ABSTRACT

There has been increasing interest in the use of integral transform (IT) functions for ab initio quantum mechanical calculations and many alternative methods of employing the integral transformation concept have been developed.

This thesis is concerned with the performance of exponential IT functions (as opposed to Gaussian IT functions) in variational calculations of the energy of small atomic and molecular systems. The characteristics of an IT function and the reasons for selecting the exponential IT function for constructing approximate wavefunctions are given and the use of these functions for H^-, He, and Li^+, H_2^+ and H_2 is described. The results obtained in each case are analyzed and compared with the energies calculated from linear combinations of exponential functions. A comparison of different Gaussian and exponential IT functions for each atomic and molecular system is also made. A novel version of the IT method which generalizes the principal quantum number, n, is introduced and tested for H_2^+.

The calculations confirm that exponential IT functions, when used to construct approximate wavefunctions, produce energies which are better than those obtained by using the corresponding Gaussian IT functions, yet they contain the same number of variational parameters.

In some cases it was found that on optimization the exponential IT function reduces to the primitive function. That

this can be avoided by carefully choosing the combination of the constituent parts of the IT function (i.e. the shape function, the generalized parameter, and the primitive function) is illustrated in the case of H_2^+ by using the new n-transform function.

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To V. H. P.

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LIST OF SYMBOLS

(A,B)	integration domain
e	electronic charge
E	energy
h	Planck's constant
H_{ij}	H-matrix element
$\mathcal{H}$	Hamiltonian
$k_\nu(x)$	reduced modified Bessel function of the 2nd kind
$K_\nu(x)$	modified Bessel function of the 2nd kind
ℓ	angular momentum quantum number
$L_i(x)$	Laguerre polynomials
λ	elliptic coordinate
m	electronic mass
μ	elliptic coordinate
n	principal quantum number
ν	non-linear parameter
$P_n(x)$	Legendre polynomial
q	non-linear parameter
r	electron-nucleus distance
R	internuclear separation
S_{ij}	overlap matrix element
x,y,z	cartesian coordinates
ζ	orbital exponent
Z	nuclear charge

LIST OF ABBREVIATIONS

AO	Atomic orbital
MO	Molecular orbital
STO	Slater type orbital
GTO	Gaussian type orbital
LC	Linear combination
SCF	Self consistent field
IT	Integral transform

ATOMIC UNITS

1) DEFINITIONS

The atomic units of length and energy are bohrs and hartrees (Shull and Hall [1]). One bohr is the first Bohr radius of the hydrogen atom assuming infinite nuclear mass:

$$1 \text{ bohr} = h^2/(4\pi^2 me^2).$$

One hartree is (-2) times the Bohr ionization potential of the hydrogen atom assuming infinite nuclear mass:

$$1 \text{ hartree} = 4\pi^2 me^4/h^2,$$

where h is Planck's constant, m is the electronic mass, and e is the electronic charge.

2) CONVERSION FACTORS

The following conversion factors are based on the values of physical constants established by Taylor et al. [2].

$$1 \text{ bohr} = 0.529\ 177 \text{ Ångström}$$

and

$$1 \text{ hartree} = 27.211\ 652 \text{ eV}$$

$$1 \text{ hartree} = 219\ 474.624 \text{ cm}^{-1}$$

$$1 \text{ hartree} = 627.52 \text{ kcal/mole}$$

CHAPTER I

GENERAL INTRODUCTION

This introductory chapter serves the twofold purpose of providing the background information required to understand the terminology used and describing those features which are common to all the calculations in the chapters that follow. First a brief summary of the principles underlying the quantum mechanical calculations will be given to show the connection between the integral transform (IT) method applied in this work and the general procedures used in other calculations. Second, the characteristic parts of an IT function will be discussed and several examples of IT functions will be given. Third, the publications where IT functions have been used for systems similar to those dealt with here will be reviewed. Fourth, the computational methods employed in the calculations of this work will be described. Finally, a brief outline will be given of the contents of the thesis.

SECTION A. QUANTUM MECHANICAL PRINCIPLES

1) THE SCHRÖDINGER EQUATION

The working expression of quantum mechanical calculations is the Schrödinger equation

$$H\psi = E\psi \, . \tag{1}$$

This equation is an eigenvalue problem; the operator H is known but both the eigenfunction, ψ, and the eigenvalue, E, are unknown. The wavefunction, ψ, is a function of all nuclear and electronic coordinates. In the Born-Oppenheimer approximation the set of nuclear coordinates is kept fixed. In the orbital approximation ψ is assumed to be composed of one-electron functions, the orbitals. Both approximations will be used in this work.

The Born-Oppenheimer approximation leads to an electronic-Schrödinger equation similar to Eq. (1) which can be solved in a closed mathematical form for the H-atom and for H_2^+. For all other cases, the variational principle provides a constructive procedure to obtain wavefunctions with any desired degree of accuracy. An alternative method is given by the perturbation theory. The variational method will be employed here. It consists of minimizing the following expression

$$W = \langle\psi H\psi\rangle / \langle\psi\psi\rangle \, , \tag{2}$$

where the Dirac brackets are used as a notation for the definite multi-dimensional integration over all the coordinates of all electrons, and the variational principle states that

$$W \geq W_o, \qquad (3)$$

where W_o is the ground state energy.

To achieve a systematic variation in trial functions use is made of mathematical parameters. They can be non-linear, e.g. if they appear in the argument of an exponential function, $\exp(-\zeta r)$, i.e. the orbital exponent, ζ, is the non-linear parameter. Or they can be linear parameters as in the case when the trial wavefunction is written as a linear combination of some set of known basis functions, $\{\chi_i\}$, so that

$$\psi = \sum_{i=1}^{\infty} c_i \chi_i \ , \qquad (4)$$

i.e. the coefficients, c_i, are linear variational parameters. The justification for doing this is given by the expansion theorem which states the conditions to be met by the set of functions. In practice finite sets of functions are used, and the series is then said to be truncated, and the variational principle ensures that the energy is as close as possible to the true energy for the basis set chosen. For wavefunctions of the type given by Eq. (4), the integrals for W in Eq. (2) are expressed as sums of integrals over the functions χ_i, i.e. as sums of integrals such as

$$H_{ij} = \langle \chi_i H \chi_j \rangle \qquad (5)$$

and

$$S_{ij} = \langle \chi_i \chi_j \rangle \; . \tag{6}$$

In ab initio calculations all the integrals H_{ij} and S_{ij} are calculated exactly; in semi-empirical calculations some or all of the integrals H_{ij} and S_{ij} are replaced by numbers which are estimated or deduced from experimental results. All calculations in this work are ab initio calculations. The minimization of W with respect to each of the coefficients, c_i, leads to the following system of linear equations:

$$\sum_{j=1}^{k} (H_{ij} - E\, S_{ij})\, c_j = 0, \text{ for } i=1,2,3,\ldots,k, \tag{7}$$

where k is the number of basis functions in the expansion. The energy which comes closest to the ground state energy is given by the lowest root, E_1, of the secular equation

$$\det\,(\underline{H} - \underline{E}\;\underline{S}) = 0, \tag{8}$$

and the coefficients are the solutions of the system of linear equations, Eq. (7), with E replaced by E_1.

2) BASIS FUNCTIONS

The set of functions, $\{\chi_i\}$, is called a basis set. The completeness, convergence and convenience of a basis set are important factors. If the basis functions do not form a complete set, the variational method will lead to a wrong limit. The convergence of a basis set should be good, i.e. the first term should already be a good approximation to the final function. The convenience of a basis set is judged by whether the integrals over such functions which arise in the energy expression are mathematically easy to evaluate.

(a) Conventional Basis Functions

In conventionally used basis functions a separation into a radial part, which is a function of the electronic coordinate r, and an angular part, which depends on the angles θ and ϕ, is carried out. The angular parts are given by the spherical harmonics, $Y_{\ell m}(\theta,\phi)$, and are the same for all conventional basis functions. Different members of the set are distinguished by the 3 quantum numbers (n,ℓ,m). For ℓ, the angular momentum quantum number, the spectroscopic notation s,p,d... is often used, these symbols denoting $\ell=0,1,2...$ respectively.

By far the most important basis sets used to-day are the Slater type orbitals (STOs), the radial parts of which are given by

$$r^{n-1} \exp(-\zeta r) \,, \tag{9}$$

and the Gaussian type orbitals (GTOs), the radial parts of which are given by

$$r^{n-1}\exp(-\zeta r^2). \tag{10}$$

These sets of STOs and GTOs are complete. The integration formulae for GTOs are especially convenient but their rate of convergence is rather slow. The opposite is true of the STOs, since their convergence is usually very good but their integration formulae are somewhat complicated. About twice as many basis functions are required to produce a given energy in a given system, if GTOs are used instead of STOs. In this work only the s-type STOs and GTOs will be used, for which ℓ=m=0 and the angular part $Y_{\ell m}(\theta,\phi) = 1$.

The difficulties in quantum mechanical calculations are generally not of a fundamental nature but are due to computational problems. This explains why further improvement of mathematical methods is sought, and unconventional basis functions, such as those described here, are tested in calculations for small molecules.

(b) Unconventional Basis Functions

Basis functions which are more flexible than GTOs and STOs have been proposed by several authors. The basis function,

$$\exp(-\zeta r^{\lambda}), \tag{11}$$

was introduced by Carrier and Pilar [3], the ellipsoidal Gaussian function,

$$\exp(-\alpha(x^2+y^2)-\beta z^2), \tag{12}$$

was used by Katriel and Adam [4], the non-integer-n-STO,

$$r^{\lambda}\exp(-\zeta r), \tag{13}$$

was employed, e.g. in single centre calculations by Bishop [5], and a non-integer-ℓ- STO was used by Ludwig and Parr [6]. A summary of the results of various unconventional 2-parameter basis functions for He has been given by Bishop and Leclerc [7].

One important group of unconventional basis functions is the class of integral transform (IT) functions. Since these will be the main point of interest in this thesis, they will be dealt with in more detail.

SECTION B. INTEGRAL TRANSFORM FUNCTIONS

1) MATHEMATICAL FORMULATION

Integral transform functions are relatively new to the quantum chemistry scene. In order to introduce them use will be made of their relation to linear combinations of other basis functions. An IT function can be regarded as a generalization of a linear combination in the following way: whereas the basis function $\chi(\zeta,r)$ remains unchanged, the discrete set $\{\zeta_i\}$ of the non-linear parameter ζ is transformed into a continuous range (A,B) of its values, the sum over n terms is transformed into a definite integral, and the set of coefficients $\{c_i\}$ is transformed into a weight factor function $c(\zeta)$, i.e.

$$\sum_{i=1}^{k} c_i\chi(\zeta_i,r) \qquad (14)$$

becomes

$$\int_A^B c(\zeta)\chi(\zeta,r)d\zeta. \qquad (15)$$

Graphically one can demonstrate the above generalization by plotting the spectrum of the coefficients c_i as a function of the orbital exponent ζ. The weight factor $c(\zeta)$, or the "shape function" of the IT function, is then given by the envelope function (see Fig. 1).

It should be mentioned that the replacement of a set of coefficients by a shape function, as is shown in Fig. 1, restricts the flexibility offered by a linear combination, in which the linear parameters are varied independently of each other and can have positive and negative signs. However, the case shown in Fig. 1 is very common, especially with Gaussian type orbitals.

2) CHARACTERISTICS OF AN IT FUNCTION

Any IT function is defined if the primitive function, the shape function, and the domain of integration are specified.

(a) Primitive Function

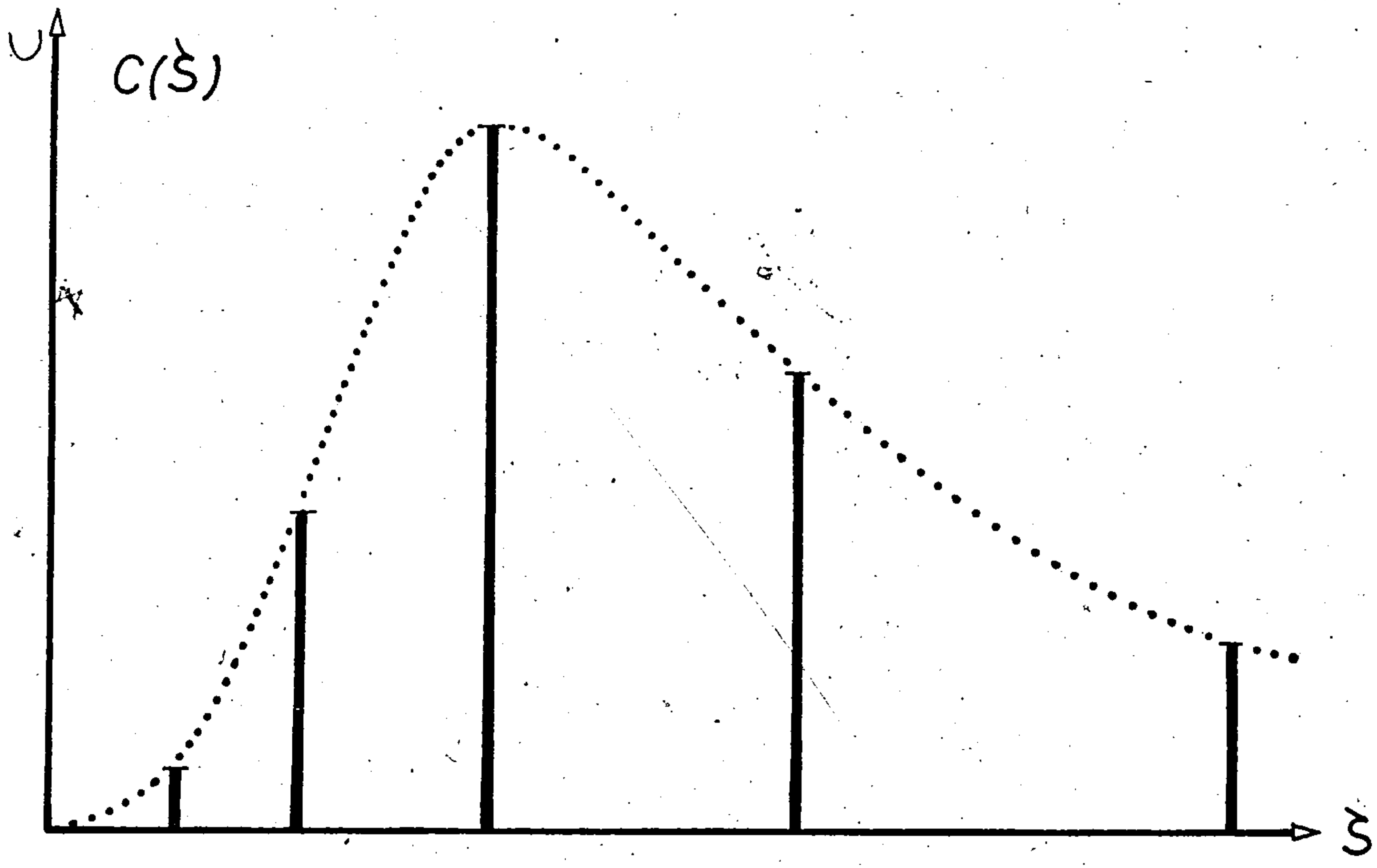
Integral transforms of trigonometric functions are called "Fourier transforms", and ITs of the exponential function are known as "Laplace transforms". In this work use will be made of primitive functions, $\exp(-\zeta r)$ and $\exp(-\zeta r^2)$, i.e. the 1s-STO and the 1s-GTO, and the functions will be called exponential ITs and Gaussian ITs respectively.

Caption to Fig. 1.

The set of coefficients of a linear combination as a function of the orbital exponent ζ.

—— ———————— coefficients c_i

.... envelope function


U
$C(\xi)$
ξ

(b) Shape Function

The problem of finding the coefficients in a linear combination is now replaced by that of finding an appropriate shape function. One possibility is to choose a shape function with adjustable parameters. A small number of parameters (normally two) is usually sufficient.

Several shape functions have been used in atomic and molecular calculations. Schematic drawings of several shape functions as functions of ζ are given in Fig. 2. Shape functions can be divided into two groups having a finite or an infinite domain of integration.

(i) Finite Domain of Integration

The rectangular shape function,

$$G(A,B;\zeta) = \left\{ \begin{array}{ll} 0 & , \zeta < A \\ \text{const}, & A \leq \zeta \leq B \\ 0 & , \zeta > B \end{array} \right\}, \qquad (16)$$

produces the Hulthén basis function if $\exp(-\zeta r)$ is the primitive function:

$$\phi(r) = N\, r^{-1} \left[\exp(-Ar)-\exp(-Br)\right]. \qquad (17)$$

A similar expression is obtained if $\exp(-\zeta r^2)$ is the primitive function. A and B are variational parameters, and N is a normalization constant.

Caption to Fig. 2.

Schematic drawings of several shape functions.

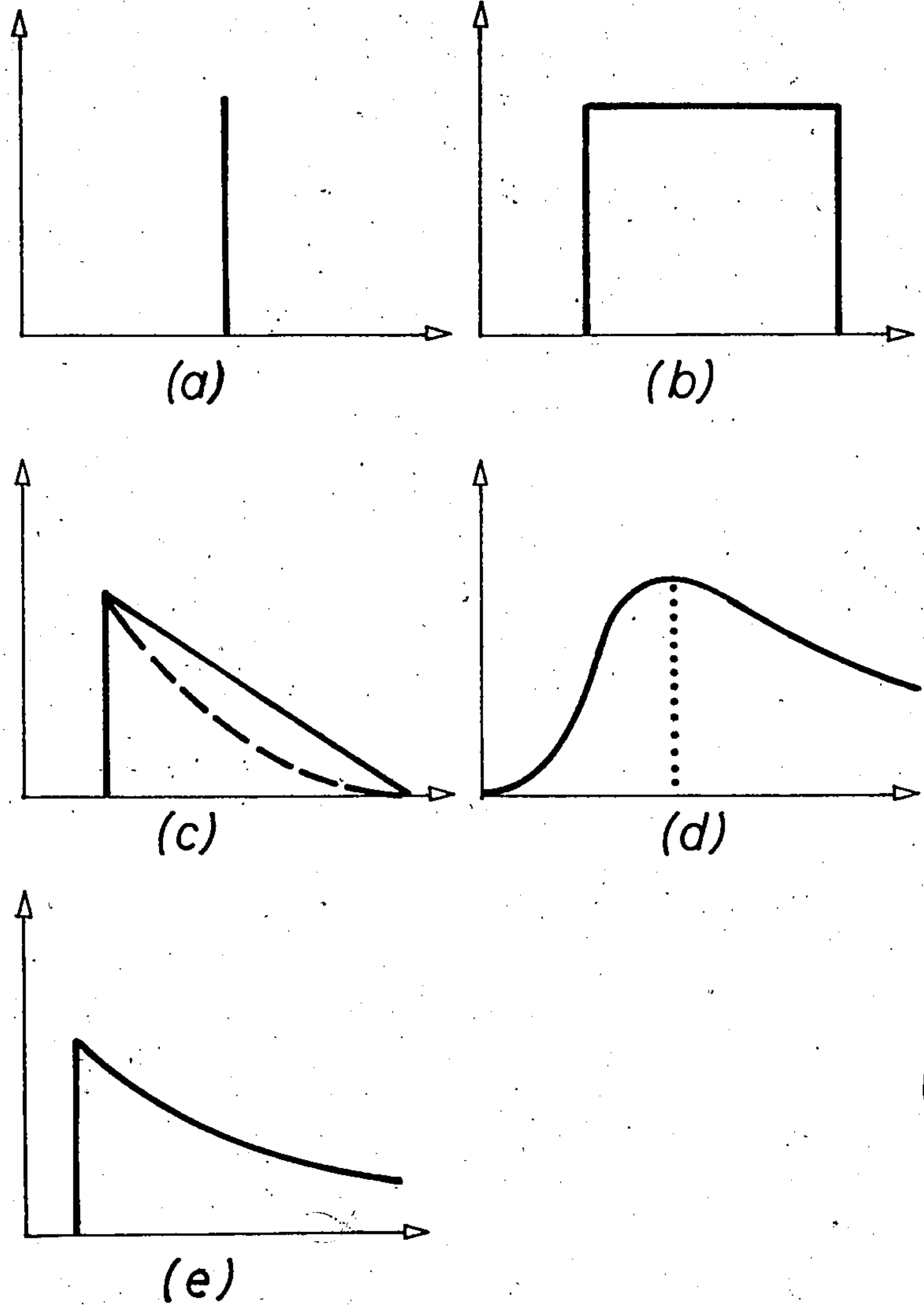
(a) Delta function $\delta(\zeta-\zeta_{max})$.

(b) Hulthén type.

(c) Fractional integral class, ▬▬▬ m=1, — — — m=2.

(d) Continuous shape functions over the integration domain $(0, \infty)$ e.g. $G(\nu,q;\zeta)$ or $G(n,p;\zeta)$, ... ζ_{max}.

(e) Shape function $G(A,\alpha;\zeta)$ of the rational function.



(a)

(b)

(c)

(d)

(e)

A generalization of the Hulthén shape function is the 3-parameter function,

$$G(A,B,m;\zeta) = \left\{ \begin{array}{cc} 0, & \zeta < A \\ (B-\zeta)^m, & A \leq \zeta \leq B \\ 0, & \zeta > B \end{array} \right\}, \qquad (18)$$

where m is 1,2,3 etc. (m=0 is the Hulthén shape function). With both the $\exp(-\zeta r)$ and the $\exp(-\zeta r^2)$ primitive functions, the resulting IT functions belong to the "fractional integral class", and A,B, and m are variational parameters.

(ii) Infinite Domain of Integration

The shape function,

$$G(\nu,q;\zeta) = \zeta^{-(\nu+1)}\exp[-q^2/(4\zeta)], \; 0 \leq \zeta < \infty \; , \qquad (19)$$

has been used with both Gaussian and exponential primitive functions, since it constitutes a good method of representing the envelope of a set of coefficients. It contains two variational parameters ν and q. For a Gaussian primitive function the resulting IT function is

$$\phi(r) = N\, k_\nu(qr), \qquad (20)$$

and for an exponential primitive function the resulting IT function is

$$\phi(r) = N\, k_\nu(q\sqrt{r}); \qquad (21)$$

the functions $k_\nu(x)$ are reduced modified Bessel functions of the second kind.

The shape function,

$$G(n,p;\zeta) = \zeta^{n} \exp(-p\zeta), \; 0 \leq \zeta < \infty, \qquad (22)$$

is related to Eq. (19) by the transformation $\zeta \rightarrow \zeta^{-1}$. The IT function which combines $G(n,p;\zeta)$ with the exponential primitive function is called a Slater transform function (STF) and contains the two parameters n and p:

$$\phi(r) = N \cdot \frac{1}{(r + p)^{n+1}} \; . \qquad (23)$$

The above basis function is of striking simplicity, yet very effective in achieving good approximate wavefunctions.

Another shape function with an infinite domain of integration is

$$G(A,a;\zeta) = \left\{ \begin{array}{ll} 0, & \zeta < A \\ A^{-1} \exp[-\frac{a}{A}(\zeta-A)], & A \leq \zeta < \infty \end{array} \right\} . \qquad (24)$$

This shape function when combined with an exponential primitive function is the "rational function" [8]:

$$\phi(r) = N \, (Ar + a)^{-1} \exp(-Ar). \qquad (25)$$

(iii) The Delta Function

All shape functions in an IT function must contain the delta function as a special case for a certain value of one of the parameters. This condition, the "delta-convergence", implies also that shape functions must be normalized to unity over the integration domain. This is a small restriction, since there are many ways to form a delta-convergent series. All shape functions listed in the preceding paragraph meet the delta-convergence condition. Proof of the delta-convergence of the shape function $G(\nu,q;\zeta)$ for $\nu \to \infty$ is given in Appendix 1.

In the case where a shape function reduces to a delta function $\delta(\zeta-\zeta_o)$, the IT function reduces to its primitive function, since, e.g.,

$$\int_o^\infty \delta(\zeta-\zeta_o) \exp(-\zeta r)d\zeta = \exp(-\zeta_o r). \tag{26}$$

(c) The Resulting IT Function

(i) Completeness

The Gaussian as well as the exponential functions form a complete set. The completeness of the sets of the corresponding IT functions, $k_\nu(qr)$ and $k_\nu(q\sqrt{r})$, was discussed by Bishop and Leclerc [7], who showed that both functions satisfy a Sturm-Liouville differential equation. Since the eigenfunctions of the latter are known to form a complete set, the completeness of the sets, $\{k_\nu(qr)\}$ and $\{k_\nu(q\sqrt{r})\}$, with either ν fixed and q varied, or q fixed and ν varied is ensured.

(ii) Special Cases

The special cases $\nu\to\infty$ and $\nu = 1/2$ for both $k_\nu(qr)$ and $k_\nu(q\sqrt{r})$ are of interest since they satisfy the following relationships.

The Gaussian IT function, $k_\nu(qr)$, is proportional to the exponential function for $\nu = 1/2$ and $q = \zeta$, i.e.

$$k_{1/2}(\zeta r) = \sqrt{\pi/2}\,\exp(-\zeta r) \quad , \tag{27}$$

and for $\nu\to\infty$ and $q = \sqrt{4\zeta(\nu+1)}$, it reduces to the primitive Gaussian function, i.e.,

$$\lim_{\nu\to\infty} [C(\nu)\; k_{\nu}(qr)] = \exp(-\zeta r^{2}), \tag{28}$$

with

$$C(\nu) = [\Gamma(\nu)\cdot 2^{\nu-1}]^{-1}. \tag{29}$$

The exponential IT function, $k_{\nu}(q\sqrt{r})$, is proportional to $\exp(-\zeta\sqrt{r})$ for $\nu=1/2$ and $q=\zeta$, i.e.,

$$k_{1/2}(\zeta\sqrt{r}) = \sqrt{\pi/2}\,\exp(-\zeta\sqrt{r}), \tag{30}$$

and for $\nu\to\infty$ and $q = \sqrt{4\zeta(\nu+1)}$ it reduces to the primitive function, i.e.,

$$\lim_{\nu\to\infty}[C(\nu)\cdot k_{\nu}(q\sqrt{r})] = \exp(-\zeta r), \tag{31}$$

with $C(\nu)$ as given in Eq. (29).

3) ALTERNATIVE IT METHODS AND FUNCTIONS

In this work a given mathematical function containing variational parameters is used to approximate the shape function. However, there are several other ways of finding shape functions, e.g., Somorjai and Power [9] have solved the appropriate integral equation directly making no *a priori* assumption about the form of the shape function.

There are many functions other than $\exp(-\zeta r)$ and $\exp(-\zeta r^2)$ which can be chosen as primitive functions, e.g., 2s, 3s, 4s, ...2p, 3d etc. functions can be used.

There are other non-linear parameters besides the orbital exponent, ζ, which can be 'generalized', such as the position coordinate of "floating" basis functions which are not centred at the nuclei, see Somorjai [10], or the principal quantum number, n, which is 'generalized' in the n-transform functions introduced in this work in Section III E.

In a scheme proposed by Somorjai [11] one integral transform function is used as the primitive function in the second integral transformation. Starting from a poor approximation, convergence to a good final shape function is obtained by iteration.

The integral transformation is, of course, not restricted to functions of the spherical coordinate r, but can be used in a completely analogous way for functions of elliptic or other coordinates.

Finally, there are no restrictions to using IT functions for excited states as well as for the ground state.

Many test calculations with IT functions have been reported for several small atomic and molecular systems. In the next section a review of work in this field will be given.

SECTION C. REVIEW

Prior to the advent of the IT basis functions, the integral transformations were merely used as a mathematical method in the evaluation of some molecular integrals. For example, the identity

$$r_{12} = \frac{1}{\sqrt{\pi}} \int_0^\infty s^{-1/2} \exp(-s\, r_{12}^2) ds \qquad (32)$$

was proposed by Shavitt and Karplus [12] for the calculation of two-electron integrals, and the identity

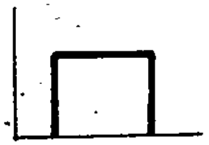
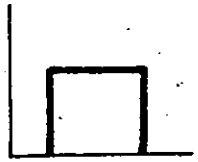
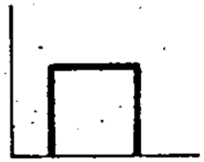
$$\exp(-\zeta r) = \frac{\zeta}{2\sqrt{\pi}} \int_0^\infty s^{-3/2} \exp[-\zeta^2/4s] \exp(-sr^2) ds \qquad (33)$$

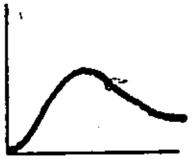
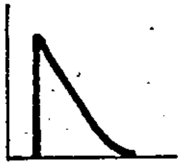
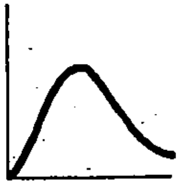
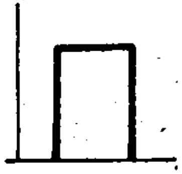
was used in the evaluation of molecular integrals over Slater type orbitals.

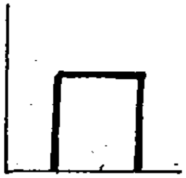
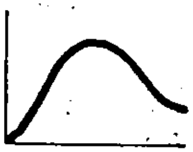
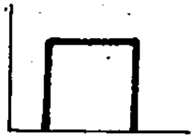
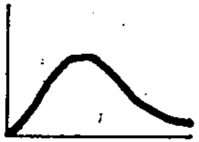
Shavitt [13] suggested that the $k_\nu(qr)$ functions could be used as the radial part of a generalized type of basis function. He also mentioned the representation of the $k_\nu(q\sqrt{r})$ function as a Laplace transform of $G(\nu,q;\zeta)$. Integral transform functions were proposed as basis functions by Somorjai [14].

Table 1 gives a list of publications dealing with the use of IT functions in atomic and molecular calculations. For each entry the shape function, the primitive function, the name of the corresponding IT function, the systems under investigation and the reference are indicated.

Table 1. Review of calculations using parametrized shape functions in several different integral transform functions for small atomic and molecular systems

Nr.	Shape Function	Primitive Function	Resulting IT Function	Systems Studied and Comments	Authors and Reference
1		exponential	"Os"	H^-,He,Be^{++},Ne^{8+}.	Parr and Weare [15].
2		Gaussian	Hulthén IT	H-atom; explanation of "Os" result by IT method; further uses of ITs are discussed.	Somorjai [14].
3		exponential	Slater Transform	H-atom He	Shillady [16]. and [17].
4		exponential	"1p"	B,C,N,O,F,Ne	Chandler [18].
5		exponential	"Os" and "1p"	He isoelectronic series	Weare, Weber and Parr [19].

6		exponential	Slater Transform non-integer-n	He isoelectronic series	Somorjai [20].
7		exponential	STPX extended STF	He	Billingsley and Shillady [21].
8		exponential and Gaussian	Fractional Integral Class	H^-,He,Li^+,Be^{++}; H_2.	Somorjai and Bishop [22].
9		Gaussian	$k_\nu(qr)$	H^-,He,Li^+,Be^{++}.	Bishop and Somorjai [23]. Bishop and Schneider [24].
10		Gaussian	$k_\nu(qr)$	H_2^+ at R=2.0 bohr	Yue and Somorjai [25].
11		1s-STO and 2p-STO	Hulthén Transforms	He isoelectronic series, He 2^1P state, open shell calculations.	Yue [26].

18		2p-STO and 3d-STO	"1p" and "2d"	He,Li^+,Be^{++},B^{3+}; excited states	Gruninger [33].
19		exponential	Slater Transforms	He; electron correlation; H_2 at R=1.4 bohr; elliptic coordinates.	Scherr [34].
20		exponential	Hulthen	H_2 at R=1.4 bohr; compar-ison of unconventional basis functions	Bishop and Leclerc [7]; Chapter IV.
		exponential	$k_\nu(q\sqrt{r})$		

SECTION D. COMPUTATIONAL ASPECTS

1) INTEGRATION

(a) Order of Integration

If use is made of an integral transform function two kinds of integration are involved in calculating the energy: integration over the electronic coordinates and integration over the parameter space. There are two ways of carrying out the integration. If the integration over the parameter space is performed first, the explicit forms of the basis functions are used, and if the integration over the electronic coordinates is carried out first, use is made of the implicit forms, the integral representations, of the basis functions,

$$\phi(r) = \int G(\zeta)\phi(\zeta r)\, d\zeta \tag{34}$$

and

$$\phi(r) = \int G(\zeta')\phi(\zeta' r)\, d\zeta', \tag{35}$$

so that the energy, E, is

$$E = \frac{\int\int G(\zeta)G(\zeta')\ [\int \phi(\zeta r)H\phi(\zeta' r)d\tau]d\zeta d\zeta'}{\int\int G(\zeta)G(\zeta')\ [\int \phi(\zeta r)\phi(\zeta' r)d\tau]d\zeta d\zeta'}. \tag{36}$$

When GTOs and STOs are used as primitive functions, use can be made of the well known formulae for the inner integrations over $d\tau$.

(a) Numerical Integration

It was not always possible to evaluate all integrals analytically, and therefore numerical integration techniques were employed. In Gaussian quadratures the integral is approximated by a weighted sum of values of the integrand for a special set of arguments, i.e.,

$$\int_a^b g(t)\, dt \simeq \sum_{i=1}^{N} u_i\, g(t_i). \qquad (37)$$

Tables of the weights, u_i, and arguments, t_i, are available for different values of N, e.g., in Abramowitz and Stegun [35]. Different Gaussian quadratures are distinguished by special integration domains, (-1,+1) or (0,∞), or by special forms of the integrand, such as those containing the factors $\exp(-t)$ or $\exp(-t^2)$.

A mapping technique has been proposed by McLean and Yoshimine [36], which enables one to apply Gauss-Legendre quadrature tabulated weights and points to a general integration domain (a,b), where a and b can take any values including infinity. They introduced a mapping parameter, m, ($a<m<b$), which enables one to change the distribution of points t_i; the weights, u_i, are then changed so that the quadrature still produces the best possible accuracy for a given number of points, N. This technique was used in this work in several instances and was found to be very economic with respect to the number of points required for a given accuracy.

2) MINIMIZATION

(a) Linear Parameters

In Sections III C and III D, linear combinations of basis functions are used. As was shown earlier, the minimization of the energy expression with respect to the linear coefficients reduces to the solution of a system of linear equations. These equations were solved using a standard computer subroutine.

(b) Non-linear Parameters

Since the IT basis functions, which are studied in this work, contain only two non-linear parameters, the minimization of the energy with respect to these parameters presented no difficulty. When necessary a minimization routine SEARCH was used. This routine is based on a pattern search technique and is described by Wilde [37].

All necessary computer programs were written in the programming language Fortran IV, and all computer calculations were carried out in double precision arithmetic (i.e., 16 digits) on the IBM 360/65 computer system at the University of Ottawa Computing Centre.

SECTION E. OUTLINE

The helium isoelectronic series (Chapter II), the hydrogen molecular ion (Chapter III), and the hydrogen molecule (Chapter IV) will be studied by using the integral transform functions $k_\nu(q\sqrt{r})$, which combine the shape function $G(\nu,q;\zeta)$ and the exponential primitive function. At the end of each chapter the results obtained by using these functions will be compared with those obtained by other authors using exponential IT functions with different shape functions. The results will also be compared with the results obtained when linear combinations of 1s-STOs are used. A comparison of the results obtained using different shape functions in Gaussian ITs will also be given.

In Section III E a novel IT function which generalizes the principal quantum number, n, rather than the orbital exponent, ζ, will be introduced and tested in calculations on H_2^+.

CHAPTER II

THE HE ISOELECTRONIC SERIES

SECTION A. INTRODUCTION

The atoms and ions of the He isoelectronic series, H$^-$, He, Li$^+$, and Be^{++} ..., are two-electron one-centre systems. They are important in theoretical investigations because of their simplicity, which makes them amenable to rather accurate *ab initio* calculations including the study of electron correlation. They are often used for testing new kinds of basis functions. The SCF (self-consistent field) energies of the He isoelectronic series have been calculated by Roothaan, Sachs and Weiss [38]. The most accurate calculations for He have been made by Pekeris [39] who included configuration interaction terms and used an expansion with a large number of functions to represent the wavefunction. Many different approximate wavefunctions have been proposed, some of the ones which are pertinent to this study are referred to in Section C.

In this chapter, results for H$^-$, He, and Li$^+$ using the exponential integral transform functions, $k_\nu(q\sqrt{r})$, are reported. A discussion of the wavefunctions, the shape functions, the limit for infinite nuclear charge, and some expectation values of powers of r is also given. In Section C the results are analysed and compared with those obtained for $k_\nu(qr)$, the analogous Gaussian integral transform function.

SECTION B. THE EXPONENTIAL INTEGRAL TRANSFORM FUNCTIONS, $k_\nu(q\sqrt{r})$

1) MOTIVATION

Since exponential functions are known to be better basis functions than Gaussian functions it was anticipated that the exponential IT functions should be better than the Gaussian IT functions. The latter produced good results for the He isoelectronic series (Bishop and Somorjai[23]). The use of the basis functions, $k_\nu(q\sqrt{r})$, was therefore explored for H^-, He, and Li^+. The functions, $k_\nu(x)$, are reduced modified Bessel functions of the second kind. They are related to the normal modified Bessel functions of the second kind, $K_\nu(x)$, by the equation

$$k_\nu(x) = K_\nu(x)\ x^\nu . \qquad (38)$$

However, the fact that they are related to Bessel functions is less important than the fact that they can be regarded as the generalized form of a linear combination of exponential functions. This becomes clear by using the following Laplace transformation,

$$[q^{2\nu}/2^{\nu+1}]k_\nu(q\sqrt{r}) = \int_0^\infty G(\nu,q;\zeta)\ \exp(-\zeta r)\ d\zeta , \qquad (39)$$

where $G(\nu,q;\zeta)$ is the shape function described in Chapter I. If the $k_\nu(q\sqrt{r})$ functions are written in this form, it can be seen that they are equivalent to linear combinations of an infinite number of screened exponential functions with orbital exponents, ζ, ranging continuously from zero to infinity. The shape function has the effect of appropriately weighting the orbital exponent space.

2) MATHEMATICAL FORMULATION

The total wavefunction, $\Psi = \phi(r_1)\ \phi(r_2)$, is constructed from the orbitals ϕ,

$$\phi(r) = k_\nu(q\sqrt{r}), \tag{40}$$

where ν and q are variational parameters. With these trial functions and the Hamiltonian (in atomic units),

$$H = -\frac{1}{2}\,[\nabla_1^2 + \nabla_1^2] - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\ , \tag{41}$$

where Z denotes the nuclear charge, the electronic energy,

$$E = \int\int \Psi H \Psi d\tau_1 d\tau_2 / \int\int \Psi\Psi d\tau_1 d\tau_2\ , \tag{42}$$

is given by the expression

$$E = [2\ S(T + V_n) + V_e]/S^2, \tag{43}$$

where the overlap integral is

$$S = \int \phi^*(r)\, \phi(r) d\tau = 2^{2\nu+6}\, q^{-6}\, \pi[\Gamma(\nu+3)]^2\, B(2\nu+3,3), \qquad (44)$$

the kinetic energy integral is

$$T = \int \phi^*(r)\, (-\tfrac{1}{2}\nabla^2)\, \phi(r) d\tau = -2^{2\nu+1}\, q^{-2}\, \pi[\Gamma(\nu+2)]^2\, B(2\nu+1,3), \qquad (45)$$

the electron nuclear attraction integral is

$$V_n = \int \phi^*(r)\, (-\frac{Z}{r})\, \phi(r) d\tau = -Z\, 2^{2\nu+4}\, q^{-4}\, \pi[\Gamma(\nu+2)]^2\, B(2\nu+2,2), \qquad (46)$$

and the two-electron integral is

$$\begin{aligned} V_e &= \int\int \phi^*(r_1)\, \phi(r_1)\, (\frac{1}{r_{12}})\, \phi^*(r_2)\, \phi(r_2)\, d\tau_1\, d\tau_2 \\ &= 64q^{-10}\, (2\nu+2)^{-1}\, \pi^2 \int_0^\infty p^{4\nu+9}\, K_\nu^2(p)\, [(2\nu+3)^{-1}\, K_{\nu+2}^2(p) \\ &\quad + (2\nu+2)\, (2\nu+3)^{-1}\, K_{\nu+1}^2(p) - K_\nu^2(p)]dp. \end{aligned} \qquad (47)$$

In the above expressions, $B(x,y)$ is the beta function. The integral V_e was derived by closely following the description given by Bishop and Somorjai [23] for the Gaussian integral transform. The electronic energy is thus finally given as a function of ν and q, and the nuclear charge Z.

3) COMPUTATIONAL DETAILS

The integral in the expression for V_e is evaluated numerically using Gauss-Laguerre quadrature in the same way as the similar integral was treated in [23]. Values for ν and q for He and Li$^+$ were found to be very large, and special care had to be taken to avoid loss of accuracy in the evaluation of V_e. The accuracy of the calculation of V_e was tested for half-integer values of ν where analytical formulae for the $k_\nu(x)$ exist. Agreement to at least eight significant figures was found.

Optimization of the parameters ν and q was reduced to a one-dimensional problem since optimization with respect to q could be done analytically.

4) RESULTS AND DISCUSSION

Table 2 shows the optimum parameters and the corresponding minimum energies for H$^-$, He and Li$^+$.

(a) Energies

The results obtained by using $k_\nu(q\sqrt{r})$ functions for H$^-$, He, and Li$^+$ are very good. In Table 3 the energies obtained are compared with the Hartree-Fock values and are found to represent 99.95%, 99.98%, and 99.99% of the Hartree-Fock energy for H$^-$, He, and Li$^+$, respectively. The Hartree-Fock energy is the best energy that one can achieve within the orbital approximation. It can be seen from this table that the energies are, as was expected, superior to those calculated by Somorjai and Bishop [23] using the Gaussian integral transform functions, $k_\nu(qr)$. They are not, however, as

Table 2. Parameters and energies for H^-, He, and Li^+, using the exponential integral transform functions $k_\nu(q\sqrt{r})$.

Atom or Ion	Parameters ν	Parameters q	Energy (hartree)
H^-	3.261	3.27	-0.487 704
He	10.426	8.61	-2.861 194
Li^+	18.17	14.18	-7.235 565

Table 3. Comparison of energies (hartree) for H^-, He, and Li^+.

Atom or Ion	$k_\nu(q\sqrt{r})$	Hartree-Fock [38]	$k_\nu(qr)$, [23]	Fractional integral class [22]
H^-	-0.487704	-0.48793	-0.48296	-0.4878879
He	-2.861194	-2.86168	-2.85853	-2.861450
Li^+	-7.235565	-7.23641	-7.23366	-7.235760

good as the energies calculated for the same isoelectronic series by Bishop and Somorjai [22], using a different shape function (the $G(A,B,m;\zeta)$ described in Chapter I) in an exponential integral transform function, namely

$$\int_A^B (B-\zeta)^m \exp(-r\zeta)d\zeta.$$

This is understandable since these fractional integral class functions contain three variational parameters.

(b) Wavefunctions

The customary one-electron radial functions defined by

$$P(r) = r\phi(r) \tag{48}$$

for the exponential and the Gaussian integral transform functions,

$$P_1(r) = N_1\, r\, k_\nu(q\sqrt{r}), \tag{49}$$

and

$$P_2(r) = N_2\, r\, k_\nu(qr), \tag{50}$$

(for the latter see Bishop and Schneider [24]), were compared with the Hartree-Fock radial function, P_{HF}, which was found by using the coefficients given by Roothaan et al. [38]. N_1 and N_2 were chosen such that

$$4\pi\int P^2(r)dr = 1. \tag{51}$$

The top half of Fig. 3 shows as an example the radial function, P_{HF}, for He and the bottom half shows the differences between

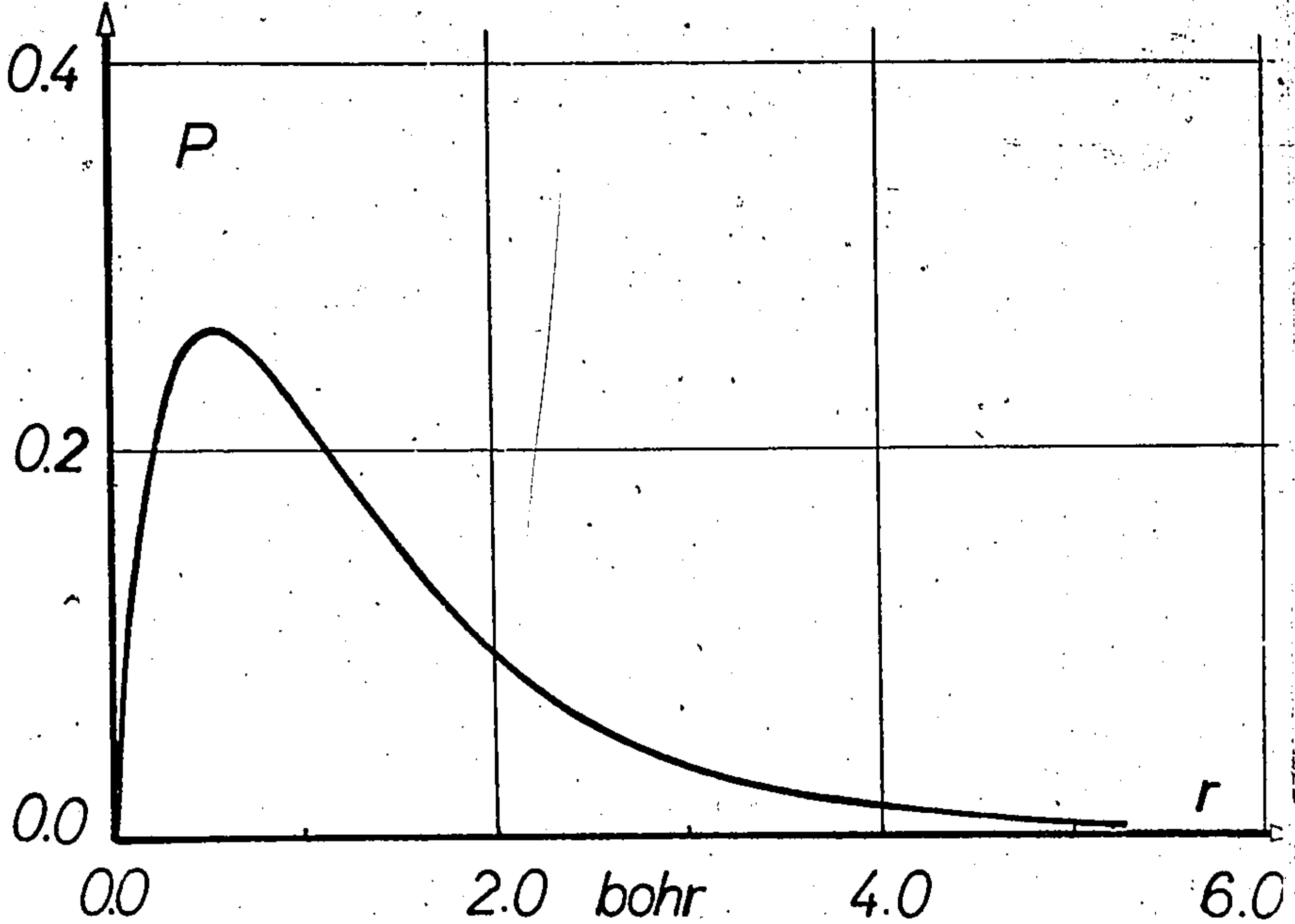
Caption to Figure 3

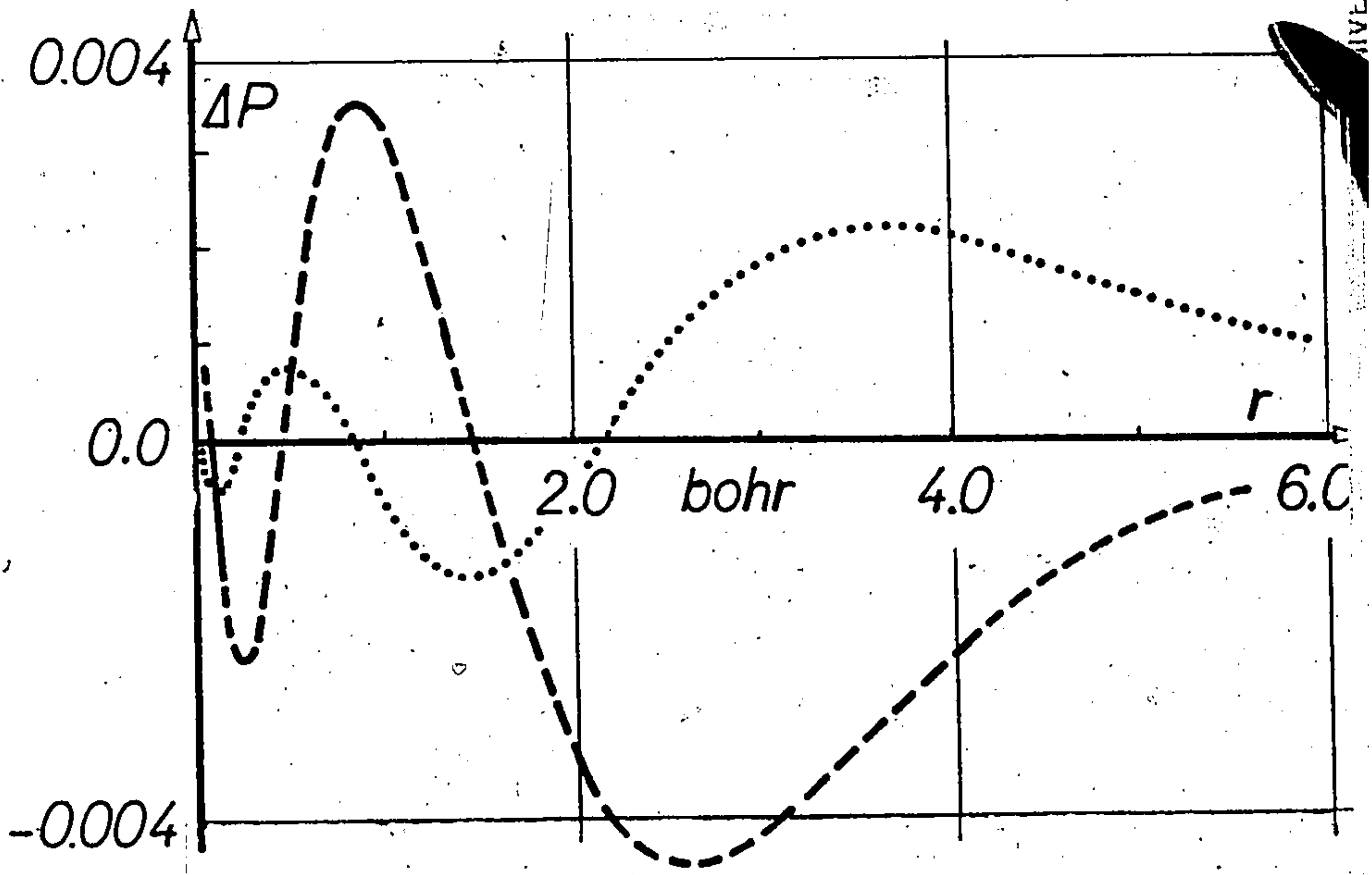
Wavefunctions for helium

—————— indicates P_{HF} = Hartree-Fock radial function.

.... indicates $P_1 - P_{HF}$, where $P_1 = N\ r\ k_\nu(q\sqrt{r})$, $\nu = 10.426$ and $q = 8.61$.

-------- indicates $P_2 - P_{HF}$, where $P_2 = N\ r\ k_\nu(qr)$, $\nu = 0.3575$ and $q = 1.52167$.


0.4
P
0.2
0.0
r
0.0
2.0
bohr
4.0
6.0


0.004
ΔP
0.0
r
2.0
bohr
4.0
6.0
-0.004

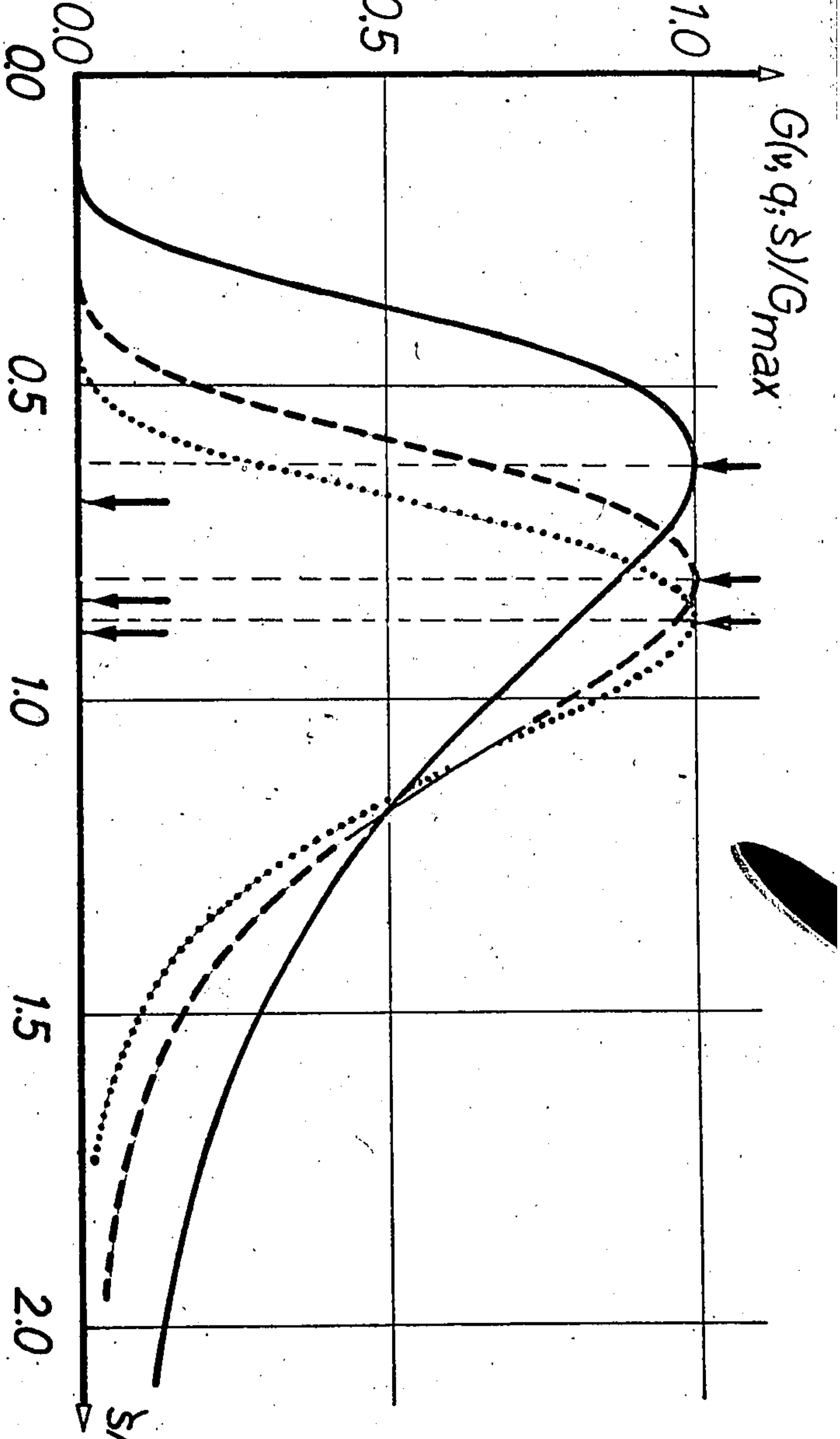
Caption to Figure 4 .

The shape functions (plotted versus the ratio ζ/Z) for optimum parameters for H^-, He, and Li^+, using the exponential IT functions $k_\nu(q\sqrt{r})$. The arrows on the abscissa mark ζ_{H^-}, ζ_{He} and ζ_{Li^+}, and the arrows in the top part of the figure mark ζ_{max} for each case.

▬▬▬▬▬▬ H^-

— — — — He

.... Li^+


G(ν,q;z)/G_max
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
z/Z

P_1 or P_2 and P_{HF} in enlarged scale. It is apparent that the differences between the $k_\nu(q\sqrt{r})$ and Hartree-Fock radial functions (dotted line) are smaller than the corresponding differences for the $k_\nu(qr)$ (broken line), especially in the region of the maximum of P_{HF}. Very similar plots were obtained for H^- and Li^+.

(c) Shape functions

Fig. 4 shows the shape functions for optimum values of the parameters ν and q. The shape functions are plotted versus the ratio ζ/Z in order to be able to compare them on the same figure. It is interesting to compare the values of ζ_{max}, for which the shape functions have a maximum, with the values of ζ_Z the orbital exponents which minimize the energy if a single screened exponential function is used as a basis function. The analytic expressions for ζ_{max} and ζ_Z are

$$\zeta_{max} = q^2/[4(\nu+1)], \tag{52}$$

and

$$\zeta_Z = (Z-5/16), \tag{53}$$

and their values are given in Table 4. Both ζ_{max}/Z and ζ_Z/Z tend to 1 in the limit $Z \to \infty$.

Fig. 5 shows how well the exponential IT function for He succeeds in imitating the set of optimum coefficients which occur in a 3-term linear combination of exponential functions used in a SCF calculation by Solomon [40].

Table 4. Values for ζ_{max} and ζ_Z for H^-, He, and Li^+, using the exponential integral transform functions $k_\nu(q\sqrt{r})$.

Z	ζ_{max}	ζ_Z	ζ_{max}/Z	ζ_Z/Z
1	0.625	0.6875	0.625	0.6875
2	1.622	1.6875	0.811	0.84375
3	2.622	2.6875	0.874	0.8958

Table 5. Expectation values of powers of r for He compared with those obtained with the Hartree-Fock function.

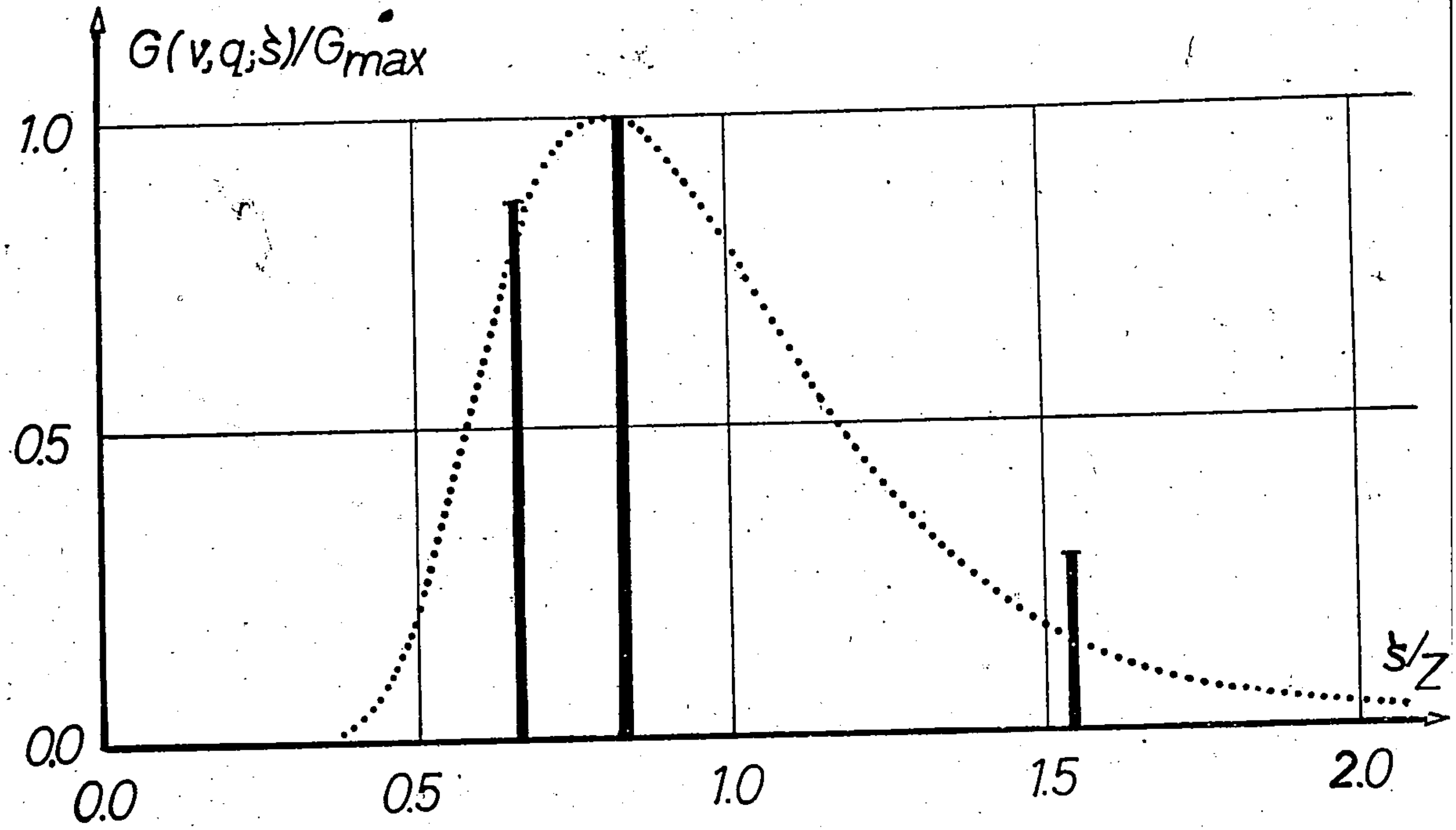
Function	$\langle r^1\rangle$	$\langle r^2\rangle$	$\langle r^3\rangle$	$\langle r^4\rangle$	Reference
$k_\nu(q\sqrt{r})$	0.9307	1.2064	2.038	4.299	This work.
Hartree-Fock	0.9273	1.1848	1.9406	3.8879	[38].

Caption to Figure 5.

Comparison of the shape function, $G(\nu,q;\zeta)$, for optimum values of the parameters ν and q for He (plotted versus the ratio ζ/Z) with the set of optimized coefficients calculated by Solomon [40].

▬▬▬▬▬ coefficients

.... $G(\nu,q;\zeta)$


G(v,q;ŝ)/Gmax
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
ŝ/Z

(d) Expectation values of r^n.

Expectation values of r^n are given by the expression

$$\int \phi(r) r^n \phi(r) d\tau = S^{-1}\ 2^{2(3+n+\nu)} q^{-2(n+3)} \pi \Gamma^2(\nu+3+n) B(2\nu+3+n, 3+n). \tag{54}$$

In Table 5 results for He for n = 1,2,3 and 4 are compared with the corresponding results using the Hartree-Fock wavefunction. The agreement between the two sets of numbers is very good.

(e) The limit for infinite nuclear charge

Using the $k_\nu(q\sqrt{r})$ functions the energies of the He isoelectronic series with optimum values for q may be expressed as a function of ν and Z as:

$$E = -Z^2\left[\frac{4\nu^2 + 12\nu+5}{4\nu^2 + 12\nu+8}\right] + Z\ f(\nu) - \frac{f^2(\nu)}{4}\left[\frac{\nu^2+3\nu+2}{\nu^2+3\nu+5/4}\right] . \tag{55}$$

Since ν goes to infinity for $Z \to \infty$ (see Table 2), the rational expressions for ν in square brackets in Eq.(55) tend to 1. $f(\nu)$ is a fairly complicated function of ν, which for large ν tends to 5/8. This result was found by evaluating $f(\nu)$ for large ν ($\nu \doteq 25$), and fitting the expression

$$f(\nu) = a_o + a_1\nu^{-1} + a_2\nu^{-2} , \tag{56}$$

and then letting ν increase towards ∞. Hence the limiting form of E for $Z \to \infty$ is:

$$E = -Z^2 + (5/8)Z \quad -(25/256)$$
$$= -Z^2 + 0.625\ Z \ -0.097\ 656\ 25. \qquad (57)$$

This can be compared with the result of Linderberg [42], who found the Hartree-Fock energy to be

$$E = -Z^2 + 0.625\ Z - 0.111\ 003\ 17 - 0.001\ 055\ 25\ Z^{-1}. \qquad (58)$$

In the next section the results of the above calculations will be compared with the results obtained by using other integral transform functions. He will be taken as a prototype for the whole series.

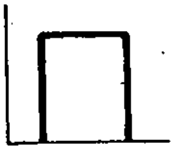
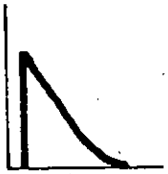
SECTION C. COMPARISON OF I.T. FUNCTIONS FOR He.

In Table 6 several shape functions which have been used in conjunction with the Gaussian primitive function are listed. For ease of identification schematic drawings of the shape functions as functions of the orbital exponent, ζ, are included as well as the number of non-linear parameters. Some linear combinations of 1s-GTOs are given in this table, since they can be regarded as the case of a shape function which is a sum of delta functions located at different optimum orbital exponents, ζ_i, i.e.,

$$\text{shape}(\zeta) = \sum_{i=1} \delta(\zeta - \zeta_i). \qquad (59)$$

The entries in Table 6 are given in order of decreasing energy.

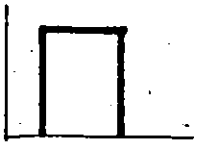
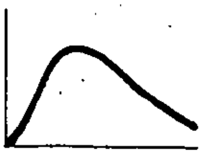
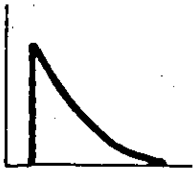
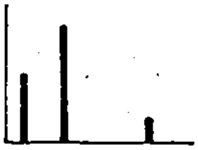
Table 6. Different basis functions for He expressed as Gaussian integral transforms.

Basis	Shape function	Energy (hartree)	Number of non-linear parameters	Reference
1s-GTO		-2.300 99	1	Reeves [43].
Hulthén		-2.697 004	2	Somorjai and Bishop [22].
Fractional Integral Class		-2.765 787	3	Somorjai and Bishop [22].
4-term 1s-GTO		-2.855 160 3	4	Huzinaga [44].
$k_\nu(qr)$		-2.858 53	2	Bishop and Somorjai [23], Bishop and Schneider [24].
SCF		-2.861 68		Roothaan et al. [38].

From Table 6 it is apparent that, though the single 1s-GTO gives a poor energy, the situation may be improved by using a linear combination of 1s-GTOs (e.g., the 4-term linear combination given in this table). Both the Hulthén-type and the fractional integral class functions improve the energy considerably compared with the 1s-GTO case, although they use 2 and 3 parameters to do so. The $k_\nu(qr)$ function is excellent, exceeding even the 4-term linear combination of Huzinaga [43], yet it contains only 2 parameters. The SCF energy is included for the sake of comparison.

In Table 7, it can be seen that the single 1s-STO, which is used as a point of reference for all the other functions in this table, produces an energy which is lower than the first three energies in the preceding table. Nevertheless, the 2-parameter Slater transform function (proposed independently by Shillady [17] and Somorjai [20]) and the Hulthén-type function used by Somorjai and Bishop [22] are able to give an energy improvement. Of the 2-parameter integral transform functions, the $k_\nu(q\sqrt{r})$ function gives the best energy. The 3-parameter wavefunction of the fractional integral class is nearly as good as the three-term linear combination of 1s-STOs, however the latter contains a total of five parameters. It has already been pointed out (see Section B) that the exponential integral transform functions produce energies close to the Hartree-Fock value given in the last line of this table.

Table 7. Different basis functions for He expressed as exponential integral transforms.

Basis	Shape function	Energy (hartree)	Number of nonlinear parameters	References
1s-STO		-2.847 656	1	Kellner [41].
Slater Transform		-2.860 555	2	Shillady [17], Somorjai [20].
Hulthén		-2.860 8	2	Somorjai and Bishop [22].
$k_\nu(q\sqrt{r})$		-2.861 19	2	this work, Bishop and Schneider [29].
Fractional Integral Class		-2.861 450	3	Somorjai and Bishop [22].
3-term 1s-STO		-2.861 679	3	Solomon [40].
SCF		-2.861 68		Roothaan et al. [38].

The success of both the Gaussian IT function, $k_\nu(qr)$, and the exponential IT function, $k_\nu(q\sqrt{r})$, for the He isoelectronic series led to the idea of testing them in molecular systems. While the $k_\nu(qr)$ function was used by Yue and Somorjai [25] for H_2^+, the use of $k_\nu(q\sqrt{r})$ for H_2^+ and H_2 will be explored in this work (Chapters III and IV, respectively).

CHAPTER III

THE HYDROGEN MOLECULAR ION

SECTION A. INTRODUCTION

1) IMPORTANCE OF H_2^+

The hydrogen molecular ion is encountered in theoretical investigations in a number of different contexts. Experimentally some H_2^+ energy levels have been measured by Herzberg and Jungen [45] from the limits of the Rydberg series in H_2. However, the spectrum of H_2^+ has not yet been found directly. The photoelectron spectrum has been reported by Cornford et al. [46].

For H_2^+, the smallest possible molecule, and its isotopic and isoelectronic series, the Schrödinger equation for the motion of the electron in the field of the fixed nuclei (i.e., in the Born Oppenheimer approximation) can be solved in closed mathematical form. Theoretical electronic energy eigenvalues and eigenfunctions can be determined very accurately as functions of the internuclear separation. For this reason H_2^+ is useful for testing approximate methods.

2) THE EXACT WAVEFUNCTION

Bates [47] gives a number of references to early determinations of the exact electronic energies, eigenfunctions and equilibrium internuclear separations of H_2^+.

The Schrödinger equation in the Born-Oppenheimer approximation for H_2^+ is separable in elliptical coordinates (λ,μ,ϕ), i.e., the wavefunction is a product of three parts each depending on one of the elliptical coordinates only:

$$\psi = \Lambda(\lambda)\ M(\mu)\ \Phi(\phi). \tag{60}$$

For the ground state of H_2^+, $\Phi(\phi)$ is a constant, and $\Lambda(\lambda)$ and $M(\mu)$ satisfy the following equations:

$$\frac{d}{d\mu}\left[(1-\mu^2)\ \frac{dM(\mu)}{d\mu}\right] + (-A+p^2\mu^2)M(\mu) = 0, \tag{61}$$

and

$$\frac{d}{d\lambda}\left[(\lambda^2-1)\frac{d\Lambda(\lambda)}{d\lambda}\right] + (A+2R\lambda-p^2\lambda^2)\Lambda(\lambda) = 0. \tag{62}$$

For a given internuclear separation, R, the separation constant, A, and the eigenparameter, p, completely define the wavefunction.

In all cases the task of finding the exact λ and μ dependence is transformed to the task of finding the set of coefficients in infinite expansions of $\Lambda(\lambda)$ and $M(\mu)$ in terms of some known set of polynomials. Thus we have for the ground state of H_2^+:

$$M(\mu) = \sum_{\text{even } s=0}^{\infty} f_s\ P_s(\mu), \tag{63}$$

where the $P_s(\mu)$ are Legendre polynomials, and

$$\Lambda(\lambda) = \exp(-p(\lambda-1)) \sum_{i=0}^{\infty} (c_i/i!)L_i(2p(\lambda-1)), \tag{64}$$

where the $L_i(x)$ are Laguerre polynomials, or alternatively $\Lambda(\lambda)$ may be expressed as [47]:

$$\Lambda(\lambda) = (\lambda+1)^{R/p-1} \exp(-p\lambda) \sum_{t=0}^{\infty} g_t \left(\frac{\lambda-1}{\lambda+1}\right)^t . \qquad (65)$$

(a) H_2^+ for the equilibrium internuclear separation

Quite accurate calculations have been carried out recently and precise values are now available for the ground state energy and wavefunction. The energy of the electronic ground state has been found to be E = -0.602 634 619 hartree. The equilibrium internuclear separation has been found to be R_e = 1.997 193 320 bohr. The values are taken from Bishop [48] who used Peek's method [49] to evaluate the coefficients f_s and c_i of Eqs.(63) and (64). They agree with those of Beckel et al. [50] and Power [51]. The coefficients f_s and c_i [52] for the ground state wavefunction for H_2^+ at $R = R_e$ are given in Table 8. The exact wavefunction as a function of the electronic coordinate x(bohr) which lies along the internuclear axis is given in Table 9. The values were calculated using the coefficients of Table 8, and the analytical formula for the normalization constant given by Katriel and Adam [53].

(b) H_2^+ at R = 2.0 bohr

For the sake of standardization most approximate calculations are carried out for H_2^+ at R = 2.0 bohr. Therefore the exact results for this internuclear separation are included here.

Table 8. Coefficients c_i and f_s of Eqs.(63) and (64) for the exact H_2^+ wavefunction at $R = R_e$, the equilibrium internuclear distance.

Λ(λ)			M(μ)		
i	c_i		s	f_s	
			0	0.100 000 000 000	(1)
0	0.100 000 000 000	(1)	2	0.260 054 049 048	(0)
1	-0.483 662 229 906	(-1)	4	0.996 543 674 108	(-2)
2	-0.356 927 348 660	(-2)	6	0.159 359 936 532	(-3)
3	-0.564 019 974 772	(-3)	8	0.140 447 567 234	(-5)
4	-0.124 623 621 094	(-3)	10	0.784 957 131 799	(-8)
5	-0.337 074 566 111	[illegible]	12	0.303 169 107 552	(-10)
6	-0.104 783 136 439	[illegible]	14	0.857 744 346 094	(-13)
7	-0.361 168 415 836	(-5)	16	0.185 449 654 494	(-15)
8	-0.134 926 859 134	(-5)	18	0.316 394 391 062	(-18)
9	-0.537 916 615 118	(-6)	20	0.436 834 538 651	(-21)
10	-0.226 293 502 954	(-6)	22	0.498 109 538 772	(-24)
11	-0.995 660 501 658	(-7)	24	0.477 014 658 719	(-27)
12	-0.454 187 523 575	(-7)	26	0.389 081 330 926	(-30)
13	-0.211 811 591 338	(-7)	28	0.273 553 206 628	(-33)
14	-0.971 981 002 488	(-8)	30	0.167 496 469 095	(-36)
15	-0.376 569 864 334	(-8)	32	0.901 200 007 496	(-40)
			34	0.429 441 078 579	(-43)
			36	0.182 505 430 483	(-46)
			38	0.696 037 188 659	(-50)

The numbers in brackets indicate powers of ten.

Table 9. The exact wavefunction for H_2^+ for the equilibrium internuclear distance, $R = R_e$, as a function of the electron coordinate x (bohr) along the internuclear axis.

λ	μ	x(bohr)	ψ_{exact}
1.000	0.0	0.0	0.315 153 730 412
1.000	0.025	0.024 964 9165	0.315 233 489 172
1.000	0.050	0.049 929 8330	0.315 472 834 006
1.000	0.075	0.074 894 7495	0.315 871 970 650
1.000	0.100	0.099 859 6660	0.316 431 242 223
1.000	0.125	0.124 824 5825	0.317 151 129 575
1.000	0.150	0.149 789 4990	0.318 032 251 772
1.000	0.175	0.174 754 4155	0.319 075 366 714
1.000	0.200	0.199 719 3320	0.320 281 371 899
1.000	0.225	0.224 684 2485	0.321 651 305 323
1.000	0.250	0.249 649 1650	0.323 186 346 528
1.000	0.275	0.274 614 0815	0.324 887 817 784
1.000	0.300	0.299 578 9980	0.326 757 185 420
1.000	0.325	0.324 543 9145	0.328 796 061 300
1.000	0.350	0.349 508 8310	0.331 006 204 445
1.000	0.375	[illegible]374 473 7475	0.333 389 522 801
1.000	0.400	0.399 438 6640	0.335 948 075 167
1.000	0.425	0.424 403 5805	0.338 684 073 262
1.000	0.450	0.449 368 4970	0.341 599 883 956
1.000	0.475	0.474 333 4135	0.344 698 031 660
1.000	0.500	0.499 298 3300	0.347 981 200 866
1.000	0.525	0.524 263 2465	0.351 452 238 862
1.000	0.550	0.549 228 1630	0.355 114 158 601
1.000	0.575	0.574 193 0795	0.358 970 141 749
1.000	0.600	0.599 157 9960	0.363 023 541 898
1.000	0.625	0.624 122 9125	0.367 277 887 956
1.000	0.650	0.649 087 8290	0.371 736 887 721
1.000	0.675	0.674 052 7455	0.376 404 431 630
1.000	0.700	0.699 017 6620	0.381 284 596 704
1.000	0.725	0.723 982 5785	0.386 381 650 676
1.000	0.750	0.748 947 4950	0.391 700 056 325
1.000	0.775	0.773 912 4115	0.397 244 475 999
1.000	0.800	0.798 877 3280	0.403 019 776 355
1.000	0.825	0.823 842 2445	0.409 031 033 300
1.000	0.850	0.848 807 1610	0.415 283 537 160
1.000	0.875	0.873 772 0775	0.421 782 798 057
1.000	0.900	0.898 736 9940	0.428 534 551 526
1.000	0.925	0.923 701 9105	0.435 544 764 359
1.000	0.950	0.948 666 8270	0.442 819 640 692
1.000	0.975	0.973 631 7435	0.450 365 628 338
1.000	1.000	0.998 596 6600	0.458 189 425 374
1.025	1.000	1.023 561 5765	0.443 504 126 446
1.050	1.000	1.048 526 4930	0.429 264 707 885
1.075	1.000	1.073 491 4095	0.415 459 077 035
1.100	1.000	1.098 456 3260	0.402 075 375 827
1.125	1.000	1.123 421 2425	0.389 101 983 307

Table 9. (continued)

1.150	1.000	1.148 386 1590	0.376 527 517 403
1.175	1.000	1.173 351 0755	0.364 340 836 029
1.200	1.000	1.198 315 9920	0.352 531 037 576
1.225	1.000	1.223 280 9085	0.341 087 460 844
1.250	1.000	1.248 245 8250	0.329 999 684 490
1.275	1.000	1.273 210 7415	0.319 257 526 013
1.300	1.000	1.298 175 6580	0.308 851 040 351
1.325	1.000	1.323 140 5745	0.298 770 518 104
1.350	1.000	1.348 105 4910	0.289 006 483 447
1.375	1.000	1.373 070 4075	0.279 549 691 749
1.400	1.000	1.398 035 3240	0.270 391 126 944
1.425	1.000	1.423 000 2405	0.261 521 998 675
1.450	1.000	1.447 965 1570	0.252 933 739 244
1.475	1.000	1.472 930 0735	0.244 618 000 389
1.500	1.000	1.497 894 9900	0.236 566 649 916
1.525	1.000	1.522 859 9065	0.228 771 768 201
1.550	1.000	1.547 824 8230	0.221 225 644 589
1.575	1.000	1.572 789 7395	0.213 920 773 700
1.600	1.000	1.597 754 6560	0.206 849 851 660
1.625	1.000	1.622 719 5725	0.200 005 772 281
1.650	1.000	1.647 684 4890	0.193 381 623 185
1.675	1.000	1.672 649 4055	0.186 970 681 904
1.700	1.000	1.697 614 3220	0.180 766 411 952
1.725	1.000	1.722 579 2385	0.174 762 458 889
1.750	1.000	1.747 544 1550	0.168 952 646 381
1.775	1.000	1.772 509 0715	0.163 330 972 261
1.800	1.000	1.797 473 9880	0.157 891 604 614
1.825	1.000	1.822 438 9045	0.152 628 877 869
1.850	1.000	1.847 403 8210	0.147 537 288 924
1.875	1.000	1.872 368 7375	0.142 611 493 306
1.900	1.000	1.897 333 6540	0.137 846 301 353
1.925	1.000	1.922 298 5705	0.133 236 674 453
1.950	1.000	1.947 263 4870	0.128 777 721 315
1.975	1.000	1.972 228 4035	0.124 464 694 295
2.000	1.000	1.997 193 3200	0.120 292 985 766
2.025	1.000	2.022 158 2365	0.116 258 124 550
2.050	1.000	2.047 123 1530	0.112 355 772 394
2.075	1.000	2.072 088 0695	0.108 581 720 513
2.100	1.000	2.097 052 9860	0.104 931 886 189
2.125	1.000	2.122 017 9025	0.101 402 309 424
2.150	1.000	2.146 982 8190	0.097 989 149 667
2.175	1.000	2.171 947 7355	0.094 688 682 590
2.200	1.000	2.196 912 6520	0.091 497 296 935
2.225	1.000	2.221 877 5685	0.088 411 491 422
2.250	1.000	2.246 842 4850	0.085 427 871 721
2.275	1.000	2.271 807 4015	0.082 543 147 487
2.300	1.000	2.296 772 3180	0.079 754 129 460
2.325	1.000	2.321 737 2345	0.077 057 726 625
2.350	1.000	2.346 702 1510	0.074 450 943 446
2.375	1.000	2.371 667 0675	0.071 930 877 148
2.400	1.000	2.396 631 9840	0.069 494 715 074
2.425	1.000	2.421 596 9005	0.067 139 732 098
2.450	1.000	2.446 561 8170	0.064 863 283 103
2.475	1.000	2.471 526 7335	0.062 662 825 517

The electronic energy of the H_2^+ ground state at R = 2.0 bohr is (from Bishop [54]) E = -0.602 634 214 495 hartree. The coefficients for H_2^+ wavefunction for R = 2.0 bohr are given in Table 10. They are taken from Bishop [52]. The exact wavefunction for H_2^+ at R = 2.0 bohr as a function of the electronic coordinate x(bohr) which lies along the internuclear axis is given in Table 25 of Section E of this chapter, where it is compared with several approximate wavefunctions. A plot of the exact wavefunction can be found in Fig. 12 in the same section.

3) APPROXIMATE WAVEFUNCTIONS

Commonly, there are two kinds of approximate wavefunction for H_2^+: first, wavefunctions which have separate λ- and μ-dependences, and second, LCAO wavefunctions which are formed from a linear combination of atomic orbitals.

(a) $\Lambda(\lambda)\,M(\mu)$-type

In the past $\Lambda(\lambda)$, see Eq. (65), has frequently been approximated by the simple exponential factor with a variational parameter α,

$$\exp(-\alpha\lambda), \tag{66}$$

and $M(\mu)$, see Eq. (63), has been approximated by even functions of μ such as

$$(1+\beta\mu^2) \tag{67}$$

Table 10. Coefficients c_i and f_s of Eqs. (63) and (64) for the exact H_2^+ wavefunction for R = 2.0 bohr.

$\Lambda(\lambda)$		$M(\mu)$	
i	c_i	s	f_s
		0	0.100 000 000 000 (1)
		2	0.260 648 909 971 (0)
0	0.100 000 000 000 (1)	4	0.100 102 072 592 (-1)
1	-0.483 869 105 774 (-1)	6	0.160 425 704 900 (-3)
2	-0.356 602 442 114 (-2)	8	0.141 695 120 648 (-5)
3	-0.563 022 882 484 (-3)	10	0.793 654 447 217 (-8)
4	-0.124 315 929 584 (-3)	12	0.307 195 421 997 (-10)
5	-0.336 035 800 180 (-4)	14	0.871 026 959 950 (-13)
6	-0.104 402 307 081 (-4)	16	0.188 731 103 609 (-15)
7	-0.359 672 245 143 (-5)	18	0.322 693 183 371 (-18)
8	-0.134 304 083 119 (-5)	20	0.446 499 975 282 (-21)
9	-0.535 194 743 379 (-6)	22	0.510 237 885 421 (-24)
10	-0.225 053 450 616 (-6)	24	0.489 691 854 066 (-27)
11	-0.989 809 101 734 (-7)	26	0.400 290 063 542 (-30)
12	-0.451 349 289 065 (-7)	28	0.282 045 679 005 (-33)
13	-0.210 416 522 700 (-7)	30	0.173 071 871 316 (-36)
14	-0.965 306 847 841 (-8)	32	0.933 222 468 926 (-40)
15	-0.373 913 077 416 (-8)	34	0.445 667 259 708 (-43)
		36	0.189 813 048 710 (-46)
		38	0.725 480 643 815 (-50)

The numbers in brackets indicate powers of ten.

or

$$\cosh(\beta\mu) \qquad (68)$$

with a variational parameter β. Calculations of this type are given in [55] to [66]. But more recently better approximate functions, containing only two parameters, have been reported. In Table 11 the λ- and μ-part, the optimum parameters, and the minimum energies for some of these functions for R = 2.0 bohr are given.

Included in this table is the function:

$$V(\mu) = \cosh(\beta\mu) + \cosh(2\beta\mu), \qquad (69)$$

which Varshni and Lam [67] introduced for the μ-dependence, and the function used for the λ-dependence by Weinhold and Chinen [69]. The latter consists of the first term in the exact expansion of Λ(λ) (see Eq. (65)), i.e.,

$$W(\lambda) = (\lambda+1)^{R/\alpha-1} \exp(-\alpha\lambda). \qquad (70)$$

How well both V(μ) and W(λ) of Eqs. (69) and (70) approximate the exact wavefunction is demonstrated by a short calculation with an approximate function, the "V-W-function", composed of these two functions. The optimum parameters must be the same as those obtained for V(μ) [70] and W(λ) in the original calculations. The energy (obtained by numerical integration) in fact coincides up to five decimals with the exact energy of H_2^+ at R = 2.0 bohr (see Table 11). It also is better than the energy calculated recently by Llugano, Gupta and Rothstein with a 3-parameter function [71].

Table 11. Comparison of several approximate functions separable into $\Lambda(\lambda)$ and $M(\mu)$ for H_2^+ at $R = 2.0$ bohr.

$M(\mu)$	$\Lambda(\lambda)$	Energy (hartree)	Ref.
$\cosh(\beta\mu)+\cosh(2\beta\mu)$, $\beta = 0.57531$	$\exp(-\alpha\lambda)$, $\alpha = 1.3540$	−0.602 451	Varshni and Lam [67].
$\cosh(\beta\mu)$, $\beta = 0.9192$	$\exp(-\alpha\lambda)\left[\frac{1+c(\alpha)\lambda}{d(\alpha)+\alpha\lambda}\right]$ where $c(\alpha) \equiv R/(\alpha(3-\sigma))$ $d(\alpha) \equiv \alpha(3+\sigma)/(1-\sigma)$ $\sigma \equiv R/\alpha-1$ $\alpha = 1.4792$	−0.602 623 5	Padé-approximant, Rothstein [68].
$\cosh(\beta\mu)$, $\beta = 0.9192$	$\exp(-\alpha\lambda)(1+\lambda)^{R/\alpha-1}$, $\alpha = 1.4815$	−0.602 623 7	Weinhold and Chinen [69].
$\cosh(\beta\mu)$ $\beta = 0.9192$	$\exp(-\alpha\lambda)(1+\lambda)^{\sigma}$ $\alpha = 1.4890$ $\sigma = 0.3706$	−0.602 624 2	Llugano, Gupta and Rothstein [71
$\cosh(\beta\mu)+\cosh(2\beta\mu)$, $\beta = 0.57531$	$\exp(-\alpha\lambda)(1+\lambda)^{R/\alpha-1}$, $\alpha = 1.4815$	−0.602 631 434	"V-W-function", This work.
$M_{ex}(\mu)$,	$\Lambda_{ex}(\lambda)$,	−0.602 634 214	Peek [49], Bishop [48], Power [51].

Though it is possible to study the effect of integral transformations on the functions of the $\Lambda(\lambda)$, $M(\mu)$-type, it is, however, better to do so with approximate wavefunctions which are linear combinations of atomic orbitals since molecular systems other than H_2^+ are not generally separable in elliptical coordinates. The only calculation reported so far which uses an integral transformation on elliptical coordinates is the one by Scherr [34], who replaced $\exp(-\alpha\lambda)$ and $\exp(+\beta\mu)$ by Slater transform functions in the wavefunction for H_2.

(b) LCAOs

Among the LCAO approximate wavefunctions for H_2^+, those using 1s-GTOs by Schwartz [72], and those using 1s-STOs by Hoyland [73] should be mentioned since they are closely related to the integral transform functions described in this work. The molecular orbital ψ for H_2^+ is formed by centering an AO on each of the nuclei:

$$\psi = N[\phi(r_a) + \phi(r_b)]. \tag{71}$$

The atomic orbitals, $\phi(r)$, are written as a sum of a number of terms with the coefficients and orbital exponents, ζ_i, as variational parameters. Thus for STOs

$$\phi(r) = \sum_{i=0}^{k} c_i \, r^{n_i} \exp(-\zeta_i \, r), \tag{72}$$

and for GTOs

$$\phi(r) = \sum_{i=0}^{k} c_i \, r^{n_i} \exp(-\zeta_i \, r^2). \tag{73}$$

4) OUTLINE OF CHAPTER III

In the remaining sections several approximate wavefunctions for H_2^+ will be dealt with in order to assess the applicability and accuracy of integral transform functions.

Section B describes the calculations using the exponential integral transform functions, $k_\nu(q\sqrt{r})$, which gave good results for the He-isoelectronic series (see Chapter II). Section C contains calculations using s-type STOs which were necessary to clarify the results of Section B. In Section D, LCAOs of STOs with a common orbital exponent are used to investigate the possibilities of a new type of integral transformation. In Section E the n-transform function will be introduced, described, and tested.

SECTION B. EXPONENTIAL INTEGRAL TRANSFORM FUNCTIONS

1) MATHEMATICAL FORMULATION

In this section the exponential integral transform function will be used to construct approximate wavefunctions for the hydrogen molecular ion since these functions produced very accurate energy values for the He-like series.

The exponential integral transform function is characterized by the primitive function $\exp(-\zeta r)$, the shape function $G(\nu,q;\zeta)$, and the domain of integration for ζ $(0,\infty)$. The resulting function is $k_\nu(q\sqrt{r})$ (see Chapter I).

The wavefunction for the electron in H_2^+ is constructed by placing one atomic orbital on each nucleus

$$\psi = N[\phi(r_a) + \phi(r_b)], \tag{74}$$

where

$$\phi(r) = \int_0^\infty G(\nu,q;\zeta)\exp(-\zeta r)\,d\zeta, \tag{75}$$

and N is the normalization constant.

The Hamiltonian for H_2^+ is (in atomic units)

$$H = -1/2\,\nabla^2 - 1/r_a - 1/r_b + 1/R. \tag{76}$$

We write

$$H = H' + 1/R \tag{77}$$

and keep R fixed at 2.0 bohr. The total energy of H_2^+ is then given by

$$E = \int \psi H' \psi \, d\tau / \int \psi\psi \, d\tau + 1/R. \tag{78}$$

Introducing Eq. (75) for the atomic orbitals, $\phi(r_a)$ and $\phi(r_b)$, and interchanging the order of integration (i.e., carrying out the integration over physical space first), we obtain the energy as a function of the variational parameters ν and q:

$$E = \int_0^\infty \int_0^\infty G(\nu,q;\zeta)G(\nu,q;\zeta') H(1,1;\zeta,\zeta')d\zeta d\zeta' / \int_0^\infty \int_0^\infty G(\nu,q;\zeta)G(\nu,q;\zeta')S(1,1;\zeta,\zeta') \, d\zeta d\zeta' + 1/R \tag{79}$$

where the function $H(1,1;\zeta,\zeta')$ is defined by

$$H(1,1;\zeta,\zeta') = \int[\exp(-\zeta r_a) + \exp(-\zeta r_b)]H'[\exp(-r_a\zeta') + \exp(-r_b\zeta')]d\tau \tag{80}$$

and similarly

$$S(1,1;\zeta,\zeta') = \int[\exp(-\zeta r_a) + \exp(-\zeta r_b)][\exp(-r_a\zeta') + \exp(-r_b\zeta')]d\tau. \tag{81}$$

(The ones in the symbol $S(1,1;\zeta,\zeta')$ denote that two 1s-STOs are used).

The integration over physical space is done analytically (see Appendix 2) and the integration over the parameter space is done numerically.

2) COMPUTATIONAL ASPECTS

(a) Integration

The functions $H(1,1;\zeta,\zeta')$ and $S(1,1;\zeta,\zeta')$ are symmetric with respect to interchange of ζ and ζ', since the two orbital-exponent integration-variables are equivalent. Therefore it was sufficient to take twice the integral evaluated over half the integration domain (i.e., $0 < \zeta' < \infty$ and $\zeta > \zeta'$). Gauss-Legendre quadrature in conjunction with mapping was used (see Chapter I). The lower and upper integration limits were kept flexible: they were chosen as the values of ζ for which the shape function is only 10^{-8} of its maximum value. This was necessary to ensure sufficient accuracy for both very broad and very narrow shape functions. Furthermore, provisions were made for very high values of ν. Here the shape function was evaluated by calculating its logarithm first in order to avoid numerical inaccuracy.

(b) Minimization

The optimization of the parameters ν and q was guided by the following consideration. The position of the maximum of the shape function, ζ_{max}, should lie in the range $0.5 < \zeta < 2.0$, since the energy for wavefunctions using 1s-STOs with ζ outside this range is very high. Hence very small or very high orbital exponents should not be weighted heavily. In the (ν,q)-plane, with ranges $(-1, \infty)$ for ν and $(0, \infty)$ for q, the two parabolic branches obtained from

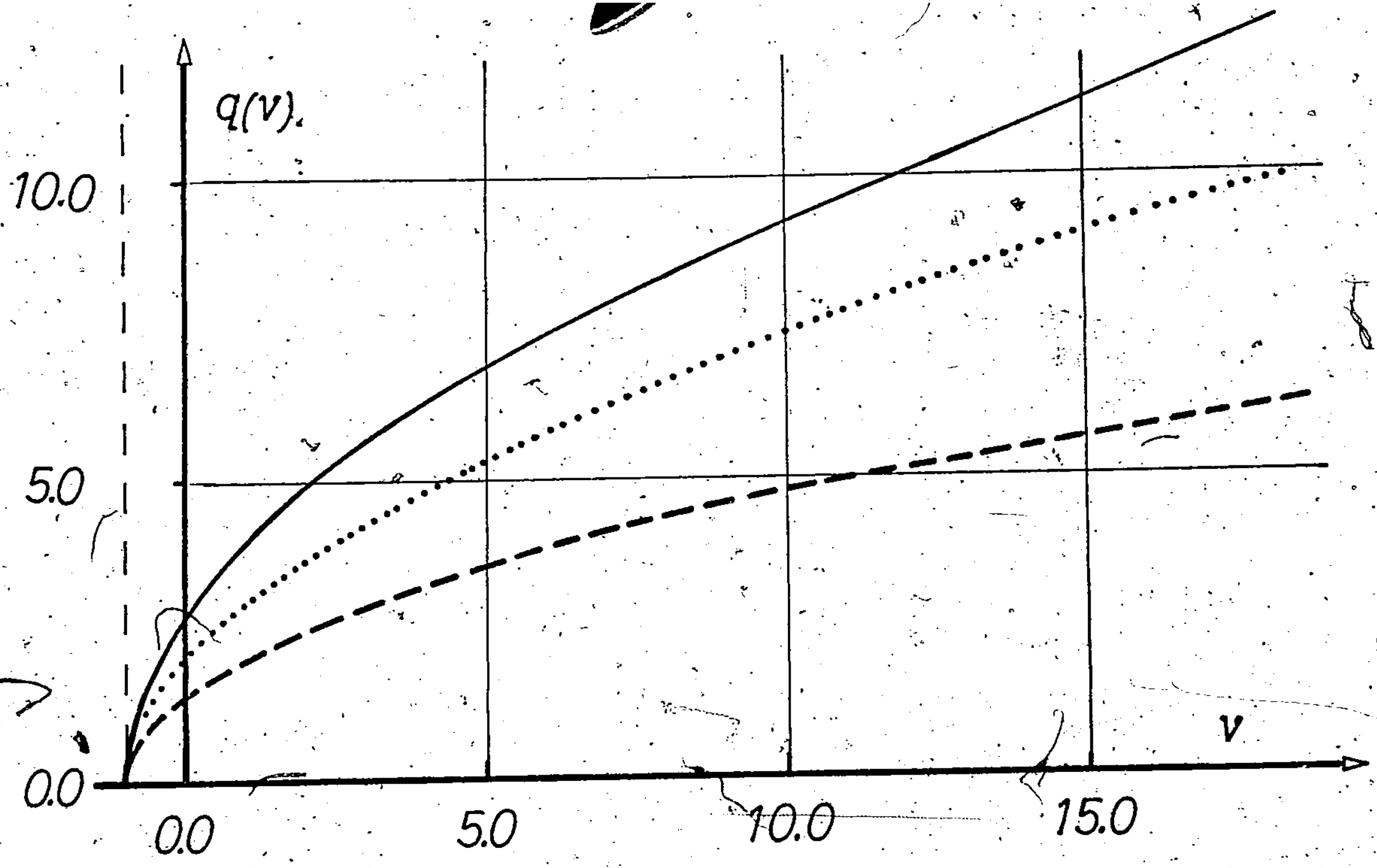
Caption to Fig. 6

The parameter q as a function of ν for constant ζ_{max}, i.e. $q = [4(\nu+1)\zeta_{max}]^{1/2}$.

——————— $\zeta_{max} = 2.0$

••••••••••••••••• $\zeta_{max} = \zeta_{1s}$

- - - - - - - - - - $\zeta_{max} = 0.5$


q(v).
10.0
5.0
0.0
0.0
5.0
10.0
15.0
v

$$q = [4(\nu+1)\zeta_{max}]^{1/2} \tag{82}$$

by inserting $\zeta_{max} = 0.5$ and $\zeta_{max} = 2.0$ enclose the region of (ν,q) pairs for which the energy is low (see Fig. 6). This was confirmed by the calculation of energies for a grid of (ν,q) values in the range (0.0 to 10.0) for both ν and q. The minimum energy was obtained with the highest ν value, $\nu = 10.0$.

Further minimization showed that the minimum energy is obtained for $\nu \to \infty$. The corresponding optimum value of the parameter q for each ν was found to be such that the ζ_{max} of the shape function approached ζ_{1s}, the orbital exponent which minimizes the energy for a wavefunction constructed from 1s-STOs.

With the help of the delta-convergence property of $G(\nu,q;\zeta)$ for $\nu \to \infty$ (see Appendix 1) it was shown (see Chapter I) that the $k_\nu(q\sqrt{r})$ function (i.e. the exponential integral transform function with $G(\nu,q;\zeta)$ as shape function) reduces to the 1s-STO for $\nu \to \infty$. Therefore the minimum energy obtained for $\nu \to \infty$ must be equal to E_{1s}. Table 12 demonstrates this fact. Some energies obtained for high values of ν and values of q such that $\zeta_{max} = \zeta_{1s}$ together with the half-widths of the shape function are given in this table. Plots of the shape function versus ζ/ζ_{1s} are shown in Fig. 7.

Table 12. H_2^+ energies and half-widths of the shape functions for ζ_{max} = const. = ζ_{1s}. $\Delta\zeta = (\zeta_2 - \zeta_1)$, where $G(\nu,q;\zeta_2) = G(\nu,q;\zeta_1) = 0.5\ G_{max}$.

ν	q	Half-width $\Delta\zeta$	Energy (hartree)
10.00	7.384285	3.0840	-0.572 748
20.00	10.202855	1.9258	-0.580 489
40.00	14.256208	1.2745	-0.583 774
80.00	20.038010	0.8709	-0.585 218
160.00	28.250428	0.6052	-0.585 883
320.00	39.890052	0.4242	-0.586 199
640.00	56.369100	0.2986	-0.586 354
1280.00	79.686849	0.2107	-0.586 430
2560.00	112.672227	0.1488	-0.586 468
5120.00	159.327036	0.1052	-0.586 487
10240.00	225.311454	0.0744	-0.586 496
	∞	0.0	-0.586 505

Caption to Fig. 7

Convergence of the set of shape functions to the delta function for $\nu = \infty$.

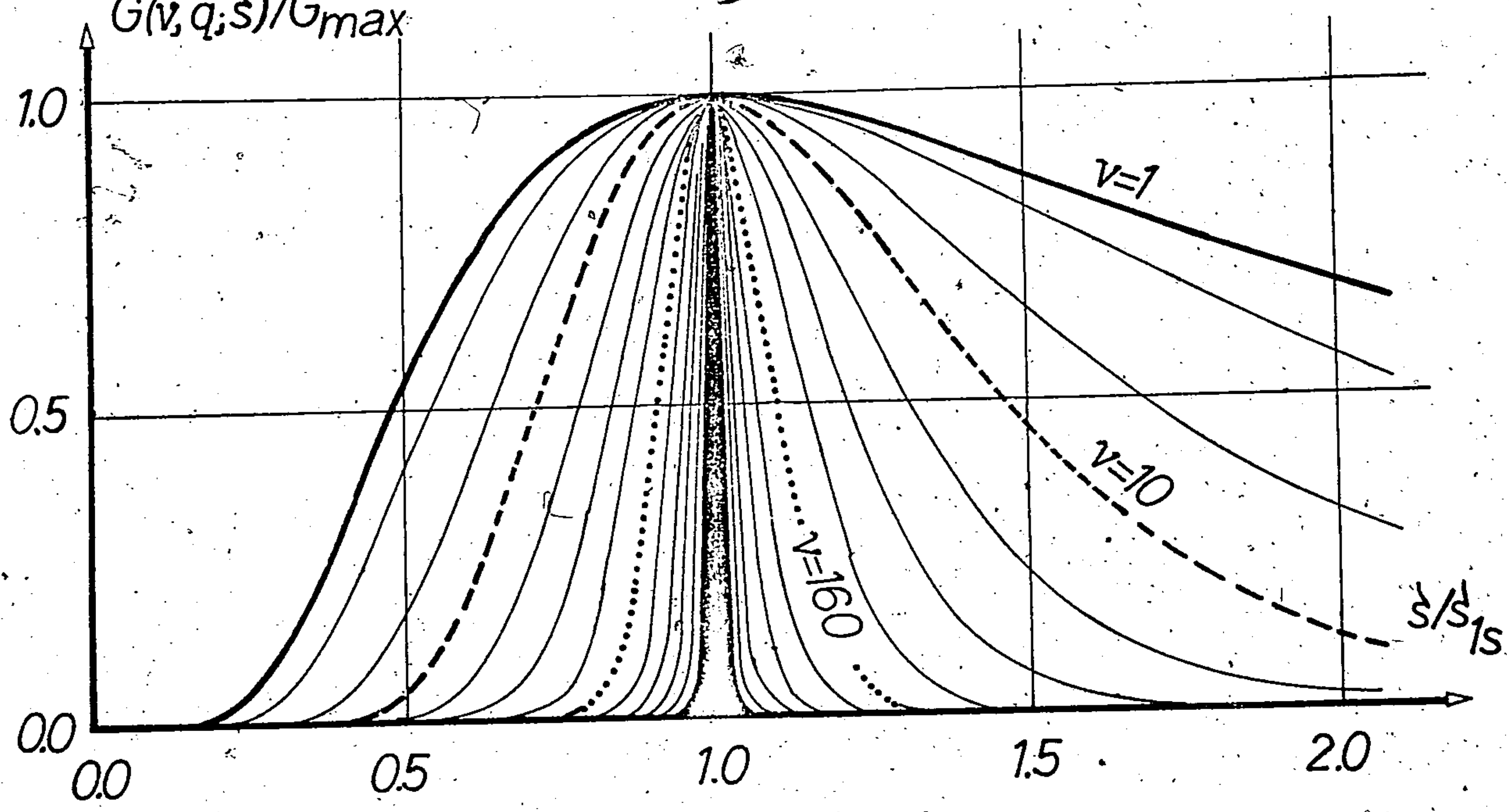
$G(\nu,q;\zeta)/G_{max}$ is plotted as a function of the ratio ζ/ζ_{max} for q such that $\zeta_{max} = \text{const.} = \zeta_{1s}$ · ν = 1, 2, 5, 10, 20, 40, 80, 160, 320, 640, 1280, 2560, and 5120. For ease of identification some ν values are marked:

——————— $\nu = 1$

- - - - - - - - - $\nu = 10$

··········· $\nu = 160$

▬▬▬▬▬ $\nu = 5120$


G(ν, q; s)/Gmax
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
ν=1
ν=10
ν=160
s/s1s

3) RESULTS

Using the exponential integral transform function for H_2^+ the minimum energy, $E = -0.586\ 505$ hartree $= E_{1s}$, was obtained for $\nu = \infty$ and q having the value such that the shape function reduces to the delta-function at $\zeta = \zeta_{max}$, where $\zeta_{max} = 1.239265 = \zeta_{1s}$. For this case the integral transform function, when optimized, reduces to the primitive 1s function.

4) DISCUSSION

(a) General

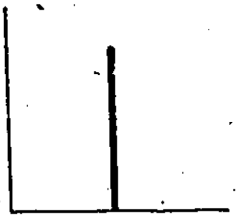
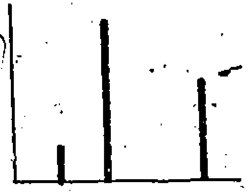
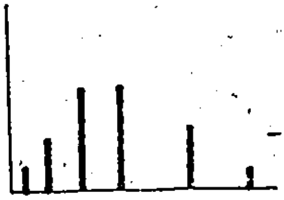
The results of this section are surprising since the shape function used, $G(\nu,q;\zeta)$, produced good results in the calculation for H_2^+ with the Gaussian primitive function, [25], and the primitive function used, the exponential function, produced very good results for the He-series when used with the same shape function [29].

In order to clarify this situation the available calculations on H_2^+ using Gaussian and exponential integral transform functions will be described briefly.

(b) Gaussian integral transform functions for H_2^+

Table 13 shows a comparison of Gaussian integral transforms for various shape functions. Schematic drawings of the shape functions as well as the number of non-linear parameters in

Table 13. Comparison of several Gaussian integral transform functions for H_2^+ at R = 2.0 bohr.

Basis	Shape function	Energy (hartree)	Number of non-linear parameters	Reference
GTO		-0.530 409	1	Schwartz and Schaad [72].
GTO, 3-term		-0.588 379	3	Schwartz and Schaad [72].
$k_\nu(qr)$		-0.589 5	2	Yue and Somorjai [25].
GTO n-term		-0.590 891	n	Schwartz and Schaad [72], Katriel and Adam [74].
exact		-0.602 634		Peek [49], Bishop [48].

the trial wavefunctions are included. The entries in this table are in order of decreasing energy.

It is remarkable that the Gaussian integral transform function, $k_\nu(qr)$, used by Yue and Somorjai [25] is better than the 3-term function using 1s-GTOs when one considers that it contains only two non-linear and no linear variational parameters.

The energy attainable in the limit of placing n 1s-GTOs on each nucleus was determined by Schwartz [72] and Katriel and Adam [74].

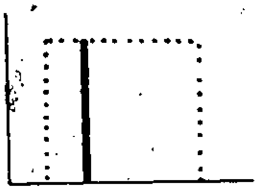
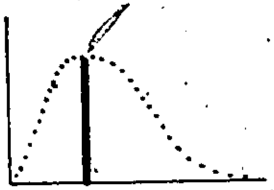
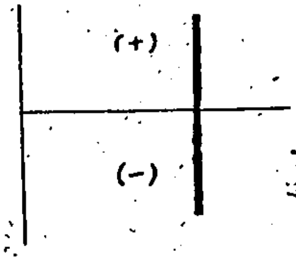
(c) Exponential integral transforms

Table 14 shows a comparison of vari~~ous~~ exponential integral transforms. The energy for a 1s-STO centered on each nucleus has been known for a long time. However, calculations with several 1s-STOs centered on the nuclei have not been reported in the literature. Konowalow and Barker [75] reported that the minimum H_2^+ energy for wavefunctions of the Hulthén type is obtained for a delta-type shape function (i.e., for the case that both integration limits coincide). Jakab and Randić [28] have used the Slater transform (see Chapter I) as a trial function for H_2^+. They could not complete the minimization due to the high parameter values encountered which led to numerical difficulties. If one determines the position,

$$\zeta_{max} = (n+3)/p, \tag{83}$$

of the maximum of Jakab and Randić's shape function, which was

Table 14. Comparison of several exponential integral transform functions for H_2^+ at R = 2.0 bohr.

Basis	Shape function	Energy (hartree)	Number of non-linear parameters	Reference
1s-STO		-0.586 505	1	Finkelstein and Horowitz [76], this work.
Hulthén		-0.586 505	2	Konowalow and Barker [75].
Slater-trans-form		-0.586 505	2	Jakab and Randić [28].
$k_\nu(q\sqrt{r})$		-0.586 505	2	Section III B.
2-term STO		-0.590 450	2	Section III C.

$$G(n,p;\zeta) = \zeta^{(n+3)/2}\exp(-\zeta p/2),$$

for the optimized parameter values quoted, a trend of $n \to \infty$, $\zeta_{max} \to \zeta_{1s}$, and $p \to (n+3)/\zeta_{1s}$ becomes clear (Jakab and Randić noted that, if optimized the two parameters n and p are no longer independent but related in an almost constant ratio n/p). It can be assumed that the minimum energy is obtained at $n = \infty$ and coincides with E_{1s}, and that the shape function reduces to the delta function $\delta(\zeta-\zeta_{1s})$.

Thus in the calculations carried out by Konowalow and Barker, Jakab and Randić and in this work, the exponential integral transform functions with three different shape functions reduce to the primitive function when optimization is performed. This effect has been reported in the literature for systems other than H_2^+, e.g., by Yue [30] for the He 2^1P excited state using a Hulthén transform and by Scherr [34] for the "open shell" calculation of the ground-states of the He series (except H^-) using Slater transforms.

Finally, for the sake of comparison the last line of Table 14 contains the result of a calculation described in the next section.

SECTION C. LINEAR COMBINATIONS OF s-TYPE STOs.

In order to explain the findings of Section B it was decided to study linear combinations of 1s-STOs, since the exponential integral transform function is a generalization of the latter to an infinite number of terms (see Chapter I). In the course of the calculations it was necessary to deal with 1s and 2s linear combinations, and this will be discussed briefly in the second part of this section. The discussion will concern mainly the resulting sets of optimized coefficients.

1) LINEAR COMBINATIONS OF 1s-STOs.

(a) 1s-STO

The energy for the wavefunction using one 1s-STO on each nucleus:

$$\psi = N[\exp(-\zeta_{1s} r_a) + \exp(-\zeta_{1s} r_b)] \qquad (85)$$

has been recalculated. The first calculation of this kind was carried out in 1928 by Finkelstein and Horowitz [76]. For R = 2.0 bohr the minimum energy, E_{1s} = -0.586 505 hartree, was obtained with the orbital exponent ζ_{1s} = 1.239 265.

(b) $1s(\zeta_{1s})+1s(\zeta_2)$.

In an integral transform function, such as $k_\nu(q\sqrt{r})$, the orbital exponent is treated as a continuous integration variable, and each orbital exponent is represented with a different weight factor. Among the orbital exponents in the range $(0,\infty)$ one is equal to ζ_{1s}.

Let us therefore consider a two term linear combination of 1s-STOs where one of the orbital exponents is ζ_{1s}. The wavefunction for this case is obtained by centering two 1s-STOs on each nucleus:

$$\psi = N[\phi(r_a) + \phi(r_b)] \tag{86}$$

with

$$\phi(r_a) = c_1 \exp(-\zeta_{1s} r_a) + c_2 \exp(-\zeta_2 r_a) \tag{87}$$

and a similar expression for $\phi(r_b)$.

The coefficients c_1 and c_2 are obtained by solving the secular equation, $\det|\underline{H} - E\,\underline{S}| = 0$, where e.g., the symmetric H-matrix is

$$\left\| \begin{array}{cc} H(1,1;\zeta_{1s},\zeta_{1s}) & H(1,1;\zeta_{1s},\zeta_2) \\ & H(1,1;\zeta_2,\zeta_2) \end{array} \right\| \tag{88}$$

(see Section B for the definition of the H and S matrix elements).

The minimum energy, $E = -0.587\,876$ hartree was obtained for $\zeta_2 = 3.64$, $c_{1s} = 0.992\,837$ and $c_2 = -0.119\,478$.

On calculating the coefficients which optimized the energy as functions of ζ_2 it was found that they have opposite signs for all ζ_2 values. This is important since shape functions do not, in general, represent a set of coefficients with positive and negative signs.

It was also found that positive coefficients produce an energy higher than E_{1s} for all ζ_2. In Appendix 3 it is shown that for a pair of positive coefficients the wavefunction of Eqs. (86) and (87) produces an energy higher than E_{1s} for all ζ_2.

(c) $1s(\zeta_1)+1s(\zeta_2)$.

The wavefunction of Eqs. (86) and (87) is used but now both orbital exponents are non-linear variational parameters.

The energy, E = -0.590 396 hartree, was found for $\zeta_1 = 1.601$, $\zeta_2 = 1.599$, $c_1 = -325.016$ and $c_2 = + 326.050$ after calculating the optimum coefficients for a large number of ζ_1 and ζ_2 values. This was not the minimum, and the results indicated that the minimum energy would be obtained for the case $\zeta_1 = \zeta_2$, with

$$\lim_{\zeta_1=\zeta_2} (c_1) = -\infty, \quad \lim_{\zeta_1=\zeta_2} (c_2) = +\infty, \text{ and } \lim_{\zeta_1=\zeta_2} (c_2/c_1) = -1. \qquad (89)$$

The question of what wavefunction corresponds to the limit $\zeta_1=\zeta_2$ will be discussed later.

The important fact here is that in the (ζ_1,ζ_2) space the regions for which the optimized coefficients are positive coincide with the regions for which the energy $E \geq E_{1s}$.

(d) $1s(\zeta_1)+1s(\zeta_2)+\ldots 1s(\zeta_k)$.

The closest approximation to an envelope function of optimized linear coefficients is given by a k-term linear combination of 1s-STOs where k is large and therefore calculations of this type were carried out. Here the wavefunction

$$\psi = N[\phi(r_a) + \phi(r_b)] \qquad (90)$$

is constructed from the k-term atomic orbitals

$$\phi(r) = \sum_{i=1}^{k} c_i \exp(-\zeta_1 r). \qquad (91)$$

The optimum coefficients are found by solving the usual secular equation for the symmetric (k×k) H- and S-matrices.

The energies obtained for sets of k equally spaced orbital exponents $(\Delta\zeta = \zeta_{i+1}-\zeta_i = 1.0)$ in a k-term linear combination of 1s-STOs are given in Table 15. With increasing number of terms the energy decreases as expected.

The optimum coefficient sets for k-term LC-STOs with the above sets $[\zeta_i]$ are given in Table 16 and Fig. 8 is a graphical representation of the coefficients $c_1\ldots c_{11}$ as functions of ζ.

Table 15. Energies obtained with linear combinations of 1s-STOs for equally spaced orbital exponents ($\Delta\zeta = 1.0$).

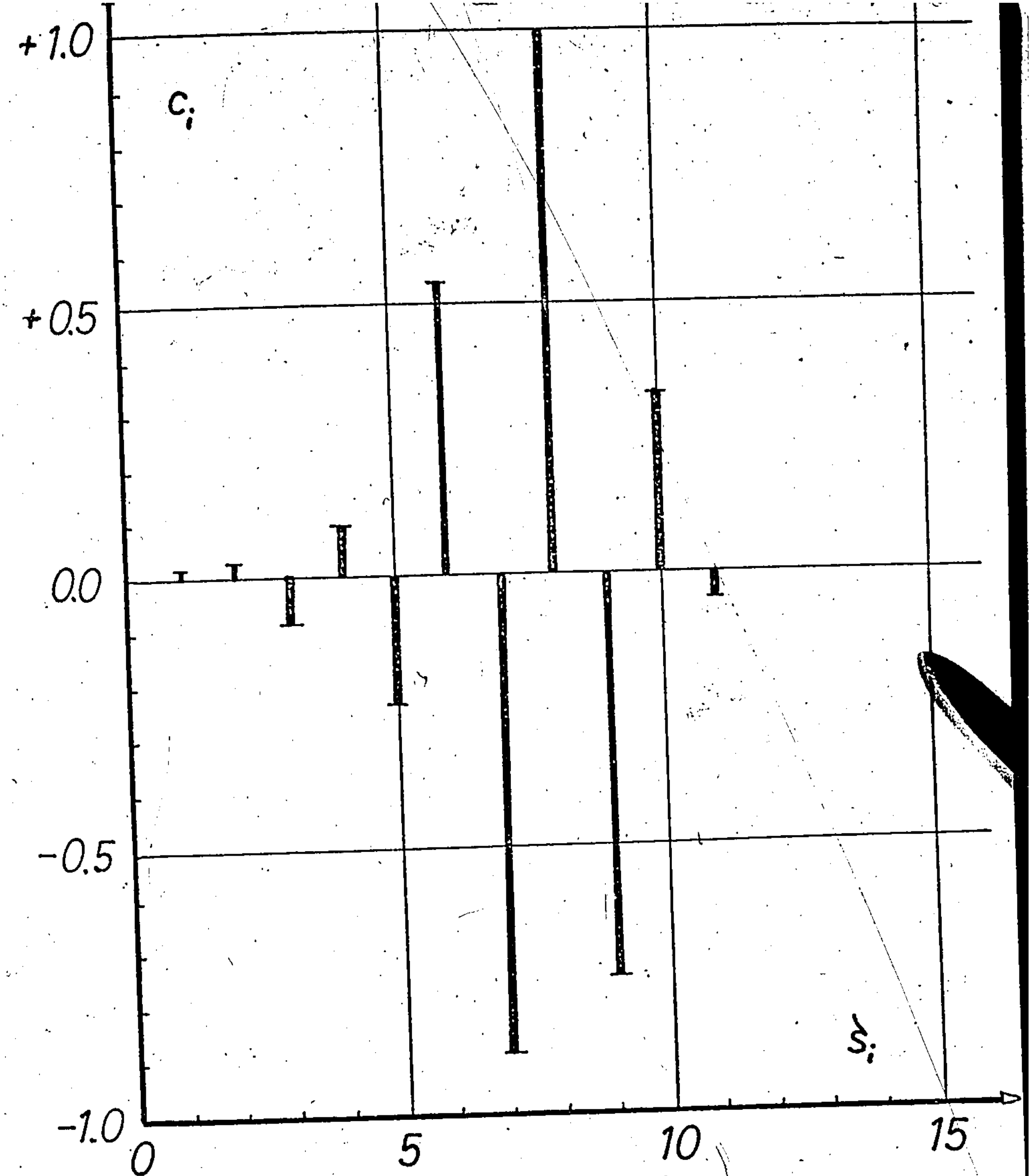
Number of terms	Energy (hartree)	Orbital Exponent Set $\{\zeta_i\}$
3	-0.583 596	1.0,2.0,3.0
4	-0.588 610	1.0,...,4.0
5	-0.590 310	1.0,...,5.0
6	-0.590 811	1.0,...,6.0
7	-0.590 918	1.0,...,7.0
8	-0.590 934	1.0,...,8.0
9	-0.590 935 8	1.0,...,9.0
10	-0.590 935 990	1.0,...,10.0
11	-0.590 936 157	1.0,...,11.0

Table 16. Sets of optimized linear coefficients for k-term linear combinations of 1s-STOs for equally spaced sets of orbital exponents, $\{\zeta_i\} = \{1.0, \ldots k \cdot \Delta\zeta\}$, $\Delta\zeta = 1.0$.

k	i	c_i	k	i	c_i
3	1	0.490013	8	1	0.182
	2	1.541758		2	6.641
	3	-1.067041		3	-28.973
				4	78.877
				5	-133.443
				6	135.876
				7	-76.000
				8	17.897
4	1	0.361100	9	1	0.178
	2	2.857032		2	6.821
	3	-4.257126		3	-31.500
	4	2.164445		4	95.124
5	1	0.275554		5	-189.635
	2	4.201694		6	247.087
	3	-9.856924		7	-201.975
	4	10.677078		8	93.815
	5	-4.275953		9	-18.860
			10	1	0.177
6	1	0.222101		2	6.890
	2	5.379924		3	-32.690
	3	-17.100841		4	104.703
	4	28.831291		5	-232.130
	5	-24.197806		6	358.995
	6	7.943002		7	-381.227
7	1	0.194513		8	265.092
	2	6.190334		9	-108.552
	3	-23.971684		10	19.797
	4	54.023492	11	1	0.175
	5	-69.383536		2	7.001
	6	46.945269		3	-34.985
	7	-12.950835		4	127.215
				5	-355.902
				6	773.218
				7	-1257.088
				8	1440.476
				9	-1078.755
				10	468.892
				11	-89.192

Caption to Fig. 8

Plot of coefficients c_i versus ζ_i for the eleven-term linear combination of 1s-STOs with equally spaced orbital exponents $[\zeta_i]$ = [1.0, 2.0,....11.0].



+1.0
c_i
+0.5
0.0
−0.5
−1.0
0
5
10
15
s_i

All the calculations with different sets of orbital exponents produced sets of optimized coefficients with repeating changes of sign. No ranges for ζ were found for which the signs of neighbouring coefficients were the same, and on increasing the number of ζs the number of sign alternations increased. This is important since for a shape function the neighbouring points have similar values.

(e) Summary

Finally Table 17 compares the results of all linear combinations of 1s-STOs discussed in this section. Schematic drawings of the coefficients as functions of ζ are included.

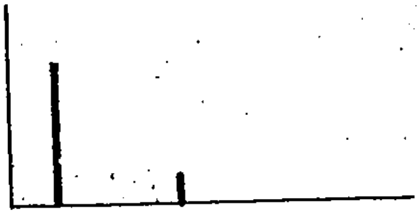
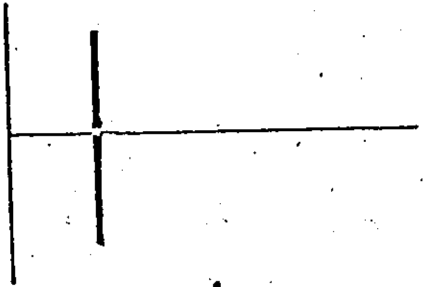
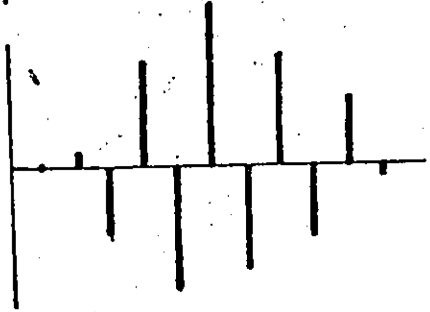
The findings of this part make it clear why the wavefunction using exponential integral transforms produces a minimum energy at $\nu = \infty$, i.e., the shape function reduces to the delta function $\delta(\zeta-\zeta_{1s})$: the sets of optimized coefficients for k-term linear combinations of STOs cannot be approximated by shape functions such as that used in Section B and those used by Konowalow and Barker or Jakab and Randić.

2) LINEAR COMBINATIONS OF 1s AND 2s STOs.

(a) The Limit Problem

Let us return to the question of the limiting ($\zeta_1 \to \zeta_2$) form of $a[1s(\zeta_1) + 1s(\zeta_2)]$ linear combination. It is shown

Table 17. Comparison of some linear combinations of 1s-STOs for H_2^+ at R = 2.0 bohr.

Basis	Shape function	Number of non-linear parameters	Energy (hartree)
$1s(\zeta_{1s})$		1	-0.586 505
$1s(\zeta_{1s})+1s(\zeta_2)$		1	-0.587 876
$1s(\zeta_1)+1s(\zeta_2)$		2	-0.590 450
$1s(\zeta_1)+1s(\zeta_2)+$ $\ldots+1s(\zeta_k)$		k = 11	-0.590 936§

§non-optimized $[\zeta_i]$, optimized $[c_i]$.

in Appendix 4 that in the limit, $\Delta\zeta = (\zeta_2 - \zeta_1) = 0$, the wavefunction is a linear combination of a 1s-STO and its derivative with respect to ζ. We have

$$\partial/\partial\zeta(\exp(-\zeta r)) = -r \exp(-\zeta r), \tag{92}$$

and therefore the limiting form of the wavefunction is given by a 1s-STO and a 2s-STO for the same ζ: 1s(ζ) +2s(ζ).

It might be mentioned that the corresponding case for GTOs is the combination of a 1s-GTO plus a 3s-GTO of the same ζ, since

$$\partial/\partial\zeta(\exp(-\zeta r^2)) = -r^2 \exp(-\zeta r^2). \tag{93}$$

Cases of coincidental orbital exponents producing a minimum energy have been reported in the literature. For example Solomon [40] found this for a 5 parameter LC of 1s-STOs for the Be sequence. A similar effect has been described by Pandres and Matsen [77] on minimizing the Weinbaum [78] hydrogen molecule wavefunction for the limit R = 0. Coulson [79] has noted that the difference between two 1s-STO orbitals on slightly separated centers has the form of a 1p orbital.

(b) <u>1s(ζ)+2s(ζ).</u>

In order to replace the energy given in part 1(c) by the true minimum energy, optimization of the non-linear variational parameter ζ and the coefficients c_1 and c_2 was carried out using a function of the form $\left[c_{1s}\ 1s(\zeta)+c_{2s}\ 2s(\zeta)\right]$ on each nucleus.

Here the symmetric 2×2 H-matrix:

$$\left\|\begin{matrix} H(1,1;\ \zeta,\zeta) & H(1,2;\ \zeta,\zeta) \\ H(2,1;\ \zeta,\zeta) & H(2,2;\ \zeta,\zeta) \end{matrix}\right\| \qquad (94)$$

had to be constructed.

For the $H(1,2;\ \zeta,\zeta)$, $H(2,2;\ \zeta,\zeta)$, $S(1,2;\ \zeta,\zeta)$ and $S(2,2;\ \zeta,\zeta)$ elements the formulae were found with the help of those given by Mulliken et al. [80] for the overlap matrix, S, and by Coulson [81] for the integrals occurring in the H-matrix. The required auxiliary functions for higher indices (up to n=4 in $A_n(p)$ and $B_n(pt)$) were obtained by recursion.

The minimum energy, E = -0.590 450 hartree, was found for $\zeta = 1.6275$, $c_{1s} = 0.409\ 458$, and $c_{2s} = 0.285\ 235$. The optimized coefficients are both positive. This fact gives rise to the question whether a linear combination using 1s and 2s STOs with two or more orbital exponents would also produce a set of positive coefficients.

(c) 1s and 2s STOs with different orbital ~~exponents~~ exponents.

In this part several linear combinations with different orbital exponents in 1s and 2s STOs were used to construct the wavefunction. Among these were the following:

$$\psi_2 = \sum_{i=1}^{2} [a_i 1s(\zeta_i) + b_i\ 2s(\zeta_i)], \text{ and} \qquad (95)$$

$$\psi_3 = \sum_{i=1}^{3} [a_i\ 1s(\zeta_i) + b_i\ 2s(\zeta_i)]\ , \qquad (96)$$

where all the a_i, b_i, and ζ_i were variational parameters, and

$$\phi_k = \sum_{i=1}^{k} [a_i\ 1s(\zeta_i) + b_i\ 2s(\zeta_i)] \text{ for } k=4,5...8 \qquad (97)$$

where the a_i and b_i were optimized for a <u>fixed</u> set of k orbital exponents $\{\zeta_i\}$. The H and S matrices required for the solution of the secular equation in each case were established easily since they contained only matrix elements whose formulae had been derived earlier.

The wavefunction obtained by placing ψ_2 on each nucleus was found to produce the minimum energy for $\zeta_1 \neq \zeta_2$, but for the wavefunction using ψ_3, although several local minima for $\zeta_1 \neq \zeta_2 \neq \zeta_3$ were found, the minimization could not be completed since the true minimum occurs for $\zeta_1 = \zeta_2 = \zeta_3$.

In the calculations with ψ_2, ψ_3, and ϕ_k no ranges of ζ were found for which the optimized were positive <u>and</u> the energies low. This is important since it implies that the integral transform of the combination of a 1s and 2s STO is presumably not advantageous.

(d) 1s and 2s STOs with coincidental orbital exponents.

In the linear combinations of Eqs. (95) and (96) the special cases $\zeta_1 = \zeta_2$ or $\zeta_1 = \zeta_2 = \zeta_3$ should not be excluded, since the minimum energy might well occur for these cases. Therefore the analytic forms of ψ_2 and ψ_3 for coincidental orbital exponents were determined. Since

$$\frac{\partial}{\partial\zeta}\,[r^n \exp(-\zeta r)] = -r^{n+1} \exp(-\zeta r) \tag{98}$$

we can derive the generalization of the limit problem, which dealt with two 1s-STOs with coincidental orbital exponents, to two ns-STOs:

$$\lim_{\zeta_1=\zeta_2} [c_1\, ns(\zeta_1) + c_2\, ns(\zeta_2)] = c_1'\, ns(\zeta) + c_2'\, ms(\zeta), \text{ where } m = n+1. \tag{99}$$

On applying repeatedly the rule given in this equation we obtain

$$\lim_{\zeta_1=\zeta_2} [\psi_2] = c_1'\, 1s(\zeta) + c_2'\, 2s(\zeta) + \ldots + c_4'\, 4s(\zeta) \tag{100}$$

and

$$\lim_{\zeta_1=\zeta_2=\zeta_3} [\psi_3] = c_1'\, 1s(\zeta) + c_2'\, 2s(\zeta) + \ldots + c_6'\, 6s(\zeta). \tag{101}$$

This result led to the consideration of a linear combination of ns-STOs with a common value for ζ and different values for n. This will be discussed in the next section. Furthermore, these linear combinations open up the possibility that, if sets of positive coefficients are obtained, they can be generalized into another kind of integral transforms.

SECTION D. COMMON-ζ-1s2s...ns-STO CALCULATIONS

1) INTRODUCTION

There are several reasons why common-ζ-1s2s...ns-STO calculations for H_2^+ were carried out. First, these orbitals arose quite naturally in the calculations of Section C, since the special case of a common exponent was encountered on minimization. Second, they are interesting in their own right since a generalization to a new type of integral transform function is possible if they produce sets of optimum coefficients with only positive signs. Third, LCAOs of s-type STOs with a common orbital exponent but with different principal quantum numbers have not been reported in the literature. Usually all orbital exponents are either set according to Slater's rules or are optimized variationally, and STOs other than the s-type are normally included.

2) MATHEMATICAL FORMULATION

In this section the atomic orbital centred on each nucleus has the following form

$$\phi(r) = \exp(-\zeta r) \cdot \sum_{i=0}^{k} c_i r^i, \qquad (102)$$

where the coefficients, c_i, and the orbital exponent, ζ, are variational parameters.

The molecular orbital is then

$$\psi = \phi(r_a) + \phi(r_b), \tag{103}$$

where r_a and r_b are the distances between the electron and each nucleus. ψ can be written as

$$\psi = \sum_{i=0}^{k} c_i[r_a^{\,i} \exp(-\zeta r_a) + r_b^{\,i} \exp(-\zeta r_b)]. \tag{104}$$

For $k = 0$, $\phi(r) = c_o \exp(-\zeta r)$ = 1s-STO, and for $k = 1$, $\phi(r) = c_o \exp(-\zeta r) + c_1 r \exp(-\zeta r)$ = 1s2s-STO.

These two cases have been dealt with in Section C.

For $k = 2$:

$$\phi(r) = \exp(-\zeta r)(c_0 + c_1 r + c_2 r^2) = \text{1s2s3s-STO}, \tag{105}$$

and for $k = 3$:

$$\phi(r) = \exp(-\zeta r)(c_0 + c_1 r + c_2 r^2 + c_3 r^3) = \text{1234s-STO}. \tag{106}$$

These two cases are discussed now. No calculations were carried out for values of k greater than 3 since all the pertinent information could be gained from a comparison of the $k = 0,1,2,3$ cases.

3) COMPUTATIONAL DETAILS

(a) Integration

In order to solve the secular equation, det$|\underline{H} - \underline{SE}|=0$, to find the coefficients, c_i, we require the integrals over the molecular orbitals. They can be expressed, as in the previous section, as a sum of integrals over products of AOs. These integrals were arranged in symmetric 3 × 3 H- and S-matrices for the 1s2s3s-STO and in 4 × 4 matrices for the 1234s-STO case; e.g. the 4 × 4 H-matrix is:

$$\left\| \begin{array}{cccc} H(1,1;\zeta,\zeta) & H(1,2;\zeta,\zeta) & H(1,3;\zeta,\zeta) & H(1,4;\zeta,\zeta) \\ & H(2,2;\zeta,\zeta) & H(2,3;\zeta,\zeta) & H(2,4;\zeta,\zeta) \\ & & H(3,3;\zeta,\zeta) & H(3,4;\zeta,\zeta) \\ & & & H(4,4;\zeta,\zeta) \end{array} \right\| \tag{107}$$

and similarly for the S-matrix. Here the first pair of integers indicates which STOs are used, e.g. $H(3,4;\zeta,\zeta)$ is defined by:

$$H(3,4;\zeta,\zeta) = \int[r_a^2\exp(-\zeta r_a) + r_b^2\exp(-\zeta r_b)]H[r_a^3\exp(-\zeta r_a) + r_b^3\exp(-\zeta r_b)]d\tau. \tag{108}$$

These matrix elements were then expressed in terms of the auxiliary functions $A_n(p)$ and $B_n(pt)$. The formulae obtained were checked with the explicit formulae given by Coulson [81] and by comparison with the values given by Rosen [82].

(b) Minimization

The linear parameters c_i in Eqs. (105) and (106) were obtained by solving the secular equation with the computer routine SECEQN. The non-linear parameter ζ was optimized by simply calculating the H_2^+ energy for various ζ values and determining the value of ζ which gave the lowest energy. The accuracy of the optimum exponent is reflected by the number of decimals given.

4) RESULTS

(a) The 1s2s3s-STO Function

The minimum energy, E = -0.590 450 hartree, was obtained for the following values of the orbital exponent and linear coefficients:

$$\zeta = 1.6275,$$
$$c_0 = 0.409\,458,$$
$$c_1 = 0.258\,235,$$
$$c_2 = 0.0.$$

(b) The 1234s-STO Function

The minimum energy, E = -0.590 502 hartree, was obtained for the following values of the orbital exponent and linear coefficients:

$$\zeta = 1.59,$$
$$c_0 = 0.411\,246,$$
$$c_1 = 0.260\,336,$$
$$c_2 = -0.000\,143,$$
$$c_3 = -0.002\,248.$$

5) DISCUSSION

The optimum coefficients, the optimum orbital exponents and the minimum energies for the 1s-, 1s2s-, 1s2s3s-, and 1234s-STO functions are listed in Table 18. The H_2^+ energies for these four common-zeta-STO functions are plotted as functions of the orbital exponent in Fig. 9. Table 19 gives a summary of the distributions of positive and negative signs of the optimized coefficients.

It can be seen from Table *18* that the 1s2s-STO function gives a considerable improvement over the energy of the 1s-STO function. It should be noted that both the coefficients are positive. The energy curve for the case where 1s2s-STOs are used (fine continuous line in Fig. 9) shows a local minimum at $\zeta = 0.978$, a tangential point with the 1s-STO curve at $\zeta=\zeta_{1s} = 1.239265$ and an absolute minimum at $\zeta=1.6275$.

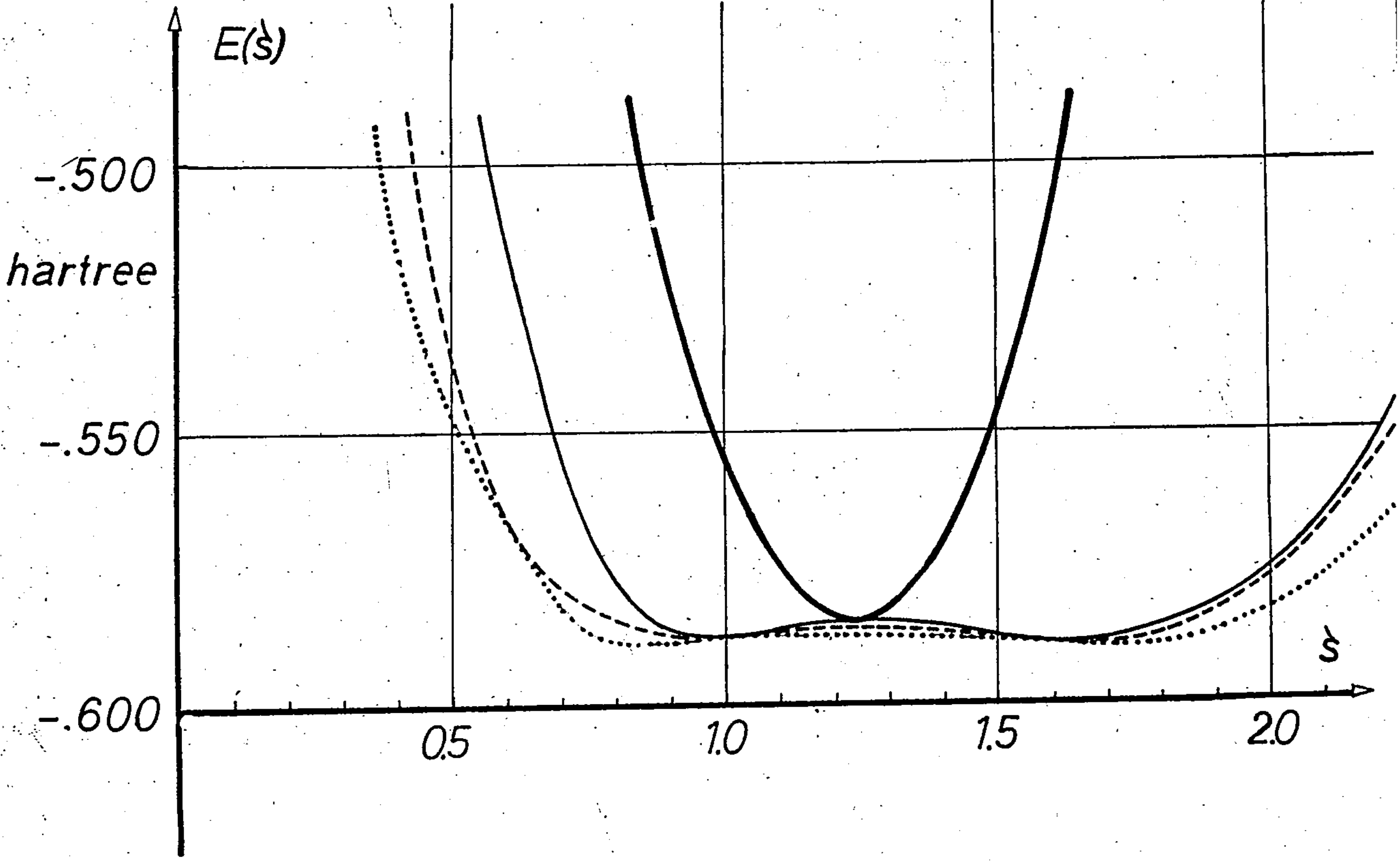
Inspection of Table 18 further shows that the optimum energy for the function which places a 1s2s3s-STO on each nucleus is no better than the optimum energy obtained when 1s2s-STOs are used. This is why $c_2 = 0$. Fig. 9 shows that the energy obtained with 1s2s3s-STOs (broken line) is less than the energy obtained with 1s2s-STOs (fine continuous line) for all orbital exponents except for the tangential points at $\zeta=0.98$ and $\zeta=1.6275$ (the optimum ζ). This finding is in agreement with the variational principle.

Table 18. The optimum coefficients, optimum orbital exponents and minimum energies for common-ζ- 1s2s...ns-STO functions for H_2^+. Internuclear separation R = 2.0 bohr.

Function	Optimum Parameters		Minimum
Name	Orbital Exponent	Coefficients	Energy (hartree)
1s-STO	1.239265	c_0 = 0.454 952	-0.586 505
1s2s-STO	1.6275	c_0 = 0.409 458	
		c_1 = 0.258 235	-0.590 450
1s2s3s-STO	1.6275	c_0 = 0.409 458	
		c_1 = 0.258 235	-0.590 450
		c_2 = 0.0	
1234s-STO	1.59	c_0 = 0.411 246	
		c_1 = 0.260 336	
		c_3 = -0.000 143	
		c_4 = -0.002 480	-0.590 502

Caption to Fig. 9 The energy (hartree) of H_2^+ for various common-ζ-1s...ns-STO functions as a function of the orbital exponent ζ.

━━━━━━━━━━	1s-STO
──────────	1s2s-STO
- - - - - - - - - -	1s2s3s-STO
··················	1234s-STO


E(s̀)
hartree
-.500
-.550
-.600
0.5
1.0
1.5
2.0
s̀

The wavefunction using the 1234s-STOs produces a minimum energy which is less than the minimum energy when the 1s2s3s-STOs are used (see Table 18). The energy curve for the 1234s-STO function (dotted line in Fig. 9) shows a local minimum at $\zeta = 0.88$. The absolute minimum occurs at $\zeta=1.59$.

The most important result of this section, however, is the fact that there is a range of orbital exponents for which the optimized coefficients are all positive and for which the energy is less than that when the 1s-STO is used. This fact is illustrated by Table 19 where the signs of the optimized coefficients are given for wavefunctions using the common-ζ-STO discussed in this section. For increasing values of ζ in this table the set of coefficients changes in a continuous way: if one coefficient changes its sign there is one special value of ζ for which the coefficient is exactly zero (this then corresponds to one of the tangential points in Fig. 9). The bottom line of Table 19 shows that an optimized set of four positive coefficients exists for $\zeta>1.655$. For these values of ζ Fig. 9 shows that the energy obtained when 1234s-STOs are used (dotted line) is less than E_{1s}, the minimum energy obtained when 1s-STOs are used, for values of ζ up to 2.0. The main conclusion of this section is therefore that a generalization of common-ζ-STOs to an integral transform function could be advantageous.

Table 19. Distribution of signs of coefficients for common-ζ-ns-STO functions

Function	Signs of coefficients				Range of orbital exponent
	1s	2s	3s	4s	
1s-STO	+				$0 < \zeta < \infty$
1s2s-STO	+	−			$0 < \zeta < 1.239265$
	+	0			$\zeta = 1.239265$
	+	+			$1.239265 < \zeta$
1s2s3s-STO	+	−	+		$\zeta < 0.975$
	+	−	0		$\zeta = 0.975$
	+	−	−		$0.975 < \zeta < 1.195$
	+	0	−		$\zeta = 1.195$
	+	+	−		$1.195 < \zeta < 1.6275$
	+	+	0		$\zeta = 1.6275$
	+	+	+		$1.6275 < \zeta$
1234s-STO	+	−	+	−	$\zeta < 0.59$
	+	−	+	0	$\zeta = 0.59$
	+	−	+	+	$0.59 < \zeta < 0.875$
	+	−	0	+	$\zeta = 0.875$
	+	−	−	+	$0.875 < \zeta < 1.025$
	+	−	−	0	$\zeta = 1.025$
	+	−	−	−	$1.025 < \zeta < 1.175$
	+	0	−	−	$\zeta = 1.175$
	+	+	−	−	$1.175 < \zeta < 1.595$
	+	+	0	+	$\zeta = 1.595$
	+	+	+	−	$1.595 < \zeta < 1.655$
	+	+	+	0	$\zeta = 1.655$
	+	+	+	+	$1.655 < \zeta$

SECTION E

n-TRANSFORM FUNCTIONS FOR H_2^+

1) INTRODUCTION

There are several non-linear parameters in conventionally used basis functions, which can be generalized. For example Somorjai [10] has proposed the generalization of position coordinates in "floating" GTOs or STOs. However, no calculations have yet been reported.

All the integral transform functions referred to in Chapter I, as well as those used in Sections IIB and IIIB, are "zeta-transform" functions, where zeta is the orbital exponent.

In this section an alternative integral transformation which generalizes n, the principal quantum number, from a non-linear parameter to an integration variable will be proposed and tested. The resulting orbitals will be called "n-transform" functions.

The mathematical background will be discussed first. A plausible form of the shape function will be chosen, and the properties of the resulting wavefunction will be described. The energy of H_2^+ will be calculated using two n-transform functions which differ in their range of integration. The results obtained on minimizing the energy will be discussed by comparing them with the results of the preceding section.

2) MATHEMATICAL FORMULATION

The n-transform function proposed is of the following general form

$$\phi(r) = \int_0^\infty \text{shape}(n)\, r^n \exp(-\zeta r)\, dn\,, \tag{109}$$

where n is no longer restricted to integer values but is a continuous integration variable.

In the previous cases of ζ-transform functions the mathematical formulation was established by several authors (see Chapter I). Since n-transform functions are used in this work for the first time, the mathematical concept must be considered in detail before actual calculations are performed.

The primitive function, the shape function and its range of integration, as well as the resulting wavefunction, will be discussed.

(a) The Primitive Function

The primitive function in Eq. (109) is the ns-STO,

$$r^n \exp(-\zeta r), \tag{110}$$

but $\exp(-\zeta r)$ is a constant with respect to the integration over n, and therefore only the properties of the function r^n are of interest. The following identity,

$$r^n = \exp((\ln r)n), \tag{111}$$

can be used to demonstrate the analogy between the primitive function of the n-transforms and the primitive functions $\exp(-r\zeta)$ or $\exp(-(r^2)\zeta)$ of the ζ-transforms which were treated earlier.

(b) The Domain of Integration

One restriction must be made in order to ensure convergence of the integral

$$\int_0^\infty \text{shape}(n)\ \exp((\ell nr)n)\ dn \tag{112}$$

for arbitrary r, $(0 < r < \infty)$; this is that the shape function must be such that the integration is carried out over a finite domain.

(c) The Shape Function

Any shape function which is defined on a finite range $A \leq n \leq B$ can be chosen as long as normalization and delta-convergence are guaranteed.

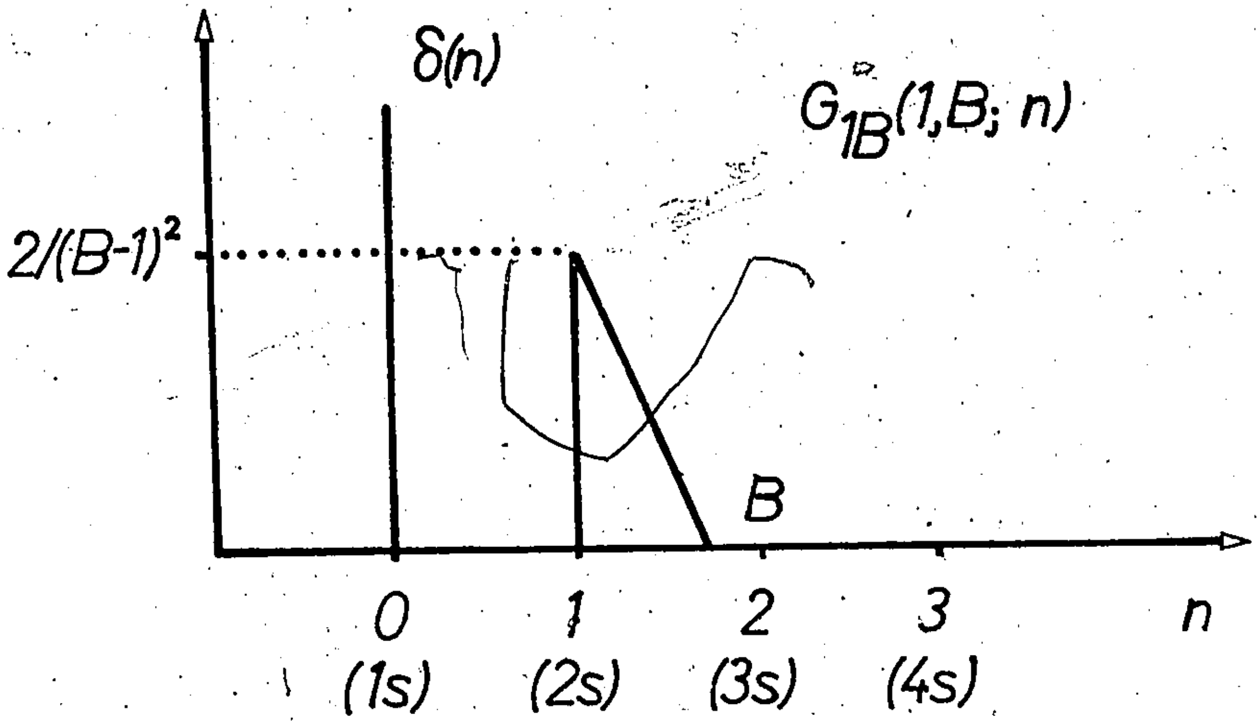
The family of shape functions (see Chapter I, Eqs. (16) and (18)) which produced, in conjunction with STOs and GTOs, wavefunctions of the fractional integral class [22] will be applicable. In Appendix 5 the normalization and delta-convergence [83] of the linear member (i.e., m = 1 in Eq. (18) of Chapter I),

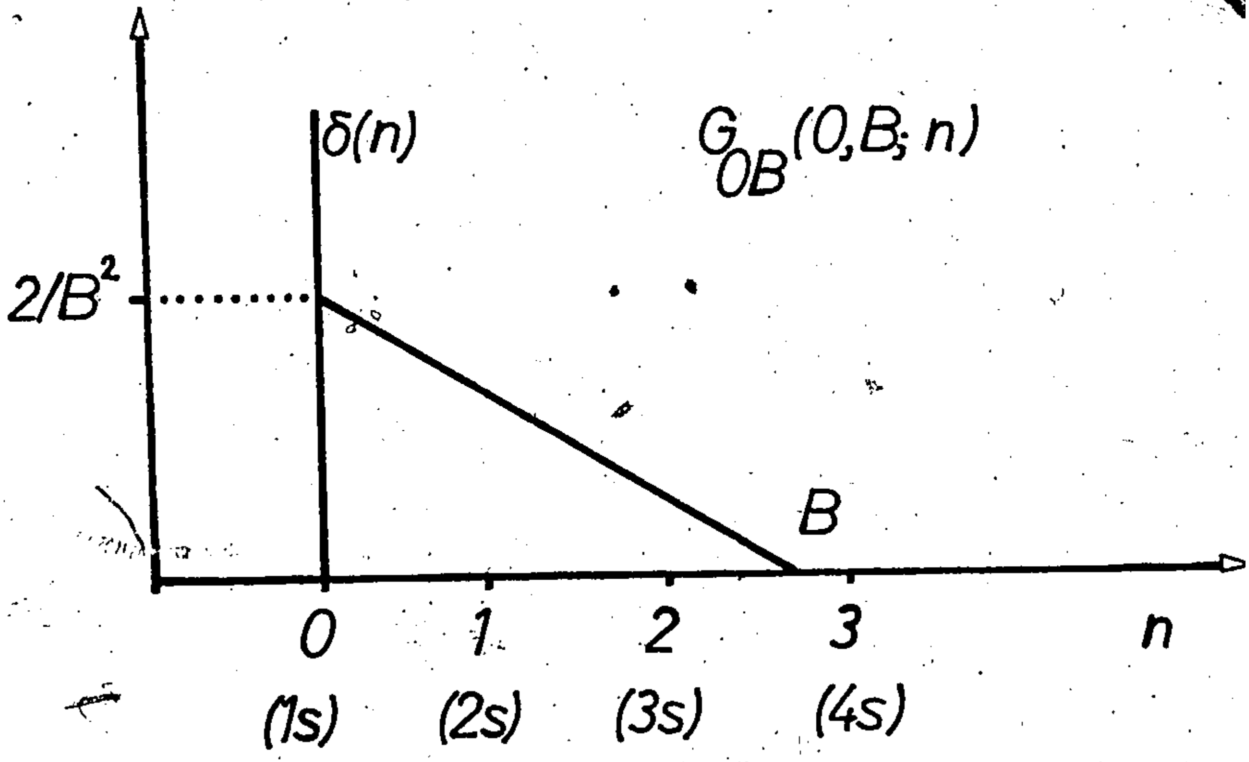
$$G_{AB}(A,\ B;n) = 2\ (B-A)^{-2}(B-n), \tag{113}$$

is proven. The graphical representations of the cases (A,B) = (0,B) and (A,B) = (1,B) are shown in Fig. 10.

Caption to Fig. 10

The shape functions used for n-transforms.


δ(n)
$G_{1B}(1,B;n)$
$2/(B-1)^2$
B
0
1
2
3
n
(1s)
(2s)
(3s)
(4s)


δ(n)
$G_{0B}(0,B;n)$
$2/B^2$
B
0
1
2
3
n
(1s)
(2s)
(3s)
(4s)

(d) The Wavefunction

The integral representation of the n-transform function with the shape function of Eq. (113) is as follows:

$$\phi(r) = \exp(-\zeta r) \cdot f_{AB}(A,B;\, r), \tag{114}$$

where

$$f_{AB}(A,B;\, r) = \int_A^B G_{AB}(A,B;\, n)\, r^n\, dn\,. \tag{115}$$

In Appendix 5 the explicit formula for $\phi(r)$ is derived. The result is:

$$\phi(r) = \begin{cases} \exp(-\zeta r)\; 2\; (B-A)^{-2}[(r^B - r^A)\,\ell n^{-2} r - r^A (B-A)\,\ell n^{-1} r] & \text{for } A \neq B,\ A \geq 0,\ B > 0 \\ \exp(-\zeta r)\; r^A, & \text{for } A = B,\ A > 0 \\ \exp(-\zeta r), & \text{for } A = B = 0\,. \end{cases} \tag{116}$$

The above functional dependences for $\phi(r)$ show clearly how the general (A,B)-n-transform function reduces to a primitive function of the non-integer-n-STO type in a natural way if B approaches A. The corresponding shape function is a delta function $\delta(n-A)$ for $A = B$.

In order that the resulting n-transform function can be used as a wavefunction we must confirm that it is "well behaved".

Therefore we must ensure that

i) it vanishes at $r = \infty$,

ii) it has no discontinuity (e.g., at $r = 1$ we apparently divide by zero in equation (116)), and

iii) it is finite at $r = 0$ (i.e., at the site of the nuclei).

The mathematical details of these investigations are found in Appendix 5. There, either the integral representation or the direct formula of $\phi(r)$, whichever was more convenient, was used to investigate the behaviour of $\phi(r)$ for $r = \infty$, $r = 1$, and $r = 0$.

The results are as follows:

$$\phi(\infty) = \begin{cases} 0 & A \neq B,\ A \geq 0,\ B > 0 \\ 0 & A = B,\ A > 0 \\ 0 & A = B = 0 \end{cases} \tag{117}$$

and

$$\phi(1) = \begin{cases} \exp(-\zeta) & A \neq B,\ A \geq 0,\ B > 0 \\ \exp(-\zeta) & A = B,\ A > 0 \\ \exp(-\zeta) & A = B = 0 \end{cases} \tag{118}$$

but

$$\phi(0) = \begin{cases} 0 & A \neq B,\ A \geq 0,\ B > 0 \\ 0 & A = B,\ A > 0 \\ 1 & A = B = 0\ . \end{cases} \tag{119}$$ *

For both $r = \infty$ and $r = 1$, the primitive functions, $r^A \exp(-\zeta r)$, and their n-transform functions have the same behaviour.

In Eq. (119), the ($A = B$, $A > 0$) and ($A = B = 0$) cases give the behaviour of the primitive functions at $r = 0$. The n-transform for the general case $A \neq B$, $A > 0$ vanishes, since it contains an infinite number of primitive functions which all vanish at $r = 0$. It is, however, surprising that $\phi(0) = 0$ for the case

---

* Here the case $A \neq B$, $A \geq 0$, $B > 0$ corresponds to the general n-transform function, the case $A = B$, $A > 0$ corresponds to the primitive functions (except the 1s-STO), and the case $A = B = 0$ corresponds to the 1s-STO.

$A \neq B$, $A = 0$, since this n-transform function places the maximum weight factor on the 1s-STO primitive function which is finite at $r = 0$.

A minimization of the H_2^+ energy for an n-transform with $G_{OB}(0,B;n)$ as a shape function would certainly produce an optimum value of B equal to zero, since this value would provide the only possibility to ensure a finite value of $\phi(0)$. The minimum energy then would be that of the 1s-STO [76].

There is, however, a possibility of avoiding this artifact by simply adding in a $\delta(n)$ term (i.e., a delta function at $n = 0$) into the shape function. Thus we form a new version of the shape function, namely:

$$C_{OB}(n) = \delta(n) + a\, G_{OB}(0,B;n), \tag{120}$$

or in general

$$C_{AB}(n) = \delta(n) + a\, G_{AB}(A,B;n). \tag{121}$$

Here a linear parameter, a, is added in to allow the delta function part and the $G_{AB}(n)$ part to have different weights.

In what follows two n-transform functions, which differ in their range of integration, will be applied to the hydrogen molecular ion:

1) the "(0,B)-n-transform" function which contains the shape function $C_{OB}(n)$ (see Eq. (120)), and

2) the "(1,B)-n-transform" function, which contains the shape-function $C_{1B}(n)$ (see Eq. (121) with A = 1).

The integral representations of both trial functions are as follows

$$\phi_{0,B}(r) = N \int_0^\infty [C_{0B}(n)\, r^n]\, dn\, \exp(-\zeta r) \qquad (122)$$

and

$$\phi_{1,B}(r) = N \int_0^\infty [C_{1B}(n)\, r^n]\, dn\, \exp(-\zeta r). \qquad (123)$$

The explicit formulae of both types of trial function are the following:

$$\phi_{0,B}(r) = N \exp(-\zeta r)\, [1 + a\cdot 2\cdot B^{-2}((r^B-1)\ln^{-2}r - B\cdot \ln^{-1}r)] \qquad (124)$$

and

$$\phi_{1,B}(r) = N \exp(-\zeta r)\, [1 + a\cdot 2\cdot (B-1)^{-2}((r^B-r)\ln^{-2}r - r(B-1)\ln^{-1}r)]. \qquad (125)$$

It is easily verified that for both the (0,B)-n-transform and the (1,B)-n-transform, we have $\phi_{0B}(0) = N$ and $\phi_{1B}(0) = N$, i.e., both are finite at the nucleus on which they are centred (N is a normalization constant).

3) COMPUTATIONAL DETAILS

(a) Integration

If the energy expression for H_2^+ with n-transform functions is evaluated by integrating over the physical space first, i.e.,

$$E = \frac{\int\int C(n)\cdot C(n')\ H(n,n')\ dn\ dn'}{\int\int C(n)\cdot C(n')\ S(n,n')\ dn\ dn'}\ , \qquad (126)$$

where

$$H(n,n') = \int [r_a{}^n \exp(-\zeta r_a) + r_b{}^n \exp(-\zeta r_b)] H [r_a{}^{n'} \exp(-\zeta r_a) + r_b{}^{n'} \exp(-\zeta r)] d\tau\ , \qquad (127)$$

and similarly

$$S(n,n') = \int [r_a^n \exp(-\zeta r_a) + r_b^n \exp(-\zeta r_b)][r_a^{n'} \exp(-\zeta r_a) + r_b^{n'} \exp(-\zeta r_b)] d\tau \qquad (128)$$

for <u>real</u> n and n' ≥ 0, then we would have analytical expressions for the H and S integrals involving incomplete gamma-functions which themselves are defined by an integral representation. It is doubtful, whether the analytical expressions for the n and n' integrations over incomplete gamma-functions would be simple.

It was therefore decided to integrate over the parameter space first (i.e., n and n'). The remaining integration over the physical space was done by a 2-dimensional numerical quadrature in elliptical coordinates:

$$E = \int_{\lambda=1}^{\infty}\int_{\mu=-1}^{+1} \psi H \psi\ \frac{R^3\pi}{4}\ (\lambda^2-\mu^2)\ d\mu\ d\lambda \Big/ \int_{\lambda=1}^{\infty}\int_{\mu=-1}^{+1} \psi\psi\ \frac{R^3\pi}{4}\ (\lambda^2-\mu^2)\ d\mu\ d\lambda\ . \qquad (129)$$

The Gauss-Legendre quadrature formula in conjunction with the McLean-Yoshimine [36] mapping parameter (see Chapter I) was used after setting the upper integration limit for $\int d\lambda$ (i.e. replacing the infinite limit with an approximate finite limit), the number of points, and the value of the mapping parameter. The optimum set of these integration specifications (i.e., the one which produced the highest accuracy for the least number of points) was obtained with the help of test calculations on 1s-STO functions (see Tables 20a-c).

The results were as follows:

upper integration limit	20
number of points	16 × 16
mapping parameter	0.3.

The accuracy obtained for the 1s-STO calculations was 14 valid decimals in the overlap and energy integrals.

(b) Minimization

The pattern search concept (see Chapter I) was used for the minimization of the energy with respect to the non-linear parameters ζ and B. The linear parameter, a, was found by solving the usual secular equation.

The non-linear parameters were optimized up to the number of decimals with which their values are quoted in the tables. Minimization was not carried out further than changes in the ninth decimal of the energy value.

4) RESULTS

(a) General Remarks

In order to give the results of n-transform calculations of the energy of H_2^+ in a convenient way, and to make comparison with

Table 20. Overlap integrals for the 1s-STO function.

a. Mapping parameter = 0.5, number of points = 16 × 16.

Upper integration limit	Overlap integral
5.0	4.827 ... ...
10.0	4.831 36 ... .
20.0	4.831 364 ... .
50.0	4.829 ... ...
analytical	4.831 364 257 370 2

b. Upper integration limit = 20.0, mapping parameter = 0.5.

Number of points	
16 × 16	4.831 363 ... .
20 × 20	4.831 364 257 ... .
24 × 24	4.831 364 257 370 .
32 × 32	4.831 364 257 370 2
40 × 40	4.831 364 257 370 2
64 × 64	4.831 364 257 370 2
80 × 80	4.831 364 257 370 2

c. Number of points = 16 × 16, upper integration limit = 20.0.

Mapping parameter	Overlap integral
0.5	4.831 363 ... .
0.4	4.831 364 257 37 .
0.3	4.831 364 257 370 2
0.2	4.831 364 257 370 .
0.1	4.831 364 257 ... .

the results of the preceding section easier, the functions under discussion are listed by name and number in Table 21.

Table 22 gives the explicit formulae of all atomic orbitals, $\phi(r)$, which are involved, and Table 23 gives the same set of functions in their integral representations.

Table 23 shows clearly the close resemblance between the n-transform functions and the group of common-ζ-ns Slater type orbitals.

The latter can be regarded as n-transform functions, where the shape functions are composed of a number of delta functions at various integer n values. For example the "Common-ζ-1234s-STO" is obtained, if the shape function,

$$\text{shape }(n) = \sum_{i=0}^{3} c_i \delta(n - i), \tag{130}$$

and the primitive function, $r^n \exp(-\zeta r)$, are combined in an n-transformation (see function 5 in Table 23).

(b) Parameters

The optimum values of the non-linear parameters ζ and B, the linear parameter a, as well as the normalization constant N for the (0,B)-n-transform function (function 2) and for the (1,B)-n-transform function (function 6) are given in Table 24.

(c) Wavefunctions

The wavefunction corresponding to the (1,B)-n-transform is given in Table 25 as a function of the electronic coordinate along

Table 21. List of common-ζ-ns-STO and n-transform functions by name and number

Function Number	Name
1	1s Slater type orbital (STO)
2	(0,B)-η-transform function
3	Common-ζ-1s2s-STO
4	Common-ζ-1s2s3s-STO
5	Common-ζ-1s2s3s4s-STO
6	(1,B)-n-transform function

Table 22. Explicit formulae for the functions of Table 21

Function number	Explicit form
1	$N\cdot\exp(-\zeta r)$
2	$N\cdot\exp(-\zeta r)(1 + a\, f_{0B}(B;r))$, where $f_{0B}(B;r) = 2B^{-2}\,((r^{B} - 1)\, \ell n^{-2} r - B\, \ell n^{-1} r)$
3	$N\cdot\exp(-\zeta r)\ (1 + a\ r)$
4	$N\cdot\exp(-\zeta r)\ (1 + a\ r + b\ r^{2})$
5	$N\cdot\exp(-\zeta r)\ (1 + a\ r + b\ r^{2} + c\ r^{3})$
6	$N\cdot\exp(-\zeta r)\ (1 + a\, f_{1B}(B;r))$, where $f_{1B}(B;r) = 2(B-1)^{-2}((r^{B} - r)\, \ell n^{-2} r - r(B-1)\ell n^{-1} r)$

Table 23. Integral representations of the functions of Table 21.

Function number	Range of integration	Shape function	Primitive function
1	$n = 0$	$\delta(n)$	$r^n\exp(-\zeta r)$
2	$n = 0,\ 0 \leq n \leq B$	$\delta(n) + a\ G_{0B}(B;n)$	$r^n\exp(-\zeta r)$
3	$n = 0,\ 1$	$\delta(n) + a\ \delta(n-1)$	$r^n\exp(-\zeta r)$
4	$n = 0,\ 1,\ 2$	$\delta(n) + a\ \delta(n-1) + b\ \delta(n-2)$	$r^n\exp(-\zeta r)$
5	$n = 0,\ 1,\ 2,\ 3$	$\delta(n)+a\delta(n-1)+b\delta(n-2)+c\delta(n-3)$	$r^n\exp(-\zeta r)$
6	$n = 0,\ 1 \leq n \leq B$	$\delta(n) + a\ G_{1B}(B;n)$	$r^n\exp(-\zeta r)$

Table 24. Normalization constants and optimum parameters for the functions of Table 21.

Function number	Normalization constant	Optimum parameters	
		linear	non-linear
1	N = 0.454 952	---	$\zeta = 1.239265$
2	N = 0.302 225	a = +1.915 583	$\zeta = 1.874$ B = 2.992
3	N = 0.409 458	a = +0.696 616	$\zeta = 1.6275$
4	N = 0.409 458	a = +0.696 616 b = 0.0	$\zeta = 1.6275$
5	N = 0.411 246	a = +0.633 042 b = −0.000 349 c = −0.006 032	$\zeta = 1.59$
6	N = 0.430 845	a = +0.952 997	$\zeta = 1.81608$ B = 1.8402

the internuclear axis. This table contains also the exact wavefunction which was calculated as outlined in Section A, the 1234s-STO and the 1s-STO for the sake of comparison.

(d) Energies

The minimum energy obtained for the (0,B)-n-transform function is: $E_{0B} = -0.589\ 499$ hartree, and the energy for the (1,B)-n-transform function is $E_{1B} = -0.590\ 802$ hartree (see Table 26).

5) DISCUSSION

(a) General Remarks

Table 26 gives a summary of the minimum energies obtained for the 1s-STO, the (0,B)-n-transform function, the 1s2s-, the 1s2s3s-, and the 1s2s3s4s-STO functions, as well as that of the (1,B)-n-transform function in order of decreasing energy. Included in this table, in the same manner as in previous chapters, are the schematic drawings of the shape functions belonging to the different wavefunctions. The number of non-linear parameters necessary to achieve these energy values are also given.

(b) The (0,B)-n-transform

For B = 0 the shape function reduces to

$$\delta(n) + a\ \delta(n) \qquad (131)$$

and the resulting n-transform orbital reduces to

Table 25. The exact, (1,B)-n-transform, 1234s-STO and 1s-STO wavefunctions for H_2^+ as functions of the electronic coordinate along the internuclear axis. Internuclear distance R = 2.0 bohr.

X(bohr)	Exact	(1,B)-n-transform	1234s-STO	1s-STO
0.0	0.314 692	0.273 741	0.272 835	0.263 505
0.025	0.314 772	0.273 845	0.272 947	0.263 632
0.050	0.315 012	0.274 159	0.273 280	0.264 011
0.075	0.315 411	0.274 683	0.273 837	0.264 644
0.100	0.315 971	0.275 416	0.274 615	0.265 531
0.125	0.316 691	0.276 359	0.275 617	0.266 673
0.150	0.317 573	0.277 512	0.276 840	0.268 071
0.175	0.318 617	0.278 877	0.278 287	0.269 727
0.200	0.319 825	0.280 452	0.279 956	0.271 641
0.225	0.321 196	0.282 240	0.281 848	0.273 816
0.250	0.322 732	0.284 240	0.283 963	0.276 253
0.275	0.324 435	0.286 454	0.286 301	0.278 956
0.300	0.326 307	0.288 884	0.288 862	0.281 927
0.325	0.328 347	0.291 529	0.291 645	0.285 168
0.350	0.330 560	0.294 392	0.294 652	0.288 683
0.375	0.332 945	0.297 474	0.297 881	0.292 476
0.400	0.335 507	0.300 778	0.301 334	0.296 549
0.425	0.338 245	0.304 306	0.305 009	0.300 906
0.450	0.341 164	0.308 060	0.308 906	0.305 553
0.475	0.344 265	0.312 044	0.313 026	0.310 493
0.500	0.347 552	0.316 261	0.317 368	0.315 731
0.525	0.351 027	0.320 715	0.321 931	0.321 271
0.550	0.354 693	0.325 412	0.326 716	0.327 121
0.575	0.358 553	0.330 356	0.331 721	0.333 284
0.600	0.362 611	0.335 556	0.336 946	0.339 768
0.625	0.366 870	0.341 017	0.342 390	0.346 577
0.650	0.371 334	0.346 748	0.348 052	0.353 719
0.675	0.376 007	0.352 762	0.353 931	0.361 201
0.700	0.380 892	0.359 068	0.360 025	0.369 029
0.725	0.385 995	0.365 682	0.366 333	0.377 212
0.750	0.391 320	0.372 620	0.372 854	0.385 757
0.775	0.396 871	0.379 904	0.379 585	0.394 672
0.800	0.402 654	0.387 557	0.386 523	0.403 966
0.825	0.408 672	0.395 609	0.393 668	0.413 647
0.850	0.414 933	0.404 097	0.401 015	0.423 726
0.875	0.421 441	0.413 067	0.408 561	0.434 212
0.900	0.428 201	0.422 580	0.416 304	0.445 114
0.925	0.435 221	0.432 719	0.424 239	0.456 444
0.950	0.442 505	0.443 607	0.432 362	0.468 211
0.975	0.450 062	0.455 451	0.440 668	0.480 429
1.000	0.457 896	0.468 884	0.449 151	0.493 107
1.025	0.443 205	0.452 868	0.438 132	0.478 064
1.050	0.428 961	0.438 438	0.427 288	0.463 480
1.075	0.415 150	0.424 961	0.416 623	0.449 341
1.100	0.401 762	0.412 225	0.406 138	0.435 633
1.125	0.388 786	0.400 106	0.395 837	0.422 343

1.150	0.376 208	0.388 518	0.385 719	0.409 459
1.175	0.364 019	0.377 400	0.375 788	0.396 968
1.200	0.352 207	0.366 701	0.366 043	0.384 858
1.225	0.340 762	0.356 384	0.356 484	0.373 117
1.250	0.329 674	0.346 415	0.347 113	0.361 734
1.275	0.318 931	0.336 769	0.337 928	0.350 699
1.300	0.308 524	0.327 422	0.328 930	0.340 000
1.325	0.298 444	0.318 356	0.320 117	0.329 628
1.350	0.288 680	0.309 554	0.311 490	0.319 572
1.375	0.279 224	0.301 001	0.303 046	0.309 823
1.400	0.270 066	0.292 634	0.294 786	0.300 372
1.425	0.261 199	0.284 594	0.286 706	0.291 208
1.450	0.252 612	0.276 719	0.278 806	0.282 325
1.475	0.244 298	0.269 051	0.271 083	0.273 712
1.500	0.236 249	0.261 582	0.263 537	0.265 362
1.525	0.228 456	0.254 305	0.256 164	0.257 266
1.550	0.220 913	0.247 214	0.248 964	0.249 418
1.575	0.213 610	0.240 302	0.241 933	0.241 809
1.600	0.206 542	0.233 564	0.235 069	0.234 432
1.625	0.199 701	0.226 994	0.228 371	0.227 281
1.650	0.193 080	0.220 590	0.221 835	0.220 347
1.675	0.186 673	0.214 345	0.215 459	0.213 625
1.700	0.180 472	0.208 256	0.209 241	0.207 108
1.725	0.174 471	0.202 319	0.203 178	0.200 790
1.750	0.168 665	0.196 531	0.197 267	0.194 665
1.775	0.163 047	0.190 888	0.191 505	0.188 726
1.800	0.157 611	0.185 386	0.185 891	0.182 969
1.825	0.152 352	0.180 023	0.180 422	0.177 387
1.850	0.147 265	0.174 795	0.175 094	0.171 975
1.875	0.142 343	0.169 700	0.169 905	0.166 729
1.900	0.137 582	0.164 735	0.164 852	0.161 643
1.925	0.132 976	0.159 896	0.159 933	0.156 711
1.950	0.128 521	0.155 182	0.155 144	0.151 931
1.975	0.124 212	0.150 589	0.150 484	0.147 296
2.000	0.120 044	0.146 115	0.145 950	0.142 802
2.025	0.116 014	0.141 758	0.141 538	0.138 446
2.050	0.112 116	0.137 515	0.137 246	0.134 222
2.075	0.108 346	0.133 384	0.133 072	0.130 128
2.100	0.104 700	0.129 362	0.129 012	0.126 158
2.125	0.101 174	0.125 447	0.125 066	0.122 309
2.150	0.097 765	0.121 637	0.121 228	0.118 578
2.175	0.094 469	0.117 929	0.117 499	0.114 961
2.200	0.091 281	0.114 321	0.113 873	0.111 454
2.225	0.088 200	0.110 812	0.110 351	0.108 054
2.250	0.085 220	0.107 398	0.106 928	0.104 757
2.275	0.082 339	0.104 078	0.103 602	0.101 561
2.300	0.079 554	0.100 850	0.100 372	0.098 463
2.325	0.076 862	0.097 711	0.097 234	0.095 459
2.350	0.074 259	0.094 660	0.094 187	0.092 547
2.375	0.071 743	0.091 695	0.091 228	0.089 724
2.400	0.069 310	0.088 813	0.088 356	0.086 987
2.425	0.066 959	0.086 013	0.085 567	0.084 333
2.450	0.064 686	0.083 293	0.082 860	0.081 760
2.475	0.062 490	0.080 650	0.080 232	0.079 2[illegible]6

$$N \exp(-\zeta r)\ (1 + a). \tag{132}$$

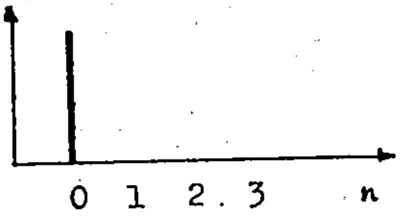
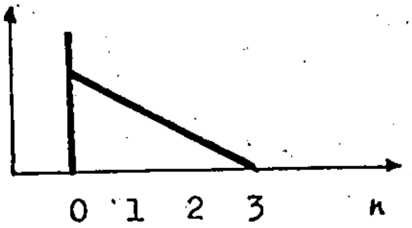
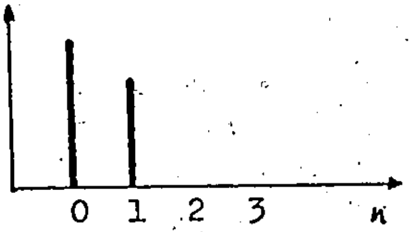
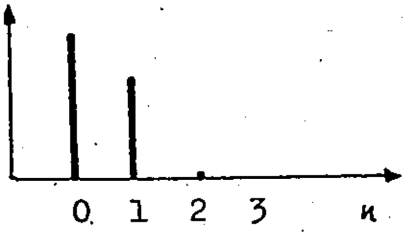
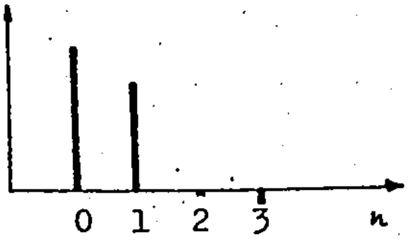
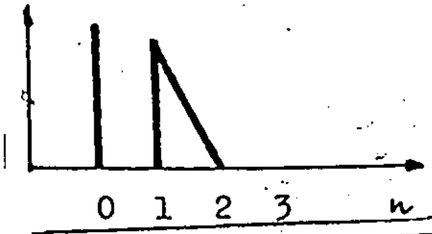
This means that the 1s-STO is contained in the (0,B)-n-transforms as the special case of B = 0.

Therefore, the minimum energy for an optimized value of the parameter B must be equal to or better than the energy of the 1s-STO. A look at Table 26 shows that the minimum energy for a (0,B)-n-transform function is in fact lower than that of the 1s-STO for H_2^+. The value found, E = -.589 499 hartree, lies actually very close to that found using a Gaussian integral transform function [25], E = -.589 5 hartree.

From the results of Section D it was expected that the optimum orbital exponent, ζ_{opt}, should be in the range $\zeta > 1.65$, since in this range all four coefficients of the 4-term LCAO have positive signs. Table 24 gives $\zeta_{opt} = 1.874$ for function 2. Similarly it was expected that the optimum parameter, B_{opt}, should be close to 3.0, since higher n values gave only insignificant improvements (see Section D) in ns-STO linear combinations.

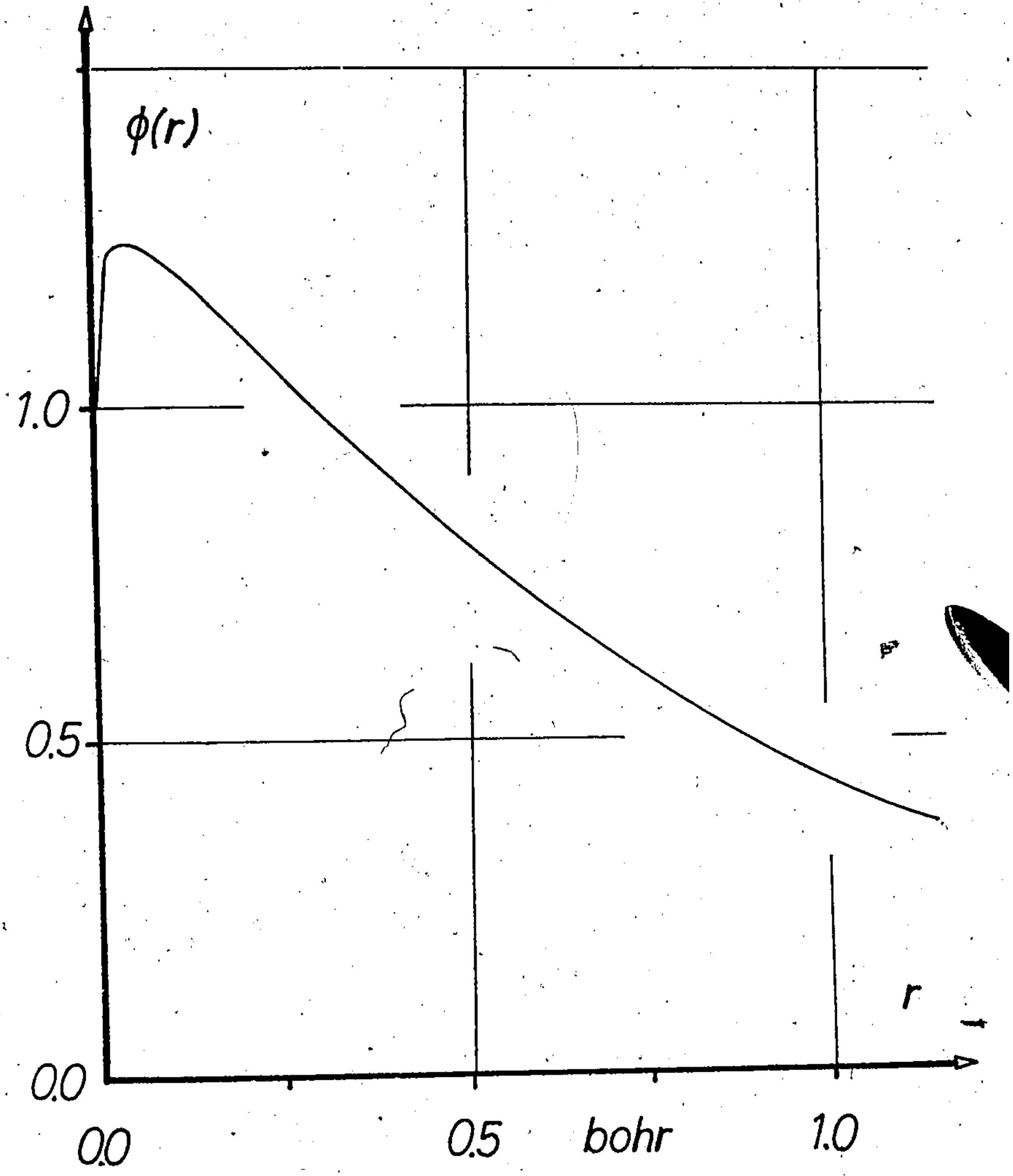
However, a plot of the atomic orbital, $\phi(r)$, for the (0,B)-n-transform function shows (see Fig. 11) that, despite its good energy, it is not a wavefunction suitable for describing the physical reality of H_2^+ since it has no peak at the site of the nuclei (i.e., for r = 0).

Table 26. N-transform functions for H_2^+. Internuclear distance R = 2.0 bohr.

Shape (n)	Function	Number of non-linear parameters	Energy (hartree)	Reference
	1s-STO	1	-0.586 506	Finkelstein, Horowitz [76], this work.
	(0,B)-n-transform	2	-0.589 499	Section E
	1s2s-STO	1	-0.590 450	Section C
	1s2s3s-STO	1	-0.590 450	Section D
	1234s-STO	1	-0.590 502	Section D
	(1,B)-n-transform	2	-0.590 802	Section E

Caption to Fig. 11.

The (O,B)-n-transform atomic orbital $\phi(r)$ as a function of the electron-nucleus distance r (bohr).


φ(r)
1.0
0.5
0.0
0.0
0.5
bohr
1.0
r

In this context the cusp value, γ, for a molecular wavefunction must be discussed. A negative finite cusp value ensures the existence of a wavefunction peak at the position of the nuclei. The cusp value for the exact wavefunction of H_2^+ is $\gamma = -1.0$. In Appendix 6 a derivation of the cusp value for wavefunctions constructed from the general (A,B)-n-transform is given. It is found that, in fact, the wavefunction using the (0,B)-n-transform has the improper cusp value $\gamma = +\infty$.

(c) The (1,B)-n-transform

For B = 1, the shape function reduces to $\delta(n) + a\,\delta(n-1)$ and the resulting n-transform function reduces to $N \exp(-\zeta r)\cdot(1 + a\,r)$.

This means that the 1s2s-STO is contained in the set of (1,B)-n-transforms as the special case of B = 1, a = 0.696 616. Table 27 clearly demonstrates this fact. In this table the optimum values of ζ, N, a, and E for a prescribed value of B are compared. For B approaching the value 1.0, all other parameters approach the values that correspond to the 1s2s-STO given in the last line of Table 27. Therefore, the minimum energy for an optimized parameter B must be equal to or better than that for a 1s2s-STO placed on each nucleus. In Table 26, it is in fact found that the minimum energy for the (1,B)-n-transform function is lower than that of the 1s2s-STO for H_2^+. Moreover, it is found that it is even better than that of the 1234s-STO.

From the results of Section D, it was expected that the optimum orbital exponent, ζ, should be in the range $\zeta > 1.65$.

Table 27. Comparison of the (1,B)-n-transform energies of H_2^+ for several prescribed values of B and optimized values of the remaining parameters with the energy of the 1s2s-STO.

B	ζ	N	a	Energy (hartree)
1.8402	1.81608	+0.430 845	+0.952 997	-0.590 801 6028
1.6	1.75648	+0.424 699	+0.865 509	-0.590 768 0254
1.4	1.71030	+0.419 634	+0.801 639	-0.590 694 0798
1.2	1.66727	+0.414 581	+0.745 357	-0.590 586 0997
1.1	1.64696	+0.412 036	+0.720 012	-0.590 521 4822
1.05	1.63711	+0.410745	+0.708 034	-0.590 486 8679
1s2s-STO	1.6275	+0.409 458	+0.696 616	-0.590 450 8564

Table 28. The (1,B)-n-transform energy of H_2^+ for a = 1.0.

	Parameters		
Normalization constant	linear	non-linear	Energy (hartree)
N = 0.419 859	a = 1.0	ζ = 1.81608	-0.590 689
		B = 1.8402	

The optimum $\zeta = 1.81608$ (see Table 24 for function 6) is indeed in this range.

The optimum value of a is 0.952 997 and indicates that this parameter adds little to the flexibility of $\phi(r)$, since even on forcing $a = 1.0$, we find for $\zeta = \zeta_{opt}$, and $B = B_{opt}$ that the energy is -0.590 689 hartree (see Table 28). The optimum energy for a (1,B)-n-transform without any linear parameter must therefore be equal to or better than this value. We thus conclude that the main improvement of the (1,B)-n-transform over the common-ζ-ns-STO is due to the integral transform concept rather than to the additional linear parameter a.

Fig. 12 shows a comparison of the exact wavefunction (bold line), the 1s-STO (dotted line), the 1234s-STO (broken line), and the (1,B)-n-transform function (fine continuous line). All functions are plotted as functions of the electronic coordinate x for points along the internuclear axis. Because of the symmetry of H_2^+, only one half ($x > 0$) is shown. The coordinate origin is at the molecular midpoint, and $x = \pm 1.0$ bohr correspond to the positions of the protons, since the internuclear distance is taken as $R = 2.0$ bohr.

Table 29 lists the $x = 0$, $x = 1.0$ and $x = 2.0$ values of the four wavefunctions given in Fig. 12. Table 30 lists the differences between the three approximate wavefunctions and the exact wavefunction again for $x = 0$, $x = 1.0$, and $x = 2.0$. From inspection of Tables 29 and 30, we see that the improvement of the (1,B)-n-transform and the 1234s-STO over the simple 1s-STO is due to a

Caption to Fig. 12.

Comparison of several H_2^+ wavefunctions as functions of the coordinate x (bohr) along the internuclear axis. Interatomic distance R = 2.0 bohr.

....	1s-STO
----------	1234s-STO
――――	(1,B)-n-transform
▬▬▬▬	exact

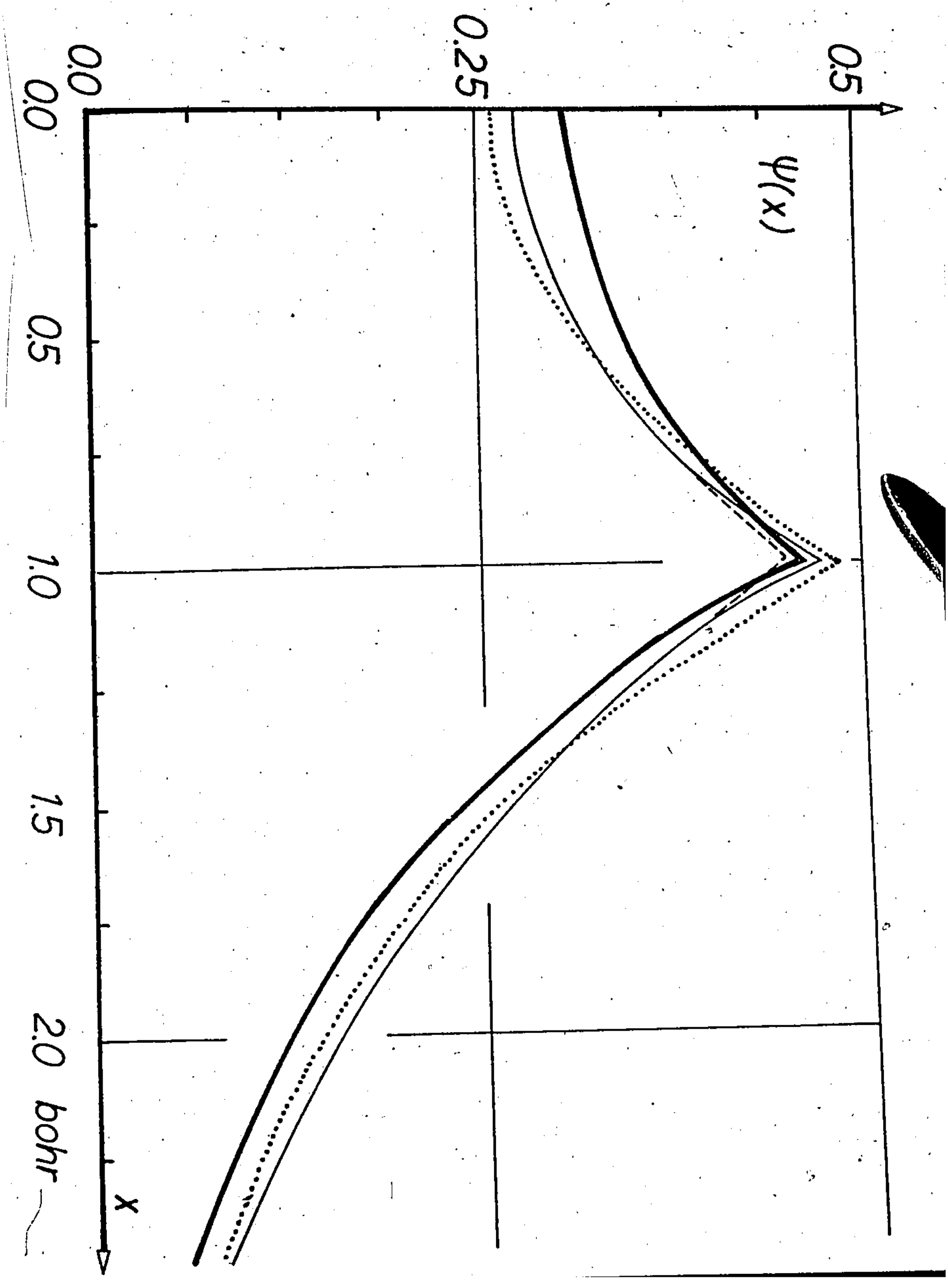

0.5
0.25
0.0
ψ(x)
0.0
0.5
1.0
1.5
2.0 bohr
x

Table 29. The x = 0.0, x = 1.0 and x = 2.0 values of the four wavefunctions for H_2^+ given in Fig. 12

Function	$\psi(0)$	$\psi(1.0)$	$\psi(2.0)$
1s-STO	+0.236 505	+0.493 107	+0.142 802
1234s-STO	+0.272 835	+0.449 151	+0.145 949
(1,B)-n-transform	+0.273 740	+0.468 883	+0.146 115
exact	+0.314 692	+0.457 896	+0.120 044

Table 30. The differences between the three approximate wavefunctions and the exact wavefunction for H_2^+ given in Fig. 12 at x = 0, x = 1.0 and x = 2.0. Internuclear distance R = 2.0 bohr.

Function	$\psi(0)-\psi_{ex}(0)$	$\psi(1.0)-\psi_{ex}(1.0)$	$\psi(2.0)-\psi_{ex}(2.0)$
1s-STO	-.051 187	+.035 211	+.022 758
1234s-STO	-.041 857	-.008 745	+.025 905
(1,B)-n-transform	-.040 952	+.010 987	+.026 071
exact	0.0	0.0	0.0

better approximation of the exact wavefunction in the region of the molecular midpoint and at the peak at $x = 1.0$ bohr. The wavefunctions constructed from the (1,B)-n-transform and the 1234s-STO almost coincide within an accuracy of about 10^{-3} (see Table 29) except for the region around $x = 1.0$ bohr, where the (1,B)-n-transform has a higher, and the 1234s-STO has a lower peak than the exact wavefunction.

All four functions in Fig. 12 show a cusp. Table 31 lists the cusp values, γ, for the functions given in this figure in order of decreasing energy. It is found that an approximate wavefunction which produced a rather good energy does not necessarily have an equally good cusp value. For example the wavefunctions using a 1234s-STO or a (1,B)-n-transform on each nucleus are not better than ψ_{1s} in terms of their cusp value. The property of γ less than -1.0 or γ greater than -1.0 goes parallel with the property of $\psi(1.0)$ higher than or lower than $\psi_{ex}(1.0)$ in Fig. 12.

Table 32 contains values of r_{max}, the position of the maximum of the atomic orbitals, after removal of the $\exp(-\zeta r)$ term, for the n-transforms and the common-ζ-ns-STOs (see Fig. 13). Except for the (0,B)-n-transform, which has already been rejected because of its irregular cusp value, all values of r_{max} are close to each other. For the 1s2s-STO and the 1s2s3s-STO, r_{max} is given by the quotient n/ζ. For the 1234s-STO and both n-transforms, r_{max} was obtained numerically.

The wavefunctions constructed from the atomic orbitals 3 to 6 in this table give a lower energy than the wavefunction constructed from a 1s-STO on each nucleus because they

Table 31. The cusp value for the wavefunctions given in Fig. 12.

Function	Cusp Value	
	Formula	Value
1s-STO	$-\zeta N/\psi_A$	-1.143
1234s-STO	$(-\zeta+a)\ N/\psi_A$	-0.87
(1,B)-n-transform	$-\zeta N/\psi_A$	-1.668
exact	$-Z_A$	-1.0

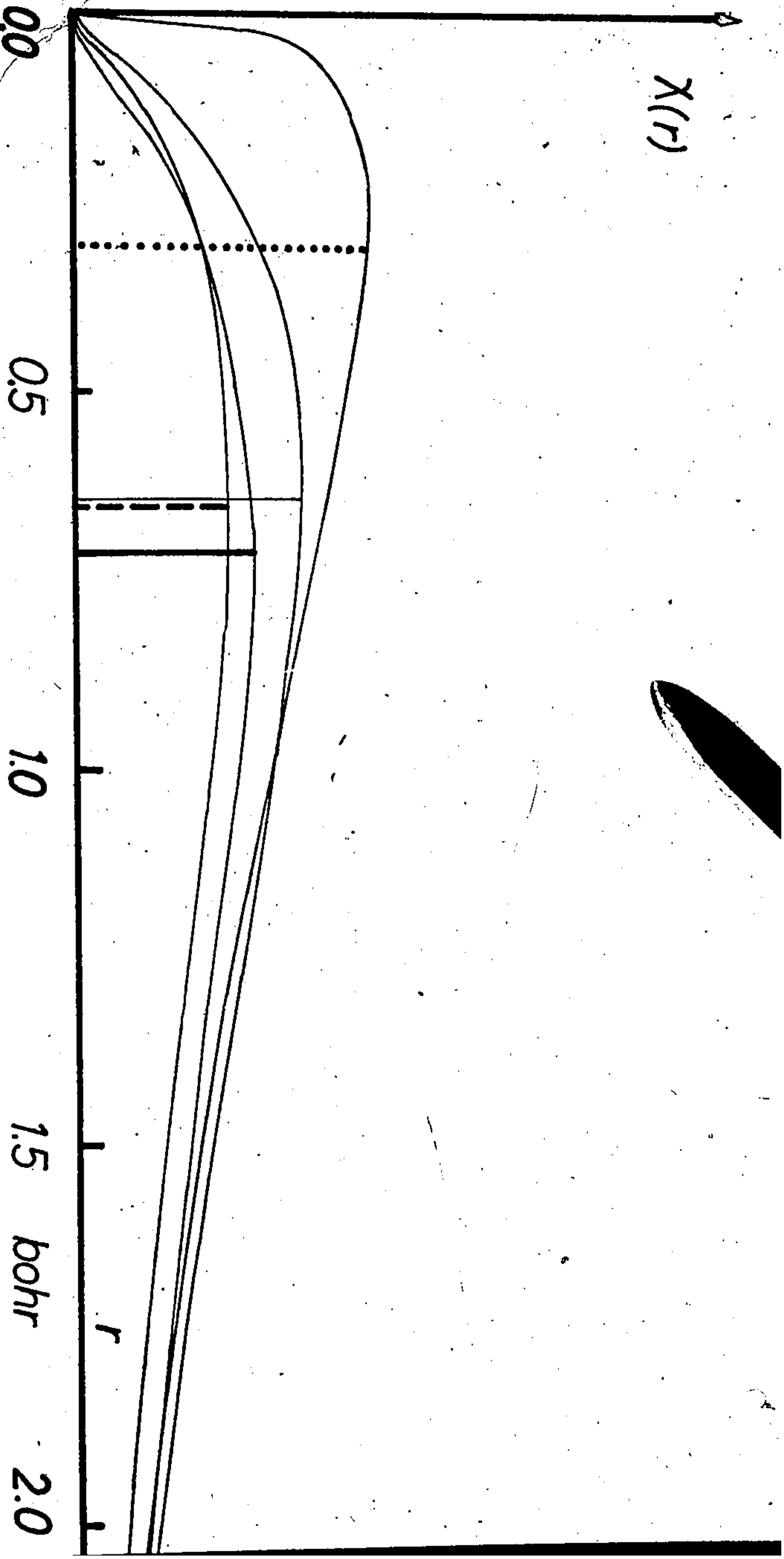
Table 32. The values of r_{max}(bohr), the position of the maximum of the atomic orbitals after removal of the exp($-\zeta r$) term.

Function number	Name	r_{max}(bohr)
1	1s-STO	----
2	(0,B)-n-transform	0.30
3	1s2s-STO	0.6144
4	1s2s3s-STO	0.6144
5	1234s-STO	0.625
6	(1,B)-n-transform	0.70

Caption to Fig. 13

Plot of the atomic orbitals after removal of the exp($-\zeta r$) term as functions of the electron-nucleus distance r (bohr). The scale on the ordinate in arbitrary units.

━━━━━━━━━━	(1,B)-n-transform orbital
- - - - - - - - - -	1234s-STO
──────────	1s2s- and 1s2s3s-STO
··················	(0,B)-n-transform orbital


χ(r)
0.0
0.5
1.0
1.5
2.0
r
bohr

enhance the latter in the mid-bond region and reduce it at the positions of the nuclei and this brings them closer to the exact wavefunction. This is possible because the AOs contain the flexibility of increasing their value considerably over a range of r values though not at r=0 and only to a small extent at r=2.0 (at the position of one nucleus the molecular wavefunction adds the r=0 value of the AO centred on it and the r=2.0 value of the AO centred on the other nucleus; at the molecular midpoint it adds the r=1.0 contributions of both AOs).

The success of the (1,B)-n-transform function seems to lie in the fact that its AOs are enhanced for a rather broad range of r and have a rather high value of r_{max}.

CHAPTER IV

THE HYDROGEN MOLECULE

SECTION A. INTRODUCTION

The hydrogen molecule plays an important rôle in theoretical investigations since it is complex enough to display many of the features which occur in larger molecular systems, e.g. electron correlation, yet small enough to be handled quite accurately in ab initio calculations. Also highly accurate spectroscopic data are available. Unlike the H_2^+ case, the Schrödinger equation for H_2 cannot be solved in a closed mathematical form. Theoretical calculations, therefore, rely on approximate methods. Calculations were first made by Wang [84], Rosen [85], and Weinbaum [78]. The SCF energy was calculated by Kołos and Roothaan [86]. Also Kołos and Wolniewicz [87] have calculated the energy of H_2 at both the Born-Oppenheimer and adiabatic levels of approximation. For the sake of standardization, most approximate calculations are carried out at the internuclear separation $R = 1.4$ bohr which is close to the equilibrium value of R. Wavefunctions which are a simple product of two identical functions for the two electrons, $\Psi = \phi(1)\phi(2)$, are called closed shell wavefunctions, and those of the $\Psi = \phi(1)\phi'(2)$ type are called open shell type. Both one-center and two-center wavefunctions have been used. In the course of calculations carried out by a member of this department (see Bishop and Leclerc [7]), an opportunity presented itself to test the applicability of the exponential integral transform function, $k_\nu(q\sqrt{r})$, to H_2. The results obtained will be discussed in this chapter. A comparison of the available Gaussian and exponential integral transform functions will also be given.

SECTION B. EXPONENTIAL INTEGRAL TRANSFORMS $k_\nu(q\sqrt{r})$

1) MATHEMATICAL FORMULATION

In the Born-Oppenheimer approximation the Hamiltonian in atomic units for H_2 is:

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{R}, \qquad (133)$$

where r_{a1} etc. are the electron-nucleus distances, and R is fixed at 1.4 bohr. The total wavefunction, Ψ, is

$$\Psi = \phi(1)\phi(2), \qquad (134)$$

where the molecular orbital $\phi(1)$ is

$$\phi(1) = \chi_a(1) + \chi_b(1), \qquad (135)$$

and a similar expression for $\phi(2)$. The atomic orbitals, χ, are the exponential integral transform functions:

$$\chi_a(1) = k_\nu(q\sqrt{r_{a1}}) \tag{136}$$

and similarly for $\chi_b(1)$, $\chi_a(2)$, and $\chi_b(2)$. The total energy is

$$E = \iint \Psi H \Psi d\tau_1 d\tau_2 / \iint \Psi \Psi d\tau_1 d\tau_2. \tag{137}$$

2) COMPUTATIONAL DETAILS AND RESULTS

Leclerc's computer program [7] was written in order to compare a series of unconventional basis functions, χ, within the common framework of H_2. The formulae required for the one-electron and two-electron integrals were expressed in elliptical coordinates. The main idea of this concept was to perform all the integrations over physical space numerically, so that basis functions of several kinds could be used without changing the integration procedure on going from one basis function to another. Only the basis function, its first and its second derivative with respect to the elliptical coordinates had to be supplied. The actual calculations used Gauss-Legendre quadratures and the mapping technique of McLean and Yoshimine [36]. The optimum values for the integration limits and the mapping parameter, and the most economic number of points were obtained by using the 1s-STO basis for which all the integrals could be evaluated analytically.

The $k_\nu(q\sqrt{r})$ function was one of the test functions Bishop and Leclerc investigated. As in the He calculations with this function (see Chapter II), the values for the $k_\nu(q\sqrt{r})$ function were obtained by an analytical formula if ν was a half-integer, and by an extended trapezoidal rule in conjunction with recurrence relations if ν was not. In order to express the Laplacian operator in elliptical coordinates use was made of the relationship:

$$\partial k_\nu(z)/\partial z = -z\ k_{\nu-1}(z). \qquad (138)$$

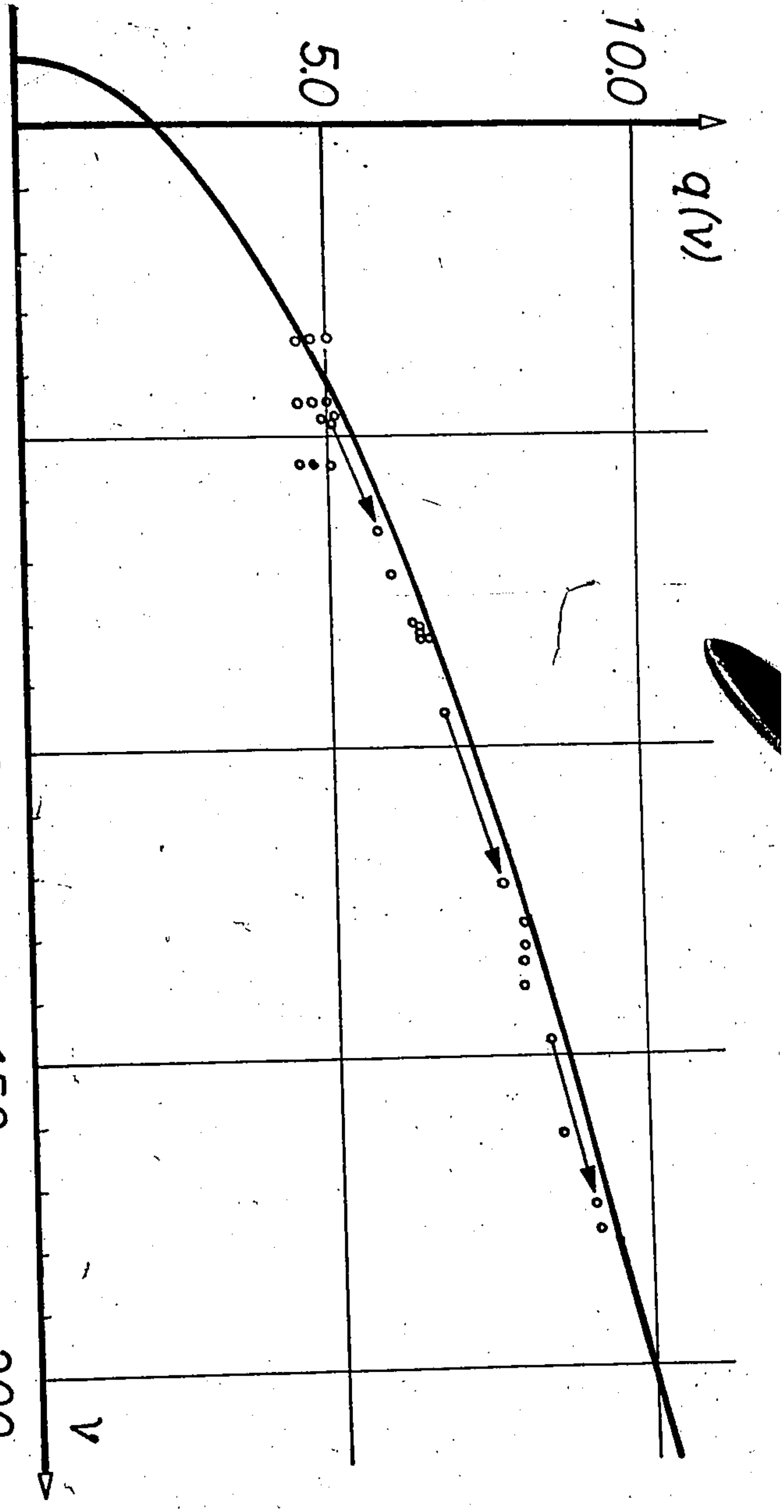
Due to the additional integration for the evaluation of each function, Bishop and Leclerc found that the calculating time for a single energy value was much longer for the $k_\nu(q\sqrt{r})$ functions than for the other basis functions studied. Therefore the optimization of the parameters ν and q could not be completed due to the lack of computer time, and also because numerical difficulties were encountered at high values of ν during the minimization of the energy.

What follows is an analysis of the values $E(\nu,q)$ they found and an attempt to explain their results, in the light of the findings of the preceding chapter on H_2^+. This will be done with the help of Figs. 14 to 16, and Table 33.

Let us start the discussion with Fig. 14. The circles in this figure indicate ν,q values for which energies were calculated in the course of minimization. The arrows indicate the direction of the steepest descent of the energy as a function of ν and q. It can be seen from this figure that the arrows are close and parallel

Caption to Fig. 14

ν and q values for H_2 with exponential integral transform functions (see text).


q(v)
10.0
5.0
0.0
5.0
10.0
15.0
20.0
v

to the parabolic curve for which the shape functions, $G(\nu,q;\zeta)$, have their maxima at a constant value, ζ_{max} and that they point towards $\nu \to \infty$.

Here $\zeta_{max} = \zeta_{1s} = 1.1895$, the orbital exponent which minimizes the H_2 energy if the 1s-STO is used as a basis function. The equation of this curve is

$$q = [4(\nu+1)\ \zeta_{max}]^{1/2}. \tag{139}$$

Fig.15 shows shape function plots for constant $\zeta_{max} = \zeta_{1s}$ for several values of ν. The decrease in half-width with increasing ν leads to the delta-type shape function $\delta(\zeta-\zeta_{1s})$. In order to clarify the situation, the energy values for several ν,q pairs such that $\zeta_{max} = \zeta_{1s}$ were calculated. Table 33 gives a comparison of these energies with those obtained from a rough minimization with respect to q for a given value of ν. Both sets of energies are plotted as functions of ν in Fig.16, where the energy E_{1s} is also indicated. The energies for which $\partial E/\partial q = 0$ (shaded circles in this figure) are, in all cases considered, below those for which $\zeta_{max} = \zeta_{1s}$ (blank circles) but still above E_{1s}. The findings derived from Figs.14-16 together with the results for the $k_\nu(q\sqrt{r})$ function for H_2^+, strongly support the conclusion that the $k_\nu(q\sqrt{r})$ function, when optimized, reduces to the 1s primitive function. Therefore the minimum energy, $E = E_{1s} = -1.128\,190$ hartree, is obtained for $\nu = \infty$, where the shape function is a delta function, $\delta(\zeta-\zeta_{max})$, and for q such that $\zeta_{max} = \zeta_{1s} = 1.1895$.

Caption to Fig. 15

The shape functions $G(\nu,q;\zeta)/G_{max}$ versus the ratio ζ/ζ_{max} for q such that $\zeta_{max} = \zeta_{1s}$, and for a set of ν values.

▬▬▬	$\delta(\zeta-\zeta_{1s})$
– – – –	$\nu = 3.75$
———	$\nu = 5.00$
———	$\nu = 7.50$
———	$\nu = 10.00$
———	$\nu = 15.00$

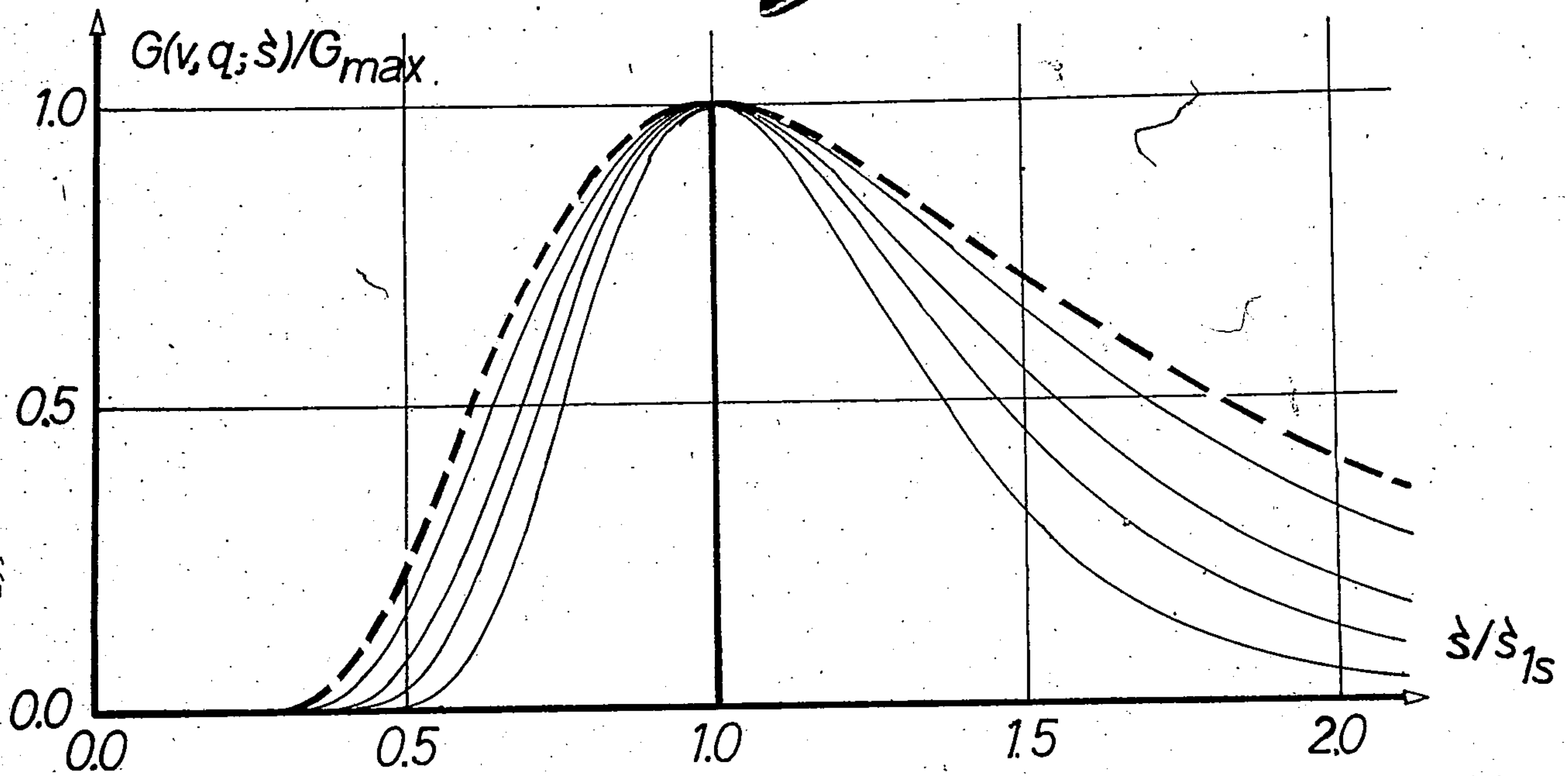

$G(v,q;\grave{s})/G_{max}$
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
$\grave{s}/\grave{s}_{1s}$

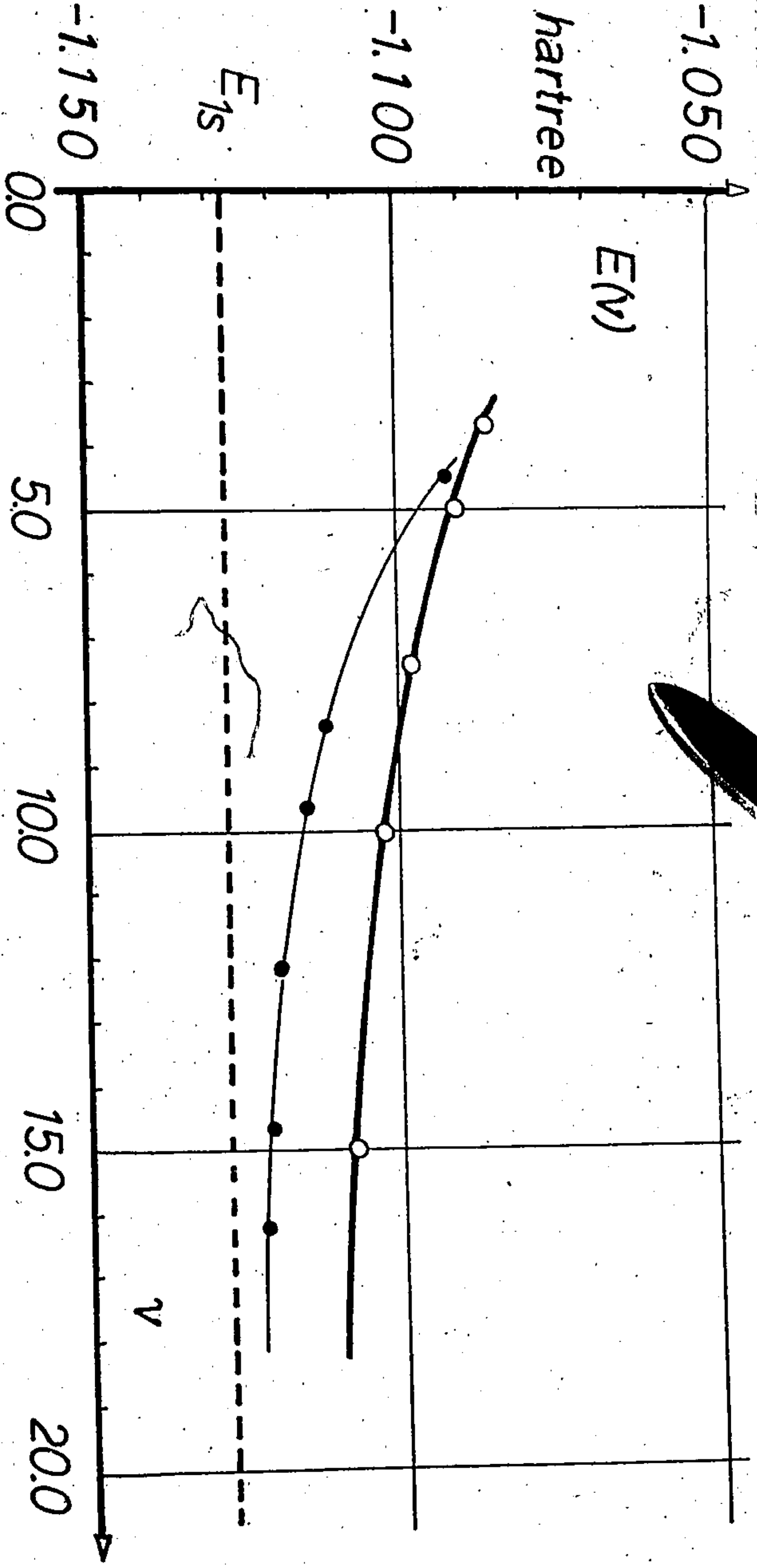
Table 33. Energy values for $\zeta_{max} = \zeta_{1s}$ and $\partial E/\partial q = 0$

	$\zeta_{max} = \zeta_{1s}$		$\partial E/\partial q = 0$	
ν	q	E(hartree)	q	E(hartree)
3.75	4.753 998	-1.086 385		
4.50			5.0	-1.109
5.00	5.343 032	-1.090 867		
7.50	6.359 481	-1.097 824		
8.40			6.5	-1.112
9.50			6.8	-1.117
10.00	7.234 500	-1.102 792		
12.20			7.7	-1.119
14.50			8.5	-1.121
15.00	8.725 136	-1.107 97		
16.25			8.8	-1.123
$\nu = \infty$		E_{1s} = -1.128 190		

Caption to Fig. 16.

H_2 with exponential integral transform functions. The energies (in hartrees) encountered on minimization plotted against the parameter ν.

—○——○—	E for q such that $\zeta_{max} = \zeta_{1s} = 1.1895$.
—●——●—	E such that $\partial E/\partial q = 0$ for ν = const.
------------	E_{1s}, the minimum energy if 1s-STOs are used to construct the wavefunction.


-1.050
hartree
-1.100
E_{1s}
-1.150
E(v)
0.0
5.0
10.0
15.0
20.0
v

In the next section this result will be brought into context with the results of available exponential and Gaussian integral transform functions.

SECTION C. COMPARISON OF I.T. FUNCTIONS FOR H_2

Table 34 contains the exponential integral transform functions for H_2 in order of decreasing energy. The schematic diagrams of the respective shape functions are included. It will be seen from this table that Bishop and Leclerc found a minimum energy for the Hulthén-type shape function (with a finite width $\Delta\zeta = 0.523$) which is below the E_{1s}. This result is different from what was found for H_2^+ where the Hulthén shape function as well as the shape function of $k_\nu(q\sqrt{r})$ reduced to a delta function on minimization, and did not produce an energy lower than E_{1s}.

Table 35 shows several Gaussian integral transform functions for H_2 in order of decreasing energy. The single 1s-GTO basis is a much poorer approximation than the single 1s-STO. A rather high number of terms (e.g. the 5-term linear combination by David and Mely [88] in this table) must be taken if GTOs are to be successful. The integral transform function of the fractional integral class used as basis functions by Somorjai and Bishop [22] is better than the 2-term GTO basis. The integral transform function using $G(\nu,q;\zeta)$ as a shape function together with a Gaussian primitive function, i.e., the $k_\nu(qr)$ function, is not available for H_2. However, since it contains the 1s-STO as a special case (i.e., $\nu = 1/2$), it must give an energy, $E \leq E_{1s\text{-}STO} = -1.128\ 190$ hartree.

Table 34. Different basis functions expressed as exponential integral transform functions for H_2 at R = 1.4 bohr

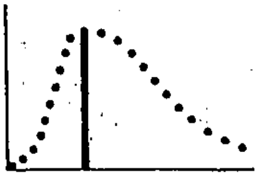
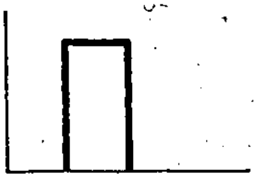
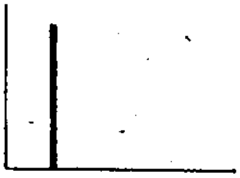
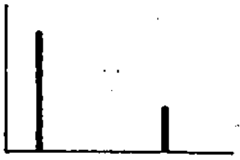
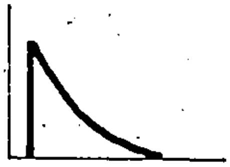
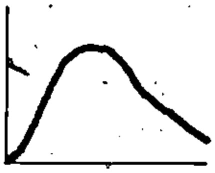
Basis	Shape function	Parameters	Energy (hartree)	Reference
1s-STO		$\zeta_{1s}=1.1895$	-1.128 190	Gordon and Secrest [88]
$k_\nu(q\sqrt{r})$		$\nu \to \infty$ $q^2=4(\nu+1)\zeta_{1s}$	-1.128 190	Bishop and Leclerc [7], this work
Hulthén		$\zeta_1=0.962$ $\zeta_2=1.485$	-1.128 236	Bishop and Leclerc [7]
SCF			-1.133 63	Kołos and Roothaan [86]
Exact			-1.174 4699	Kołos and Wolniewicz [87]

Table 35. Different basis functions expressed as Gaussian integral transform functions for H_2 at R = 1.4 bohr.

Basis	Shape function	Non-linear parameters	Energy (hartree)	Reference
1s-GTO		ζ = 0.397	-0.976 172	Katriel and Adam [90]
2-term 1s-GTO		ζ_1 = 0.259 97 ζ_2 = 1.178 90	-1.098 78	David and Mely [88]
fractional integral class		ζ_1 = 0.06 ζ_2 = 4.330	-1.109 03	Bishop and Somorjai [22]
5-term 1s-GTO		ζ_1 = 0.120 558 ζ_2 = 0.382 161 ζ_3 = 1.364 69 ζ_4 = 6.018 97 ζ_5 =40.036 8	-1.127 990	David and Mely [88]
$k_\nu(qr)$			≤-1.128 190	none
SCF			-1.133 63	Kołos and Roothaan [86]
Exact			-1.174 4699	Kołos and Wolniewicz [87]

CHAPTER V. CONCLUSIONS

The results of the calculations on the He-isoelectronic series, H_2^+, and H_2 in this thesis are important in several respects.

(a) The Integral Transformation Method

It was shown that the failure of the ζ-transform (with the exponential primitive function) to produce an energy better than that of the 1s-STO for H_2^+ or H_2 is an exceptional case which does not affect the applicability of the integral transformation concept in general.

(b) The Generalized Parameter

The calculations, supported with mathematical proofs and numerical evidence from actual examples, showed that the non-linear parameter n of ns-STOs can be generalized successfully within the scope of an integral transformation.

(c) The Primitive Function

The results obtained confirmed the fact that Slater type orbitals are better than Gaussian type orbitals, whether they are used in linear combinations of atomic orbitals or in integral transform functions.

(d) The Shape Function

The importance of constructing shape functions which mimic the set of optimized coefficients obtained for the corresponding linear combination of primitive functions was demonstrated.

(e) The Combination

The results of the H_2^+ calculations stress furthermore the fact that the combination of constituent parts of an IT function (i.e., the generalized parameter, the set of primitive functions, and the shape function) must be chosen to produce an integral transform function which does not reduce to one of the primitive functions on optimization.

CLAIMS TO ORIGINAL RESEARCH

1. Exponential integral transform functions were studied for the He-isoelectronic series, the hydrogen molecular ion, and the hydrogen molecule.

2. The minimum energies and the corresponding optimum parameters for the H^-, He, and Li^+ ground states were determined.

3. The energy limit for infinite nuclear charge as well as the expectation values for powers of r were calculated for H^-, He, and Li^+. The results obtained were better than the corresponding results for the Gaussian integral transform functions and very close to the Hartree-Fock values.

4. The minimum energies and the optimum parameters for the hydrogen molecular ion, H_2^+, were determined using an exponential integral transform function. The minimum energy was obtained for $\nu = \infty$, for which the function becomes a 1s-STO wavefunction.

5. These H_2^+ results were discussed by comparison with results obtained with n-term LCAO of 1s-STOs. The properties of the sets of optimum coefficients of the 1s-STOs made it clear that this set cannot be approximated by the given integral transform function.

6. Various n-term LCAO calculations with 1s2s-STO functions were performed for H_2^+ in order to investigate the possibilities of their generalization into an integral transform function.

The properties of the sets of optimum coefficients obtained indicated that such an integral transformation would not be likely to give an improvement.

7. Subsequently several n-term 1,2,3,...ns-STO LCAO functions with a common orbital exponent were studied to investigate their generalization into an integral transform function. The properties of the sets of optimum coefficients obtained indicated that such a generalization could be advantageous.

8. A novel integral transformation, which generalizes n, the principal quantum number, rather than ζ, the orbital exponent, was proposed. It was shown that such n-transform functions satisfy all the necessary mathematical requirements, which must be met by any integral transform function if it is to be used as a wavefunction. The minimum energy and the corresponding optimum parameters for H_2^+ were determined. The result obtained confirmed that the n-transform function can produce an energy improvement over the minimum energy obtained when the primitive function alone is used, even in cases where the ζ-transform fails to do so. The energy found by employing the n-transform was better than the energies obtained when either a 4-term linear combination of ns-STOs with a common orbital exponent or the Gaussian ζ-transform were used.

9\. For the hydrogen molecule, H_2, the minimum energy and the optimum parameters for the $k_\nu(q\sqrt{r})$ function were determined. The minimum energy was obtained for $\nu = \infty$, where it is equal to that of an 1s-STO wavefunction. This result was explained by arguments analogous to those which explained the results for H_2^+.

APPENDIX 1

DELTA-CONVERGENCE OF $G(\nu,q;\zeta)$

(a) The delta-convergence criteria for 1-parameter functions have been described by Gel'fand and Shilov [83]. The 1-parameter subset of the set of $G(\nu,q;\zeta)$ functions for which the maximum occurs at a constant value, ζ_{max}, is given by

$$G_\nu(\zeta) \equiv G(\nu,q \equiv \sqrt{4\zeta_{max}(\nu+1)}\ ;\ \zeta). \tag{140}$$

The explicit formula of $G_\nu(\zeta)$ is

$$G_\nu(\zeta) = [\zeta^{-1} \exp(-\zeta_{max}/\zeta)]^{\nu+1}. \tag{141}$$

The normalization constant, N, is

$$N = [\int_0^\infty G_\nu(\zeta)d\zeta]^{-1} = [\zeta_{max}(\nu+1)]^\nu/\Gamma(\nu). \tag{142}$$

The delta-convergence of $N \cdot G_\nu(\zeta)$ for $\nu \to \infty$ to $\delta(\zeta-\zeta_{max})$ will be shown.

(b) Proof that

$$\lim_{\nu\to\infty} [N \cdot G_\nu(\zeta)] = \delta(\zeta-\zeta_{max}). \tag{143}$$

The first requirement given by Gel'fand and Shilov [83] is:

"For any $M>0$ and for $|a| \leq M$ and $|b| \leq M$, the quantity $|\int_a^b N \cdot G_\nu(\zeta)d\zeta|$ must be bounded by a constant independent of a, b, or ν".

Since

$$\left|\int_a^b N\cdot G_\nu(\zeta)d\zeta\right| \leq N \int_0^\infty G_\nu(\zeta)d\zeta, = 1.0, \tag{144}$$

the first requirement is met.

The second requirement is:

"For any fixed non-vanishing a and b, we must have

$$\lim_{\nu\to\infty} [\int_a^b N\cdot G_\nu(\zeta)d\zeta] = \begin{cases} 0, & a < b < \zeta_{max} \\ 0, & \zeta_{max} < a < b \\ 1, & a < \zeta_{max} < b \end{cases} \text{."} \tag{145}$$

This will be shown in three separate steps.

(i) For $a < b < \zeta_{max}$, we must have

$$\lim_{\nu\to\infty} [\int_a^b N\cdot G_\nu(\zeta)d\zeta] = 0. \tag{146}$$

It is sufficient to show this for the integration domain (0,b):

$$\lim_{\nu\to\infty} [\int_0^b N\cdot G_\nu(\zeta)d\zeta] = 0.$$

On substituting $s = \zeta^{-1}$, we obtain

$$\lim_{\nu\to\infty} [\int_{1/b}^\infty N\cdot \exp[-\zeta_{max}(\nu+1)s]s^{\nu-1}ds]. \tag{147}$$

Use will be made of the general formula

$$\int_x^\infty t^a \exp(-t)\, dt = \Gamma(a+1) - \gamma(a+1, x), \tag{148}$$

where Γ and γ are the gamma function and the incomplete gamma function respectively (as defined by Gradsteyn and Ryshnik [91]). Therefore, for the limit in Eq. (147) we obtain

$$\lim_{\nu\to\infty}\left\{\frac{N}{[\zeta_{max}(\nu+1)]^{\nu}}\cdot\left[\Gamma(\nu)-\gamma\left(\nu,\frac{\zeta_{max}(\nu+1)}{b}\right)\right]\right\} \tag{149}$$

and, with the explicit expression for N,

$$\lim_{\nu\to\infty}\left\{1-\frac{\gamma\left(\nu,\frac{\zeta_{max}(\nu+1)}{b}\right)}{\Gamma(\nu)}\right\} . \tag{150}$$

Since the second term is equal to 1 for $\nu\to\infty$, i.e.,

$$\frac{\gamma(\nu,\zeta_{max}(\nu+1)/b)}{\Gamma(\nu)}=\frac{\int_0^{\zeta_{max}(\nu+1)/b} t^{\nu-1}e^{-t}\,dt}{\int_0^{\infty} t^{\nu-1}e^{-t}\,dt}=1, \tag{151}$$

the limit in Eq. (150) is zero, q.e.d.

(ii) For $\zeta_{max} < a < b$ we have to show that

$$\lim_{\nu\to\infty}\left[\int_a^b N\,G_\nu(\zeta)\,d\zeta\right]=0. \tag{152}$$

On substituting $s = \zeta^{-1}$, we obtain for the left hand side

$$\lim_{\nu\to\infty}\left\{\int_{1/b}^{1/a} N\,s^{\nu-1}\exp[-\zeta_{max}(\nu+1)s]\,ds\right\}, \tag{153}$$

and on substituting $t = \zeta_{max}(\nu+1)s$, we obtain

$$\lim_{\nu\to\infty} \{N[\zeta_{max}(\nu+1)]^{-\nu} \cdot \int_{\zeta_{max}(\nu+1)/b}^{\zeta_{max}(\nu+1)/a} \exp(-t)\, t^{\nu-1} dt\}. \qquad (154)$$

Use will be made of the general formula

$$\int_0^x t^a\, e^{-t}\, dt = \gamma(a+1,\, x). \qquad (155)$$

Hence we obtain

$$\lim_{\nu\to\infty}[\Gamma^{-1}(\nu)\cdot\gamma(\nu,\zeta_{max}(\nu+1)/a)-\Gamma^{-1}(\nu)\cdot\gamma(\nu,\zeta_{max}(\nu+1)/b)]. \qquad (156)$$

Since, analogous to Eq. (151), both

$$\Gamma^{-1}(\nu)\cdot\gamma(\nu,\zeta_{max}(\nu+1)/a)$$

and

$$\Gamma^{-1}(\nu)\cdot\gamma(\nu,\zeta_{max}(\nu+1)/b)$$

are equal to unity for $\nu\to\infty$, the limit in Eq. (156) is zero, q.e.d.

(iii) For $a < \zeta_{max} < b$, we have to show that

$$\lim_{\nu\to\infty}[\int_a^b N\cdot G_\nu(\zeta)\, d\zeta] = 1. \qquad (157)$$

To do this we make use of the fact that $G_\nu(\zeta)$ is normalized, and that the integration domain $(0, \infty)$ can be divided into three parts $(0,a)$, (a,b), and (b,∞), i.e.

$$\lim_{\nu\to\infty}[\int_a^b N\, G_\nu(\zeta)d\zeta] = [\int_0^\infty N\, G_\nu(\zeta)d\zeta - \int_0^a N\, G_\nu(\zeta)d\zeta - \int_b^\infty N\, G_\nu(\zeta)d\zeta]. \tag{158}$$

The integral from 0 to ∞ is unity and the remaining two integrals on the right hand side are zero, since they belong to the cases dealt with in steps (i) and (ii) above. Hence

$$\lim_{\nu\to\infty}[\int_a^b N\, G_\nu(\zeta)d\zeta] = 1, \text{ q.e.d.} \tag{159}$$

Thus the first and second requirements are met by the function $N\, G_\nu(\zeta)$, and therefore

$$\lim_{\nu\to\infty}[N\, G_\nu(\zeta)] = \delta(\zeta-\zeta_{max}), \text{ q.e.d.} \tag{160}$$

APPENDIX 2

H AND S INTEGRALS OVER 1s-STOs FOR H_2^+.

(a) $\zeta \neq \zeta'$.

Using the notation

$$p = (R/2)(\zeta+\zeta') \qquad (161)$$

and

$$t = (\zeta-\zeta')/(\zeta+\zeta'), \qquad (162)$$

the overlap integral may be written as

$$S(1,1;\zeta,\zeta') = (R^3\pi/4)2(A_2(p)[B_o(p)+B_o(pt)]-A_o(p)[B_2(p)+B_2(pt)]). \qquad (163)$$

In Eq.(163)use has been made of the auxiliary functions $A_n(p)$ and $B_n(pt)$ which are defined as some special definite integrals (see e.g. Eyring et al. [92] or Mulliken et al. [80]). The functions $B_n(pt)$ are sometimes called Kotani functions. The definitions of the auxiliary functions are:

$$A_n(p) = \int_1^\infty \lambda^n \exp(-p\lambda)\, d\lambda \qquad (164)$$

and

$$B_n(pt) = \int_{-1}^{+1} \mu^n \exp(-\, pt\mu)\, d\mu. \qquad (165)$$

$H(1,1;\zeta,\zeta')$ is the integral

$$\int[(\exp(-r_a\zeta)+\exp(-r_b\zeta)](-(1/2)\nabla^2-1/r_a-1/r_b)[(\exp(-r_a\zeta')+\exp(-r_b\zeta')d\tau. \qquad (166)$$

Using a more convenient form of the operator, either:

$$-(1/2)\nabla^2-\zeta/r_a + (\zeta-1)/r_a -1/r_b \ , \qquad (167)$$

or:

$$-(1/2)\nabla^2 -\zeta/r_b +(\zeta-1)/r_b -1/r_a, \qquad (168)$$

and making use of the fact that

$$[-(1/2)\nabla^2 -\zeta/r_a]\exp(-\zeta r_a) = -(\zeta^2/2)\cdot\exp(-\zeta r_a), \qquad (169)$$

we can write

$$H(1,1;\zeta,\zeta') = \int[\exp(-r_a\zeta)+\exp(-r_b\zeta)](-\zeta'^2/2+(\zeta'-1)/r_a-1/r_b)\cdot$$

$$\exp(-\zeta' r_a)d\tau + \int[\exp(-r_a\zeta)+\exp(-r_b\zeta)](-\zeta'^2/2+(\zeta'-1)/r_b-1/r_a)\exp(-r_b\zeta')d\tau. \qquad (170)$$

Hence:

$$H(1,1;\zeta,\zeta') = -\zeta'^2/2\int[\exp(-\zeta r_a)+\exp(-\zeta r_b)][\exp(-\zeta' r_a)+\exp(-\zeta' r_b)]d\tau \qquad (171)$$

$$+ 2\int[\exp(-\zeta r'_a)+\exp(-\zeta r_b)][(\zeta'-1)/r_a-1/r_b]\cdot\exp(-\zeta' r_a)d\tau.$$

The factor 2 in front of the second integral in Eq. (171) is due to the fact that r_a and r_b are equivalent. The first integral in the same equation is the same as $S(1,1;\zeta,\zeta')$ and the second integral can be expressed in terms of the auxiliary function $A_n(p)$ and $B_n(pt)$. We have, finally,

$$H(1,1;\zeta,\zeta') = (R^3\pi/4)[(-\zeta'^2/2)\cdot S(1,1;\zeta,\zeta') + \\ + (4\zeta'/R)(A_1(p)[B_o(p)+B_o(pt)] - A_o(p)\,[B_1(p)-B_1(pt)]) + \\ + (8/R)\,A_1(p)\,[B_o(p) + B_o(pt)]. \qquad (172)$$

As a check the above formulae were developed further, and the explicit formulae were obtained and these could be compared with those given by Coulson [81]. Some values could also be checked numerically with the values given by Mulliken et al. [80].

(b) $\zeta = \zeta'$.

For this case $p = R\zeta$ and $t = 0$, and for zero argument the Kotani auxiliary functions satisfy the following relations:

$$B_n(0) = \left\{ \begin{array}{ll} 0 & \text{for} \quad n = \text{odd} \\ \frac{2}{n+1} & \text{for} \quad n = \text{even} \end{array} \right\}. \qquad (173)$$

(c) $\zeta \approx \zeta'$.

In actual computations the case $\zeta \approx \zeta'$ has to be considered separately. We then have $pt \approx 0$ and it is advisable to use the Taylor expansion for the Kotani auxiliary functions (see for example DeJeu [93] and Guillemin and Zener [94]):

$$B_n(pt) = \left\{ \begin{array}{l} 2 \sum\limits_{k=0,2,4\ldots}^{\infty} \frac{(pt)^k}{k!(k+n+1)}, \text{ for } n = \text{even} \\ -2 \sum\limits_{k=1,3,5}^{\infty} \frac{(pt)^k}{k!(k+n+1)}, \text{ for } n = \text{odd} \end{array} \right\}. \qquad (174)$$

APPENDIX 3

THE ENERGY OF THE $1s(\zeta_{1s})+1s(\zeta_2)$ LINEAR COMBINATION

(a) The formula for the energy of H_2^+ for the $[1s(\zeta_{1s})+1s(\zeta_2)]$ linear combination is

$$E(\zeta_{1s},\zeta_2) = \frac{c_1^2H(\zeta_{1s},\zeta_{1s})+2c_1c_2H(\zeta_{1s},\zeta_2)+c_2^2H(\zeta_2,\zeta_2)}{c_1^2S(\zeta_{1s},\zeta_{1s})+2c_1c_2S(\zeta_{1s},\zeta_2)+c_2^2S(\zeta_2,\zeta_2)} . \qquad (175)$$

Here $H(\zeta_{1s},\zeta_2)$ is used as a notation for the integral $H(1,1;\zeta_{1s},\zeta_2)$ and similarly for the remaining integrals. Using the abbreviations

$$a = H(\zeta_{1s},\zeta_2)/H(\zeta_{1s},\zeta_{1s}), \qquad c = S(\zeta_{1s},\zeta_2)/S(\zeta_{1s},\zeta_{1s}),$$
$$b = H(\zeta_2,\zeta_2)/H(\zeta_{1s},\zeta_{1s}), \qquad d = S(\zeta_2,\zeta_2)/S(\zeta_{1s},\zeta_{1s}),$$

and $p = c_2/c_1$, we have

$$E(\zeta_{1s},\zeta_2) = \frac{H(\zeta_{1s},\zeta_{1s})}{S(\zeta_{1s},\zeta_{1s})} \cdot \frac{(1+2ap+bp^2)}{(1+2cp+dp^2)} . \qquad (176)$$

We write

$$E_{1s} = H(\zeta_{1s},\zeta_{1s})/S(\zeta_{1s},\zeta_{1s}). \qquad (177)$$

The expression Eq.(176) can be transformed algebraically into:

$$E(\zeta_{1s},\zeta_2) = E_{1s} + \frac{2cp[H(\zeta_{1s},\zeta_2)/S(\zeta_{1s},\zeta_2) - E_{1s}]}{(1+2cp+dp^2)} + \frac{dp^2[H(\zeta_2,\zeta_2)/S(\zeta_2,\zeta_2) - E_{1s}]}{(1+2cp+dp^2)} \qquad (178)$$

(b) Proof that for a positive ratio of coefficients, p,

$$E(\zeta_{1s},\zeta_2) \geq E_{1s} \text{ for all } \zeta_2. \qquad (179)$$

In Eq. (178) the quantities c and d are positive by their definition as the quotients of two overlap integrals, p is positive by the assumption, and $[H(\zeta_2,\zeta_2)/S(\zeta_2,\zeta_2)-E_{1s}]$ is positive by the definition of E_{1s} being the minimum energy among all $H(\zeta_2,\zeta_2)/S(\zeta_2,\zeta_2)$ energies. Numerical results show (see Fig. 17) that

$$H(\zeta_{1s},\zeta_2)/S(\zeta_{1s},\zeta_2) \geq E_{1s} \text{ for all } \zeta_2. \qquad (180)$$

Therefore only positive terms are added to E_{1s} in Eq. (178) which leads to the inequality Eq. (179), q.e.d.

(c) For the 1s-GTOs the opposite is true. Numerical results show (see Fig. 17)

$$H(\zeta_{1s\text{-}GTO},\zeta_2)/S(\zeta_{1s\text{-}GTO},\zeta_2) \leq E_{1s\text{-}GTO}, \qquad (181)$$

and hence for positive p,

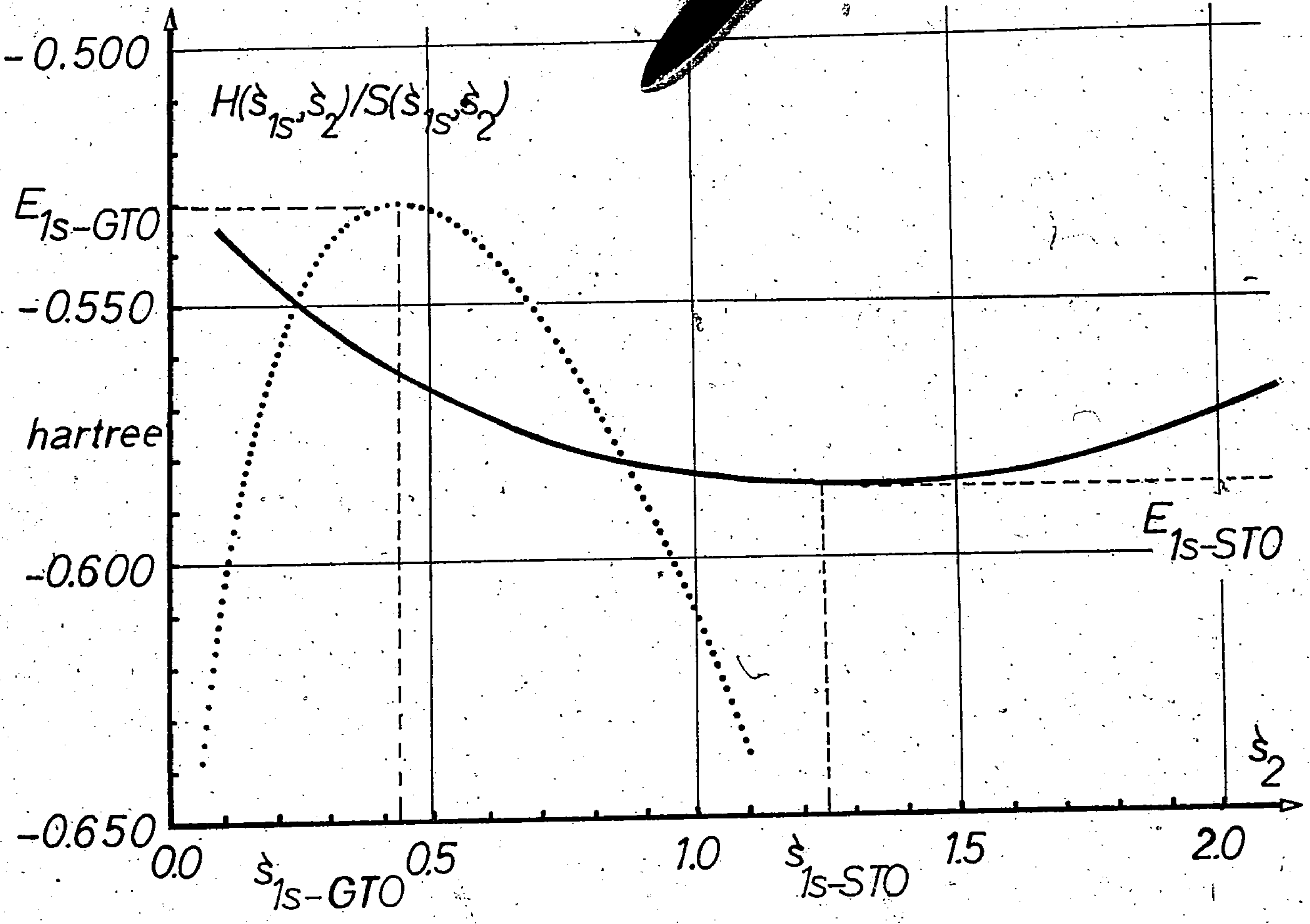
$$E(\zeta_{1s\text{-}GTO},\zeta_2) \leq E_{1s\text{-}GTO} \text{ for all } \zeta_2. \qquad (182)$$

Caption to Fig. 17.

The ratios $H(\zeta_{1s},\zeta_2)/S(\zeta_{1s},\zeta_2)$ in hartrees for GTOs and STOs as functions of ζ_2. The optimum orbital exponents ζ_{1s} and minimum energies E_{1s} for both cases are indicated by broken lines.

——————— STO

··················· GTO.


-0.500
-0.550
-0.600
-0.650
hartree
E_{1s-GTO}
E_{1s-STO}
$H(\zeta_{1s},\zeta_2)/S(\zeta_{1s},\zeta_2)$
0.0
0.5
1.0
1.5
2.0
ζ_{1s-GTO}
ζ_{1s-STO}
ζ_2

APPENDIX 4

THE LIMIT PROBLEM

Let Ψ_1 be the following one-parameter wavefunction and E_1 the corresponding energy and let Ψ_2 be the following two-parameter wavefunction with two almost equal orbital exponents and E_2 the corresponding energy:

$$\Psi_1 = \psi(\zeta) \text{ and } \Psi_2 = c_1\ \psi(\zeta+\Delta) + c_2\ \psi(\zeta-\Delta). \qquad (183)$$

Ψ_2 can be written as

$$\Psi_2 = c_1'\chi_1 + c_2'\chi_2 \qquad (184)$$

with $\chi_1 = [\psi(\zeta+\Delta) + \psi(\zeta-\Delta)]/2$,

$\chi_2 = [\psi(\zeta+\Delta) - \psi(\zeta-\Delta)]/(2\Delta)$,

$c_1' = \Delta(c_1 + c_2)$, and

$c_2' = \Delta(c_1 - c_2)$.

For $\Delta = 0$ we have

$$\lim_{\Delta=0} \Psi_2 = c_1'\psi + c_2'\psi' \text{ where } \psi' = \partial\psi(\zeta)/\partial\zeta. \qquad (185)$$

Assuming $\psi' \neq (\text{const.}\ \psi)$ we see that

$$\lim_{\Delta=0} \Psi_2 \neq \psi \text{ and } \lim_{\Delta=0} \Psi_2 \neq 0. \qquad (186)$$

(b) If $\zeta = \zeta_{opt}$, the orbital exponent which minimizes E_1, then

$$\langle\psi(H-E_1)\psi\rangle = 0 \qquad (187)$$

by definition of E_1, and

$$\langle\psi'(H-E_1)\psi\rangle = 0 \qquad (188)$$

by definition of ζ_{opt}.

The secular equations with $\zeta = \zeta_{opt}$ are

$$\langle\psi\psi\rangle(E_1-E_2)c_1' + \langle\psi\psi'\rangle(E_1-E_2)c_2' = 0 \text{ and} \qquad (189)$$

$$\langle\psi\psi'\rangle(E_1-E_2)c_1' + [\langle\psi' H\psi'\rangle - E_2\langle\psi'\psi'\rangle]c_2' = 0. \qquad (190)$$

There are two roots:

(i) $$E_1 = E_2, \quad c_1' \neq 0, \quad c_2' = 0, \quad \psi_2 = \psi(\zeta_{opt}). \qquad (191)$$

(ii) $E_1 \neq E_2$,

$$\frac{c_1'}{c_2'} = -\frac{\langle\psi\psi'\rangle}{\langle\psi\psi\rangle} = \frac{E_2\langle\psi'\psi'\rangle - \langle\psi' H\psi'\rangle}{\langle\psi\psi'\rangle(E_1-E_2)}. \qquad (192)$$

APPENDIX 5

n-TRANSFORM FUNCTIONS

(a) Normalization of the shape function $G_{AB}(A,B;n)$.

$$G_{AB}(A,B;\,n) = \left\{ \begin{array}{ll} 0.0\,, & \text{for } n < A \\ 2(B-A)^{-2}(B-n), & \text{for } A \leq n \leq B \\ 0.0\,, & \text{for } B < n \end{array} \right\} \tag{193}$$

is normalized such that:

$$\int_A^B G_{AB}\,dn = 1.0 \quad \text{for all } (A,B)\,, \tag{194}$$

since

$$\int_A^B G_{AB}\,dn = 2\,(B-A)^{-2}\cdot\int_A^B (B-n)\,dn = 2(B-A)^{-2}\cdot(Bn-n^2/2)_A^B =$$

$$= 2\,(B-A)^{-2}\cdot(B-A)^2/2 = 1.0 \text{ for all } (A,B). \tag{195}$$

(b) Delta-convergence of the shape function $G_{AB}(A,B;n)$.

If for a fixed pair (a,b) and B=A+d,

$$\lim_{d=0}\left(\int_a^b G_{AB}\,dn\right) = \left\{ \begin{array}{l} 0.0,\ \text{for } a < b < A \\ 1.0,\ \text{for } a < A < b \\ 0.0,\ \text{for } A < a < b \end{array} \right\}, \begin{array}{r} (196a) \\ (196b) \\ (196c) \end{array}$$

then

$$\lim_{d=0}\,(G_{AB}) = \delta(n-A), \tag{197}$$

Condition (196a) holds, since for $a < b < A$,

$$G_{AB} \equiv 0. \tag{198}$$

Condition (196b) holds, since for $a < A < b$, we have

$$\int_a^b G_{AB}\, dn = \int_A^{A+d} G_{AB}\, dn = 1 \tag{199}$$

for any d(including $d = 0$) because of the normalization condition.

Condition (196c) holds, since for $A < a < b$,

$$\int_a^b G_{AB}\, dn = 0 \tag{200}$$

for any d such that $(A+d) < a$ including $d = 0$.

(c) Derivation of the explicit form of the n-transform orbital

The integral representation of the n-transform orbital is as follows:

$$\phi(r) = \exp(-\zeta r)\; f_{AB}(A,B;\ r), \tag{201}$$

where

$$f_{AB}(A,B;\ r) = \int_A^B G_{AB}(A,B;\ n)\ r^n\ dn\ . \tag{202}$$

In order to give the explicit form of the n-transform orbital use is made of the following relationships:

$$r^n = \exp((\ln r)\ n), \tag{203}$$

$$\int r^n dn = r^n \ln^{-1} r, \tag{204}$$

and

$$\int n\, r^n\, dn = r^n \ln^{-1} r\, (n - \ln^{-1} r). \tag{205}$$

We obtain for the n-transform orbital

$$\phi(r) = \exp(-\zeta r)\, f_{AB}(A,B;\, r), \tag{206}$$

where

$$f_{AB}(A,B;\, r) = 2(B-A)^{-2} \int_A^B (B-n) \exp((\ln r)n)\, dn$$

$$= 2(B-A)^{-2} \ln^{-1} r((r^B - r^A) \ln^{-1} r - r^A(B-A)). \tag{207}$$

Thus

$$\phi(r) = \exp(-\zeta r) \cdot 2(B-A)^{-2} \cdot \ln^{-1} r((r^B - r^A) \ln^{-1} r - r^A(B-A)) \tag{208}$$

is the explicit form for $\phi(r)$ for the general case of (A,B).

(i) For the special case $(A,B) = (0,B)$, we have

$$\phi(r) = \exp(-\zeta r)\; 2\, B^{-2} \ln^{-1} r((r^B - 1) \ln^{-1} r - B). \tag{209}$$

(ii) For the special case $(A,B) = (1,B)$, we have

$$\phi(r) = \exp(-\zeta r) 2(B-1)^{-2} \ln^{-1} r((r^B - r) \ln^{-1} r - r(B-1)). \tag{210}$$

(iii) For the special case $A = B$, $A > 0$, we have the shape function

$$G_{AA}\,(A,A;\, n) = \delta(n-A) \tag{211}$$

which leads to

$$f_{AA}(A,A;\, r) = r^{A}\,, \tag{212}$$

since

$$\int \delta(n-A)\, r^{n}\, dn = r^{n} \text{ at } n = A. \tag{213}$$

Therefore

$$\phi(r) = r^{A} \exp(-\zeta r) \tag{214}$$

which is of the non-integer-n-STO type.

(iv) For the special case A = B = 0, we have the shape function

$$G_{00}(0,0;\, n) = \delta(n) \tag{215}$$

which leads to

$$f_{00}(0,0;\, r) = r^{0} \tag{216}$$

and

$$\phi(r) = r^{0} \exp(-\zeta r) \qquad \text{(21[illegible])}$$

which is the 1s-STO.

(d) <u>The behaviour of the n-transform function for r = ∞</u>

The vanishing of $\phi(r)$ for $r = \infty$ can best be shown if use is made of the explicit formula given by Eqs. (206) and (207).

$$\begin{aligned} \lim_{r=\infty} \phi(r) &= \lim_{r=\infty}[\exp(-\zeta r)\, f_{AB}(A,B;\, r)] = \\ &= 2(B-A)^{-2}(\lim_{r=\infty}[\exp(-\zeta r)\, \ell n^{-2} r\, (r^{B} - r^{A})] + \\ &+ \lim_{r=\infty}[\exp(-\zeta r)\, \ell n^{-1} r\, r^{A})]. \end{aligned} \tag{218}$$

Due to the presence of the exponential and logarithmic factors, it is found that both limits for $r = \infty$ in Eq.(218) are zero, hence, irrespective of the values of (A,B), we have

(i) for $A \neq B$

$$\lim_{r=\infty}[\phi(r)] = 0, \quad \text{and} \tag{219}$$

(ii) for $A = B, \phi(r) = r^A \exp(-\zeta r)$ which vanishes at $r = \infty$.

(e) <u>The behaviour of the n-transform orbital for r = 1</u>

The explicit formula in Eq.(207) contains apparently a division by zero, since $\ln r = 0$ for $r = 1$. But inspection of the integral representation (see Eq.(202)) reveals that $r = 1$ is a regular point of $\phi(r)$:

(i) $$\phi(r) = \exp(-\zeta) \quad \text{for} \quad r = 1 \tag{220}$$

for any (A,B), since we have

$$f_{AB}(A,B;\, r) = 1.0 \quad \text{for} \quad r = 1. \tag{221}$$

This can be shown as follows:

$$\lim_{r=1} f_{AB}(A,B;\, r) = \int_A^B G_{AB}(A,B;\, n)\, [\lim_{r=1} r^n]dn = 1 \tag{222}$$

for all (A,B) because of the normalization of the shapefunction.

(ii) For $A = B$, $G(n) = \delta(n-A)$, $f(r) = r^A$, $\phi(r) = r^A\exp(-\zeta r) = e^{-\zeta}$ for $r = 1$.

(f) The behaviour of the n-transform orbital at r = 0 (i.e. at the position of the nuclei)

Distinction must be made between the following cases of parameter values:

1) the general cases with $A \neq B$, $A \geq 0$, $B > 0$,

2) the special cases $A = B$, $A > 0$, and

3) the single case, where $A = B = 0$.

On inspection of the integral representation of the n-transform orbital $\phi(r)$ it is found that

$$\text{for } r = 0, \phi(r) = \begin{Bmatrix} 0 & \text{for all } A \neq B,\ A \geq 0,\ B > 0 \\ 0 & \text{for all } A = B,\ A > 0 \\ 1 & \text{for } A = B = 0. \end{Bmatrix} . \qquad (223)$$

This will be shown separately for each of the three cases.

1) For $A \neq B$, $A \geq 0$, $B > 0$, we have

$$G_{AB}(A,B;\ n) = 2\,(B-A)^{-2}\,(B-n)$$

and

$$f_{AB}(A,B;\ r) = \int_A^B G_{AB}(A,B;\ n) \cdot \lim_{r=0}(r^n)\,dn. \qquad (224)$$

Since

$$\lim_{r \to 0}\left[r^n\right] = \begin{Bmatrix} 0 \text{ for } n > 0 \\ 1 \text{ for } n = 0 \\ \infty \text{ for } n < 0 \end{Bmatrix}, \qquad (225)$$

we have

$$\lim_{r=0} f_{AB}\,(A,B;\ r) = 0\,, \qquad (226)$$

because the integrand in equation (224) vanishes identically throughout the range (A,B).

Therefore:

$$\phi(r) = 0 \text{ at } r = 0. \tag{227}$$

2) For A = B and A > 0, we have the n-transform of a delta-shape function at n = A, and therefore

$$G_{AB}(A,B;\, n) = \delta(n-A) \tag{228}$$

and

$$f_{AB}(A,B;\, r) = r^A, \tag{229}$$

which leads to

$$\phi(r) = r^A \exp(-\zeta r) \tag{230}$$

and finally

$$\phi(0) = 0. \tag{231}$$

3) For A = B = 0, we have the n-transform of a delta-shape function at n = 0, and therefore

$$G_{AB}(A,B;\, n) = \delta(n) \tag{232}$$

and

$$f_{AB}(A,B;\, r) = r^0, \tag{233}$$

which leads to

$$\phi(r) = r^0 \cdot \exp(-\zeta r) \tag{234}$$

and finally

$$\phi(0) = 1. \tag{235}$$

(g) First and second derivatives of the (A,B)-n-transform.

The Laplacian in the kinetic energy integral makes it necessary to evaluate the first and second derivatives of the (A,B)-n-transform orbital.

(i) Integral representations.

Derivatives of the integral representations are obtained by differentiating with respect to r in the integrand: *for* the orbital

$$\phi(r) = N \int_0^\infty C_{AB}(n)\, r^n \, dn \cdot \exp(-\zeta r), \qquad (236)$$

the first derivative is

$$d/dr(\phi(r)) = N \int_0^\infty C_{AB}(n)[n\, r^{n-1} - \zeta r^n]dn \cdot \exp(-\zeta r), \qquad (237)$$

and the second derivative is

$$d^2/dr^2(\phi(r)) = N \int_0^\infty C_{AB}(n)[n(n-1)\, r^{n-2} - 2\zeta n r^{n-1} + \zeta^2 r^n]dn \cdot \exp(-\zeta r). \qquad (238)$$

(ii) Explicit formulae.

For the orbital,

$$\phi(r) = N\,(1 + a\, f_{AB}(r))\cdot\exp(-\zeta r), \qquad (239)$$

where

$$f_{AB}(r) = 2\,(B-A)^{-2}\cdot[(r^B - r^A)\ln^{-2} r - r^A (B-A) \ln^{-1} r], \qquad (240)$$

the first derivative is

$$d/dr(\phi(r)) = N\,(-\zeta + a\, f'_{AB}(r))\cdot \exp(-\zeta r), \qquad (241)$$

where for r = 1.0

$$f'_{AB}(1) = (B^3 + A^2(2A - 3B))/(3(B-A)^2), \qquad (242)$$

for $r \neq 1.0$

$$f'_{AB}(r) = 2(B-A)^{-2}\, r^{-1}\, \ell n^{-1} r \cdot [2(r^A - r^B)\ell n^{-2} r + (Br^B + r^A(B-2A))\ell n^{-1} r - A(B-A)\, r^A], \qquad (243)$$

and for r = 0.0

$$f'_{AB}(0) = \int_A^B 2(B-A)^{-2}(B-n)n \lim_{r=0} r^{n-1} dn$$

$$= \left\{\begin{matrix} 0.0 \\ \infty \end{matrix}\right. , B \neq A, \left.\begin{matrix} \text{for } A \geq 1 \\ \text{for } A < 1 \end{matrix}\right\} . \qquad (244)$$

The second derivative is

$$d^2/dr^2(\phi(r)) = N\,[\zeta^2 - a\,\zeta\, f'_{AB}(r) + a\, f''_{AB}(r)]\, \exp(-\zeta r), \qquad (245)$$

where for r = 1.0

$$f''_{AB}(1) = 2\,(B-A)^{-2}[B^2(B^2/12 - B/6) + A^2(A^2/4 - (B+1)A/3 + B/2)], \qquad (246)$$

and for $r \neq 1.0$

$$f''_{AB}(r) = 2\,(B-A)^{-2}\, r^{-2}\, \ell n^{-1} r\, [(2r^B(1-2B) + 2r^A(3A-B-1))\ell n^{-2} r + 6(r^B - r^A)\ell n^{-3} r + (Br^B(B-1) + r^A(2AB - 3A^2 - B + 2A))\cdot \ell n^{-1} r + Ar^A(A^2 - BA - A + B)]. \qquad (247)$$

APPENDIX 6

THE CUSP CONDITION

(a) Introduction

For a system of charged particles the Hamiltonian contains Coulomb potential terms which give rise to singularities when any two particles coalesce (i.e. when the corresponding interparticle distance is equal to zero). The nature of these singularities were described by Kato [95], who also showed that the partial derivatives of the eigenfunctions are bounded. These coalescence conditions are called cusp conditions when the wavefunction has a finite non-zero value at the singularity. There are electron-electron and electron-nucleus cusp conditions.

(b) Definition

If the wavefunction ϕ is expressed as

$$\phi = \phi(r_{12} = 0)\ [1 + \gamma r_{12} + \vec{r}_{12}\,\vec{u}_{12} + O(r_{12}^{2})], \qquad (248)$$

where $\phi\ (r_{12} = 0)$ is the wavefunction for an interparticle distance of zero, and the vector $\vec{u}_{12}$ depends on the other particles in the system, then the coefficient γ is called the cusp value.

(c) Atoms

An alternative way to define the cusp is

$$(\partial\hat{\phi}/\partial r_{12})_{r_{12}=0} = \gamma\phi(r_{12}=0). \qquad (249)$$

In Eq. (249) $\hat{\phi}$ is ϕ averaged over a small sphere about the singularity. The cusp value γ is given by the formula:

$$\gamma = Z_1 Z_2 \mu_{12} , \qquad (250)$$

where μ_{12} is the reduced mass of the particles. For example, we have (in atomic units of mass and charge) for electron-electron coalescence $Z_1 = Z_2 = -1$ and $\mu_{12} = m_1 m_2/(m_1+m_2) = 1/2$, and therefore

$$\gamma = 1/2 , \qquad (251)$$

and for electron-nucleus coalescence we have charges Z and -1 and the reduced mass is $(1+1/M)^{-1}$, where M is the mass of the nucleus, and therefore

$$\gamma = -Z/(1+1/M) \qquad (252)$$

which reduces to

$$\gamma = -Z \qquad (253)$$

if infinite nuclear mass is assumed.

(d) Diatomic Molecules

The electron 1-nucleus A cusp condition for diatomic molecules has been discussed by Pack and Byers-Brown [96]. In this case we have $r_{12} = r_{1a}$ and $\gamma = -Z_A$ in Eqs. (248) and (249). Pack and Byers-Brown showed that the spherical average $\hat{\phi}$ in Eq. (249) can be replaced by a cylindrical average, $\bar{\phi}$, in view of the cylindrical symmetry of diatomics around the molecular axis, and hence:

$$[\partial\bar{\phi}/\partial r_{1a}]A,(\theta_{1a} = \pi/2) = [-Z_A\phi_A], \qquad (254)$$

where $\theta_{1a} = \pi/2$ indicates that the derivative of $\bar{\phi}$ w.r.t. r_{1a} for constant R and r_{1b} has to be taken at A in a direction perpendicular to the molecular axis.

The equivalent equation to Eq. (248) for diatomics is

$$\bar{\phi} = \phi_A[1 - Z_A r_{1a} + 0(r_{1a}{}^2)]. \qquad (255)$$

If a wavefunction is given in elliptical coordinates rather than two-center coordinates r_a and r_b, the cusp condition assumes the following form:

$$[(\partial\bar{\phi}/\partial\lambda)_A + (\partial\bar{\phi}/\partial\mu)_A]/R = -Z_A\phi_A\,. \qquad (256)$$

Since, if $\lambda = (r_{1a} + r_{1b})/R$ and $\mu = (r_{1a} - r_{1b})/R$, we have

$$\partial/\partial r_{1a} = (\partial/\partial\lambda + \partial/\partial\mu)/R.$$

(e) Testing Approximate Functions

The exact wavefunction of course, satisfies the cusp condition. Approximate wavefunctions generally have a cusp value different from $-Z_A$, or they are constrained to have γ equal to $-Z_A$, (this often results in a sacrifice of energy).

On solving Eq. (254) for γ we obtain

$$\gamma = \lim_{r_{1a}\to 0} (d/dr(\ell n(\bar{\phi}))). \qquad (257)$$

This form has been used, for example, by Somorjai [20] for atomic systems. Eqs.(254) to (257), whichever is most convenient, can be used for the determination of the cusp value for a diatomic molecule.

(f) The cusp value for approximate wavefunctions of the LCAO type.

In a LCAO type wavefunction ϕ is constructed by placing one AO, $\psi(r)$, on each nucleus:

$$\phi = N[\psi(r_a)) + \psi(r_b)], \tag{258}$$

and N is the normalization constant.

ϕ at nucleus A is given by

$$\phi_A = N[\psi(0) + \psi(R)], \tag{259}$$

where R is the internuclear separation.

By evaluating the left hand side of Eq.(254) we obtain, since the symmetry of the ground state wavefunction is such that $\bar{\phi}$ is ϕ,

$$(\partial\bar{\phi}/\partial r_a)_A = N\cdot[\partial\psi(r_a)/\partial r_a]_A \equiv N\cdot\psi'(0), \tag{260}$$

and setting this result equal to the right hand side of Eq.(254) we obtain

$$N\psi'(0) = \gamma\phi_A,$$

and solving for γ we find

$$\gamma = N\psi'(0)/\phi_A. \tag{261}$$

(g) The cusp value γ for common-ζ and n-transform functions.

(i) For the common-ζ- STO we have

$$\psi(r_a) = \exp(-\zeta r_a)\ (1 + a\ r_a + b\ r_a^{\ 2} + \ldots) \tag{262}$$

and

$$\begin{aligned}\psi'(r_a) = \exp(-\zeta r_a)[-\zeta(1 + a\ r_a + b\ r_a^{\ 2} + \ldots) + \\ + a + 2b\ r_a + 3c\ r_a^{\ 2} + \ldots],\end{aligned} \tag{263}$$

which reduces at $r_a = 0$ to

$$\psi'(0) = -\zeta + a\ . \tag{264}$$

(ii) For the (A,B)-n-transform orbital we have

$$\psi(r_a) = \exp(-\zeta r_a)(1 + f_{AB}(r_a)) \tag{265}$$

and

$$\psi'(r_a) = \exp(-\zeta r_a)[-\zeta(1+f_{AB}) + a\ f'_{AB}\ ]\ , \tag{266}$$

which reduces at $r_a = 0$ to

$$\psi'(0) = -\zeta \text{ for } A \geq 1,\ B \neq A\ , \tag{267}$$

since

$$f_{AB}(0) = \begin{Bmatrix} 0 & A \geq 0 \\ \infty & A < 0 \end{Bmatrix} \tag{268}$$

and

$$f'_{AB}(0) = \begin{Bmatrix} 0 & A \geq 1 \\ \infty & A < 1 \end{Bmatrix}\ . \tag{269}$$

The last two equations are derived in Appendix 5.

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$$|\psi(N,L,M;n,\alpha)\rangle \equiv \sqrt{\frac{(2n-1)(2n-2)(2n-3)\alpha^{2n-2N-1}}{(2N)!}}\,\frac{r^{N-1}}{(r+\alpha)^{n}}\cdot Y_{LM}(\theta,\phi).$$

and Eq. (14) should read:

$$\alpha_{opt} = (\hbar^2/Zme^2)\,\frac{n(2n-2)}{(2n+1)}\,.$$

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