING EXPANSIONS.

terms is associated with the better energy, around the coefficient sign crossover point, is consistent with the observed energy advantage of the r^{-1} -weighted over the unweighted expansions. The greater the number of contracted GTO terms, the better fit are the functions in regions close to the nucleus, which are, of course, just the regions favored by r^{-1} weighting.

TABLE 3. COEFFICIENTS AND EXPONENTS FOR THE WEIGHTED GAUSSIAN EXPANSIONS OF THE 2P SCF FUNCTION OF NITROGEN (4S)

N	⟨R**N⟩	3-TERM			4-TERM			5-TERM		
		EXPONENT	COEFFICIENT	EPSBAR 1-S	EXPONENT	COEFFICIENT	EPSBAR 1-S	EXPONENT	COEFFICIENT	EPSBAR 1-S
-2	1.33630(0)	3.27889(-1)	6.97685(-1)	1.31(-3)	2.38190(-1)	5.24853(-1)	2.11(-4)	1.86634(-1)	3.86585(-1)	3.91(-5)
		1.68063(0)	4.38242(-1)	4.26(-3)	9.72339(-1)	5.14822(-1)	8.84(-4)	6.48961(-1)	5.19599(-1)	1.92(-4)
		1.09290(1)	6.89252(-2)		4.09944(0)	1.69143(-1)		2.23398(0)	2.65297(-1)	
					2.46140(1)	2.06549(-2)		8.87817(0)	6.20266(-2)	
								5.04176(1)	6.54723(-3)	
-1	9.57733(-1)	2.45460(-1)	5.50305(-1)	1.35(-3)	1.81998(-1)	3.77608(-1)	2.04(-4)	1.44820(-1)	2.55973(-1)	3.48(-5)
		1.08449(0)	5.31847(-1)	1.26(-3)	6.46487(-1)	5.38788(-1)	2.00(-4)	4.43955(-1)	4.92533(-1)	3.14(-5)
		5.80092(0)	1.42019(-1)		2.40114(0)	2.71245(-1)		1.39147(0)	3.55164(-1)	
					1.20705(1)	5.22089(-2)		4.81405(0)	1.21619(-1)	
								2.29914(1)	1.99759(-2)	
0	1.00001(0)	1.92197(-1)	4.15644(-1)	1.33(-3)	1.45557(-1)	2.61890(-1)	1.89(-4)	1.17733(-1)	1.65778(-1)	3.00(-5)
		7.46574(-1)	5.72017(-1)	6.60(-4)	4.61632(-1)	5.14008(-1)	8.95(-5)	3.28080(-1)	4.35619(-1)	9.70(-6)
		3.44669(0)	2.37401(-1)		1.56851(0)	3.60646(-1)		9.48360(-1)	4.05909(-1)	
					6.81282(0)	1.01930(-1)		2.95997(0)	1.93687(-1)	
								1.24142(1)	4.46204(-2)	
1	1.40925(0)	1.56631(-1)	3.05032(-1)	1.26(-3)	1.20700(-1)	1.78033(-1)	1.70(-4)	9.91595(-2)	1.06713(-1)	2.53(-5)
		5.49448(-1)	5.69184(-1)	1.17(-3)	3.50015(-1)	4.66984(-1)	1.92(-4)	2.56335(-1)	3.66731(-1)	3.03(-5)
		2.27451(0)	3.38579(-1)		1.10186(0)	4.21280(-1)		6.86158(-1)	4.22021(-1)	
					4.25268(0)	1.67483(-1)		1.99208(0)	2.65205(-1)	
								7.47105(0)	8.16175(-2)	
2	2.54464(0)	1.32839(-1)	2.24128(-1)	1.27(-3)	1.03460(-1)	1.21617(-1)	1.55(-4)	8.59592(-2)	6.92417(-2)	2.14(-5)
		4.26164(-1)	5.41770(-1)	2.68(-3)	2.79957(-1)	4.07957(-1)	5.79(-4)	2.08850(-1)	2.98341(-1)	1.27(-4)
		1.67092(0)	4.30157(-1)		8.23021(-1)	4.51898(-1)		5.22251(-1)	4.15097(-1)	
					2.93376(0)	2.41317(-1)		1.43495(0)	3.23443(-1)	
								4.92570(0)	1.29748(-1)	
3	5.66322(0)	1.16365(-1)	1.67568(-1)	1.34(-3)	9.12986(-2)	8.50560(-2)	1.49(-4)	7.64153(-2)	4.59839(-2)	1.89(-5)
		3.51553(-1)	5.04678(-1)	4.98(-3)	2.34047(-1)	3.50353(-1)	1.32(-3)	1.76304(-1)	2.39056(-1)	3.58(-4)
		1.33097(0)	5.07227(-1)		6.49666(-1)	4.61268(-1)		4.17533(-1)	3.95598(-1)	
					2.22002(0)	3.14111(-1)		1.09311(0)	3.62719(-1)	
								3.56154(0)	1.84504(-1)	

SIX SIGNIFICANT FIGURES ARE TABULATED FOR EACH GAUSSIAN PARAMETER. THE APPROPRIATE POWER OF 10 IS ENCLOSED IN PARENTHESES TO THE RIGHT OF EACH ENTRY. THE RADIAL WEIGHTING FACTOR IS N, AND ⟨R**N⟩ IS THE EXPECTATION VALUE FOR THE OPERATOR (R**N) COMPUTED WITH THE SCF ORBITAL. EPSBAR IS EPS/⟨R**N⟩ AND S IS THE OVERLAP BETWEEN THE SCF AND GAUSSIAN ORBITALS.

R	EXP FUNCT	DENSITY ON A PER ELECTRON BASIS AT R (AU)					
		GAUSS FUNCT (WTS)					
		-2	-1	0	1	2	3
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
		0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
		0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
.05000	.17352	.11752	.08026	.05141	.03255	.02205	.01613
		.14656	.11278	.08117	.05615	.03955	.02944
		.16386	.13753	.10799	.08084	.05976	.04558
.25000	1.29528	1.39354	1.25071	.94087	.65307	.46564	.35990
		1.29551	1.35242	1.23045	.98906	.76155	.59734
		1.27952	1.30982	1.32606	1.21256	1.02377	.84711
.50000	1.43654	1.35751	1.49445	1.54009	1.35244	1.11292	.91582
		1.46070	1.39905	1.46454	1.50771	1.42285	1.27899
		1.43176	1.44585	1.41640	1.45674	1.49265	1.45978
1.00000	.64276	.67170	.65416	.68014	.65586	.72192	.75507
		.63514	.64337	.65415	.63144	.63926	.67668
		.64471	.64277	.63990	.64874	.64044	.63755

N	EXP FUNCT	EXPECTATION VALUES OF R**N					
		GAUSS FUNCT (WTS)					
		-2	-1	0	1	2	3
-2	1.33630	1.33816	1.31517	1.25592	1.16397	1.07277	.99516
		1.33673	1.33033	1.30791	1.26027	1.19807	1.13669
		1.33640	1.33449	1.32592	1.30334	1.26601	1.22278
-1	.95773	.96158	.95734	.94754	.92709	.90254	.87653
		.95854	.95767	.95514	.94739	.93467	.92001
		.95791	.95772	.95703	.95423	.94825	.94003
0	1.00001	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
		1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
		1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
1	1.40925	1.38091	1.40168	1.40938	1.41728	1.42793	1.44096
		1.40156	1.40774	1.40926	1.41108	1.41451	1.41937
		1.40714	1.40893	1.40924	1.40969	1.41078	1.41258
2	2.54464	2.36253	2.48720	2.53379	2.55562	2.57376	2.59508
		2.48629	2.53138	2.54264	2.54718	2.55204	2.55641
		2.52641	2.54150	2.54424	2.54524	2.54664	2.54865
3	5.66322	4.73654	5.31094	5.56611	5.66264	5.70282	5.73292
		5.31091	5.56656	5.64276	5.66441	5.67348	5.68059
		5.53672	5.63706	5.65878	5.66371	5.66602	5.66797
4	15.07203	10.67765	13.07417	14.37391	14.91318	15.09518	15.16469
		13.10147	14.41828	14.89897	15.04335	15.08333	15.09591
		14.29839	14.86811	15.02943	15.06675	15.07593	15.07865

IN SUB-ROW ORDER, FOR THE 3-, 4- AND 5-TERM EXPANSIONS, OBTAINED WITH THE WEIGHTING SPECIFIED BY COLUMN HEADING.

Table 4. Energies for $N(4s)$ from the Weighted Gaussian Expansions of the SCF Functions^{a,b}

n	3-term	4-term	5-term
-2	-53.591496	-54.175475 (-54.114936)	-54.332092
	54.711468	54.261225 (54.360109)	54.261179
-1	-53.898145 (-53.621450)	-54.234054 (-54.244324)	-54.360021
	54.420081 (54.681354)	54.398677 (54.332928)	54.372410
0	-53.469122 (-53.688345)	-54.138958	-54.321897 (-54.260156)
	53.166807 (53.424447)	54.057232	54.295181 (54.224478)
1	-52.967555	-53.878588 (-53.662956)	-54.110339 (-54.199511)
	50.977425	53.129560 (52.538013)	53.673782 (53.910561)
2	-52.302572	-53.259828 (-53.470111)	-53.825663
	49.071870	51.206655 (52.258718)	52.825644
3	-51.525990	-52.685363	-53.426163
	47.645092	49.745718	51.807211

^aIn sub-row order, total energy and kinetic energy in hartrees. All AO (1s, 2s and 2p) expansions obtained with the same weighting, r^n . Parenthesized values are obtained using the alternative, poorer fitting (by ϵ_n criteria) 2s expansions.

^bThe Hartree-Fock energies are -54.400911 and 54.401562 [4]. The energy optimized 3-, 4- and 5-term expansions have total energies -54.062880, -54.319468 and -54.379474, respectively [7].

To pursue these matters further, r^{-1} -weighting improves the total energy (relative to the unweighted expansions) by from 56–66% of the improvement accomplished by freeing all the GTO parameters and energy optimizing them [7]. The larger the expansion, the greater the relative improvement. The absolute improvement (relative to the Hartree-Fock energy) accomplished by this weighting ranges from 30–48%, again being greater, the greater the expansion length. It is also of interest to note that regular, almost completely general progression trends exist for the GTO parameters themselves. The parameter values for the 1s and 2p orbital expansions obtained with r^{-1} weighting are fairly centrally

Table 5. Energies for $C(^3P)$ from the Mixed Weighted Gaussian Expansions of the SCF Functions^{a,b}

$n \backslash n_{1s}$	0	-1	-2
n_{2s}	-37.19357, 37.01441		
	-37.50473, 37.44806		
	-37.63294, 37.61454		
0	-37.20433, 37.07250	-37.33789, 37.60918	
	-37.50919, 37.46385	-37.56712, 37.59288	
	-37.63451, 37.61891	-37.65857, 37.64981	
	<i>-37.19801, 37.10101</i>	<i>-37.33148, 37.63768</i>	
	<i>-37.50799, 37.46940</i>	<i>-37.56592, 37.59844</i>	
	<i>-37.63426, 37.62009</i>	<i>-37.65832, 37.65099</i>	
-1		-37.32873, 37.64874	-37.15816, 37.70946
		-37.57609, 37.62783	-37.53259, 37.52062
		-37.65822, 37.66454	-37.64684, 37.57091
	-37.20536, 37.17651	-37.33945, 37.70684	-37.16906, 37.76756
	-37.52239, 37.51672	-37.58054, 37.64362	-37.53701, 37.53641
	-37.63572, 37.63817	-37.65978, 37.66891	-37.64841, 37.57527
	<i>-37.19894, 37.20501</i>	<i>-37.33293, 37.73534</i>	
	<i>-37.52114, 37.52227</i>	<i>-37.57929, 37.64918</i>	
	<i>-37.63546, 37.63935</i>	<i>-37.65953, 37.67009</i>	
		-37.29478, 37.75939	-37.11537, 37.82779
-2		-37.57126, 37.68285	-37.52766, 37.57244
		-37.64985, 37.67804	-37.63850, 37.58606
		-37.30542, 37.81748	-37.12621, 37.88588
		-37.57571, 37.69863	-37.53208, 37.58823
		-37.65142, 37.68241	-37.64008, 37.59043

^aThe total energy, the kinetic energy, in hartrees. In sub-row order, the 3-, 4- and 5-term results. Variation in the 2p function weighting, $r^{**}n_{2p}$, indicated by change in typeface; small typeface for the function determined without weighting, regular type for n_{2p} equal -1 and italics for -2.

^bThe Hartree-Fock energies are -37.68861 and 37.68854 [4]. The total energies are -37.45306, -37.63172, -37.67356 for the 3-, 4- and 5-term energy optimized GTO expansions [7].

located between those of the unweighted and energy optimized expansions. The 2s parameter comparisons are considerably more complicated because of the node production requirement, viz., the energy optimized 3- and 5-level sets have fewer subtractive contracted terms than those obtained by the space filling optimization methods. However, examination of the somewhat poorer (by ϵ_n standards) functions and their density contributions, combined with the above observation and the 4-term results reinforces the generalization that energy improvement accompanies contraction of the overlap optimized function.

Variations in the individual AO contributions to energy through use of GTO expressions obtained by variable weighting may be obtained by examination of Table 5. The results for $C(^3P)$, which are typical, are shown; this is the ground

state for the atom with equal numbers of 1s, 2s and 2p electrons which provides a useful normalization of the individual orbital effects². It may be quickly ascertained that the greatest effects accompany changes in the 1s expansions. This is not a surprising result considering the relative AO contributions to total energy. The total energy increments are typically 0.01–0.1 hartrees (on the total energy), an order or more in magnitude greater than the effects noted upon variation in the 2s and 2p functions. The effects of variation in the latter are similar except as noted below.

The r^{-1} -weighted functions are most favorable as regards total energy for all AO's and for the 1s and 2p functions the effects of weighting are most profound for the 3-term and least important for the 5-term expansions. For the 2s AO, comparing the r^{-1} -weighted expansions, the greatest difference, by an order of magnitude, is noted for the 4-term expansion, an effect which may be a ramification of coefficient crossover. The r^{-1} -weighted 4-term expansion function has 3 negative coefficients, the unweighted has 2. In the 3-term expansions both have 2 negative coefficients and in the 5-term expansions both have 3. Comparison of the r^{-1} - and r^{-2} -weighted functions reveals for all AO's the effects of weighting decrease as the expansion length increases.

Discussion and Conclusions

The values of weighting, with relatively simple weighting functions, in the course of expansion of real molecule wavefunctions are apparent from the foregoing results. The weighting functions employed may be considered as useful first-order corrections in the process of orbital representation matching, the ultimate and usually completely impractical correction for optimization of a particular expectation value being in the use of the operator itself as weighting function (i.e., weighting with the Hamiltonian for energy matching). The previously recognized fact that least-squares fitting in an overlap maximization procedure tends to stress the more diffuse regions of space [2] is reiterated by the density and expectation value results as well as the energy comparisons presented. Weighting effects as exercised through parameter variation in the GTO's are smaller on the computed densities and $\langle r^n \rangle$, the larger are r and n , respectively. In fact, for the expectation values with large n , the unweighted or smaller n -weighted functions give as good and occasionally better results than those generated with matching n . Total energies are uniformly better from the r^{-1} -weighted functions; the expansions obtained under r^{-2} -weighting are uniformly as good or better for all the first row atoms at the 4-term or higher expansion levels than those obtained without weighting.

Limited tests of the effects on molecular properties of weighting of constituent AO's are in progress. In a most stringent test, one of the few completed so far, the variously weighted SCF atom expansions for N(⁴S) were used without scaling in the variational computation of geometry and energy optima for N₂. While

² The best 2s expansion by total energy criteria is used at each weighting level. It should be noted that the 1s and 2s GTO expansions are not completely orthogonal because fit to the SCF AO's (which are of course orthogonal) is not perfect. The differences are however very small. In the course of the SCF procedure for energy calculation, orthogonality is assured by appropriate linear combination.

the r^{-1} -weighted functions were found to be as good or better than the unweighted functions as far as binding energies go, they were as often as not poorer with respect to prediction of the equilibrium value of the internuclear distance, and both properties were never better than poorly represented at best. These results are not at all remarkable, considering the molecule chosen and that significant scaling is necessary to make the energy optimized GTO expansions for atoms acceptable for use in molecular calculations [8]. Weighting is clearly not a panacea for improvements of trial functions. Further tests are underway to better define the limits of what weighting of AO functions, both of SCF and STO type, can accomplish as regards molecular calculations.

Another example worth mentioning of the potential utility of the radially-weighted expansions presented here, which does not explicitly involve their use in variational MO calculations, is to be found in the computation of X-ray scattering factors. Stewart [2] has found upon Fourier analysis that unweighted least-squares GTO expansions are satisfactory for low-angle scattering but poorer than those from variational fitting constraints at higher angles. It appears likely, since variation in the angle of scattering varies spatial regions stressed, that even better representations may be had employing the appropriately weighted functions. Direct expansion of empirical functions obtained from scattering, which represents a reverse situation, would also benefit from weighting, with regions of the highest and/or most reliable informational content stressed.

Appendix: Accurate Evaluation of the Error Function, $F_l(\alpha, \zeta)$

The integral of Eq. (4) may be cast in the error function form,

$$F_l(\alpha, \zeta) = \frac{\sqrt{\pi}}{2} \frac{e^{Z^2}}{\alpha^{(l+1)/2}} l! i^l \operatorname{erfc} Z \quad (\text{A.1})$$

with,

$$Z = \zeta/2\alpha^{1/2}. \quad (\text{A.2})$$

For small Z , the power series [9, Eq. (7.2.4)],

$$i^l \operatorname{erfc} Z = \sum_{k=0}^{\infty} \frac{(-1)^k Z^k}{2^{l-k} k! \Gamma\left(1 + \frac{l-k}{2}\right)} \quad (\text{A.3})$$

may be used to accurately evaluate the error function for L and $L-1$, where L is the maximum value of l required, followed by downward recurrence employing the relationship [9, Eq. (7.2.5)],

$$i^{l-2} \operatorname{erfc} Z = 2l i^l \operatorname{erfc} Z + 2Z i^{l-1} \operatorname{erfc} Z, \quad (\text{A.4})$$

which is unencumbered by serious differencing errors for small Z .

It is well known that for larger arguments, Z , power series representations for $i^l \operatorname{erfc} Z$ such as (A.3) cannot yield sufficiently accurate results [2, 10], especially if subsequent recursion is necessary. For very large Z (higher than 10 or 15, depending upon machine capacity, extent of recurrence necessary, accuracy desired, etc.), however, asymptotic series approximations are available [9, Eq. (7.1.23); 10].

Integral evaluation in the intermediate Z -range and definition of the range boundaries are therefore the central matters here. All previous investigators of the least-squares fitting problem cited have relied on Gauss-Laguerre quadrature in the intermediate range, with quadrature point choices ranging from 12 to 36, depending upon where the lower Z boundary was set, and upon similar criteria to those mentioned above for application of the asymptotic approximations.

We have employed the recursive non-quadrature technique of Gautschi [5] for intermediate and high Z -values.

Let the sequence $\omega_\mu^m(Z)$ ($\mu = m, m-1, \dots, 1, 0, -1$) be generated by backward use of the recurrence relation,

$$\omega_{\mu-2}^m(Z) = 2m\omega_\mu^m(Z) + 2Z\omega_{\mu-1}^m(Z), \quad (\text{A.5})$$

whose similarity to (A.4) is to be noted. Starting with $\omega_{m+2}^m = 0$ and $\omega_{m+1}^m = \gamma$, where $\gamma > 0$, then for any l , it may be shown,

$$\lim_{m \rightarrow \infty} \frac{\omega_l^m(Z)}{\omega_{m-1}^m(Z)} = \frac{\sqrt{\pi}}{2} e^{Z^2} i^l \operatorname{erfc} Z \quad (\text{A.6})$$

Since all $\omega_\mu^m(Z)$ values are generated in the course of obtaining $\omega_{m-1}^m(Z)$, all $F_l(\alpha, \zeta)$ are obtained, and all exceed in accuracy the limit chosen for $F_L(\alpha, \zeta)$.

The number of terms in the sequence, m , required if $i^L \operatorname{erfc} Z$ is to have a fractional error less than 10^{-p} is known, [5, Eq. (5.3)],

$$m \approx \left(\frac{2\sqrt{2LZ + p \ln 10 + \ln 2}}{2\sqrt{2} Z} \right)^2 \quad (\text{A.7})$$

or, for example, with $L = 12$ and a convergence limit of 3×10^{-11} , $m = 49$ with $Z = 2.5$, and $m = 37$ with $Z = 3.5$. Eq. (A.7) and these cited examples show how rapidly the sequence length decreases with increasing Z ; the only practical limit for application in the high- Z range is machine overflow which can to a very great extent be extended by appropriate choice of γ .

At the lower end, Z -values much below 2 require extensive sequence generation. This introduces a time factor consideration, and the possibility of roundoff accumulation, both factors of course being machine dependent. (It should be recognized at the same time, however, that quadrature procedures suffer in a similar way.) A reasonable compromise for a machine having 14 significant figure carry would be a Z -boundary at 2.5. Here, 8 or more significant figures from (A.3) and (A.4), and 10 or more significant figures from (A.6) (with a 3×10^{-11} convergence criterion) are obtained for all l (zero to 12), as calibrated by a 24 point quadrature test.

Consequently, for the calculations described herein, only two Z -ranges are recognized and the boundary is set at Z equal 2.5.

It is a matter of some interest to note that the criterion used in Ref. [3] for judging accuracy of the error functions, i.e., comparison of $i^0 \operatorname{erfc} Z$ obtained from (A.3) and (A.4) with values for the same integral as obtained directly by power series representations, is deceptive. Even though agreement was found to 13 figures for Z up to 3.5 (using double precision arithmetic, or about 27 figure carry), the $i^{12} \operatorname{erfc} Z$ generated as the first step by (A.3) in this Z -region is seriously

in error. Recurrence compensation, an effect of the type which enters favorably in the Gautschi method, is obviously responsible for this apparently enigmatic difference. Viz., ω_l^m/ω_{-1}^m can yield accurate estimations of $i^l \operatorname{erfc} Z$ for $m > l$, with the required difference ($m - l$) dependent upon l and the goodness of choice of ω_{m+2}^m and ω_{m+1}^m [recall, the arbitrary choices of these sequence originators in (A.5) and (A.6)]. Similar recurrence compensation effects for simpler error functions have been pointed out by Shavitt [11].

Following this revelation, all error functions for all tabulated quantities in Ref. [3] were checked. They have been verified to be good to at least 8 significant figures: N.B., all correspond to $Z < 2.61$.

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