Zeitschrift: Helvetica Physica Acta
Band: 47 (1974)
Heft: 3

Artikel: Expansion of Gaussian functions in hydrogen eigenfunctions

Autor: Dose, V. / Semini, C.

DOI: https://doi.org/10.5169/seals-114573

Helvetica Physica Acta
Vol. 47, 1974

Birkhäuser Verlag Basel

Expansion of Gaussian Functions in Hydrogen Eigenfunctions

by **V. Dose**[1])

Physik-Institut der Universität Zürich

and **C. Semini**[2])

Institut für Theoretische Physik der Universität Zürich and Ciba-Geigy Photochemie AG, Fribourg

(4. IV. 74)

Abstract. Methods have been developed which allow the expansion of Gaussian functions $r^j Y_l^m(\vartheta, \varphi) \cdot \exp(-\alpha r^2)$ in discrete and continuous eigenfunctions of the hydrogen atom. Different approaches are presented for application in different regions of an α–k and α–n plane respectively where k is the electron momentum in a continuous state and n is the principal quantum number of a discrete state. Detailed numerical results have been obtained for the special case $l = j = 0$ and exponent parameters α in the range $10^{-5} \leqslant \alpha \leqslant 10^2$. An overall check of the accuracy of the results is possible with the help of the closure relation which is in all cases satisfied to better than 10^{-5}, demonstrating the satisfactory reliability of the proposed methods.

I. Introduction

In 1950 Gaussian functions were proposed as basis functions for molecular structure calculations by Boys [2], because all multicenter integrals may be evaluated analytically. The type of function used is

$$\Psi_G = r^j Y_l^m(\vartheta, \varphi) \exp(-\alpha r^2)$$

where α is positive and j is equal to or greater than l. For j greater than l, $j - l$ must be even. Y_l^m is the usual spherical harmonic.

A considerable amount of atomic and molecular structure calculations have been carried out in the past using this computationally convenient set of functions. We shall not attempt to review this work. It has not always been successful. The failure was frequently attributed to the Gaussian factor in contrast to the exponential in hydrogen eigenfunctions and Slater orbitals. Consequently there have been attempts to expand exponentials and Slater orbitals in terms of Gaussians to combine the physical significance of Slater orbitals and the computational convenience of Gaussians (Kiyosi O-ohata et al. [7], Shavitt and Karplus [11], Hiroshi Taketa et al. [6]). The present paper is concerned with the problem the other way round. To get an idea of the

---

1) Now at Physikalisches Institut der Universität Würzburg, Röntgenring 8, Germany.
2) Now at Landis & Gyr AG, Zug, Switzerland.

physical meaning of a Gaussian function an expansion in hydrogen eigenfunctions both discrete and continuous

$$r^j \exp(-\alpha r^2)\, Y_l^m = \sum_{n=1}^{\infty} a_n(l,j,\alpha)\, R_{nl}(r)\, Y_l^m + \int_0^{\infty} dk A(k,l,j,\alpha)\, R_{kl}(r)\, Y_l^m \tag{I.1}$$

is presented. R_{nl} is the radial part of a hydrogen eigenfunction for a discrete state with principal quantum number n and orbital angular momentum l. R_{kl} is the corresponding function for a continuous state with electron momentum k. Using the orthonormality of the hydrogen functions we have for the expansion coefficients a_n and A

$$a_n(l,j,\alpha) = \int_0^{\infty} R_{nl}(r) \exp(-\alpha r^2)\, r^{j+2}\, dr \tag{I.2}$$

and

$$A(k,l,j,\alpha) = \int_0^{\infty} R_{kl}(r) \exp(-\alpha r^2)\, r^{j+2}\, dr. \tag{I.3}$$

R_{kl} is given explicitly by (Landau and Lifschitz [9])

$$R_{kl} = C_{kl} \exp(-ikr)\, r^l\, {}_1F_1\left(\frac{i}{k} + 1 + l;\ 2l+2;\ 2ikr\right) \tag{I.4}$$

$$C_{kl} = \frac{(2k)^{l+1}}{(2l+1)\,!}\left\{k\left(1 - \exp\left(-\frac{2\pi}{k}\right)\right)^{-1} \prod_{S=0}^{l}\left(s^2 + \frac{1}{k^2}\right)\right\}^{1/2}. \tag{I.5}$$

From (I.4) R_{nl} may be obtained by substituting $k = (in)^{-1}$. In this case the normalizing factor C_{nl} is

$$C_{nl} = \frac{2^{l+1}}{n^{2+l}} \cdot \frac{1}{(2l+1)\,!}\left\{\frac{1}{n} \prod_{S=0}^{l} (n^2 - s^2)\right\}^{1/2}. \tag{I.6}$$

Occasionally we shall use the abbreviations $a = i/k + l + 1$ and $c = 2l + 2$ for the first two arguments of the confluent hypergeometric function ${}_1F_1$ in (I.4).

We were not able to carry out the integrations (I.2) and (I.3) analytically and therefore used numerical methods. During the course of this work, it soon became

Table I
The four methods and their regions of convergence

Section	Method	Discrete states	Continuous states
II	Termwise integrations of Kummer's series	$n \to 1$	$k \to 0$ $\alpha \to \infty$
III	Termwise integration of Bessel function expansion	$n \to \infty$ $\alpha \to \infty$	$k \to 0$ $\alpha \to \infty$
IV	Asymptotic series in $\frac{1}{\sqrt{\alpha}}$	$n \to \infty$ $\alpha \to \infty$	$k \to 0$ $\alpha \to \infty$
V	Asymptotic series in α	$n \to 1$ $\alpha \to 0$	$k \to \infty$ $\alpha \to 0$

obvious that there is no simple procedure which would apply to all possible combinations (k, α) and (n, α) respectively. In fact four different approaches have been needed to cover all cases of interest. Table I characterizes these methods in short and gives an indication of their respective regions of convergence.

In Sections II to V of this paper we shall outline the analysis for the different methods. Section VI presents numerical results.

Numerical methods to compute some non-elementary functions arising in the analysis are described in the Appendix.

II. Termwise Integration of Kummer's Series

We shall first be concerned with the evaluation of (I.3), that is, overlap with the continuum. The modifications to be made in the case of (I.2) will be discussed subsequently.

Since it is the confluent hypergeometric function in R_{kl} which prevents analytical integration in (I.3) it is natural to expand

$$ {}_1F_1\left(\frac{i}{k} + l + 1; 2l + 2; 2ikr\right) = \sum_{m=0}^{\infty} B_m r^m \tag{II.1} $$

with coefficients B_m given by

$$ B_0 = 1, \quad B_{m+1} = 2B_m \frac{ik(l+1+m) - 1}{(m+1)(2l+2+m)} \quad m = 0, 1, \ldots . \tag{II.2} $$

Defining

$$ I_m(\alpha, \beta) = \int_0^{\infty} \exp(-\alpha r^2 + i\beta r)\, r^m\, dr \quad m = 0, 1, \ldots \tag{II.3} $$

we obtain the series expansion for A

$$ A(k, l, j, \alpha) = C_{kl} \sum_{m=0}^{\infty} B_m I_{2+l+j+m}(\alpha, -k). \tag{II.4} $$

The functions $I_m(\alpha, \beta)$ satisfy the recurrence relation

$$ I_m(\alpha, \beta) = \frac{\delta_{1m}}{2\alpha} + \frac{i\beta}{2\alpha} I_{m-1}(\alpha, \beta) + \frac{m-1}{2\alpha} I_{m-2}(\alpha, \beta), \quad m = 1, 2, \ldots \tag{II.5} $$

where δ_{1m} is the Kronecker delta. The function $I_0(\alpha, \beta)$ needed to start the recurrence is given by

$$ I_0(\alpha, \beta) = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \exp\{-\beta^2/4\alpha\} + \frac{i}{\sqrt{\alpha}} \exp\{-\beta^2/4\alpha\} \int_0^{\beta/2\sqrt{\alpha}} \exp(t^2)\, dt. \tag{II.6} $$

If β is real, the integral appearing on the right-hand side of (II.6) is known as Dawson's integral $D(\beta/2\sqrt{\alpha})$. Tables of $D(x)$ are available (Abramowitz and Stegun [1]).

It may be noted that the individual terms in (II.4) are complex, while the sum is real, because R_{kl} (I.4) is a real function. However, for numerical reasons it is advantageous to retain the imaginary part of I_m in (II.4). In practice the imaginary part of the sum (II.4) is used as a criterion to truncate the series when it is sufficiently small. On the other hand, if in spite of adding further terms the imaginary part of A does not decrease further, the real part, that is the desired result, is unlikely to have converged.

To adjust the above formulae to the discrete case (I.2) we have to replace β in equation (II.3) by i/n. With the additional substitution

$$t = \sqrt{\alpha}\left(r + \frac{1}{2n\alpha}\right) \tag{II.7}$$

we obtain

$$I_m\left(\alpha, \frac{i}{n}\right) = \exp\left(1/4\alpha n^2\right) \int_{\frac{1}{2\sqrt{\alpha}\,n}}^{\infty} \exp\left(-t^2\right)\left(t - \frac{1}{2n\sqrt{\alpha}}\right)^m \frac{dt}{\alpha^{(m+1)/2}} \tag{II.8}$$

$$I_m\left(\alpha, \frac{i}{n}\right) = \tfrac{1}{2}\sqrt{\pi}\, \frac{m!\exp\left(1/4n^2\alpha\right)}{\alpha^{(m+1)/2}}\, i^m \operatorname{erfc}\left(\frac{1}{2n\sqrt{\alpha}}\right). \tag{II.9}$$

The last factor, $i^m \operatorname{erfc}(z)$ is known as the repeated integral of the error function (Abramowitz and Stegun [1]). We shall describe numerical procedures to compute $i^m \operatorname{erfc}(z)$ in the Appendix.

The accuracy of the expansion coefficients $a_n(l, j, \alpha)$ is essentially limited by the accuracy obtainable in the computation of $i^m \operatorname{erfc}(z)$, since, in contrast to the continuum case, only the first $n - l$ terms in the sum (II.4) are different from zero. This, of course, is due to the fact that the confluent hypergeometric function in (I.4) reduces to a simple Laguerre polynomial for $i/k = -n$.

III. Bessel Function Expansion

The regular Coulomb wave function is expanded in (essentially spherical) Bessel functions (Abramowitz and Stegun [1])

$$(kr)^l \exp(-ikr)\, {}_1F_1(a; b; 2ikr) = (2l+1)!! \sum_{\nu=l}^{\infty} \frac{b_\nu}{k^{\nu-l}} \sqrt{\frac{\pi}{2kr}}\, J_{\nu+1/2}(kr). \tag{III.1}$$

The expansion coefficients $b\nu$ are given by

$$b_l = 1 \quad b_{l+1} = -\frac{2l+3}{l+1}$$

$$b\nu = -\frac{2\nu+1}{\nu(\nu+1) - l(l+1)}\left\{2b_{\nu-1} + \frac{(\nu-1)(\nu-2) - l(l+1)}{2\nu-3} k^2 b_{\nu-2}\right\}. \tag{III.2}$$

Substituting (III.1) into (I.3) and reversing the order of integration and summation yields

$$A(k,l,j,\alpha) = C_{kl}(2l+1)!!\sqrt{\frac{\pi}{2k}}\sum_{\nu=l}^{\infty}\frac{b_\nu}{k^\nu}\int_0^\infty \exp(-\alpha r^2)\, r^{3/2+j} J_{\nu+1/2}(kr)\,dr. \tag{III.3}$$

The integral appearing under the sum is well known (Gradshteyn and Ryzhik [5]). We obtain

$$A(k,l,j,\alpha) = (2l+1)!!\sqrt{\pi}\cdot C_{kl} \tag{III.4}$$

$$\sum_{\nu=l}^{\infty} b_\nu \frac{\Gamma\left(\frac{\nu}{2}+\frac{j}{2}+\frac{3}{2}\right)}{2^{\nu+2}\,\alpha^{\nu/2+j/2+3/2}\,\Gamma(\nu+3/2)}\,{}_1F_1\left(\frac{\nu}{2}+\frac{j}{2}+\frac{3}{2};\nu+\frac{3}{2};-\frac{k^2}{4\alpha}\right).$$

For continuum states a numerically more convenient result may be obtained applying Kummer's transformation

$$A(k,l,j,\alpha) = (2l+1)!!C_{kl}\sqrt{\pi}\cdot\exp(-k^2/4\alpha)$$

$$\sum_{\nu=l}^{\infty}\frac{b_\nu\Gamma\left(\frac{\nu}{2}+\frac{j}{2}+\frac{3}{2}\right)}{2^{\nu+2}\,\alpha^{\nu/2+j/2+3/2}\,\Gamma(\nu+3/2)}\cdot{}_1F_1\left(\frac{\nu}{2}-\frac{j}{2};\nu+\frac{3}{2};\frac{k^2}{4\alpha}\right). \tag{III.5}$$

In this form, the confluent hypergeometric function may be computed without loss of accuracy by direct summation of its series expansion.

IV. Asymptotic Series in $\alpha^{-1/2}$

The procedure of this section applies to overlap with discrete and continuous states. It is based on an integral representation of the confluent hypergeometric function (Landau and Lifschitz [9])

$${}_1F_1(a;c;z) = -\frac{1}{2\pi i}\frac{\Gamma(1-a)\,\Gamma(c)}{\Gamma(c-a)}\oint_{c'}\exp(tz)\,(-t)^{a-1}(1-t)^{c-a-1}\,dt. \tag{IV.1}$$

Since $c = 2l+2$ is an integer in the present problem the contour must enclose the points $t=0$ and $t=1$ and is otherwise arbitrary. Again we shall treat overlap with continuum first and indicate modifications for discrete states subsequently. Defining

$$X = -\frac{1}{2\pi i}\frac{\Gamma(1-a)\,\Gamma(c)}{\Gamma(c-a)} \tag{IV.2}$$

and inserting (IV.1) into (II.3) we obtain

$$A(k,l,j,\alpha) = C_{kl} \int_0^\infty \exp(-\alpha r^2)\, r^{l+j+2}$$

$$X \cdot \oint_{c'} \exp\{-ik(1-2t)\, r\}\, (-t)^{a-1} (1-t)^{c-a-1}\, dt\, dr. \tag{IV.3}$$

Expanding the exponential under the contour integral and interchanging integration and summation yields a series S, which will be shown to be the asymptotic expansion of $A(k,l,j,\alpha)$ in terms of $\alpha^{-1/2}$. Writing

$$S = \sum_{m=0}^{M} F_m \tag{IV.4}$$

we have from (IV.3)

$$F_m = \frac{C_{kl}(-ik)^m}{m!} \int_0^\infty \exp(-\alpha r^2)\, r^{l+j+m+2}\, dr$$

$$X \cdot \oint_{c'} (1-2t)^m (-t)^{a-1} (1-t)^{c-a-1}\, dt. \tag{IV.5}$$

While the integral over r is elementary, the contour integral is just an integral representation of the hypergeometric function ${}_2F_1(a,-m;c;2)$ (Landau and Lifschitz [9]). The result is

$$F_m = \frac{(-i)^m (k)^m}{2m!} C_{kl}\, \alpha^{-(l+j+m+3)/2}\, \Gamma\left(\frac{l+j+m+3}{2}\right) \cdot {}_2F_1(a,-m;c;2) \quad m = 0, 1, \ldots. \tag{IV.6}$$

Fortunately, since the second argument of ${}_2F_1$ is a negative integer, the hypergeometric series terminates and ${}_2F_1(a,-m;c;2)$ can be evaluated exactly. For practical purposes it is essential that the functions F_m can be calculated by recurrence. Using the recurrence relation (Abramowitz and Stegun [1])

$$(c-b)\, {}_2F_1(a,b-1;c;z) + (2b-c-bz+az) \cdot {}_2F_1(a,b;c;z)$$

$$+ b(z-1) \cdot {}_2F_1(a,b+1;c;z) = 0 \tag{IV.7}$$

an equivalent relation for the F_m's may be derived. This is

$$F_{m+1} = -\frac{(l+j+m+2)}{2(m+1)(2l+2+m)} \left\{ \frac{\Gamma\left(\frac{l+j+m+2}{2}\right)}{\Gamma\left(\frac{l+j+m+3}{2}\right)} \frac{2F_m}{\sqrt{\alpha}} + \frac{k^2}{\alpha} F_{m-1} \right\}. \tag{IV.8}$$

The starting values are obtained directly from (IV.6)

$$F_0 = \frac{C_{kl}}{2} \alpha^{-(l+j+3)/2} \Gamma\left(\frac{l+j+3}{2}\right) \tag{IV.9}$$

$$F_1 = -\frac{1}{\sqrt{\alpha}} \cdot F_0 \Gamma\left(\frac{l+j+4}{2}\right) \Big/ \Gamma\left(\frac{l+j+3}{2}\right). \tag{IV.10}$$

We shall prove now that the series S calculated in the way outlined above is the asymptotic expansion in $\alpha^{-1/2}$ of $A(k,l,j,\alpha)$. To this end we shall prove that (Knopp [8])

$$L = \lim_{\sqrt{\alpha}\to\infty} \left\{ A(k,l,j,\alpha) - \sum_{m=0}^{M} F_m \right\} \alpha^{M/2} = 0 \quad M = 0, 1, \ldots. \tag{IV.11}$$

If we put $x = r \cdot \sqrt{\alpha}$ and define

$$R = \exp\left\{ -\frac{ik}{\sqrt{\alpha}} (1-2t)\, x \right\} - \sum_{m=0}^{M} \left(\frac{-ik}{\sqrt{\alpha}} \right)^m \frac{(1-2t)^m x^m}{m!} \tag{IV.12}$$

we obtain, using (IV.3),

$$L = \lim_{\sqrt{\alpha}\to\infty} \frac{C_{kl}\, \alpha^{M/2}}{\alpha^{(l+j+3)/2}} \int_0^\infty \exp\{-x^2\}\, x^{(l+j+2)/2}$$

$$X \cdot \oint_{c'} R(-t)^{a-1}(1-t)^{c-a-1}\, dt\, dx. \tag{IV.13}$$

From Lagrange's formula (see for example Courant [3]) we have

$$R = \frac{x^{M+1}}{(M+1)!} \partial_x^{M+1} \exp\left\{ -\frac{ik}{\sqrt{\alpha}} (1-2t)\, x \right\} \Bigg|_{x=\xi} \tag{IV.14}$$

with

$$0 \leqslant \xi < x.$$

Carrying out the differentiation and replacing the exponential by ϑ with $|\vartheta| = 1$ we get

$$R = \frac{x^{M+1}}{(M+1)!} \left\{ -\frac{ik}{\sqrt{\alpha}} (1-2t) \right\}^{M+1} \vartheta. \tag{IV.15}$$

Inserting (IV.15) in (IV.13) yields

$$L = \lim_{\sqrt{\alpha}\to\infty} \frac{C_{kl}}{\alpha^{(l+j+4)/2}} \int_0^\infty \exp\{-x^2\}\, x^{l+2}$$

$$X \oint_{c'} \frac{x^{M+1}}{(M+1)!} (-ik(1-2t))^{M+1} \cdot \vartheta(-t)^{a-1}(1-t)^{c-a-1}\, dt\, dx. \tag{IV.16}$$

The expression under the lim is proportional to $\alpha^{-(l+j+4)/2}$ and therefore $L = 0$, q.e.d.

Numerically, asymptotic series are convenient, since the first neglected term is an estimate for the achieved accuracy. The above formulae may be adapted for the calculation of overlaps with discrete states replacing k by $(in)^{-1}$ and C_{kl} by C_{nl}. Convergence is rapid for large values of n. Moreover, the recurrence relation (IV.8) may be used to obtain the general behaviour of the overlap integrals (I.2) for large n.

Inspection of (I.6), (IV.9), and (IV.10) shows that the first two terms in the expansion of $a_n(l, j, \alpha)$ depend on n through $n^{-3/2}$ independent of l. From (IV.8) we see that the third term is proportional to $n^{-7/2}$. This fact may be used to estimate

$$Y = \sum_{n=0}^{\infty} |a_n(l, j, \alpha)|^2 \tag{IV.17}$$

from a finite number of terms, M.

$$Y = \sum_{n=0}^{M} |a_n(l, j, \alpha)|^2 + \sum_{n=M+1}^{\infty} |a_n(l, j, \alpha)|^2 \tag{IV.18}$$

where the terms of the second sum have not been computed. To a good approximation we may write, using the n^{-3} scaling law,

$$Y \simeq \sum_{n=0}^{M} |a_n(l, j, \alpha)|^2 + |a_M(l, j, \alpha)|^2 \sum_{n=M+1}^{\infty} \frac{M^3}{n^3}. \tag{IV.19}$$

V. Asymptotic Expansion in α

For a rigorous derivation of this expansion it is necessary to introduce a convergence factor $\exp\{-\epsilon \cdot r\}$ with ϵ positive but arbitrarily small. With the help of this factor we define

$$\bar{A}(\epsilon, k, l, j, \alpha) = C_{kl} \int_0^{\infty} \exp\{-\alpha r^2 - \epsilon r - ikr\} \cdot r^{2+l+j} {}_1F_1(a; c; 2ikr)\, dr. \tag{V.1}$$

The limit $\epsilon \to 0$ may at this step of course be interchanged with the integration to yield

$$\lim_{\varepsilon \to 0} \bar{A}(\epsilon, k, l, j, \alpha) = A(k, l, j, \alpha). \tag{V.2}$$

Expanding the Gaussian in (V.1) and interchanging summation and integration we obtain

$$\bar{A}(\epsilon, k, l, j, \alpha) = \sum_{\nu=0}^{\infty} (-\alpha)^{\nu} U_{\nu}(\epsilon) \tag{V.3}$$

with

$$U_{\nu}(\epsilon) = \frac{C_{kl}}{\nu!} \int_0^{\infty} r^{2+2\nu+j+l} \exp(-\epsilon r - ikr) \cdot {}_1F_1(a; c; 2ikr)\, dr. \tag{V.4}$$

Interchanging summation and integration in the last step is not necessarily a valid operation. Before turning to practical aspects, we shall therefore prove that the series (V.3) is the asymptotic expansion of $\bar{A}(\epsilon,k,l,j,\alpha)$ in α that is

$$L=\lim_{\alpha\to 0}\left\{\bar{A}(\epsilon,k,l,j,\alpha)-\sum_{\nu=0}^{N}(-\alpha)^{\nu}U_{\nu}(\epsilon)\right\}\frac{1}{\alpha^{N}}=0 \quad N=0,1,\ldots. \tag{V.5}$$

Denoting the expression in brackets by R it may be shown by an analysis similar to that in Section IV

$$R=(-\alpha)^{N+1}\frac{C_{kl}}{(N+1)!}\int_{0}^{\infty} r^{2N+4+l+j}\exp\{-\epsilon r-ikr\}\cdot\vartheta\,{}_1F_1(a;c;2ikr)\,dr. \tag{V.6}$$

Here ϑ is between 0 and 1. Since R is proportional to α^{N+1} equation (V.5) is satisfied, q.e.d.

As in Section IV, this semi-convergent series is suitable for the calculation of $A(k,l,j,\alpha)$ as long as the smallest term is smaller than the desired accuracy.

For application of the above formulae, we are left with the evaluation of the integral in (V.4). We define

$$G_m=\lim_{\varepsilon\to 0}C_{kl}\int_{0}^{\infty} r^{m}\exp(-\epsilon r-ikr)\,{}_1F_1(a;c;2ikr)\,dr. \tag{V.7}$$

The integration may be carried out (Landau and Lifschitz [9]) and yields

$$G_m=\lim_{\varepsilon\to 0}\frac{C_{kl}\Gamma(m+1)}{(\epsilon+ik)^{m+1}}\cdot{}_2F_1\left(a,m+1;c;\frac{2ik}{\epsilon+ik}\right). \tag{V.8}$$

With the help of the recurrence relation (IV.7) we get the recurrence relation for the functions G_m

$$m(m-2l-1)\,G_{m-1}+2G_m+k^2G_{m+1}=0 \quad m=1,2,\ldots \tag{V.9}$$

and observing that ${}_2F_1\,(a,0;c;2)=1$

$$2G_0+k^2G_1=C_{kl}(2l+1). \tag{V.10}$$

It remains to determine a starting value G_0. To this end we note, that (Abramowitz and Stegun [1])

$${}_2F_1(a,b;b;z)=(1-z)^{-a} \tag{V.11}$$

with the restriction that the term on the right-hand side has to be taken with the smallest absolute value of its phase. This gives

$$G_{2l+1}=C_{kl}(2l+1)!\lim_{\varepsilon\to 0}\frac{1}{(\epsilon^2+k^2)^{l+1}}$$

$$\cdot\exp\left\{-\frac{i}{k}\left(i\pi+\frac{2ik\epsilon}{k^2+\epsilon^2}\right)+2n\pi i\right\} \quad n=0,\pm1,\pm2,\ldots. \tag{V.12}$$

Since $\epsilon > 0$, the argument is smallest for $n = -1$ and we obtain after $\epsilon \to 0$

$$G_{2l+1} = C_{kl} \frac{(2l+1)!}{k^{2l+2}} \exp\{-\pi/k\}. \tag{V.13}$$

Now, since the recurrence relation (V.9) is linear, we may determine G_0 from two different trial values G_0^1 and G_0^2 respectively. G_0^1 and G_0^2 will generate corresponding values G_{2l+1}^1 and G_{2l+1}^2. From the linearity of (V.9) and (V.10) follows

$$G_0 = \beta G_0^1 + \gamma G_0^2$$

$$G_{2l+1} = \beta G_{2l+1}^1 + \gamma G_{2l+1}^2$$

$$1 = \beta + \gamma. \tag{V.14}$$

As in the foregoing sections, these formulae may be adjusted to the case of discrete states replacing k by $(in)^{-1}$ and C_{kl} by C_{nl}. However, it turns out that, though the method described in this section is powerful for calculation of overlap integrals for continuous states, it is of rather limited value for discrete states.

VI. Numerical Results

The methods described in Sections II to V have been used on an IBM 360/50 computer (double precision, 15 significant decimal places) to evaluate overlap integrals between hydrogen S-functions and Gaussian functions with $l = j = 0$ and exponents α in the range $10^{-5} \leqslant \alpha \leqslant 10^2$.

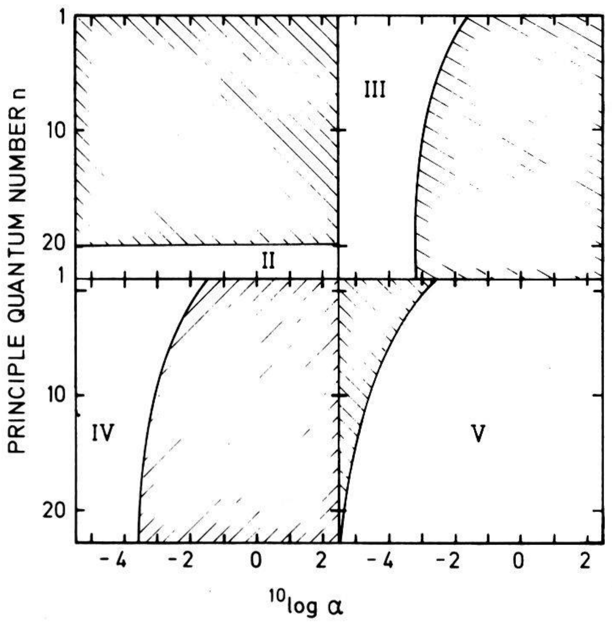

Figure 1
The hatched areas in this figure give the empirically determined regions, where the methods described in the text converge when applied to computation of overlap integrals with discrete states. Roman numbers in the plots refer to the section where the respective method is discussed.

Figure 1 shows the regions of convergence of the four methods when applied to overlap with discrete hydrogen eigenstates. Figure 2 is a similar plot for the hydrogen continuum. A method is considered to have converged if the respective normalized overlap integral is correct to six decimal places. A check on this accuracy is obtained using two complementary methods in the region where they overlap. This region also serves to establish convergence criteria. Breakdown of a method may occur for several

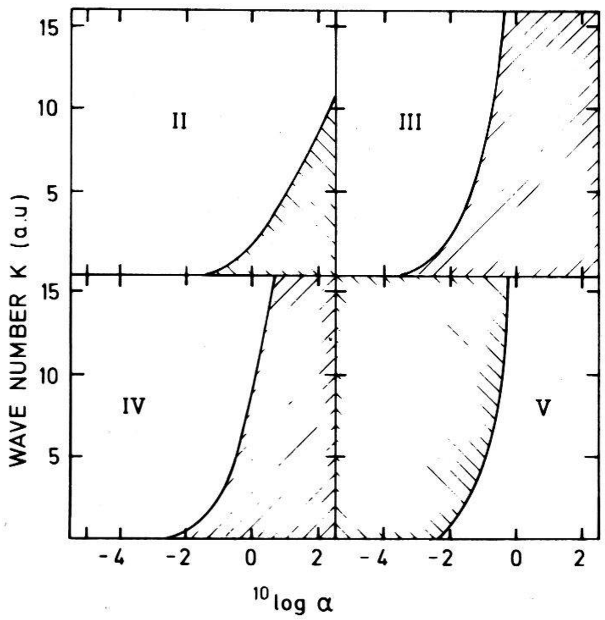

Figure 2
The hatched areas in this figure give the empirically determined regions, where the methods described in the text converge when applied to computation of overlap integrals with continuous states. Roman numbers in the plots refer to the section where the respective method is discussed.

reasons. Table II indicates the nature of the breakdown near the limit of convergence and gives the number of terms in a series expansion used at this limit.

An overall check of the accuracy of a projection calculation is, of course, provided by the closure relation. From (I.1) we obtain

$$1 = \frac{1}{N(\alpha,j)^2}\left\{\sum_{n=1}^{\infty} |a_n|^2 + \int_0^{\infty} |A(k,l,j,\alpha)|^2\, dk\right\} \tag{VI.1}$$

Table II
Breakdown of the four methods

	Discrete States		Continuous States	
Method section	Application limit	Max. number of terms	Application limit	Max. number of terms
II	rounding errors	20	rounding errors	25
III	rounding errors	45	exponent overflow	75–100
IV	rounding errors	60	rounding errors	120
V	divergent character of series	1–30	divergent character of series	1–30

where $N(\alpha, j)$ is given by

$$N^2(\alpha, j) = \int_0^\infty r^{2j} \exp\{-2\alpha r^2\} r^2 \, dr \tag{VI.2}$$

$$N^2(\alpha, j) = \frac{\Gamma(j + 3/2)}{2(2\alpha)^{j+3/2}} \,. \tag{VI.3}$$

While the infinite sum in (VI.1) is evaluated with the help of (IV.19) choosing $M = 8 \div 40$, the integral in (VI.1) was taken between $0 \leqslant k \leqslant 125$. The upper limit was again determined empirically.

Table III
Squared normalized overlap integrals for $l = j = 0$

	Exponent parameter α							
	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10	100
n	Discrete states							
1	.000003	.000102	.003154	.081852	.746861	.647359	.079396	.004009
2	.000103	.003206	.085933	.770894	.090647	.051262	.009543	.000499
3	.000799	.022947	.379569	.127086	.022365	.013943	.002807	.000148
4	.003232	.083407	.438929	.012269	.008721	.005708	.001181	.000062
5	.009564	.188671	.092285	.003060	.004296	.002882	.000604	.000032
$N^{-2} \sum_{n=1}^{\infty} a_n^2$	1.000005	1.000014	.999994	.998193	.881335	.726976	.094767	.004816
k	Continuous states							
1	.0	.0	.000006	.000207	.054031	.187788	.071640	.003977
3	.0	.0	.0	.000007	.000249	.000173	.160810	.013040
5	.0	.0	.0	.0	.000017	.001045	.141164	.024564
7	.0	.0	.0	.0	.000003	.000127	.066044	.036770
9	.0	.0	.0	.0	.0	.000026	.017162	.047393
$N^{-2} \int_0^\infty A^2 \, dk$	$<10^{-9}$	2.10^{-7}	6.10^{-6}	.001808	.118668	.273026	.905240	.995183
	Closure relation							
1-S	$-5 \cdot 10^{-6}$	$-1 \cdot 10^{-5}$	$2 \cdot 10^{-7}$	$-1 \cdot 10^{-6}$	$-3 \cdot 10^{-6}$	$-2 \cdot 10^{-6}$	$-7 \cdot 10^{-6}$	$8 \cdot 10^{-7}$

Table III gives a sample of squared normalized overlap integrals of hydrogen functions with Gaussians in the exponent range $10^{-5} \leqslant \alpha \leqslant 10^2$. In all cases we were able to obtain the closure relation to better than $1 \cdot 10^{-5}$. From Table III it is apparent that a Gaussian function may overlap considerably with continuous hydrogen functions if the exponent parameter is not too small. An application of this fact will be given in a subsequent paper.

Though detailed numerical results have, up to now, only been obtained for the case $j = l = 0$, exploratory computations for $l = j = 1, 2$ indicate a rather similar convergence behaviour in these cases of non-vanishing angular momentum.

Acknowledgements

The authors are grateful to Professor K. Bauknecht from the University of Zürich computing center for providing most generously computing time and the permission to use the computing center facilities outside the normal opening time. Some computations have been done in the computing center of Ciba-Geigy Photochemie AG, Fribourg. Provision of computing time is also gratefully acknowledged. The work of one of us (V.D.) has been supported financially by the Schweizerischer Nationalfonds.

APPENDIX

In this Appendix we describe the evaluation of the repeated integral of the error function defined by

$$i^m \operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty \frac{(t-z)^m}{m!} \exp(-t^2)\, dt. \tag{A.1}$$

By partial integration it may be shown that

$$i^m \operatorname{erfc}(z) + \frac{z}{m} i^{m-1} \operatorname{erfc}(z) - \frac{1}{2m} i^{m-2} \operatorname{erfc}(z) = 0. \tag{A.2}$$

If we define

$$i^{-1} \operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \exp(-z^2) \tag{A.3}$$

it may be shown that (A.2) holds for $m = 1, 2, \ldots$. Since

$$i^0 \operatorname{erfc}(z) = \operatorname{erfc}(z), \tag{A.4}$$

$i^m \operatorname{erfc}(z)$ could be calculated for arbitrary m in principle. However, in contrast to the recurrence relations derived in the main text, which empirically turned out to be stable, equation (A.2) is extremely unstable for upward recurrence. (A.2) is therefore used in downward recurrence putting $i^M \operatorname{erfc}(z) = 0$, $\alpha i^{M-1} \operatorname{erfc}(z) = 1$. With this choice $\alpha i^{-1} \operatorname{erfc}(z)$ is evaluated and by comparison with (A.3) the factor α determined. Since (A.2) is homogeneous all functions $i^K \operatorname{erfc}(z)$ with K sufficiently smaller than M may be obtained by dividing the trial values by α. This technique, originally proposed by Miller [10] for the evaluation of Bessel functions, was applied to the repeated integral of the error functions by Gautschi [4]. From the work of Gautschi it is apparent that the method will show poor convergence for $z \to 0$. In the present work we used this procedure for $z \geqslant 1.1$ only. For $0 < z \leqslant 1.1$ the same technique may be applied to a four-term recurrence relation. Consider the identity

$$i^m \operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \cdot \int_0^\infty \frac{(t-z)^m}{m!} \exp(-t^2)\, dt - \frac{2}{\sqrt{\pi}} \int_0^z \frac{(t-z)^m}{m!} \exp(-t^2)\, dt. \tag{A.5}$$

The first integral on the right-hand side is

$$\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{(t-z)^m}{m!} \exp(-t^2)\, dt = \frac{1}{\sqrt{\pi}} \cdot \sum_{j=0}^{m} \frac{(-z)^{m-j}}{j!\,(m-j)!} \Gamma\left(\frac{m+1}{2}\right) \tag{A.6}$$

while the second one obeys the recurrence relation

$$Y_{m-2} = \frac{1}{z} \{2m(m-1)\, Y_{m+1} + 4(m-1) \cdot z \cdot Y_m + (2z^2 - m + 1) \cdot Y_{m-1}\}$$

$$m = 2, 3, \ldots \tag{A.7}$$

with

$$Y_m = \frac{2}{\sqrt{\pi}} \int_0^z \frac{(t-z)^{m-1}}{(m-1)!} \exp(-t^2)\, dt$$

$$Y_0 = -\frac{2}{\sqrt{\pi}} \exp(-z^2). \tag{A.8}$$

Applying the above described downward recurrence procedure to (A.7) yields, together with (A.6), $i^m \operatorname{erfc}(z)$ for $z \leqslant 1.1$ with satisfactory accuracy.

Table IV
Starting values for recursive computation of i^m erfc (z)

Recurrence relation	Starting index M	Y_{M+1}	Y_M	Y_{M-1}	Range
A2	$2m + \frac{45}{z} + 10$		0	10^{-25}	$1.1 \leqslant z < \infty$
A7	$m + 30 \cdot z + 6$	10^{-50}	$M \cdot 10^{-50}$	$M^2 \cdot 10^{-50}$	$0 < z \leqslant 1.1$

Starting indices M depend of course on m and z and were determined empirically. Values given in Table IV will produce $i^m \operatorname{erfc}(z)$ for $0 \leqslant m \leqslant 11$ to relative accuracy of better than 10^{-5}.

REFERENCES

[1] M. Abramowitz and J. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).
[2] S. F. Boys, Proc. Roy. Soc A, *200*, 542 (1950).
[3] R. Courant, *Vorlesungen über Differential- und Integralrechnung* (Springer-Verlag, Berlin, 1955).
[4] W. Gautschi, Math. Comp. *15*, 227 (1961).
[5] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals Series and Products* (Academic Press, 1965).
[6] Taketa Hiroshi, Huzinaga Sigeru and O-Ohata Kiyosi, J. Phys. Soc. Japan *21*, 2313 (1966).
[7] O-Ohata Kiyosi, Taketa Hiroshi and Huzinaga Sigeru, J. Phys. Soc. Japan *21*, 2306 (1966).
[8] K. Knopp, *Theorie und Anwendung der unendlichen Reihen* (Springer-Verlag, Berlin, 1964).
[9] L. D. Landau and E. M. Lifschitz, *Quantenmechanik* (Akademie-Verlag, Berlin, 1965).
[10] J. C. P. Miller, in *British Association for the Advancement in Science, Besselfunctions, Part I. Functions of Orders Zero and Unity, Mathematical Tables*, Vol. VI (Cambridge University Press, 1950).
[11] I. Shavitt and M. Karplus, J. Chem. Phys. *43*, 398 (1965).