A thesis

on

SPATIAL LOCALIZATION OF THE HYDROGEN ATOM

by

B.A.R. Kuppers

in partial fulfillment

of the requirements for

the Master of Science Degree

from the

University of Manitoba

THE UNIVERSITY OF MANITOBA ELIZABETH DAFOE LIBRARY

c B.A.R. Kuppers 1970

PREFACE

The present thesis is one aspect of a general study of low energy collision theory that the author has been involved with in the past year. Besides the material which will be discussed in the following text, a simulation of low energy collisions has been studied in collaboration with B. Pettitt. The combined results of both investigations have suggested new areas of study which will be discussed in future work.

ABSTRACT

A set of local wave functions are defined for the Hydrogen atom and the values of various physical observables are calculated using these functions. The results of these calculations are then compared with previously known results obtained by use of the eigenfunctions of the Hydrogen atom after which the two functional types - local and non-local - are examined in various representations. Next some of the fundamental properties and relationships of the local representation are developed. Finally the possibility of using local bound states in collision theory is considered.

CONTENTS

		Page
0.	INTRODUCTION	1
1.	LOCALIZED WAVE FUNCTIONS FOR THE HYDROGEN SYSTEM	6
.1	DEFINITION OF LOCALIZED FUNCTIONS	6
.2	USE OF COMPLETE SET RELATIONSHIP TO AVOID DISTRIBUTION PRODUCTS	8
.3	TRANSFORMATION FROM POSITION TO MOMENTUM STATE	12
.4	DIRECT SOLUTION OF DISTRIBUTION PRODUCT INTEGRALS	18
.5	AN EXAMINATION OF THE RESULTS OF SECTIONS 1.3, 1.4, 1.5.	21
.6	SOME PROPERTIES AND RELATIONSHIPS OF THE LOCAL REPRESENTATION	23
.7	A DISCUSSION OF SOME POSSIBLE APPLICATIONS OF THE LOCAL REPRESENTATION TO COLLISION THEORY	29
2.	SOME CONCLUDING REMARKS	32
APPENDICES		
A.	THE HYDROGEN ATOM HAMILTONIAN	34
B.	RELATIONSHIPS AND INTEGRALS INVOLVING THE HEAVISIDE FUNCTION	36
C.	FORM AND NORMALIZATION OF NON-LOCAL AND LOCAL HYDROGEN WAVE FUNCTIONS	42
D.	INTEGRAL TABLE	44
BIBLIOGRAPHY		45
TABLES		
1.	MEAN ENERGY AND ENERGY UNCERTAINTY FOR HYDROGEN 1S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS DERIVED BY USE OF COMPLETE SET RELATIONSHIP)	11a

Page

2. VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 1S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS DERIVED BY TRANSFORMATION TO MOMENTUM SPACE) 17a

3. VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 1S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS) 20a

4. VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 2S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS) 20h

5. VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 3S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS) 20i

6. VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 4S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS) 20k

7. VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 5S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS) 20m

8. AMPLITUDE OF NON-LOCAL (ψ_{1S}) AND LOCAL ($\overline{\psi}_{1S}$) FUNCTIONS IN X- AND K-SPACE 22a

FIGURES

1. Variation of mean energy $\overline{E}$ for the local hydrogen 1S state with change in localization radius, R. Mean energy found by use of complete set relationship (1.2.3). 11b

Page

2. Variation of energy uncertainty ΔE with changes in localization for local 1S state of hydrogen. Energy uncertainty evaluated through use of complete set relationship (1.2.8). 11c

3. Mean kinetic energy of local 1S state of hydrogen atom for varying radius of localization, R, as evaluated by expression derived by direct solution of integrals involving Distribution Products (1.4.3). 20b

4. Variation of mean potential energy of hydrogen 1S state with localization radius. Mean potential energy found by evaluation of expression derived by direct solution of integrals involving Distribution Products (1.4.2). 20c

5. Mean (total) energy for various radii of localization. Evaluated by use of expression derived by direct solution of integrals involving Distribution Products (1.4.4). 20d

6. Variation of momentum uncertainty with changing radius of localization. Momentum uncertainty found by evaluation of expression derived by direct solution of integrals involving Distribution Products (1.4.8). 20e

7. Variation of position uncertainty with localization radius. Position uncertainty was evaluated by use of expression derived by direct solution of integrals involving Distribution Products (1.4.10). 20f

8. Product uncertainty for various radii of localization. Product uncertainty obtained by use of (1.3.13) and evaluations of position and momentum uncertainties obtained by use of expressions derived by direct solution of integrals involving Distribution Products. 20g

0. INTRODUCTION

When this investigation was initiated, the field of interest was low energy atomic and molecular collisions, particularly molecular rearrangement collisions. It was soon concluded, however, that an initial step in the study of molecular rearrangement collisions was the formulation and investigation of the properties of a 'local' representation for bound systems. The simplest bound system, the hydrogen atom, was chosen as the system for investigation.

Since the conclusion stated above is not apparent, some discussion of the present state of low energy collision theory is necessary.

The most general theory of molecular rearrangement collisions is usually formulated in some form similar to S-Matrix Theory. However, as a result of present difficulties in this field (1) it was felt that direct solution of the Schrodinger equation by some method such as the Distorted Wave Method (2) would be most productive. However, it should be noted that the Born Series Approach would not be applicable since it has been demonstrated that this approach is only useful for describing high energy collisions. (3)

The usual methods used to solve the Schrodinger equation directly, however, have met with both conceptual and practical difficulties. The conceptual difficulty arises from the general use of energy eigenstates, which, being non-local, that is spread over all X-space, result in the fact that colliding

systems interact at all but infinite separation. This description of two colliding systems certainly does not correspond to one's intuitive concept of such an interaction. Various practical problems can arise from this diffuse nature of the wave functions, but the most general problem to appear is the asymptotic states problem. It has been found that for approaches such as the perturbed stationary state method it is almost impossible in practice to obtain suitable wave functions that satisfy the boundary conditions at large nuclear separation. These difficulties have been discussed by Mott and Massey (2) and various other authors (4, 5).

Various workers in this field have overcome these problems but by the use of some approximation such as enclosing the colliding systems in "boxes" when they are outside a chosen region of interaction (6), neglecting certain coupling terms at large separations in methods such as the distorted wave approach (7), or neglecting overlap integrals at large separations (8).

To resolve the conceptual problems introduced into collision theory by the use of the energy representation, which has been stated to be a non-local representation, it was concluded that a local representation, that is one constrained to a finite region of X-space, would be necessary to describe the interaction of colliding systems. Some apparant and useful properties of local representations lead to the above conclusion. Concepts such as the isolated system are allowed in such a representation,

and systems can be orthogonal, that is not interact, at finite separations. Coupled to this concept is the useful idea of regions of space where interaction may take place and others where it may not. Such practical difficulties as the asymptotic states problem are also removed by the use of local states.

Local representations are far from new; for instance, wave packets are used to describe freely moving particles. In the case of the free particle, the need for a different representation than the normal eigenstate or energy representation, resulting from solution of the Schrodinger equation for the system, was obvious because this description was physically unacceptable since the functions are not square integrable. The uncertainty relations also demonstrate the physically unacceptable nature of the eigenfunctions. It is well known that the momentum operator and Hamiltonian for the system commute. Then since the energy uncertainty $\Delta E = 0$, the momentum uncertainty $\Delta K = 0$ and from

$$\Delta K \cdot \Delta x = h/4\pi$$
$$\Delta E \cdot \Delta t = h/4\pi \qquad (0.1)$$

$\Delta x = \infty$, $\Delta t = \infty$ where Δx is the position uncertainty, and Δt the time interval characteristic of the rate of change of the system. A physically valid description was obtained by multiplying by a shaping function, usually Gaussian, making a wave packet out of the plane wave eigenstates. The functions are then square integrable and $\Delta E \neq 0$. It then follows that

$\Delta K \neq 0$ and it is no longer necessary for $\Delta x = \infty$ and $\Delta t = \infty$.

In finding a local representation for the hydrogen system two approaches were initially considered. First, one could attempt to solve the Schrodinger differential equation for the system over a defined finite volume of X-space. Using the finite difference technique this approach was partially successful. However, the finite difference technique does not produce an analytic solution which makes calculation of various physical observables rather cumbersome and heavily dependent upon the accuracy of the various numeric methods applied at each stage of a given calculation. As a result of these difficulties, the alternate approach was used for this study.

The approach used is quite similar to that used to form wave packet states for the free particle. The hydrogen eigenstates were multiplied by a shaping function to form localized functions. The shaping function chosen was the step function which produced functions which were only non-zero in a finite volume of X-space.

It should be noted that these wave functions will spread with time. However, it has been shown by Goldberger and Watson (Page 63 - 66 of "Collision Theory" (21)) that, under conditions permitting macroscopic observations of scattering phenomena, wave packets for free particles for which $\Delta E \simeq 0$ spread a negligible amount in the time taken for collision processes, and that this spreading can be ignored in most circumstances. Since it is easy enough to see that these arguments apply equally well

to similar wave packets for bound systems this aspect will not be considered further.

In the next three sections various methods will be used to solve the set of equations evaluating various physical observables of the system. The equations were solved several ways to serve as an internal check. The reasons this was felt to be necessary will be discussed in some detail.

Next, the validity of the local representation will be considered. The calculated values of the observables will be compared with those of the eigenstates. Also the local and non-local functions will be examined in several representations.

In the following sections various properties and applications of local states will be considered.

Finally, some general remarks will be made summing up the results of the previous sections and considering some of the implications of local states.

1. LOCALIZED WAVE FUNCTIONS FOR THE HYDROGEN SYSTEM

1.1 DEFINITION OF LOCALIZED FUNCTIONS

The local representation functions in X-space, which will be referred to as localized or local wave functions, are defined to have the form (in spherical polar co-ordinates)

$$\overline{\psi}_{nlm}(r,\Theta,\phi) = \overline{N}_{nl}\,\psi_{nlm}(r,\Theta,\phi)\cdot S(R) \qquad (1.1.1)$$

where $\overline{N}_{nl}$ is the normalization term, $\psi_{nlm}(r,\Theta,\phi)$ the eigen-state wave functions (solutions of the wave equation in the energy or non-local representation), and S(R) the shaping funtion. The explicit form of (1.1.1) is given in Appendix C. R will be referred to as the localization radius and is in fact the radius of the sphere within which the atom has been localized in X-space. Since only S states will be dealt with ($l = m = 0$), and all calculations were done in spherical polar co-ordinates, for most of the text the following simplification of notation will be used.

$$\overline{\psi}_{nS} = \overline{\psi}_{n00}(r,\Theta,\phi) \qquad (1.1.2)$$

Also Dirac bra-ket notation will be used such that

$$\langle r \mid \overline{\psi}_{nS} \rangle = \overline{\psi}_{nS}$$

The next three sections are different approaches used to solve for the energy and other physical observables using the localized wave functions. The major difficulty in solving the mathematical expressions involved was the appearance of Distribution Function Products which have not been rigorously defined

in mathematical theory and in fact is presently a field of study (9, 10). The distribution products come into the equations through S(R) which is defined

$$S(R) = \left(1.-H(r-R)\right) \qquad (1.1.3)$$

where H(r-R) is the Heaviside function (a distribution or generalized function) which is defined in Appendix B.

All calculations were done in atomic units and as a consequence all expressions are given in atomic units.

1.2 USE OF COMPLETE SET RELATIONSHIP TO AVOID DISTRIBUTION PRODUCTS

In this initial solution, distribution products were avoided by the use of the complete set relationship

$$P_r = \sum_{n=1}^{\infty} |\psi_{nlm}\rangle\langle\psi_{nlm}| = 1. \qquad (1.2.1)$$

where ψ_{nlm} are chosen to be the normal eigenstates of the hydrogen atom Hamiltonian H. The form of the hydrogen atom Hamiltonian is given in Appendix A.

The mean energy for a given localized S state ($l = m = 0$)

$$\bar{E}_n = \langle \bar{\psi}_{nS} | H | \bar{\psi}_{nS} \rangle$$

Now using (1.2.1)

$$\bar{E}_n = \sum_{m=1}^{\infty} \langle \bar{\psi}_{nS} | H | \psi_{mS} \rangle\langle \psi_{mS} | \bar{\psi}_{nS} \rangle \qquad (1.2.2)$$

The sum is only over the S states since it happens that any local S state $\bar{\psi}_{nS}$ is orthogonal to eigenstates ψ_{nlm} for which $l,m \neq 0$. Solving in particular for the 1S state ($n = 1$)

$$\bar{E}_1 = E_1 |\langle \bar{\psi}_{1S} | \psi_{1S} \rangle|^2 + \sum_{m=2}^{\infty} E_n |\langle \bar{\psi}_{1S} | \psi_{nS} \rangle|^2 \qquad (1.2.3)$$

where $$E_n = \frac{-1}{2n^2} \qquad (1.2.4)$$

Evaluating the integrals involved using the relations given in Appendices B, C and D one finds using projector operators

$$|<\overline{\psi}_{1S}|\psi_{1S}>|^2 = |\int_r <\overline{\psi}_{1S}|r>dr<r|\psi_{1S}>|^2$$

$$= 4\int_o^R r^3 e^{-2r} dr$$

and

$$<\overline{\psi}_{1S}|\psi_{nS}> = \frac{1.}{\sqrt{\int_o^R r^2 e^{-2r} dr}}\left[\frac{2}{n^2}(n!(n-1.)!)^{\frac{1}{2}} \cdot \sum_{s=1}^{n}\left\{\left(\frac{-2}{n}\right)^{s-1.} \frac{\int_o^R r^{s+1.} e^{-(1.+1./n)r} dr}{(n-s)!s!(s-1.)!}\right\}\right] \quad (1.2.5)$$

where R is the localization radius.

The uncertainty in energy ΔE for the localized 1S state was also calculated where

$$\Delta E_1 = \left[<\overline{\psi}_{1S}|H^2|\overline{\psi}_{1S}> - |<\overline{\psi}_{1S}|H|\overline{\psi}_{1S}>|^2\right]^{\frac{1}{2}} \quad (1.2.6)$$

The second term has been evaluated above ((1.2.3), (1.2.4) and (1.2.5)) and the first term was solved in a similar manner

$$<\overline{\psi}_{1S}|H^2|\overline{\psi}_{1S}> = <\overline{\psi}_{1S}|H\cdot H|\overline{\psi}_{1S}>$$

Inserting (1.2.1)

$$= \sum_{m=1}^{\infty} <\overline{\psi}_{1S}|H|\psi_{nS}><\psi_{nS}|H|\overline{\psi}_{1S}>$$

$$= \sum_{m=1}^{\infty} E_n^2 \left| \langle \bar{\psi}_{1S} | \psi_{nS} \rangle \right|^2 \qquad (1.2.7)$$

For the form of E_n and $\langle \bar{\psi}_{1S} | \psi_{nS} \rangle$ refer back to (1.2.4) and (1.2.5) respectively. Then for energy uncertainty one obtains

$$\Delta E_1 = \left[\sum_{m=1}^{\infty} E_n^2 \left| \langle \bar{\psi}_{1S} | \psi_{nS} \rangle \right|^2 - \left\{ E_1 \left| \langle \bar{\psi}_{1S} | \psi_{1S} \rangle \right|^2 + \sum_{m=2}^{\infty} E_n \left| \langle \bar{\psi}_{1S} | \psi_{nS} \rangle \right|^2 \right\}^2 \right]^{\frac{1}{2}} \qquad (1.2.8)$$

The calculations must necessarily be approximate since the sums are infinite but by referring to Table 1 and examining the overlap integrals squared (column 3) it can be seen that few terms contribute significantly to the answer. Table 1 tabulates the mean energy $\bar{E}_1$ and energy uncertainty ΔE_1 for the localized 1S state for various radii of localization, R, and the same quantities are graphed in Figures 1 and 2.

The results of this and the next two sections will be discussed together since only one set of equations is being solved by various mathematical techniques.

However, some mention of the reasons for attempting the solution of the state equation by another method should be given. Although the use of the complete set relation made the equations solvable, other problems arise from this technique.

Besides the large number of integrals that may have to be computed, there is always the question of the completeness of the set. For instance, in this case the sum in (1.2.1) should include not only the discrete states but also the continuum yet in practice it is often only possible to consider the first few discrete states. To circumvent this problem the next approach was used.

TABLE 1

MEAN ENERGY AND ENERGY UNCERTAINTY FOR HYDROGEN 1S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS DERIVED BY USE OF COMPLETE SET RELATIONSHIP)

in Atomic Units

Localization Radius	Complete Set State	Overlap with Local State Squared	Mean Energy	Energy Uncertainty
1.0	1S	0.3233		
	2S	0.0342		
	3S	0.0098		
	4S	0.0041	-0.1666	0.2316
1.5	1S	0.5768		
	2S	0.0488		
	3S	0.0134		
	4S	0.0055	-0.2954	0.2403
2.0	1S	0.7619		
	2S	0.0463		
	3S	0.0119		
	4S	0.0048	-0.3875	0.2026
3.0	1S	0.9380		
	2S	0.0213		
	3S	0.0043		
	4S	0.0016	-0.4720	0.1100
4.0	1S	0.9862		
	2S	0.0057		
	3S	0.0007		
	4S	0.0002	-0.4939	0.0523
5.0	1S	0.9977		
	2S	0.0004	-0.4994	0.0160
6.0	1S	0.9995		
	2S	0.0002	-0.4998	0.0106
7.5	1S	1.0000	-0.5000	0.0031
9.5	1S	1.0000	-0.5000	0.0005
Infinity	1S	1.0000	-0.5000	0.0000

FIGURE 1. Variation of mean energy $\overline{E}$ for the local hydrogen 1S state with change in localization radius, R. Mean energy found by use of complete set relationship (1.2.3).

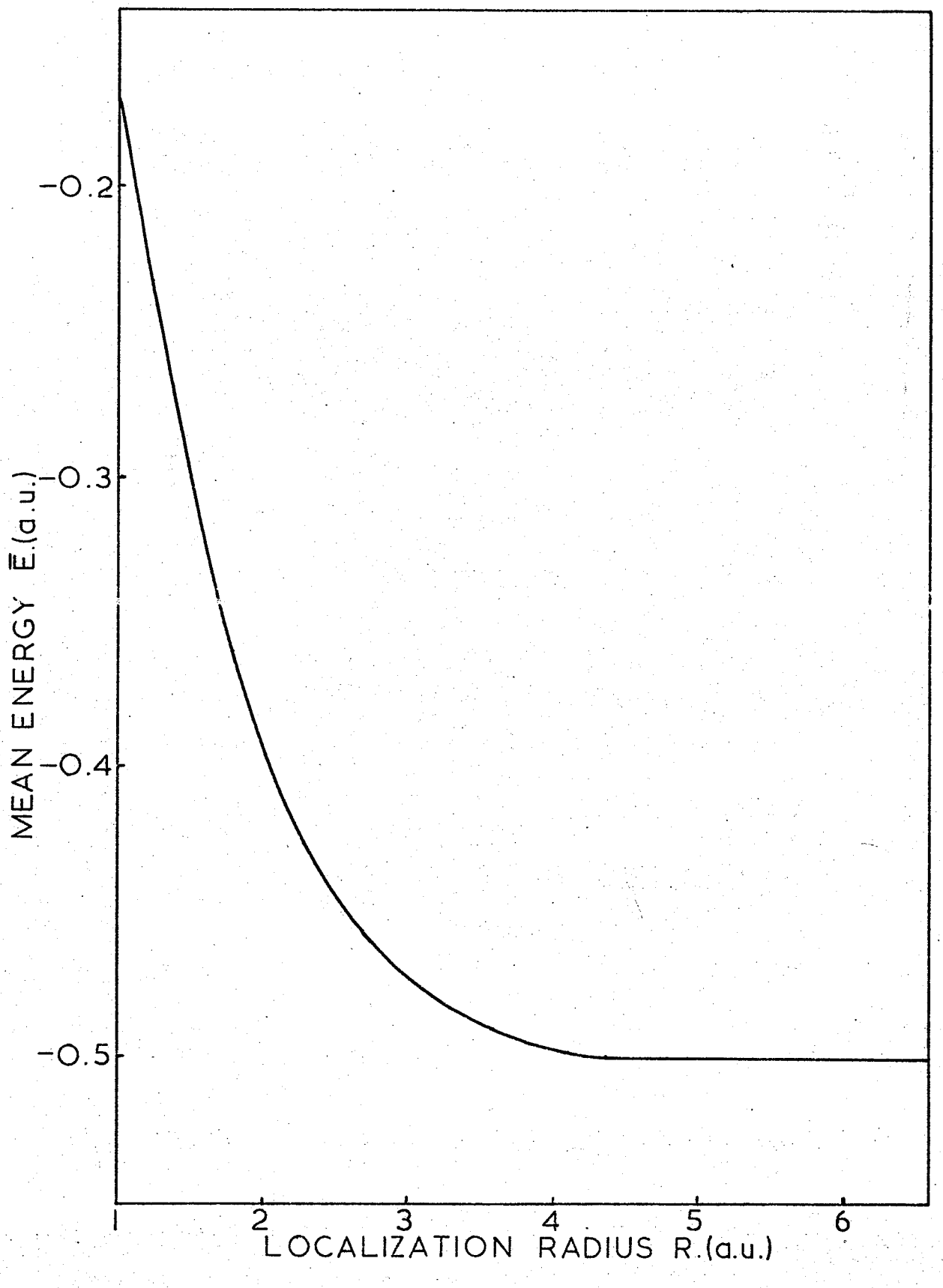
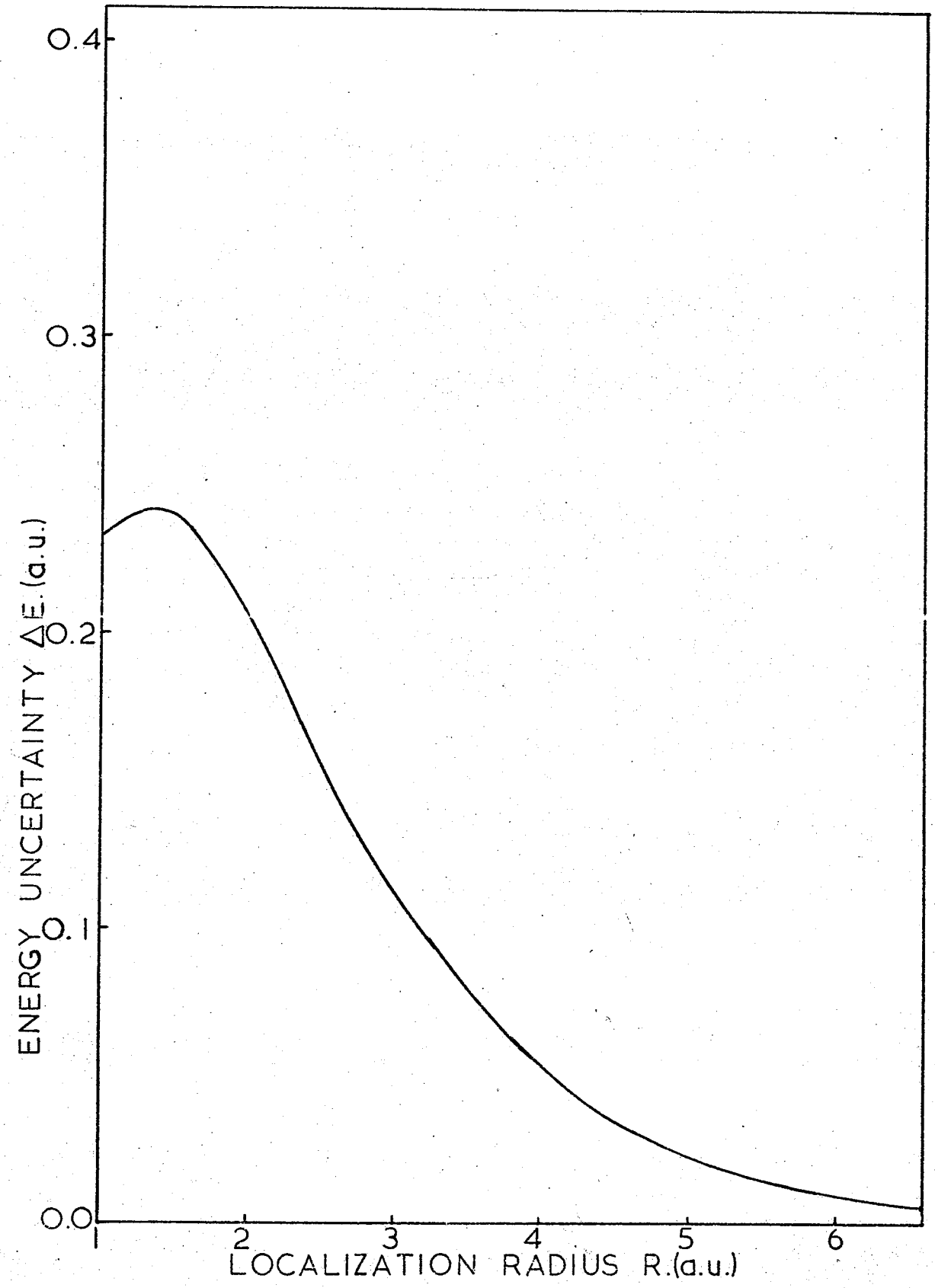

-0.2
-0.3
-0.4
-0.5
MEAN ENERGY Ē.(a.u.)
1
2
3
4
5
6
LOCALIZATION RADIUS R.(a.u.)

FIGURE 2. Variation of energy uncertainty ΔE with changes in localization for local 1S state of hydrogen. Energy uncertainty evaluated through use of complete set relationship (1.2.8).


0.4
0.3
0.2
0.1
0.0
ENERGY UNCERTAINTY ΔE.(a.u.)
1
2
3
4
5
6
LOCALIZATION RADIUS R.(a.u.)

1.3 TRANSFORMATION FROM POSITION TO MOMENTUM SPACE

The reasons for using this transformation were that in momentum representation or momentum space (K-space) the localization radius, R, became a constant in the equations rather than being an integral limit (as was the case in X-space) and also certain distribution products were avoided.

Actually the mean energy, $\overline{E}$, was not found by the use of one representation but two. The mean potential energy, $\overline{V}$, was evaluated in the position representation while the mean kinetic energy, $\overline{T}$, was evaluated in the momentum representation. In this way both the kinetic and potential energy operators were linear in form and only one distribution product resulted whose solution was known.

Then for the mean potential energy of the 1S state

$$\overline{V}_1 = \langle \overline{\psi}_{1S} \mid V \mid \overline{\psi}_{1S} \rangle$$

Using projector operators

$$\overline{V}_1 = \int_r \int_{r'} \langle \overline{\psi}_{1S} | r \rangle \, dr \langle r | V | r' \rangle \, dr' \langle r' | \overline{\psi}_{1S} \rangle$$

$$= \int_r \langle \overline{\psi}_{1S} | r \rangle \, dr \langle r | V | r \rangle \langle r | \overline{\psi}_{1S} \rangle \, \delta(r-r')$$

where $\delta(r-r')$ is the Kronecker delta. Then

$$\overline{V}_1 = - \frac{\int_0^R r e^{-2r} \, dr}{\int_0^R r^2 e^{-2r} \, dr} \qquad (1.3.1)$$

The form of the potential operator V (in X-space) for the hydrogen atom is given in Appendix A.

To evaluate the mean kinetic energy it was necessary to transform the localized wave function $\overline{\psi}_{1S}$ from co-ordinate space to momentum space. Then the localized function in momentum space

$$\overline{\psi}_{1S}(K,\Theta,\Phi) = \langle K' | \overline{\psi}_{1S} \rangle \tag{1.3.2}$$

Using projector operators

$$\overline{\psi}_{1S}(K,\Theta,\Phi) = \int_{r'} \langle K' | r' \rangle dr' \langle r' | \overline{\psi}_{1S} \rangle$$

Evaluating this expression using integrals in Appendix D

$$\overline{\psi}_{1S}(K,\Theta,\Phi) = \frac{\overline{N}_{1S}}{(\pi)^{\frac{1}{2}}} \left\{ \frac{2}{(1+K^2)^2} - \frac{1}{K(1+K^2)^2} \left[Re^{-R}(\sin(KR) + K\cos(KR)) \right] \right.$$

$$\left. - \frac{1}{K(1+K^2)^2} \left[e^{-R}\left((1-K^2)\sin(KR) + 2K\cos(KR)\right) \right] \right\}$$

$$\cdot Y_0^0(\Theta,\Phi) \tag{1.3.3}$$

where $\overline{N}_{1S}$ is the normalization constant for the localized state in co-ordinate space, R is the localization radius and Y_0^0 is a spherical harmonic function in momentum space.

In the momentum representation, the kinetic energy operator, T, has the form (in spherical polar co-ordinates)

$$T = \frac{K^2}{2} \tag{1.3.4}$$

Then the mean kinetic energy

$$\bar{T}_1 = \langle \bar{\psi}_{1S} | T | \bar{\psi}_{1S} \rangle$$

$$= \int_{K'} \int_{K''} \langle \bar{\psi}_{1S} | K' \rangle dK' \langle K' | T | K'' \rangle dK'' \langle K'' | \bar{\psi}_{1S} \rangle$$

$$= \int_{K'} \langle \bar{\psi}_{1S} | K' \rangle dK' \langle K' | T | K' \rangle \langle K' | \bar{\psi}_{1S} \rangle \delta(K' - K)$$

or

$$\bar{T}_1 = \frac{1}{\int_0^R r^2 e^{-2r} dr} \left[\int_0^\infty dK \frac{K^4}{(1+K^2)^4} \left\{ 2 - \frac{e^{-R}}{K} \left[(1-K^2)\sin(KR) + 2K\cos(KR) \right] \right\} - 2Re^{-R} \int_0^\infty dK \frac{K^3}{(1+K^2)^3} \left\{ \sin(KR) + K\cos(KR) \right\} \right.$$

$$\cdot \left\{ 2 - \frac{e^{-R}}{K} \left[(1-K^2)\sin(KR) + 2K\cos(KR) \right] \right\} + R^2 e^{-2R} \int_0^\infty \frac{dK\, K^2}{(1+K^2)^2}$$

$$\cdot \left\{ \sin^2(KR) + 2K\sin(KR)\cos(KR) \right\} + R^2 e^{-2R} \int_0^\infty \frac{K^4}{(1+K^2)^2}$$

$$\left. \cdot \cos^2(KR) dK \right] \tag{1.3.5}$$

One integral

$$\int_0^\infty \frac{dK\ K^4}{(1+K^2)^2}\cos^2(KR) \tag{1.3.6}$$

was awkward to evaluate but by writing it in another form

$$\int_0^\infty \frac{dK\ K^4}{(1+K^2)^2}\cos^2(KR) = \int_0^\infty dK\left[1-\left\{1-\frac{K^4}{(1+K^2)^2}\right\}\right]\cos^2(KR) \tag{1.3.7}$$

and noting the similarity in these integrals to those found in the normalization of plane wave states a solution was found. The solution of the integral can be found in Appendix D.

The mean energy of the 1S state can now be easily found since

$$\overline{E}_1 = \overline{T}_1 + \overline{V}_1 \tag{1.3.8}$$

The position, momentum, and product uncertainties were also evaluated. For the momentum uncertainty

$$\Delta K_1 = \left\{<\overline{\psi}_{1S}|K^2|\overline{\psi}_{1S}> - |<\overline{\psi}_{1S}|K|\overline{\psi}_{1S}>|^2\right\}^{\frac{1}{2}} \tag{1.3.9}$$

The second integral is equal to zero since the mean momentum of an S state is zero. Then

$$\Delta K_1 = (2\overline{T})^{\frac{1}{2}} \tag{1.3.10}$$

For the position uncertainty

$$\Delta r_1 = \left\{ \langle \bar{\psi}_{1S} | r^2 | \bar{\psi}_{1S} \rangle - | \langle \bar{\psi}_{1S} | r | \bar{\psi}_{1S} \rangle |^2 \right\}^{\frac{1}{2}} \qquad (1.3.11)$$

Solving in the usual manner

$$\Delta r_1 = \left\{ \tfrac{3}{4} + \frac{R^3 e^{-2R}}{2I} \left[1 - R - \frac{R^3 e^{-2R}}{2I} \right] \right\}^{\frac{1}{2}} \qquad (1.3.12)$$

where

$$I = \tfrac{1}{4} - e^{-2R} (\tfrac{1}{4} + R/2 + R^2/2)$$

and R is the localization radius. The integral solutions are in Appendix D. The product uncertainty is then easily evaluated since

$$\Delta pd_1 = \Delta r \cdot \Delta K \qquad (1.3.13)$$

The results of the various calculations performed are tabulated in Table 2.

Attempts to use this approach to evaluate other physical properties proved fruitless. For instance, in the attempted calculation of the energy uncertainty some integrals proved to be divergent.

In the calculation of the 1S state mean kinetic energy, $\bar{T}_1$, the expression had to be separated into its component integrals so that (1.3.6) could be handled successfully. Also the other integrals were evaluated numerically. These two facts combined made evaluation of the 2S mean kinetic energy practically impossible for one could not be certain if all the awkward integrals had been found and the number of complex integrals that had to be done proved prohibitive.

A third approach to the problem was then undertaken in which an attempt was made to evaluate the Distribution Products directly using the results from the previous calculations as a check.

TABLE 2

VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 1S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS DERIVED BY TRANSFORMATION TO MOMENTUM SPACE)

in Atomic Units

Localization Radius	Energies			Uncertainties		
	Kinetic	Potential	Mean	Momentum	Position	Product
1.0	2.2433	-1.8372	0.4061	2.0884	0.2218	0.4631
1.5	1.2767	-1.3884	-0.1117	1.5980	0.3453	0.5518
2.0	0.8846	-1.1923	-0.3077	1.3301	0.4663	0.6202
2.5	0.6924	-1.0962	-0.4038	1.1768	0.5756	0.6774
3.0	0.5951	-1.0476	-0.4524	1.0910	0.6665	0.7272
3.5	0.5460	-1.0230	-0.4770	1.0450	0.7362	0.7694
4.0	0.5213	-1.0109	-0.4896	1.0210	0.7858	0.8023
4.5	0.5101	-1.0050	-0.4950	1.0100	0.8187	0.8269
5.0	0.5046	-1.0023	-0.4977	1.0045	0.8393	0.8431
5.5	0.5020	-1.0010	-0.4990	1.0020	0.8514	0.8531
6.0	0.5009	-1.0004	-0.4996	1.0009	0.8583	0.8591
6.5	0.5004	-1.0002	-0.4998	1.0004	0.8621	0.8624
7.0	0.5002	-1.0001	-0.4999	1.0002	0.8640	0.8642
7.5	0.5001	-1.0000	-0.5000	1.0001	0.8651	0.8651
8.0	0.5000	-1.0000	-0.5000	1.0000	0.8656	0.8656
8.5	0.5000	-1.0000	-0.5000	1.0000	0.8658	0.8659
9.0	0.5000	-1.0000	-0.5000	1.0000	0.8659	0.8659
9.5	0.5000	-1.0000	-0.5000	1.0000	0.8660	0.8660
10.0	0.5000	-1.0000	-0.5000	1.0000	0.8660	0.8660
Infinity	0.5000	-1.0000	-0.5000	1.0000	0.8660	0.8660

1.4 DIRECT SOLUTION OF DISTRIBUTION PRODUCT INTEGRALS

The two previous methods were used to avoid certain Distribution Products. However, it was found that both methods were limited. This suggested that the problem of Distribution Products should be studied closely to see if definitions could be found for various Distribution Products.

Enough relationships were found to solve the expressions for the mean energy which involved the second derivative of the Heaviside function. However, the energy uncertainty equations involving the fourth derivative of the Heaviside function could not be solved. The relationships involving Distribution Products are given in Appendix B.

The expressions derived for the various physical observables will be for any S state.

The mean potential energy for the n^{th} S state

$$\overline{V}_n = \langle \overline{\psi}_{nS} | V | \overline{\psi}_{nS} \rangle \qquad (1.4.1)$$

Using projector operators as done previously and relations from Appendices B and C

$$\overline{V}_n = \iint_{r'} \langle \overline{\psi}_{nS} | r \rangle dr \langle r | V | r' \rangle dr' \langle r' | \overline{\psi}_{nS} \rangle$$

$$= -\overline{N}_{nS}^2 \int_0^R \left(e^{-r/n} \sum_{t=1}^{n} \left\{ \frac{(-2/n)^{t-1.} r^{t-1.}}{(n-t)!\,t!\,(t-1.)!} \right\} \right)^2 r \, dr \qquad (1.4.2)$$

In a similar manner the mean kinetic energy

$$\overline{T}_n = \langle \overline{\psi}_{nS} | T | \overline{\psi}_{nS} \rangle$$

$$= -\overline{N}_{nS}^2 \left[\int_0^R dr\, r \left\{ e^{-r/n} \sum_{t=1}^{m} \frac{(-2/n)^{t-1.}\, r^{t-1.}}{(n-t)!\,t!\,(t-1.)!} \right\} \right.$$

$$\cdot \left\{ e^{-r/n} \sum_{t=1}^{m} \frac{(-2/n)^{t-1.}}{(n-t)!\,t!\,(t-1.)!} \left((t-1.) r^{t-2} - \frac{r^{t-1.}}{n} \right) \right\}$$

$$+ \tfrac{1}{2} \int_0^R dr\, r^2 \left\{ e^{-r/n} \sum_{t=1}^{m} \frac{(-2/n)^{t-1.}\, r^{t-1.}}{(n-t)!\,t!\,(t-1.)!} \right\}$$

$$\cdot \left\{ e^{-r/n} \sum_{t=1}^{m} \frac{(-2/n)^{t-1.}}{(n-t)!\,t!\,(t-1.)!} \left[\frac{r^{t-1.}}{n^2} - \frac{2(t-1.) r^{t-2}}{n} \right. \right.$$

$$\left. \left. + (t-1.)(t-2) r^{t-3} \right] \right\} - \left. \tfrac{1}{2} R^2 \left\{ e^{-r/n} \sum_{t=1}^{m} \frac{(-2/n)^{t-1.}\, r^{t-1.}}{(n-t)!\,t!\,(t-1.)!} \right\}^2 \right] \qquad (1.4.3)$$

where R is the localization radius.

The mean energy for any given S state

$$\overline{E}_n = \overline{T}_n + \overline{V}_n \qquad (1.4.4)$$

which is just a more general form of (1.3.8).

The equations for the position, momentum and product uncertainties were also solved.

The momentum uncertainty

$$\Delta K_n = \left\{ \langle \bar{\psi}_{nS} | K^2 | \bar{\psi}_{nS} \rangle - | \langle \bar{\psi}_{nS} | K | \bar{\psi}_{nS} \rangle |^2 \right\}^{\frac{1}{2}} \qquad (1.4.5)$$

As previously noted for the 1S state

$$\langle \bar{\psi}_{nS} | K | \bar{\psi}_{nS} \rangle = 0 \qquad (1.4.6)$$

for any S state and the operator

$$K^2 = 2T \qquad (1.4.7)$$

Then using (1.4.6) and (1.4.7) in (1.4.5)

$$\Delta K_n = \left(\langle \bar{\psi}_{nS} | 2T | \bar{\psi}_{nS} \rangle \right)^{\frac{1}{2}}$$

$$= (2\bar{T}_n)^{\frac{1}{2}} \qquad (1.4.8)$$

The position uncertainty

$$\Delta r_n = \left(\langle \bar{\psi}_{nS} | r^2 | \bar{\psi}_{nS} \rangle - | \langle \bar{\psi}_{nS} | r | \bar{\psi}_{nS} \rangle |^2 \right)^{\frac{1}{2}} \qquad (1.4.9)$$

or

$$\Delta r_n = \left[\bar{N}^2_{nS} \int_0^R dr\, r^4 \left(e^{-r/n} \sum_{t=1}^{m} \frac{(-2/n)^{t-1.}\, r^{t-1.}}{(n-t)!\,t!\,(t-1.)!} \right)^2 \right.$$

$$\left. - \left\{ \bar{N}^2_{nS} \int_0^R dr\, r^3 \left(e^{-r/n} \sum_{t=1}^{m} \frac{(-2/n)^{t-1.}\, r^{t-1.}}{(n-t)!\,t!\,(t-1.)!} \right)^2 \right\}^2 \right]^{\frac{1}{2}} \qquad (1.4.10)$$

The product uncertainty, Δpd, was defined in (1.3.13) in terms of the position and momentum uncertainties.

Calculations were performed for $n = 1$ to 5. The results are tabulated in Tables 3 to 7. Also for the 1S state ($n = 1$) the results are graphed in Figures 3 to 8.

TABLE 3

VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 1S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS)

in Atomic Units

Localization Radius	Energies			Uncertainties		
	Kinetic	Potential	Mean	Momentum	Position	Product
1.0	2.1743	-1.8372	0.3371	2.0853	0.2218	0.4624
1.5	1.2768	-1.3884	-0.1116	1.5980	0.3453	0.5518
2.0	0.8846	-1.1923	-0.3077	1.3301	0.4663	0.6202
2.5	0.6924	-1.0962	-0.4038	1.1768	0.5756	0.6774
3.0	0.5951	-1.0476	-0.4524	1.0910	0.6665	0.7272
3.5	0.5460	-1.0230	-0.4770	1.0450	0.7362	0.7693
4.0	0.5218	-1.0109	-0.4891	1.0215	0.7858	0.8027
4.5	0.5101	-1.0050	-0.4950	1.0100	0.8187	0.8269
5.0	0.5046	-1.0023	-0.4977	1.0045	0.8393	0.8431
5.5	0.5020	-1.0010	-0.4990	1.0020	0.8514	0.8531
6.0	0.5009	-1.0004	-0.4996	1.0009	0.8583	0.8591
6.5	0.5004	-1.0002	-0.4998	1.0004	0.8621	0.8624
7.0	0.5002	-1.0001	-0.4999	1.0002	0.8640	0.8642
7.5	0.5001	-1.0000	-0.5000	1.0001	0.8651	0.8651
8.0	0.5000	-1.0000	-0.5000	1.0000	0.8656	0.8656
8.5	0.5000	-1.0000	-0.5000	1.0000	0.8658	0.8658
9.0	0.5000	-1.0000	-0.5000	1.0000	0.8659	0.8659
9.5	0.5000	-1.0000	-0.5000	1.0000	0.8660	0.8660
10.0	0.5000	-1.0000	-0.5000	1.0000	0.8660	0.8660
Infinity	0.5000	-1.0000	-0.5000	1.0000	0.8660	0.8660

FIGURE 3. Mean kinetic energy of local 1S state of hydrogen atom for varying radius of localization, R, as evaluated by expression derived by direct solution of integrals involving Distribution Products. (1.4.3).

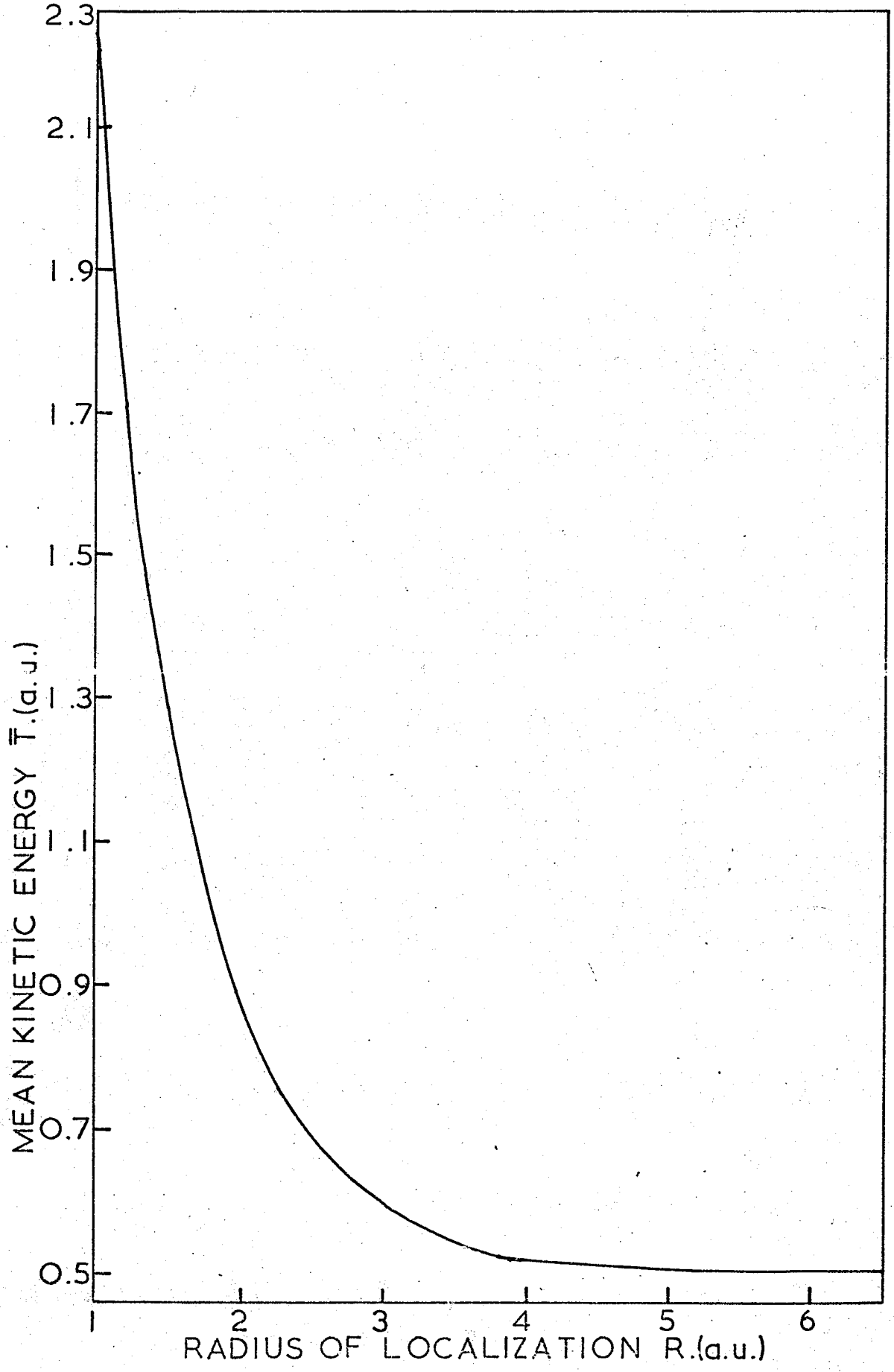

2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
MEAN KINETIC ENERGY T̄.(a.u.)
1
2
3
4
5
6
RADIUS OF LOCALIZATION R.(a.u.)

FIGURE 4. Variation of mean potential energy of hydrogen 1S state with localization radius. Mean potential energy found by evaluation of expression derived by direct solution of integrals involving Distribution Products (1.4.2).

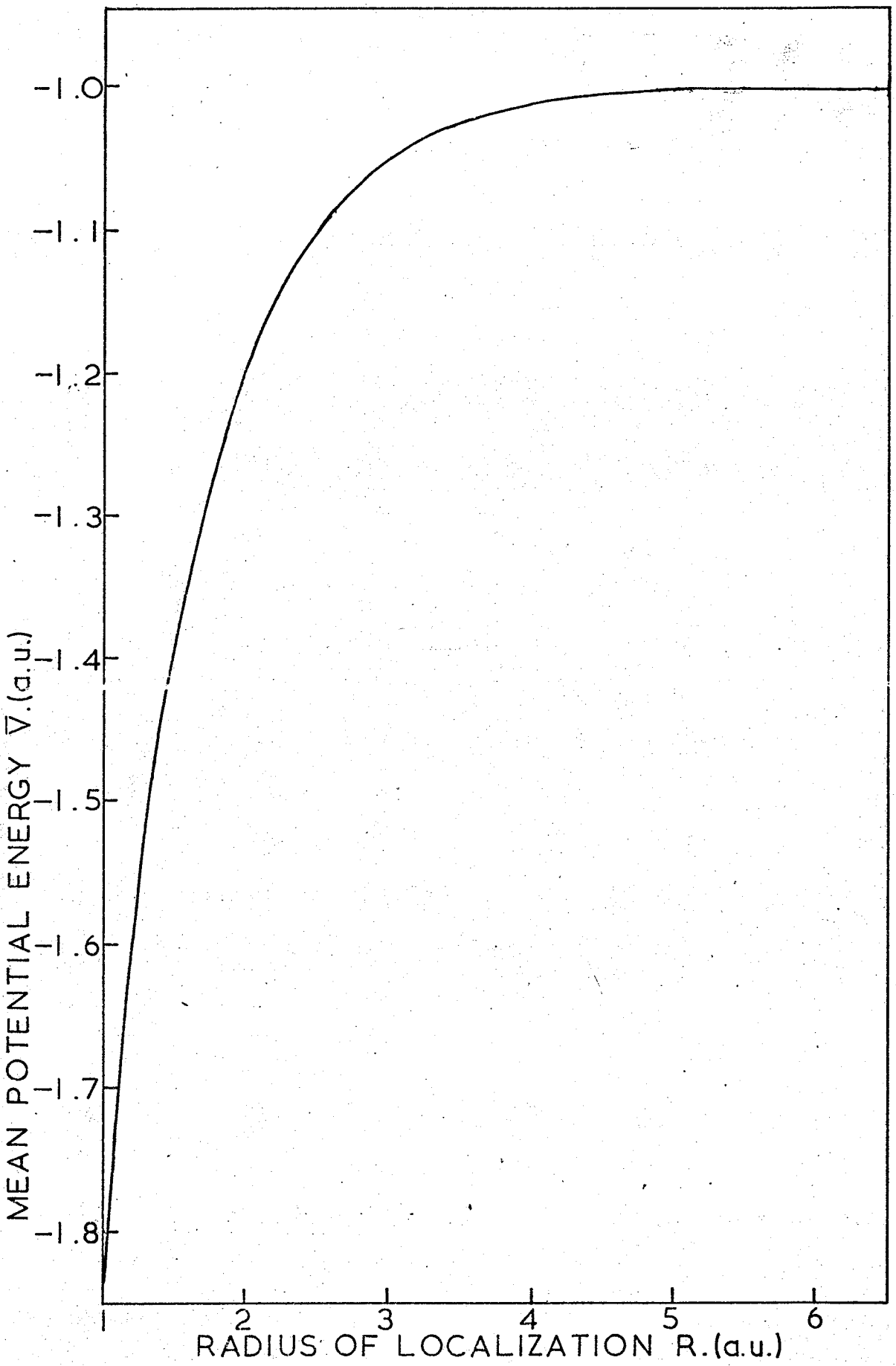

-1.0
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
MEAN POTENTIAL ENERGY $\bar{V}$.(a.u.)
1
2
3
4
5
6
RADIUS OF LOCALIZATION R.(a.u.)

FIGURE 5. Mean (total) energy for various radii of localization. Evaluated by use of expression derived by direct solution of integrals involving Distribution Products (1.4.4).

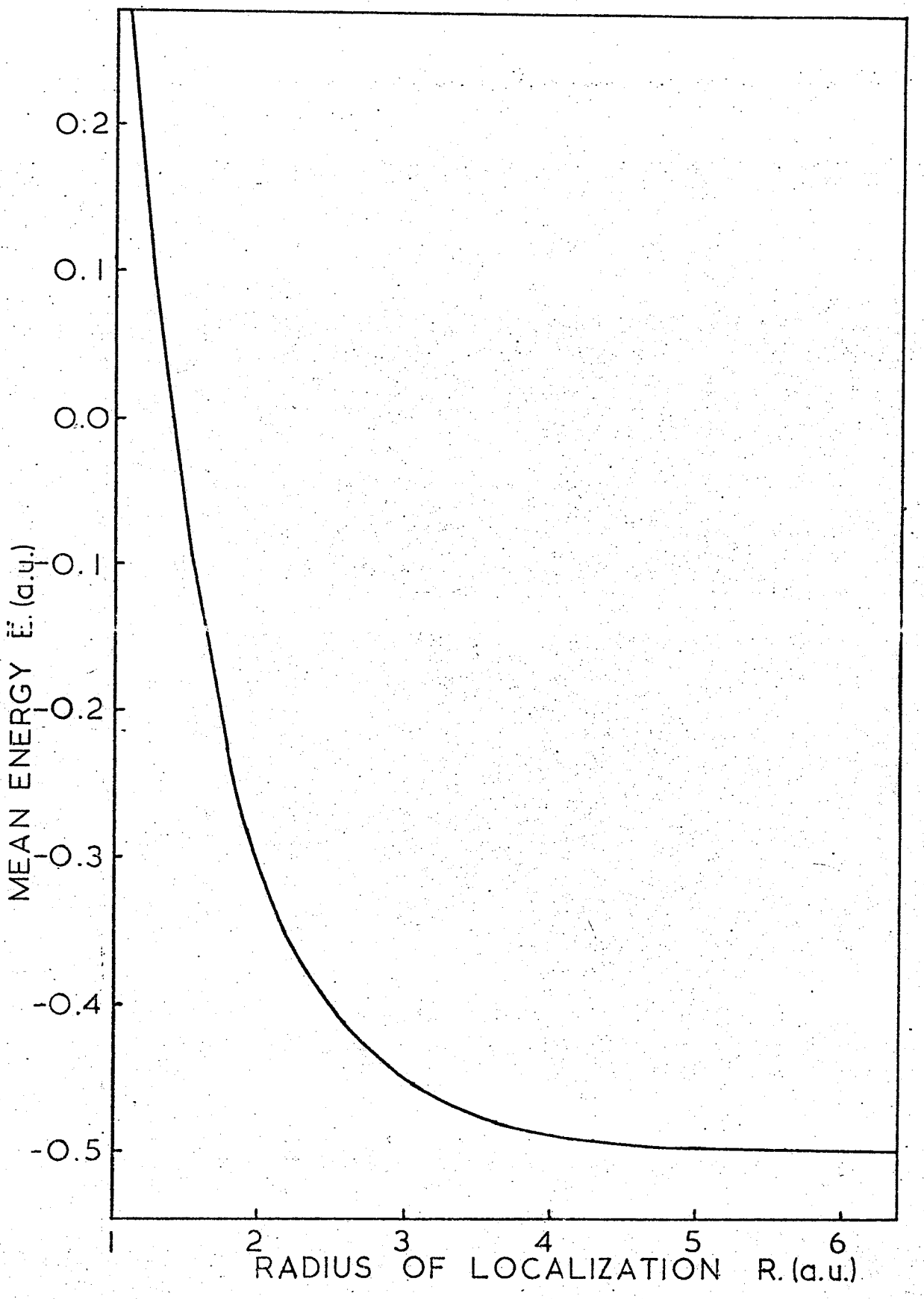

0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
MEAN ENERGY Ē. (a.u.)
1
2
3
4
5
6
RADIUS OF LOCALIZATION R. (a.u.)

FIGURE 6. Variation of momentum uncertainty with changing radius of localization. Momentum uncertainty found by evaluation of expression derived by direct solution of integrals involving Distribution Products (1.4.8).

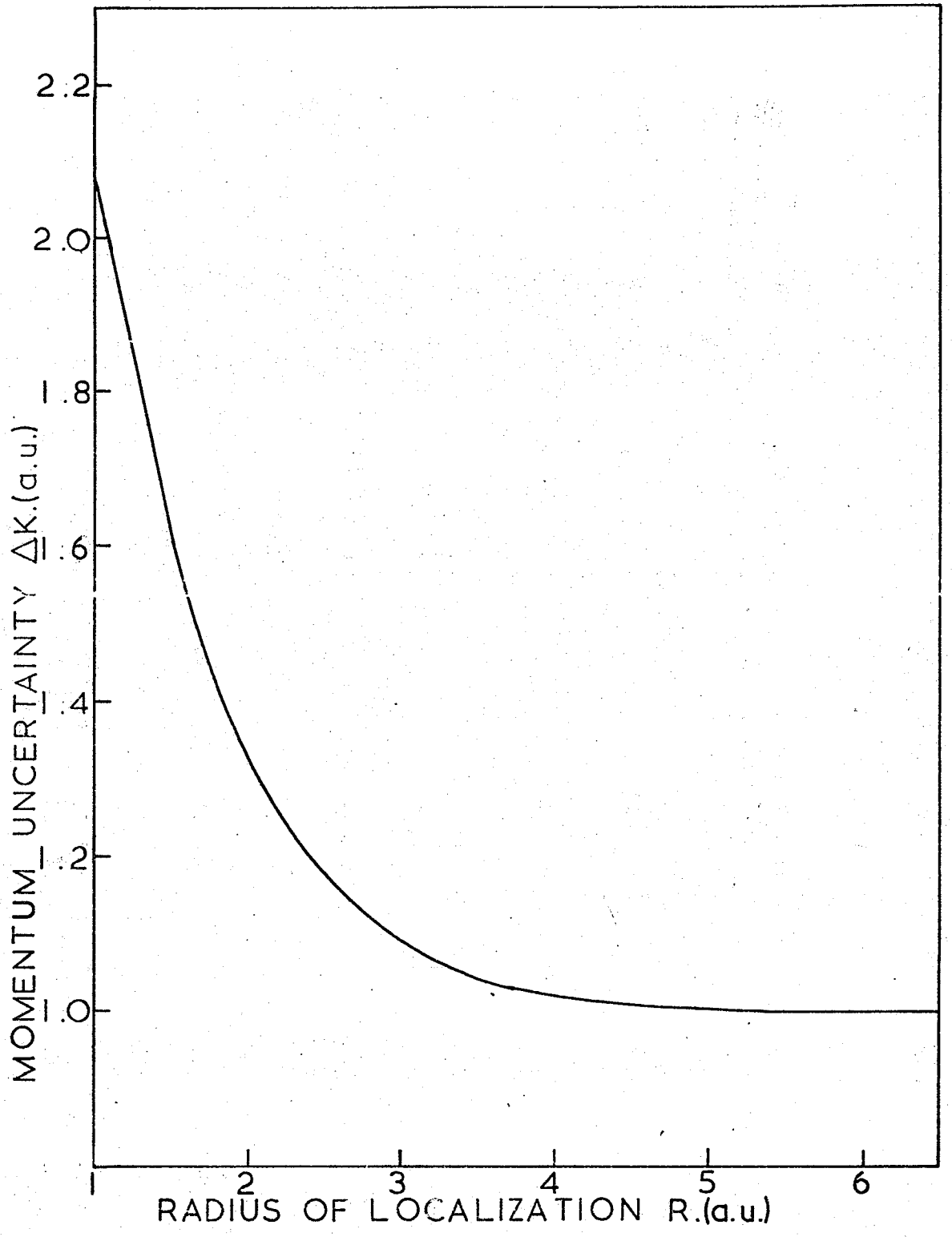

2.2
2.0
1.8
1.6
1.4
1.2
1.0
MOMENTUM UNCERTAINTY ΔK.(a.u.)
1
2
3
4
5
6
RADIUS OF LOCALIZATION R.(a.u.)

FIGURE 7. Variation of position uncertainty with localization radius. Position uncertainty was evaluated by use of expression derived by direct solution of integrals involving Distribution Products (1.4.10).

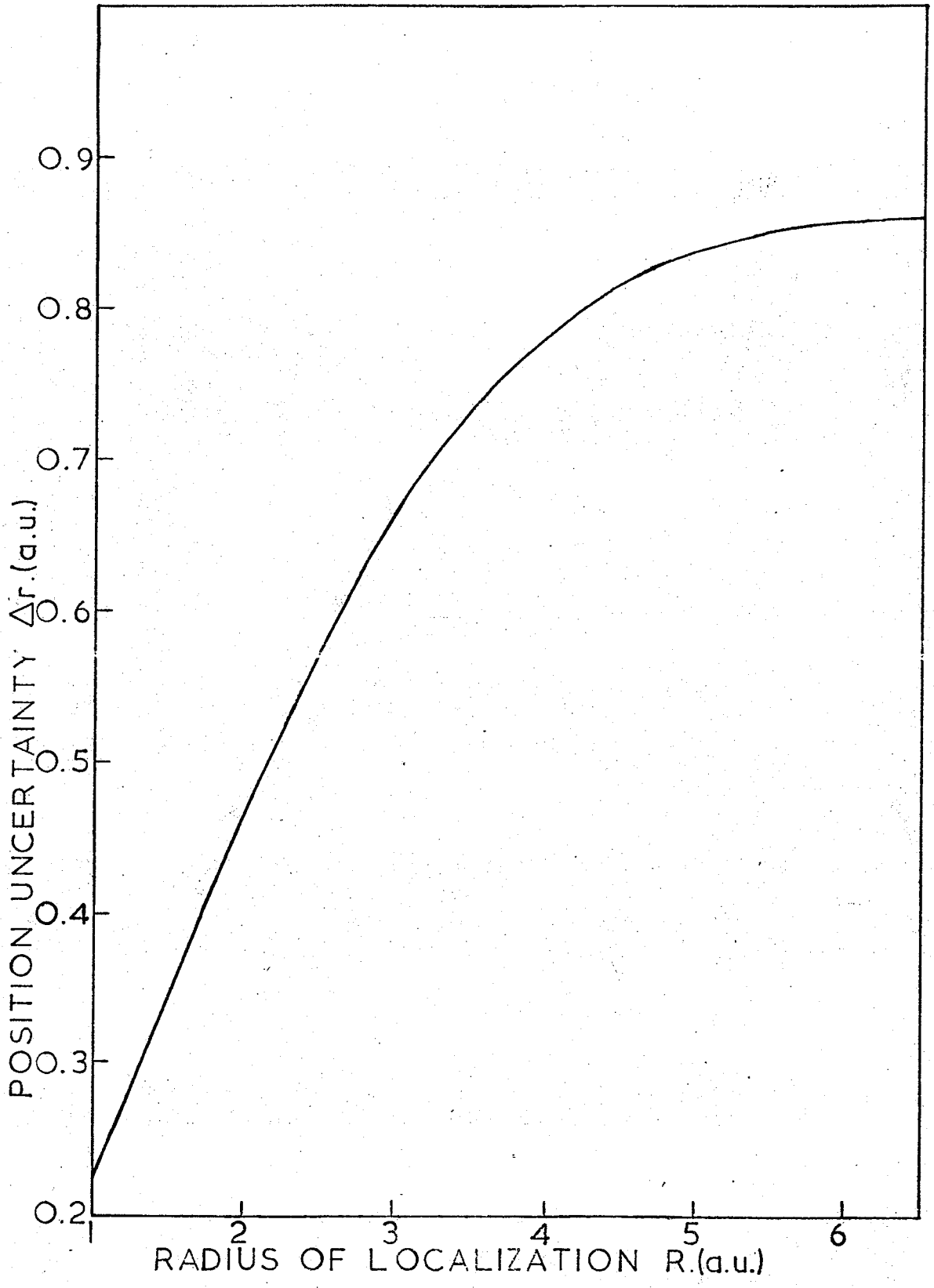

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
POSITION UNCERTAINTY Δr.(a.u.)
1
2
3
4
5
6
RADIUS OF LOCALIZATION R.(a.u.)

FIGURE 8. Product uncertainty for various radii of localization. Product uncertainty obtained by use of (1.3.13) and evaluations of position and momentum uncertainties obtained by use of expressions derived by direct solution of integrals involving Distribution Products.

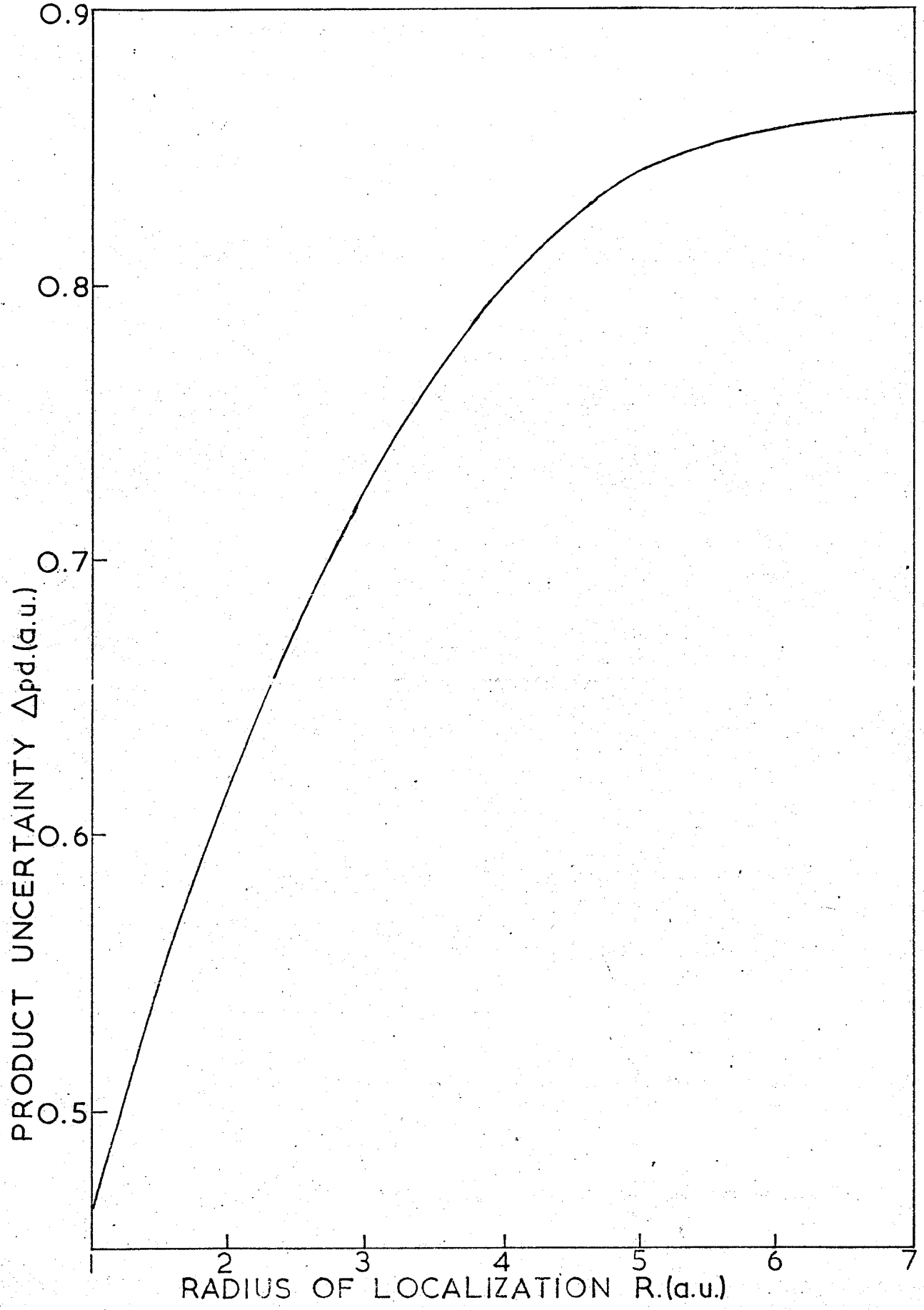

0.9
0.8
0.7
0.6
0.5
PRODUCT UNCERTAINTY Δpd.(a.u.)
2
3
4
5
6
7
RADIUS OF LOCALIZATION R.(a.u.)

TABLE 4

VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 2S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS)

in Atomic Units

Localization Radius	Energies			Uncertainties		
	Kinetic	Potential	Mean	Momentum	Position	Product
1.0	2.4700	-1.9250	0.5450	2.2226	0.2230	0.4957
1.25	1.9293	-1.6974	0.2319	1.9643	0.2814	0.5527
1.50	1.6168	-1.5848	0.0320	1.7982	0.3311	0.5954
1.75	1.4565	-1.5417	-0.0853	1.7067	0.3621	0.6180
2.0	1.4102	-1.5352	-0.1250	1.6794	0.3692	0.6201
2.25	1.4424	-1.5281	-0.0857	1.6985	0.3834	0.6512
2.5	1.5001	-1.4803	-0.0197	1.7321	0.4873	0.8441
3.0	1.4730	-1.2128	0.2601	1.7164	0.9036	1.5509
3.5	1.2275	-0.8910	0.3365	1.5668	1.1651	1.8256
4.0	0.9585	-0.6667	0.2917	1.3846	1.2460	1.7252
4.5	0.7473	-0.5304	0.2169	1.2225	1.2712	1.5541
5.0	0.5927	-0.4461	0.1465	1.0887	1.2971	1.4123
6.0	0.3953	-0.3540	0.0413	0.8892	1.3970	1.2421
7.0	0.2833	-0.3081	-0.0248	0.7528	1.5490	1.1660
8.0	0.2173	-0.2829	-0.0657	0.6592	1.7230	1.1358
10.0	0.1546	-0.2603	-0.1057	0.5560	2.0464	1.1378
15.0	0.1261	-0.2504	-0.1243	0.5022	2.4077	1.2092
20.0	0.1250	-0.2500	-0.1250	0.5001	2.4476	1.2240
25.0	0.1250	-0.2500	-0.1250	0.5000	2.4495	1.2247
Infinity	0.1250	-0.2500	-0.1250	0.5000	2.4495	1.2247

TABLE 5

VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 3S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS)

in Atomic Units

Localization Radius	Energies			Uncertainties		
	Kinetic	Potential	Mean	Momentum	Position	Product
1.0	2.5266	-1.9424	0.5842	2.2479	0.2231	0.5015
1.5	1.6918	-1.6246	0.0672	1.8394	0.3261	0.5999
2.0	1.5434	-1.5915	-0.0481	1.7570	0.3521	0.6187
2.5	1.6550	-1.4816	0.1734	1.8194	0.5585	1.0161
3.0	1.5356	-1.1471	0.3884	1.7525	0.9582	1.6793
3.5	1.2288	-0.8377	0.3912	1.5677	1.1427	1.7914
4.0	0.9486	-0.6476	0.3010	1.3774	1.2023	1.6560
4.5	0.7402	-0.5390	0.2012	1.2167	1.2415	1.5106
5.0	0.5911	-0.4763	0.1148	1.0873	1.2910	1.4038
6.0	0.4151	-0.4217	-0.0065	0.9112	1.4073	1.2824
7.0	0.3571	-0.4123	-0.0551	0.8452	1.4576	1.2319
8.0	0.3835	-0.4067	-0.0231	0.8758	1.5420	1.3506
9.0	0.4230	-0.3683	0.0547	0.9198	2.1327	1.9617
10.0	0.4088	-0.3042	0.1046	0.9042	2.8341	2.5626
11.0	0.3532	-0.2454	0.1078	0.8405	3.2166	2.7035
12.0	0.2905	-0.2034	0.0870	0.7622	3.3755	2.5727
13.0	0.2359	-0.1753	0.0606	0.6868	3.4574	2.3746
15.0	0.1582	-0.1434	0.0149	0.5626	3.6260	2.0399
20.0	0.0772	-0.1171	-0.0399	0.3929	4.2754	1.6797
25.0	0.0590	-0.1120	-0.0530	0.3435	4.7564	1.6340

TABLE 5

Continued

Localization Radius	Energies			Uncertainties		
	Kinetic	Potential	Mean	Momentum	Position	Product
30.0	0.0600	-0.1112	-0.0552	0.3346	4.9298	1.6495
40.0	0.0556	-0.1111	-0.0556	0.3333	4.9741	1.6581
50.0	0.0556	-0.1111	-0.0556	0.3333	4.9749	1.6583
Infinity	$0.055\dot{5}$	$-0.111\dot{1}$	$-0.055\dot{5}$	0.3333	4.9749	1.6583

TABLE 6

VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 4S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS)

in Atomic Units

Localization Radius	Energies			Uncertainties		
	Kinetic	Potential	Mean	Momentum	Position	Product
1.0	2.5465	-1.9485	0.5980	2.2568	0.2231	0.5035
2.0	1.5920	-1.6097	-0.0177	1.7844	0.3478	0.6205
3.0	1.5512	-1.1254	0.4257	1.7613	0.9691	1.7069
4.0	0.9470	-0.6452	0.3017	1.3762	1.1899	1.6376
5.0	0.5961	-0.4906	0.1055	1.0919	1.2881	1.4064
6.0	0.4401	-0.4501	-0.0100	0.9381	1.3873	1.3015
7.0	0.4243	-0.4469	-0.0225	0.9212	1.4083	1.2974
8.0	0.4780	-0.4199	0.0581	0.9778	1.7549	1.7159
9.0	0.4786	-0.3507	0.1279	0.9784	2.4685	2.4152
10.0	0.4112	-0.2817	0.1295	0.9069	2.9134	2.6421
11.0	0.3290	-0.2349	0.0940	0.8111	3.1159	2.5274
12.0	0.2586	-0.2072	0.0514	0.7192	3.2412	2.3310
13.0	0.2059	-0.1921	0.0138	0.6418	3.3517	2.1510
14.0	0.1712	-0.1852	-0.0140	0.5852	3.4416	2.0138
15.0	0.1541	-0.1833	-0.0292	0.5552	3.4834	1.9338
16.0	0.1537	-0.1831	-0.0294	0.5543	3.4889	1.9342
17.0	0.1660	-0.1812	-0.1517	0.5763	3.5836	2.0680
20.0	0.1963	-0.1476	0.0487	0.6266	5.2986	3.3202
25.0	0.1229	-0.0908	0.0322	0.4959	6.6140	3.2796
30.0	0.0675	-0.0717	-0.0042	0.3673	7.0678	2.5962

TABLE 6

Continued

Localization Radius	Energies			Uncertainties		
	Kinetic	Potential	Mean	Momentum	Position	Product
35.0	0.0435	-0.0653	-0.0218	0.2950	7.6431	2.2550
40.0	0.0348	-0.0633	-0.0285	0.2638	8.0983	2.1366
50.0	0.0314	-0.0625	-0.0311	0.2508	8.4423	2.1171
60.0	0.0313	-0.0625	-0.0312	0.2500	8.4830	2.1209
70.0	0.0313	-0.0625	-0.0313	0.2500	8.4852	2.1213
100.0	0.0313	-0.0625	-0.0313	0.2500	8.4853	2.1213
Infinity	0.0313	-0.0625	-0.0313	0.2500	8.4853	2.1213

TABLE 7

VARIOUS ENERGIES AND UNCERTAINTIES FOR HYDROGEN 5S LOCALIZED WAVE FUNCTION FOR VARIOUS RADII OF LOCALIZATION (CALCULATED FROM EXPRESSIONS OBTAINED BY DIRECT SOLUTION OF INTEGRALS INVOLVING DISTRIBUTION PRODUCTS)

in Atomic Units

Localization Radius	Energies			Uncertainties		
	Kinetic	Potential	Mean	Momentum	Position	Product
1.0	2.5558	-1.9514	0.6044	2.2609	0.2231	0.5044
2.0	1.6148	-1.6178	-0.0031	1.7971	0.3461	0.6220
3.0	1.5575	-1.1158	0.4417	1.7650	0.9730	1.1717
4.0	0.9466	-0.6448	0.3018	1.3760	1.1846	1.6300
5.0	0.5996	-0.4977	0.1019	1.0951	1.2861	1.4084
6.0	0.4555	-0.4636	-0.0081	0.9545	1.3740	1.3115
7.0	0.4607	-0.4601	0.0007	0.9599	1.4057	1.3493
8.0	0.5148	-0.4193	0.0955	1.0147	1.8802	1.9077
9.0	0.4895	-0.3415	0.1480	0.9894	2.5473	2.5203
10.0	0.4045	-0.2759	0.1286	0.8995	2.8990	2.6076
11.0	0.3174	-0.2358	0.0817	0.7968	3.0700	2.4460
12.0	0.2492	-0.2144	0.0348	0.7059	3.1924	2.2537
13.0	0.2043	-0.2052	-0.0008	0.6393	3.2859	2.1006
14.0	0.1842	-0.2030	-0.0188	0.6070	3.3237	2.0174
15.0	0.1877	-0.2026	-0.0149	0.6127	3.3353	2.0435
17.5	0.2296	-0.1789	0.0507	0.6777	4.3600	2.9545
20.0	0.1973	-0.1363	0.0610	0.6282	5.6071	3.5224
22.5	0.1370	-0.1118	0.0251	0.5234	6.0775	3.1809
25.0	0.0951	-0.1030	-0.0078	0.4362	6.3374	2.7645
30.0	0.0940	-0.1000	-0.0060	0.4337	6.6459	2.8821

TABLE 7

Continued

Localization Radius	Energies			Uncertainties		
	Kinetic	Potential	Mean	Momentum	Position	Product
40.0	0.0814	-0.0576	0.0239	0.4036	10.6730	4.3074
50.0	0.0357	-0.0433	-0.0076	0.2673	11.5950	3.1000
60.0	0.0227	-0.0405	-0.0178	0.2130	12.5015	2.6630
70.0	0.0203	-0.0401	-0.0197	0.2016	12.8903	2.5985
75.0	0.0201	-0.0400	-0.0199	0.2005	12.9518	2.5967
Infinity	0.0200	-0.0400	-0.0200	0.2000	12.9904	2.5908

1.5 AN EXAMINATION OF THE RESULTS OF SECTIONS 1.3, 1.4, 1.5.

Having calculated several physical observables by various techniques it is now possible to discuss the validity of the description given by local wave functions that have been defined in (1.1.1).

It is first noted that the three approaches give consistent results for corresponding quantities (Tables 1, 2, 3) and in particular the agreement between the results calculated by transformation to momentum space (Table 2) and those calculated by direct evaluation of Distribution Products (Table 3) is excellent. Also, for localization radii, R, of appropriate atomic dimensions, the values calculated for physical observables using local functions are almost indistinguishable from the values resulting from the use of eigenstates ($R = \infty$). For instance, for a localization radius, R, of 6 a.u., the mean energy, $\overline{E}_1$, of the 1S state varies from the eigenstate mean energy by less than one tenth of a percent and the corresponding energy uncertainty, ΔE, is of the order of two percent (Table 1). Figues 1 to 8 also reveal that the limiting value for the various observables of the 1S localized state, $\overline{\psi}_{1S}$, is approached quite quickly as the localization radius, R, is increased. The other four S states exhibit essentially the same properties except for larger localization radii, R.

A comparison of the local and non-local 1S state functions, $\overline{\psi}_{1S}$ and ψ_{1S}, is also revealing. In Table 8, the configuration space and momentum space representations of the two functions are tabulated with the localization radius of $\overline{\psi}_{1S}$ being 4 a.u. The functions $\overline{\psi}_{1S}(r,\Theta,\phi)$ and $\psi_{1S}(r,\Theta,\phi)$ can be found in Appendix C while the form of $\overline{\psi}_{1S}(K,\Theta,\Phi)$ is given in equation (1.3.3). Using the same transformation applied in section 1.3 on $\psi_{1S}(r,\Theta,\Phi)$ one finds that

$$\psi_{1S}(K,\Theta,\Phi) = \frac{(2)^{3/2}}{\pi} \frac{1}{(1.+K^2)^2} \qquad (1.5.1)$$

The results are tabulated rather than graphed since the K-space representation of the two functions are so similar that the difference would not be noticable graphically. Although the local state has a more undulatory nature than the non-local function in the momentum representation, the fact that the local function in the momentum representation is continuous, single valued, well behaved and almost indistinguishable from the non-local function lends support to the notion that the two functions describe essentially the same system. Considering the configuration space representation of the two functions alone one would probably not come to this conclusion.

TABLE 8

AMPLITUDE OF NON-LOCAL (ψ_{1S}) AND LOCAL ($\overline{\psi}_{1S}$) FUNCTIONS

IN X- AND K-SPACE

Radius of Localization, R = 4 a.u.

X-Representation			K-Representation		
r	ψ_{1S}	$\overline{\psi}_{1S}$	K	ψ_{1S}	$\overline{\psi}_{1S}$
0.0	2.0000	2.0139	0.0	0.2251	0.2235
0.5	1.2131	1.2215	0.5	0.1441	0.1359
1.0	0.7358	0.7409	1.0	0.0563	0.0623
1.5	0.4463	0.4494	1.5	0.0213	0.0196
2.0	0.2706	0.2726	2.0	0.0090	0.0084
3.0	0.0996	0.1003	3.0	0.0023	0.0021
4.0	0.0366	0	4.0	0.0008	0.0009
5.0	0.0135	0	5.0	0.0003	0.0002
6.0	0.0050	0	6.0	0.0002	0.0002
8.0	0.0009	0	8.0	0.0001	0.0000
10.0	0.0001	0	10.0	0.0000	0.0000

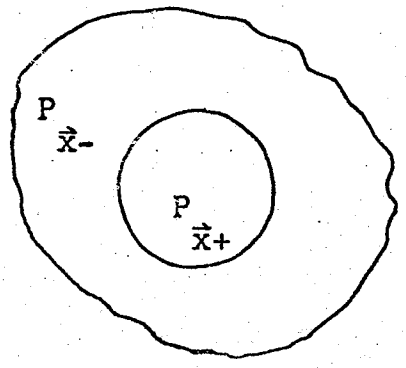
1.6 SOME PROPERTIES AND RELATIONSHIPS OF THE LOCAL REPRESENTATION.

From the results of the calculations of physical observables and considering various representations of the local and non-local functions, it has been shown that the local representation leads to a description as valid as that of the non-local representation and it would appear from the discussion of the form of the wave function in K-space that these two representations are related. This relationship in fact exists and the form of the relationship will now be derived.

First it will be necessary to derive a simple projector operator equivalent for the shaping function, S(R), used to form the local states (1.1.1). The step function, S(R), can be considered to be the configuration space respresentation in spherical polar co-ordinates of the operator $P_{\vec{x}+}$ which projects the volume of X-space for which the norm of any vector $\vec{A}_x$

$$\| \vec{A}_x \| = R \qquad (1.6.1)$$

where R is the localization radius of the previous sections.



Putting

$$1. = \int_{\vec{x}} d\vec{x}' \, |\vec{x}'><\vec{x}'| = P_{\vec{x}} = P_{\vec{x}+} + P_{\vec{x}-} \tag{1.6.2}$$

where

$$P_{\vec{x}+} = \int_{\vec{x}+} d\vec{x}+ \, |\vec{x}+><\vec{x}+| = \int_{\|\vec{A}_x\|<R} d\vec{x} \, \vec{x}><\vec{x}| \tag{1.6.3}$$

and $P_{\vec{x}-}$ is the projector for the complementary space. The X-representation of $P_{\vec{x}+}$ may be written

$$<\vec{x}'|P_{\vec{x}+}|\vec{x}''> = \int_{\|\vec{A}_x\|<R} d\vec{x} <\vec{x}'|\vec{x}><\vec{x}|\vec{x}''>$$

$$= \int_{\|\vec{A}_x\|<R} d\vec{x} \, \delta(\vec{x}'-\vec{x}) \, \delta(\vec{x}-\vec{x}'')$$

$$= \delta(\vec{x}'-\vec{x}'') \text{ if } \|\vec{A}_x\| < R$$

$$= 0 \text{ otherwise} \tag{1.6.4}$$

Since in spherical polar co-ordinates the norm of a vector $\vec{A}_x(r,\theta,\phi)$

$$\|\vec{A}_x\| = r$$

the above definition of $P_{\vec{x}+}$ (1.6.4) is the equivalent of the step function S(R). Noting that $P_{\vec{x}+}$ is diagonal and using (1.6.4) the form of the localized wave function (1.1.1) may be

rewritten

$$\overline{\psi}_{nlm} \equiv \langle \vec{x} | \overline{\psi}_{nlm} \rangle$$

$$= \overline{N}_{nl} \langle \vec{x} | P_{\vec{x}+} | \psi_{nlm} \rangle$$

$$= \overline{N}_{nl} \int d\vec{x}' \langle \vec{x} | P_{\vec{x}+} | \vec{x}' \rangle \langle \vec{x}' | \psi_{nlm} \rangle$$

$$= \overline{N}_{nl} \langle \vec{x} | P_{\vec{x}+} | \psi_{nlm} \rangle \qquad (1.6.5)$$

In this notation the normalization constant $\overline{N}_{nl}$ takes the form

$$1. = \int d\vec{x} \langle \overline{\psi}_{nlm} | \vec{x} \rangle \langle \vec{x} | \overline{\psi}_{nlm} \rangle$$

$$= (\overline{N}_{nl})^2 \int d\vec{x} \langle \psi_{nlm} | P_{\vec{x}+} | \vec{x} \rangle \langle \vec{x} | P_{\vec{x}+} | \psi_{nlm} \rangle$$

$$= (\overline{N}_{nl})^2 \langle \psi_{nlm} | P_{\vec{x}+} | \psi_{nlm} \rangle$$

the last step following from the idempotency of $P_{\vec{x}+}$. Then

$$\overline{N}_{nl} = 1./\left(\langle \psi_{nlm} | P_{\vec{x}+} | \psi_{nlm} \rangle \right)^{\frac{1}{2}} \qquad (1.6.6)$$

which is equivalent to the expression found in Appendix C for $\overline{N}_{nl}$.

Now the connection between the local and non-local representations can be established by considering the probability distribution of state vector $|\overline{\psi}_{nlm}\rangle$. For some arbitrary re-

presentation B, the probability distribution described by $|\psi'>$ is defined

$$P_{\psi'}(B) = |<B|\psi'>|^2 \qquad (1.6.7)$$

Then considering the probability distribution of $|\overline{\psi}_{nlm}>$ in the energy representation (non-local representation) from (1.6.7)

$$P_{\overline{\psi}_{nlm}}(E_{n',l',m'}) \equiv P_{\overline{\psi}_{nlm}}(\psi_{n',l',m'})$$

$$(N^2_{nl})\ |<\psi_{n',l',m'}|P_{\vec{x}+}|\psi_{nlm}>|^2$$

$$= |<\psi_{nlm}|P_{\vec{x}+}|\psi_{nlm}>|^{-1.}\ |<\psi_{n',l',m'}|P_{\vec{x}+}|\psi_{nlm}>|^2$$

(1.6.8)

From this equation one obtains the probability that the local state $|\overline{\psi}_{nlm}>$ has energy equal to that of the non-local state from which it is derived

$$P_{\overline{\psi}_{nlm}}(E_{nlm}) = <\psi_{nlm}|P_{\vec{x}+}|\psi_{nlm}> \qquad (1.6.9)$$

It follows that the probability that the local state $|\overline{\psi}_{nlm}>$ has energy not equal to energy E_{nlm} is

$$P_{\overline{\psi}_{nlm}}(\overline{E}_{nlm} \neq E_{nlm}) = <\psi_{nlm}|P_{\vec{x}-}|\psi_{nlm}> \qquad (1.6.10)$$

These two expressions are more easily understood by considering a specific case. Consider the 1S state functions for the energy

and local representations, ψ_{1S} and $\bar{\psi}_{1S}$ respectively. Then the right hand side of (1.6.10) can be interpreted as the probability that the electron described by ψ_{1S} lies outside the localization radius, R, of the local state whereas the left hand side is the probability that the corresponding local state $\bar{\psi}_{1S}$ has energy not equal to E_{1S}, the 1S eigenstate energy. Then the outer region of the wave function in the energy representation has been transformed into the 'wings' of the energy distribution curve in the local representation. Also (1.6.9) demonstrates that the energy representation is only a special case of the local representation since $P_{\bar{\psi}_{nlm}}(E_{nlm}) = 1.$ when $P_{\vec{x}+} = P_{\vec{x}}$

A rather useful property of local representations can be established by considering the mean for any operator f(B), B being an arbitrary representation, which is written

$$\langle \phi' | f(B) | \phi' \rangle = \int_B dB\, f(B) P_{\phi'}(B) \qquad (1.6.11)$$

where $P_{\phi'}(B)$ is the probability distribution defined in (1.6.7).

Now defining the local states of two colliding systems A and B

$$\langle \vec{x} | \bar{\psi}_A \rangle = \bar{N}_A \langle \vec{x} | P_{\vec{x}+} |_A \psi_A \rangle$$

$$\langle \vec{x} | \bar{\psi}_B \rangle = \bar{N}_B \langle \vec{x} | P_{\vec{x}+} |_B \psi_B \rangle \qquad (1.6.12)$$

one finds upon evaluating the overlap contribution to mean values of any given operator f(x) the expression

$$\langle \overline{\psi}_A | f(\vec{x}) | \overline{\psi}_B \rangle = \overline{N}_A \overline{N}_B \langle \psi_A | P_{\vec{x}+A} \; P_{\vec{x}+B} \; f(\vec{x}) | \psi_B \rangle$$

$$\neq 0 \text{ only if } P_{\vec{x}+A} \cap P_{\vec{x}+B} \neq 0 \qquad (1.6.13)$$

Since it has been demonstrated that projectors such as $P_{\vec{x}+A}$ and $P_{\vec{x}+B}$ operate over relatively small finite spatial volumes, it can be seen that the equations of motion of the two body system become vigorously decoupled at relatively small finite distances. This point will be developed further in the next section.

1.7 A DISCUSSION OF SOME POSSIBLE APPLICATIONS OF THE LOCAL REPRESENTATION TO COLLISION THEORY.

It has been stated that the original purpose of the study of local states was to overcome various difficulties encountered in low energy collision theory. Some discussion of this application of local states will now be undertaken.

A simple collision to which the results so far obtained can be applied is

$$H_A + H^+_B \longrightarrow H^+_A + H_B$$

where a hydrogen atom A exchanges an electron with proton B. By Mott and Massey (2), the Schrodinger equation describing this reaction may be written in two equivalent forms, one of which is

$$\left[-\frac{\hbar^2}{2m_a}\nabla^2_a - \frac{\hbar^2}{2M_b}\nabla^2_B + V_a(r_a) + V_b(r_b) + U(\vec{R}_b, \vec{r}_a) \right]\Psi = E\Psi \qquad (1.7.1)$$

By the two state approximation, Ψ is of the form

$$\Psi = \phi(\vec{r}_a)F(\vec{R}_b) + \phi(\vec{r}_b)G(\vec{R}_a) \qquad (1.7.2)$$

Considering the case where the electron is in the ground state initially and finally, the usual choice of bound states is such that

$$\phi(\vec{r}_a) = \psi_{1S}(\vec{r}_a) \text{ and } \phi(\vec{r}_b) = \psi_{1S}(\vec{r}_b)$$

Substituting (1.7.2) into (1.7.1) and its equivalent form coupled equations may be obtained for $F(\vec{R}_b)$ and $G(\vec{R}_a)$. The

equation for $F(\vec{R}_b)$ is

$$\left[\nabla^2_B + k^2_b - \frac{2M_b}{\hbar^2} \int |\psi_{1S}(\vec{r}_a)|^2 \left\{ V_b(r_b) + U(\vec{R}_b, \vec{r}_a) \right\} d\vec{r}_a \right] F(\vec{R}_b)$$

$$= -\frac{2M_b}{\hbar^2} \int \psi^*_{1S}(\vec{r}_a) \left[\frac{\hbar^2}{2M_a} (\nabla^2_A + k^2_a) - V_a(r_a) - U(\vec{R}_b, \vec{r}_a) \right]$$

$$\cdot \psi_{1S}(\vec{r}_b) G(\vec{R}_a) d\vec{r}_a \qquad (1.7.3)$$

The right hand side of (1.7.3) being non-zero for all but infinite internuclear separation expresses the fact that for non-local states reaction can occur in all regions in space. It has been suggested that this can be considered to be the cause of the asymptotic states problem.

If, however, one uses the local states $\overline{\psi}_{1S}(\vec{r}_a)$ and $\overline{\psi}_{1S}(\vec{r}_b)$ for $\phi(\vec{r}_a)$ and $\phi(\vec{r}_b)$ in (1.7.2) instead of the eigenstates, choosing the localization radius, R, large enough (5 to 10 a.u.) so that $\Delta E \simeq 0$, then the property depicted in (1.6.13) will force the right hand side of (1.7.3) to be zero for all internuclear distances greater than 10 to 20 a.u. The result is that equations for $F(\vec{R}_b)$ and $G(\vec{R}_a)$ would be uncoupled for such internuclear separations. The reaction could then be considered to occur in three stages or regions of space

I Initial Region $\Psi = \psi_{1S}(\vec{r}_a) F(\vec{R}_b)$

II Reaction Region $\Psi = \psi_{1S}(\vec{r}_a)F(\vec{R}_b) + \psi_{1S}(\vec{r}_b)G(\vec{R}_a)$

III Final Region $\Psi = \psi_{1S}(\vec{r}_b)G(\vec{R}_a)$

In the first and third regions, the colliding systems would interact by polarizing each other but would not undergo reactions such as electron exchange.

At the present time the above approach towards decoupling is being investigated by other fellow workers (11). However, at least one criterion for the validity of this approach will be the choice of states such that $\Delta E \simeq 0$ since the energy of bound systems is usually known quite accurately. Further work will hopefully lead to criterion for deciding the allowable energy uncertainty and the extent to which the systems can be localized.

Considering the concept of three reactive regions generally, one can note some hopefully productive simplifications. In the two regions where polarization only takes place the equations describing the systems are comparatively simple. Solving the equations for these two regions could then provide the starting boundary states for a two-state approximation in the interaction region which avoids the use of the asymptotic states usually employed and the problems demonstrated to be associated with these states (2).

2. SOME CONCLUDING REMARKS

Some positive as well as negative aspects of local states for bound systems were demonstrated.

First of all, it was shown to be possible to define local bound states which were physically acceptable. However, it was pointed out that various quantities could not be evaluated since the mathematical theory of distributions has not been completely developed.

By considering the probability distributions of local states, it was possible to show that the energy or non-local representation was contained within the local representation as a special case and therefore the local representation could be considered a more general and perhaps more valid description of the system.

Finally, the possibility of applying local states to collision theory was discussed. The usefulness of the form taken by the equations for the mean value of an arbitrary operator in simplifying some of the equations of interaction was indicated. Indeed, one could consider the use of local states as a formal approach to using the simplifications of various workers (6, 7, 8).

The implications of localizability lead to some of the more controversial and involved aspects of quantum theory. To go into these topics would be beyond the scope of the present study but some mention should be made of the other areas in which the present study might have application. For instance, some workers (12, 13) are interested in incorporating local representations in a general form into quantum theory. Also, in

the hidden variable controversy both protagonists (12, 14, 16, 17, 18) and antagonists (13, 15) have concerned themselves with the matter of local representations. The Einstein-Rosen-Podolsky parodox might be another topic considered to be relevant in a more general discussion of local representations.

As to the development of local representations for other bound systems by approaches similar to that used for the hydrogen atom, the possibility does not seem unfeasible. However, in the present study certain mathematical difficulties were accepted to overcome the physical difficulties encountered in the non-local representation. These mathematical difficulties would seem to restrict the general applicability of the method used for the localization of the hydrogen atom.

APPENDIX A

THE HYDROGEN ATOM HAMILTONIAN

The hydrogen atom Hamiltonian operator, H, associated with the total mean energy of the system, given on page 412 of "Quantum Mechanics" by Messiah (19), when converted to atomic units and in spherical polar co-ordinates is of the form

$$H = T + V$$

$$= -\tfrac{1}{2}\nabla^2 + \frac{l^2}{2r^2} - \frac{1.}{r} \qquad (A.1)$$

where

$$T = -\tfrac{1}{2}\nabla^2 + \frac{l^2}{2r^2} \text{ and } V = -\frac{1.}{r} \qquad (A.2)$$

are the kinetic and potential operators respectively, and l is the angular quantum number of the state whose energy is being determined. The operator

$$\nabla^2 = \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \frac{1.}{r^2 \sin(\theta)}\frac{d}{d\theta}\left(\sin(\theta)\frac{d}{d\theta}\right) + \frac{1.}{r^2 \sin^2(\theta)}\frac{d^2}{d\phi^2} \qquad (A.3)$$

which simplifies to

$$\nabla^2 = \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} \qquad (A.4)$$

when the wave function has no angular dependence. All symbols $\left(\frac{d}{dr}\right)$ represent partial differential operators. Also it should

be noted that for S states ($l = 0$) the operators for the kinetic and mean energies become

$$T = -\tfrac{1}{2}\nabla^2 \tag{A.5}$$

and

$$H = -\tfrac{1}{2}\nabla^2 - \frac{1.}{r} \tag{A.6}$$

APPENDIX B

RELATIONSHIPS AND INTEGRALS INVOLVING THE HEAVISIDE FUNCTION

a) DEFINITION OF HEAVISIDE FUNCTION

The Heaviside function is defined (9) such that

$$H(t) = \begin{cases} 1 \text{ for } t>0 \\ 0 \text{ for } t\leqslant 0 \end{cases} \qquad (B.1)$$

Then for integrals involving S(R)

$$\int_0^\infty f(x)S(R)dx = \int_0^\infty f(x)(1.-H(r-R))dx$$

$$= \int_0^\infty f(x)dx - \int_0^\infty f(x)H(r-R)dx$$

$$= \int_0^\infty f(x)dx - \int_R^\infty f(x)dx$$

$$= \int_0^R f(x)dx \qquad (B.2)$$

b) INTEGRALS INVOLVING THE HEAVISIDE FUNCTION AND ITS DERIVATIVES

The derivatives of the Heaviside function are all the same function, the Dirac delta function, defined (9) such that

$$\delta(t) = \begin{matrix} 0 \text{ if } t \neq 0 \\ \infty \text{ if } t = 0 \end{matrix} \qquad (B.3)$$

The three integrals that were evaluated are

$$\int_0^\infty f(x)H(t)H(t)dx = \int_0^\infty f(x)H(t)dx \qquad (B.4)$$

$$\int_0^\infty f(x)H(t)\,\delta(t)dx = 0 \qquad (B.5)$$

$$\int_0^\infty f(x)\,\delta(t)\,\delta(t)dx = \int_0^\infty f(x)\,\delta(t)dx \qquad (B.6)$$

The following "proofs" are not proofs in the mathematical sense since they are not rigorous. However, the results of calculations were used as a counter check on the evaluation of these integrals.

Proof of (B.4)

Consider $H(t)\cdot H(t)$

for any point t, $H(t) = 0$ or 1

then $H(t)\cdot H(t) = 0$ or 1

and in fact

$$H(t)\cdot H(t) = \begin{cases} 0 \text{ if } t \leqslant 0 \\ 1 \text{ if } t > 0 \end{cases}$$

or

$$H(t)\cdot H(t) = H(t)$$

Proof of (B.5)

Consider $H(t)\cdot \delta(t)$

$$\delta(t) \neq 0 \text{ only if } t = 0$$

but $H(t) = 0$ when $t = 0$

then $H(t)\cdot\delta(t) = 0$ for all t

Before attempting to prove (B.6) several other relations need to be developed. By Bremermann (9) the Heaviside function if considered as a generalized function may be defined to have the following form

$$H(t) = \underset{n\to\infty}{\text{Lt}}\ f_n(t) \qquad \text{(B.7)}$$

where

$$f_n(t) = (n/\pi)^{\frac{1}{2}} \int_{-\infty}^{t} e^{-nx^2} dx \qquad (B.8)$$

These functions possess derivatives and

$$H'(t) = \underset{n\to\infty}{Lt}\, f_n'(t) = \underset{n\to\infty}{Lt}\,(n/\pi)^{\frac{1}{2}} e^{-nt^2} \qquad (B.9)$$

where $H'(t)$ is understood to be in an integral

$$\int_{-\infty}^{\infty} H'(t)g(t)dt = \underset{n\to\infty}{Lt}\,(n/\pi)^{\frac{1}{2}} \int_{-\infty}^{\infty} e^{-nt^2} g(t)dt$$

$$= \langle H'(t),\ g(t)\rangle \qquad (B.10)$$

Two useful relationships given by Bremermann (9) that follow from this treatment of the Heaviside function are

$$\langle H', \phi\rangle = -\langle H, \phi'\rangle$$

or in general

$$\langle H^n, \phi\rangle = (-1)^n \langle H, \phi^n\rangle \qquad (B.11)$$

The integrals involving $H^n(t)$ are of the form

$$I = \int_0^{\infty} H(r-R)g(r)dr \qquad (B.12)$$

putting $t = r-R$, this may be rewritten

$$I = \int_{-R}^{\infty} H(t)g(R+t)dt$$

$$= \underset{n\to\infty}{Lt} \int_{-R}^{\infty} f_n(t)g(R+t)dt \qquad (B.13)$$

If n is reasonably large $f_n(t) \simeq 0$ for all but $t \geqslant 0$.

Then

$$I = \langle H(t),\ g(R+t) \rangle = \int_{-\infty}^{\infty} H(r-R)g(r)dr \qquad (B.14)$$

Then relations (B.7) to (B.11) can be applied to integrals (B.4) to (B.6) and used to express other functionals $\langle G(t),\ g(t) \rangle$ in terms of integrals (B.4) to (B.6).

Proof of (B.6)

A general "proof" could not be found. However, for specific f(x) some progress can be made. Consider for example the simplest functional $\langle H' H',\ 1 \rangle$, which is defined

$$\langle H' H',\ 1 \rangle = \underset{a\to o}{Lt} \langle H'(t)H'(t-a),\ 1 \rangle$$

$$= \underset{\substack{a\to o \\ n\to\infty}}{Lt} \left[\left(\frac{n}{\pi}\right) \int_{-\infty}^{\infty} e^{-nt^2} e^{-n(t-a)^2} dt \right] \qquad (B.15)$$

in which the limits are to be taken in such a way that the integral is well defined. This will be examined later. For convenience, (B.15) is rewritten as

$$\langle H'(t)H'(t),\ 1 \rangle = \underset{\substack{a\to o \\ n\to\infty}}{Lt} \left[I(n, a) \right] \qquad (B.16)$$

where

$$I(n, a) = \frac{n}{\pi} \int_{-\infty}^{\infty} e^{-nt^2} e^{-n(t^2 - 2at + a^2)} dt$$

$$= \frac{n}{\pi} e^{-na^2} \int_{-\infty}^{\infty} e^{-2n(t^2 - at)} dt \qquad (B.17)$$

Now regarding the constant b as a finite translation of the variable s, it is noted that

$$\int_{-\infty}^{\infty} e^{-m(s-b)^2} ds = \int_{-\infty}^{\infty} e^{-ms^2} ds = (\pi/m)^{\frac{1}{2}} \qquad (B.18)$$

Expanding the exponent of the integral on the left hand side, one obtains

$$e^{-mb^2} \int_{-\infty}^{\infty} e^{-m(s^2 - 2bs)} ds = (\pi/m)^{\frac{1}{2}}$$

hence

$$\int_{-\infty}^{\infty} e^{-m(s^2 - 2bs)} ds = e^{mb^2} (\pi/m)^{\frac{1}{2}} \qquad (B.19)$$

This integral is of the same form as that occurring in expression (B.17). Making the substitutions $m = 2n$, and $a = 2b$,

$$\int_{-\infty}^{\infty} e^{-2n(s^2 - as)} ds = e^{na^2/2} (\pi/2n)^{\frac{1}{2}} \qquad (B.20)$$

Substitution of this expression in (B.17) gives

$$I(n, a) = (n/\pi) e^{-na^2} \cdot (\pi/2n)^{\frac{1}{2}} e^{na^2/2}$$

$$= (n/2\pi)^{\frac{1}{2}} e^{-na^2/2}$$

or, putting $n/2 = m$

$$I(m, a) = (m/\pi)^{\frac{1}{2}} e^{-ma^2} \qquad (B.21)$$

Thus

$$\langle H'(t)H'(t), 1\rangle = \lim_{\substack{a\to 0 \\ m\to\infty}} \left[(m/\pi)^{\frac{1}{2}} e^{-ma^2} \right] \qquad (B.22)$$

The question now arises as to how to approach the limits in such a way that (B.22) remains well defined. This is partly suggested by the form of $I(m, a)$ which, regarding a as a variable, is none other than $H'(a) = \delta(a)$. As m becomes very large the only values of a contributing to (B.22) are those in the immediate vicinity of $a = 0$. All remaining values of a make zero contribution to (B.22). One therefore can include all such non-zero values of a without appreciable error, that is, one can integrate over all a. Making this assumption

$$\lim_{\substack{a\to 0 \\ m\to\infty}} (m/\pi)^{\frac{1}{2}} e^{-ma^2} = \int_{-\infty}^{\infty} (m/\pi)^{\frac{1}{2}} e^{-ma^2} da$$

$$= \langle H'(a), 1\rangle \qquad (B.23)$$

by definition of H'. Finally, then, one obtains the expression

$$\langle H'H', 1\rangle = \langle H', 1\rangle \qquad (B.24)$$

APPENDIX C

FORM AND NORMALIZATION OF NON-LOCAL AND LOCAL HYDROGEN WAVE FUNCTIONS

On page 483 of "Quantum Mechanics" by Messiah (19) the normalized eigenfunctions of hydrogen are found to have the following form when converted to atomic units.

$$\psi_{nlm}(r,\Theta,\phi) = N_{nl}\, F_{nl}(2r/n)\, Y_l^m(\Theta,\phi) \qquad (C.1)$$

where

$$N_{nl} = \frac{2}{n^2}\sqrt{\frac{(n-l-1.)!}{((n+l)!)^3}}$$

$$F_{nl}(x) = x^l e^{-\frac{1}{2}x} L^{2l+1.}_{n-l-1.}(x)$$

$$L^k_p(z) = \sum_{s=0}^{p} \frac{(-)^s ((p+k)!)^2 z^s}{(p-s)!(k+s)!s!}$$

n is the principal quantum number, l is the angular quantum number, and m is the magnetic quantum number. Substituting the appropriate forms into (C.1)

$$\psi_{nlm}(r,\Theta,\phi) = \frac{2}{n^2}\sqrt{(n-l-1.)!(n+l)!}\; e^{-r/n} \cdot \left(\sum_{t=1}^{n-l} \frac{(-)^t (-2/n)^{l+t+1-1.}\, r^{t+l-1.}}{(n-l-t)!(2l+t)!(t-1.)!}\, Y_l^m(\Theta,\phi) \right) \qquad (C.2)$$

where

$$\int_0^{\pi}\int_0^{2\pi} \sin(\theta)\, d\theta\, d\phi\, Y_l^m Y_{l'}^{m'} = \delta_{ll'}\,\delta_{mm'}$$

and δ_{ab} is the Kronecker delta.

Localized hydrogen wave functions will be defined to have the following form

$$\bar{\psi}_{nlm}(r,\theta,\phi) = \bar{N}_{nl}\,\psi_{nlm}(r,\theta,\phi)S(R) \qquad (C.3)$$

where

$S(R) = (1.-H(r-R))$

$H(r-R)$ being the Heaviside function.

Using the normalization condition

$$\bar{N}_{nl}^2\int_\tau \psi_{nlm}^2(r,\theta,\phi)S^2(R)d\tau = 1. \qquad (C.4)$$

Noting terms common to $\bar{N}_{nl}$ and $\psi_{nlm}(r,\theta,\phi)$ and simplifying

$$\bar{\psi}_{nlm}(r,\theta,\phi) = \bar{N}_{nl}\, e^{-r/n} \sum_{t=1}^{n-l} \frac{(-)^{t+1-1.}\,(-2/n)^{t+1-1.}}{(n-1-t)!\,(2l+t)!\,(t-1.)!}\, r^{t}\, Y_l^m(\theta,\phi) \cdot S(R) \qquad (C.5)$$

where

$$\bar{N}_{nl} = 1./\sqrt{\int_0^R e^{-2r/n}\left(\sum_{t=1}^{n-l}\frac{(-)^{t+1-1.}\,(-2/n)^{t+1}}{(n-1-t)!\,(2l+t)!\,(t-1.)!}\, r^{t}\right)^2 dr \cdot \int_0^{\pi}\int_0^{2\pi} Y_l^{m\,2}\sin(\theta)\, d\theta\, d\phi} \qquad (C.6)$$

APPENDIX D

INTEGRAL TABLE

$$\int_A^B x^m e^{ax}\,dr = \left(\sum_{r=0}^{m} (-1)^r \frac{m!\,x^{m-r}}{(m-r)!\,a^{r+1}} \right) e^{ax} \Bigg|_A^B \qquad \text{(D.1)}$$

SOURCE: Integral 398 of "Handbook of Physics and Chemistry" (20)

$$\int_o^R e^{-r} \sin(Kr)\,dr = \frac{1}{(1+K^2)} \left\{ e^{-R} (-\sin(KR) - K\cos(KR)) + K \right\} \qquad \text{(D.2)}$$

$$\int_o^R e^{-r} \cos(Kr)\,dr = \frac{1}{(1+K^2)} \left\{ e^{-R} (K\sin(KR) - \cos(KR)) + 1 \right\} \qquad \text{(D.3)}$$

$$\int_o^R r e^{-r} \sin(Kr)\,dr = \frac{2K}{(1+K^2)^2} - \frac{1}{(1+K^2)} \left\{ R e^{-R} (\sin(KR) + K\cos(KR)) \right\}$$

$$- \frac{1}{(1+K^2)^2} \left\{ e^{-R} \left[(1-K^2)\sin(KR) + 2K\cos(KR) \right] \right\} \qquad \text{(D.4)}$$

$$\int_o^\infty \cos^2(KR)\,dK = \operatorname*{Lt}_{R \to R'} \int_o^\infty \cos(KR)\cos(KR')\,dK$$

$$= \pi/2 \qquad \text{(D.5)}$$

BIBLIOGRAPHY

1. B.H. Bransden, Advances in Atomic and Molecular Physics, 1, 85, 1965.

2. N.F. Mott, H.S. Massey, "Theory of Atomic Collisions", third edn. Oxford, 1965.

3. G.G. Hall, R.D. Levine, J. Chem. Phys., 49, 51, (1968).

4. I.V. Komarov, S. Slavyanov, Soviet Physics, JETP, 25, 910, (1967).

5. B.M. Smirnov, Soviet Physics, JETP, 19, 692, (1964).

6. K.T. Tang, B. Kleinman, M. Karplus, J. Chem. Phys., 50, 1119, (1969).

7. R.D. Levine, J. Chem. Phys., 49, 51, (1968).

8. W.R. Thorson, J. Chem. Phys., 42, 3878, (1965).

9. H. Bremermann, "Distributions, Complex Variables, Fourier Transforms",Addison Wesley, 1965.

10. H. Bremermann, L. Durand, J. Math. Phys., 2, 240, (1961)

11. W. Corrigall, J. Lee, R. Wallace, personal communication.

12. J.S. Bell, Rev. Mod. Phys., 38, 447, (1966).

13. J.M. Jauch, C. Piron, Helv. Phys. Acta, 40, 559, (1967).

14. D. Bohm, J. Bub, Rev. Mod. Phys., 38, 453, (1966); 38, 470, (1966).

15. J.M. Jauch, C. Piron, Rev. Mod. Phys., 40, 228, (1968).

16. S.P. Gudder, Rev. Mod. Phys., 40, 229, (1968).

17. J.H. Tutsch, Rev. Mod. Phys., 40, 232, (1968).

18. D. Bohm. J. Bub, Rev. Mod. Phys., 40, 235, (1968).

19. A. Messiah, "Quantum Mechanics", Wiley, third printing (1965).

20. "Handbook of Chemistry and Physics", 46th. Edn., Editor in chief: R.C. Weast, Editor in charge of mathematics: S.M. Selby, Editor in chief Emeritus: C.D.Hodgman, The Chemical Rubber Co. (1965-1966).

21. M.L. Goldberger, K.M. Watson, "Collision Theory", Wiley, third printing (June, 1967).