

Elliptical Orbital Studies of

H_2^+ and H_2 Molecules

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(Submitted in partial fulfillment of
the requirements for the degree of
Master of Science)

B R O C K U N I V E R S I T Y

St. Catharines, Ontario.

August 1971

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ACKNOWLEDGMENTS

The author thanks most sincerely Dr. S. M. Rothstein for the help and guidance so freely given during the course of this project.

The author also thanks Miss Sybille Locher whose help in the typing of this thesis, has been invaluable.

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ABSTRACT

Calculations are performed on the $1\sigma_g$ ground states of the H_2^+ and H_2 molecules using a basis set of non-integral elliptical orbitals. Different variational wavefunctions constructed for H_2^+ involved one parameter to three parameter variation.

In order to reduce the number of parameters in most commonly used basis orbitals set, the importance of the term $(1+\mu)^\sigma$ over the term μ^n where n is a variational parameter and the value of σ may be given by boundary condition or cusp condition is outlined in Chapters II and III. It is found that the two parameter wavefunction for H_2^+ including the term $(1+\mu)^\sigma$, σ given by the boundary condition, gives lower variational energies than any wavefunction published to date for small and moderate internuclear separations.

In order to find out the importance of the term $(1+\mu)^\sigma$ over μ^n for the two electron problem, the variational energy is computed for the H_2 molecule from unrestricted two parameter closed shell wavefunctions including the term $(1+\mu)^\sigma$ where the value of σ is obtained from the boundary condition in one case and from the cusp condition in the second case.

In order to take into account in-out correlation partially, open shell calculation for the ground state of the hydrogen molecule for $R = 1.4$ (equilibrium internuclear separation) is performed. The results are excellent.

Chapter I

INTRODUCTION

In most of the quantum mechanical studies on diatomic molecules using basis orbitals expressed in terms of elliptical coordinates, excellent results have been obtained.¹⁻⁶ The most commonly used basis orbitals are

$$(n, s, \alpha, m, \beta) = \mu^n \nu^m \left[(\mu^2 - 1)(1 - \nu^2) \right]^{\beta/2} \times \exp(-s\mu - \alpha\nu + i\beta\phi) \quad (1)$$

In equation (1), μ and ν are the usual spheroidal coordinates, given by the following expressions:

$$\mu = (r_a + r_b) / R \quad (2)$$

$$\nu = (r_a - r_b) / R \quad (3)$$

ϕ is the angle of rotation about the internuclear axis.

The elliptical orbital basis functions have the advantage of describing the axially symmetric charge distributions associated with valence electrons. This is perhaps one of the main reasons for using the elliptical orbital basis functions. At the same time, it is more difficult to describe the representation of the spherical atomic

distributions. (See Fig. 2, Chapter II).

As early as 1933 James and Coolidge⁷ calculated the H_2 molecule energy using a wavefunction depending upon $\mu_1, \nu_1, \mu_2, \nu_2$ and λ_{12} and containing a number of variational parameters. The need to account for the correlation of the two electrons makes it necessary to include the term λ_{12} . Their wavefunction involved a factor $e^{-\alpha(\mu_1+\mu_2)}$ times a polynomial in the five variables chosen in such a way that it represents the correct type of symmetry to describe $1\sigma_g$ state. They minimized the H_2 molecular energy by varying the variational parameters.

They used three different variational wavefunctions, one of 5 terms, one of 11 terms and finally one of 13 terms. Their 5 term wavefunction (4) gave the energy of -1.166 a.u. which is quite in agreement with the experimental value of -1.1744 a.u.⁸

$$\psi = \frac{1}{2\pi} e^{-0.75(\mu_1+\mu_2)} \left[2.23779 + 0.80483(\nu_1^2 + \nu_2^2) - 0.5599\nu_1\nu_2 - 0.60985(\mu_1+\mu_2) + 0.56906\lambda_{12} \right] \quad (4)$$

After James and Coolidge, a number of quantum mechanical calculations were performed using elliptical orbital basis functions and excellent results have been obtained.¹⁻⁶

In a contrast, Slater type orbitals provide very good representation of essentially spherical charge distributions near atoms in the molecules, but they have the disadvantage of not describing the valence electrons well. Browne⁹⁻¹⁰ has carried out calculations using a mixed basis of Slater and elliptical orbitals.

The basis orbitals given by the expression (1) involve the term μ^n where n is a variational parameter. Using the above set of basis functions Hoyland¹¹ constructed a variational wavefunction (5)

$$\psi = \mu^n e^{-a\mu} \cosh(b\vartheta) \quad (5)$$

where n , a and b are the variational parameters and computed the energy for H_2^+ and H_2 molecule.

In order to reduce the number of variational parameters in the above elliptical basis functions one can replace the term μ^n by $(1 + \mu^\sigma)$ where σ is not a variational parameter but a function of other parameters, and see if it gives results comparable to wavefunction involving μ^n . The analytical expression for σ and the importance of the term $(1 + \mu^\sigma)$ is described in the next chapter.

We investigate the wavefunction (6) for H_2^+ using the term $(1 + \mu^\sigma)$.

$$\psi = (1 + \mu^\sigma) e^{-a\mu} \cosh(b\vartheta) \quad (6)$$

As described in the next chapter the above wavefunction gives better results than Hoyland's three parameter wavefunction for H_2^+ and most of the other variational wavefunctions for small and moderate internuclear separation.

Later on, in order to see how this basis orbital works for a two electron problem, a simple product wavefunction is constructed for H_2 molecule and the energy is computed.

Chapter II



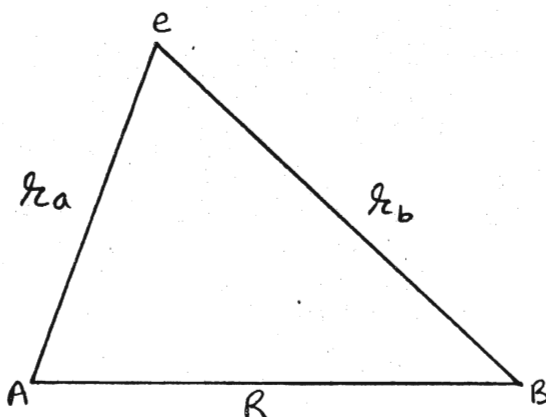
A. Exact Solution

On the basis of the Born-Oppenheimer approximation (Appendix I) the Schrodinger's equation for the electronic wave function of H_2^+ is given by equation (1)

$$\frac{1}{2} \nabla^2 \psi + \left(E + \frac{1}{r_a} + \frac{1}{r_b} - \frac{1}{R} \right) \psi = 0 \quad (1)$$

where ∇^2 is the Laplacian operator, ψ the wavefunction, E the electronic energy in atomic units, R the internuclear distance, and r_a and r_b are the distances of the electron from nucleus A and B respectively. (See Fig. 1). In equation (1) atomic units¹² are used ($\hbar = m = e = 1$)

Figure 1



Radial coordinates for the two centre problem

If the coordinate system in equation (1) is expressed in spheroidal coordinates, the laplacian operator

∇^2 is given by

$$\nabla^2 = \frac{4}{R^2(\mu^2 - \nu^2)} \times \left[\frac{\partial}{\partial \mu} \left\{ (\mu^2 - 1) \frac{\partial}{\partial \mu} \right\} + \frac{\partial}{\partial \nu} \left\{ (1 - \nu^2) \frac{\partial}{\partial \nu} \right\} + \left\{ (\mu^2 - \nu^2) / ((\mu^2 - 1)(1 - \nu^2)) \right\} \frac{\partial^2}{\partial \phi^2} \right] \quad (2)$$

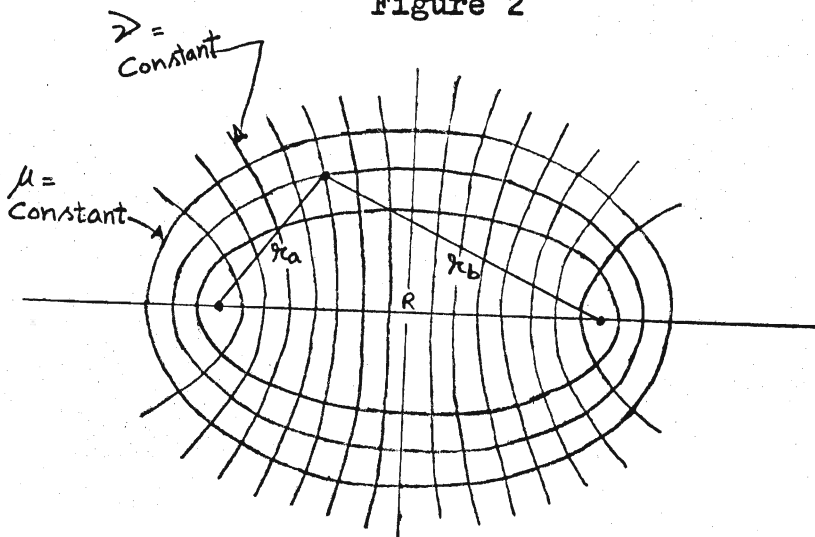
In the above equation μ and ν are the usual spheroidal coordinates,¹³ ϕ is the azimuthal angle and

μ and ν are given by the following expressions:
(See Fig. 2).

$$\mu = (r_a + r_b) / R, \quad (3)$$

$$\nu = (r_a - r_b) / R. \quad (4)$$

Figure 2



Spheroidal Coordinates
for the two-centre problem

In equation (1) by putting the value of ∇^2 from equation (2) and the value of \mathcal{L}_a and \mathcal{L}_b in terms of μ and ν , the following equation is obtained:

$$\frac{\partial}{\partial \mu} \left\{ (\mu^2 - 1) \frac{\partial \psi}{\partial \mu} \right\} + \frac{\partial}{\partial \nu} \left\{ (1 - \nu^2) \frac{\partial \psi}{\partial \nu} \right\} + \left\{ (\mu^2 - \nu^2) / (\mu^2 - 1)(1 - \nu^2) \right\} \frac{\partial^2 \psi}{\partial \phi^2} + \left\{ \frac{R^2 E}{2} (\mu^2 - \nu^2) + 2R\mu \right\} \psi = 0. \quad (5)$$

We now try to find a solution of the form

$$\psi(\mu, \nu, \phi) = M(\mu) N(\nu) \Phi(\phi) \quad (6)$$

because the variables are separable.

We separate the equation (5) into ϕ dependent part and the remaining part which depends upon μ and ν by equating

$$\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi \quad (7)$$

In the above equation $-m^2$ is the separation parameter.

The remaining part of (5) which depends upon μ and ν can be further divided into μ and ν dependent part by making use of the separational parameter A so that $M(\mu)$ and $N(\nu)$ satisfy

$$\frac{d}{d\mu} \left\{ (\mu^2 - 1) \frac{dM}{d\mu} \right\} + \left\{ A + 2R\mu - \frac{m^2}{(\mu^2 - 1)} \right\} M = 0 \quad (8)$$

and

$$\frac{d}{d\mathcal{V}} \left\{ (1-\mathcal{V}^2) \frac{dN}{d\mathcal{V}} \right\} + \left\{ -A + \frac{p^2}{2} \mathcal{V}^2 - \frac{m^2}{(1-\mathcal{V}^2)} \right\} N = 0 \quad (9)$$

where
$$p^2 = -R^2 E / R \quad (10)$$

These differential equations will have satisfactory solutions only if the separation parameters A and m as well as p have certain definite values. Obviously, the solutions to these equations yield the H_2^+ wavefunction by equation (6).

From equation (7) we at once get

$$\Phi(\phi) = e^{im\phi} \quad (11)$$

The equation (9) for $N(\mathcal{V})$ is quite familiar as it appears in many problems of wave-mechanics in spheroidal coordinates. This equation has been discussed in great detail by Stratton, Morse, Chu, and Hunter.¹⁴ They have shown that for given value of p and m , proper solutions exist only for certain discrete values of the constant A . They have also shown that the function $N(\mathcal{V})$ can be expanded in the form

$$N(l, m, p; \mathcal{V}) = \sum_{s=0}^{\infty} f_s(l, m, p) P_{m+s}^m(\mathcal{V}) \quad (12)$$

s even	l even
s odd	l odd

where $P_{m+s}^m(\vartheta)$ are the associated Legendre polynomials, and f 's are the expansion coefficients. l is a running quantum number which describes the various eigenfunctions of the equation (9). Stratton et al¹⁴ have published tables giving the separation constants and expansion coefficients as functions of p for the lower values of l and m .

Now consider the remaining differential equation

$$\frac{d}{d\mu} (\mu^2 - 1) \frac{dM(\mu)}{d\mu} + \left\{ A + 2R\mu - p^2 \mu^2 \right\} M(\mu) = 0 \quad (13)$$

which is equation (8) for $m = 0$. This corresponds to a σ state because the component of the angular momentum along the nuclear axis is zero.

In equation (13), $M(\mu)$ is the radial dependent wavefunction and is of the form

$$M(\mu) = e^{-p\mu} y(\mu) \quad (14)$$

where $y(\mu)$ is still to be found.

Now from the above equations it can be shown that the radial dependent differential equation becomes

$$\begin{aligned} (\mu^2 - 1) y'' + \left\{ -2p(\mu^2 - 1) + 2\mu \right\} y' + \\ \left\{ -p^2 - 2p\mu + A + 2R\mu \right\} y = 0 \end{aligned} \quad (15)$$

where $y' = dy/d\mu$
 and $y'' = d^2y/d\mu^2$

Equation (15) contains $\mu = \pm 1$ as regular singular points and ∞ as the irregular singular point. It can be shown that the transformation

$$u = (\mu - 1)/(\mu + 1) \quad (16)$$

where u is an independent variable, transforms the irregular singularity to $u = 1$ and regular singularities to $u = 0$ and $u = \pm\infty$.

Under the transformation (16), equation (15) takes the following form

$$\begin{aligned} (1-u)^2 u \frac{d^2 y}{du^2} + \left\{ 1 - u^2 - 4up - 2u(1-u) \right\} \frac{dy}{du} + \\ \left\{ (2R - 2p)(1+u)/(1-u) + A - p^2 \right\} y = 0 \end{aligned} \quad (17)$$

Since $u = \frac{\mu-1}{\mu+1}$ and μ varies from 1 to infinity, u can vary from 0 to 1. We also know that our differential equation (14) has the singularity at $u = 1$. We must therefore look for substitution for y in terms of u which will remove the singularity at $u = 1$ in equation (17).

It can be easily shown that the following power series expansion of y in terms of u about the point $u = 0$ does not converge at $u = 1$

$$y = u^{\alpha} \sum_K a_K u^K \quad (18)$$

If we instead substitute

$$y = (1-u)^{\alpha} Z(u) \quad (19)$$

in equation (17), the singularity at $u = 1$ can be removed. That is, we can find out the indicial equation of the differential equation (17) by equating to zero the coefficients of the lowest power of $(1-u)$. It is necessary to find the indicial equation in order to get the value of α for which singularity at $u = 1$ is removed.

The value of α is found to be

$$\alpha = 1 - R/p \quad (20)$$

From the above discussion it is clear that we must include the term $(1-u)^{\alpha}$ which is equivalent to $(1+\mu)^{R/p-1}$ in the wavefunction $M(\mu)$ in order to remove the singularity at $u = 1$ ($\mu = \infty$).

In summary, the radial wavefunction for σ states is of the form

$$M(\mu) = e^{-p\mu} (1-u)^{1-R/p} Z(u) \quad (21)$$

which combines (14), (19), and (20). By virtue of removing the singularity at $u = 1$, Z may be taken as a single power series in u .

$$Z(u) = \sum_{k=0}^{\infty} g_k u^k \quad (22)$$

The g 's are the expansion coefficients. The above two equations are the exact radial wavefunction.

The exact energy may be calculated by plotting A versus p satisfying the differential equations (8) and (9) separately for the given value of R and m . The points of intersection correspond to different excited states and exact energy may be obtained by making use of equation (10).

From the above discussion the exact wavefunction for H_2^+ ground state is given by

$$\psi(\mu, \nu) = (1-u)^{-\sigma} \left\{ \sum_{k=0}^{\infty} g_k u^k \right\} e^{-a\mu} \left\{ \sum_{\ell=0}^{\infty} f_{\ell} \nu^{2\ell} \right\}$$

where μ and ν are the usual radial and angular spheroidal coordinates. $u = (\mu-1)/(\mu+1)$,

$$\sigma = (R/a - 1), \quad a \equiv - \left(R^2 E / 2 \right)^{1/2},$$

R is the internuclear separation, and E the energy.

The g and f coefficients are calculated from recurrence formulas from the energy and separation constant.¹⁶

B. Construction of Variational wavefunctions for the ground state

1. Unrestricted two-parameter wavefunctions (28) and (29)

Obviously, an approximate (variational) wavefunction should as much as possible reflect the exact wavefunction. Thus, let the approximate wavefunction be of the form (6):

$$\psi = M(\mu) N(\nu) \Phi(\phi) \quad (23)$$

For the radial function, μ , we assume

$$M(\mu) = (1 + \mu^\sigma) e^{-a\mu} \quad (24)$$

with

$$\sigma = R/a - 1 \quad (25)$$

because of (21) and (22). In equation (25), "a" is a variational parameter.

For the angular function, $N(\nu)$, we assume

$$N(\nu) = \cosh(b\nu) \quad (26)$$

or

$$N(\nu) = (1 + b\nu^2) \quad (27)$$

because of (12). That is, (12) is an infinite series involving even powers of ν when $m = 0$.

For Φ , we take unity, for $m = 0$ (11)

Two wavefunctions are possible; i.e. (24) and (26) or (24) and (27).

$$\psi = (1+\mu) e^{\sigma - a\mu} \cosh(b\tau) [\sigma = R/a - 1] \quad (28)$$

$$\psi = (1+\mu) e^{\sigma - a\mu} (1+b\tau^2) [\sigma = R/a - 1] \quad (29)$$

We emphasize that σ is given explicitly in terms of a , so the above wavefunctions have only two variational parameters, a and b .

The expectation value of the energy, E , is given by the following expression

$$E = \int \psi^* H \psi d\tau / \int \psi^2 d\tau \quad (30)$$

The term $\int \psi^2 d\tau$ in the denominator of equation (24) accounts for the normalization. (The computation is described in Appendix II). Results obtained are given in table I.

It is quite clear from our results that when the τ dependent term of the wavefunction was changed from $\cosh(b\tau)$ to $(1 + b\tau^2)$ it did not make any significant energy change. This is not surprising, because taking into account the variational parameter b , both the terms $\cosh(b\tau)$ and $(1 + b\tau^2)$ are similar to the τ dependent terms in the exact wavefunction.

We found that the energy calculated from two parameter wavefunction (28) for the range of small and moderate separations are even lower than those obtained from three parameter wavefunction of Hoyland¹¹, equation (31), and

TABLE I Energy and parameters for $1S\sigma$ -ground state of H_2^+ for wavefunction (28) & (29)

R/a_0	$-E^b$ (Exact)	Two parameter variation			$-E^d$ (Hoyland)	$-E^e$ (Clark & Stewart)	Two parameter variation		
		$-E^c$	a	b			$-E^f$	a	b
0.2	1.9286203	1.9286203	.1964	.1135			1.9286203	.1964	.0064
0.4	1.8007540	1.8007540	.3795	.2202		1.8007272	1.8007540	.3795	.0243
0.8	1.5544801	1.5544797	.7047	.4137		1.5544656	1.5544793	.7047	.0866
1.0	1.4517863	1.4517856	.8511	.5034	1.451780	1.4517763	1.4517842	.8511	.1289
1.2	1.3623078	1.3623066	.9890	.5899		1.3623005	1.3623026	.9890	.1783
1.6	1.2159372	1.2159331	1.2451	.7566		1.2159306	1.2159150	1.2450	.2980
2.0	1.1026342	1.1026237	1.4815	.9192	1.102623	1.1026227	1.1025665	1.4810	.4480
2.4	1.0132203	1.0131977	1.7035	1.0800		1.0131974	1.0130551	1.7040	.6332
3.0	.9108962	.9108419	2.0183	1.3270	.910840	.9108420	.9104120	2.0180	.9930
4.0	.7960849	.7959439	2.5149	1.7600		.7959441	.7942059	2.5150	1.9077
5.0	.7244203	.7241933	2.9987	2.2340	.724192		.7193004	2.9990	3.4863

Table I (continued)

- a. The energies are given in atomic units and do not include the nuclear-nuclear energy $1/R$
- b. Ref. 21
- c. Equation (28)
- d. Ref. 11
- e. Ref. 17
- f. Equation (29)

Clark and Stewart's¹⁷ equation (32).

$$\psi = \mu^c \exp(-a\mu) \cosh(b\mu) \quad (31)$$

$$\psi = (1+c\mu) \exp(-a\mu) \cosh(b\mu) \quad (32)$$

The main difference between Hoyland's wavefunction (31) and wavefunction (28) is that the latter makes use of the term $(1 + \mu^\sigma)$, where σ is a function of variational parameter "a", whereas Hoyland's wavefunction uses the third parameter c in factor μ^c . In the same way, Clark and Stewart also make use of third parameter c for the term $(1 + c\mu)$ in their wavefunction (32).

In the earlier discussion of this chapter it was shown that it is necessary to include the term $(1 + \mu^\sigma)$ in the exact wavefunction, and is further verified by our two parameter variational wavefunction giving a lower energy than Hoyland's and Clark and Stewart's three parameter wavefunctions.

2. Two parameter cusp-condition wavefunction (38)

In contrast to the condition on σ given by (25), its value can be given to satisfy the "cusp-condition" instead.

Consider the H_2^+ Schrodinger equation

$$H\psi = E\psi \quad (33)$$

where

$$H = -\frac{2}{R^2(\mu^2 - \nu^2)} \left[\frac{\partial}{\partial \mu} \left\{ (\mu^2 - 1) \frac{\partial}{\partial \mu} \right\} + \frac{\partial}{\partial \nu} \left\{ (1 - \nu^2) \frac{\partial}{\partial \nu} \right\} + 2\mu R \right] \quad (34)$$

(again assume ψ is independent of ϕ)

The right hand side of the equation (33) is finite but the left hand side becomes infinite when $\mu = 1$ and $\nu = \pm 1$, because the denominator $(\mu^2 - \nu^2)$ becomes zero. In order that $H\psi$ be finite for $\mu = 1$ and $\nu = \pm 1$ the numerator of $H\psi$ must be equated to zero at these points. This necessary restriction is known as the "Cusp Condition".¹⁸

Therefore

$$\left[\frac{\partial}{\partial \mu} \left\{ (\mu^2 - 1) \frac{\partial}{\partial \mu} \right\} + \frac{\partial}{\partial \nu} \left\{ (1 - \nu^2) \frac{\partial}{\partial \nu} \right\} + 2\mu R \right] \psi \Big|_{\mu=|\nu|=1} = 0 \quad (35)$$

Upon simplification:

$$\frac{1}{R\psi} \left\{ \frac{\partial \psi}{\partial \nu} - \frac{\partial \psi}{\partial \mu} \right\} = 1 \quad (36)$$

By putting the values of $\frac{\partial \psi}{\partial \mu}$ and $\frac{\partial \psi}{\partial \nu}$ in equation (36) and using ψ given in equation (28), we get

$$\sigma = 2 \left\{ -R + a + b \tanh(b) \right\} \quad (37)$$

In this case σ is found to depend upon both the variational parameters "a" as well as "b".

The results for the following two parameter Cusp Condition wavefunction are found in Table II.

$$\psi = (1+\mu)^{\sigma} e^{-a\mu} \cosh(b\mathcal{D}) \left[\sigma = \text{Eqn. (37)} \right] \quad (38)$$

where σ is given by (37).

It can be seen from Tables I and II that for very small values of R the cusp condition wavefunction gives the same results as wavefunction (28) but as R increases, the wavefunction (28) gives better results than the cusp condition wavefunction. From the results obtained it seems that boundary condition is more important than Cusp Condition. This problem requires further investigation in order to explain why.

3. Three parameter wavefunctions

For additional flexibility, we may introduce three parameter wavefunctions.

In view of the term $\sum_{k=0}^{\infty} g_k \left[\frac{(\mu-1)}{(\mu+1)} \right]^k$

in the exact wavefunction (22), the following wavefunction which has a more complex μ dependence is tried. The wavefunction used is as follows:

$$\psi = \left[1 + g \frac{(1-\mu)}{(1+\mu)} \right] (1+\mu)^{\sigma} e^{-a\mu} \cosh(b\mathcal{D}) \quad (39)$$

TABLE II Energy and parameters for $1S\sigma$ ground state of H_2^{+a} for the
Wavefunction of Equation (28), with σ given by
Equations (25) and (37)

R/a_0	$-E^b$ (Exact)	Two-parameter variation			Two-parameter variation		
		$-E^c$	a	b	$-E^d$	a	b
0.2	1.9286203	1.9286203	.1964	.1135	1.9286203	.1964	.1135
0.4	1.8007540	1.8007540	.3795	.2202	1.8007540	.3796	.2203
0.8	1.5544801	1.5544797	.7047	.4137	1.5544797	.7054	.4152
1.0	1.4517863	1.4517856	.8511	.5034	1.4517849	.8514	.5061
1.2	1.3623078	1.3623066	.9890	.5899	1.3623042	.9881	.5940
1.6	1.2159372	1.2159331	1.2451	.7566	1.2159227	1.2369	.7643
2.0	1.1026342	1.1026237	1.4815	.9192	1.1025964	1.4561	.9305
2.4	1.0132203	1.0131977	1.7035	1.0800	1.0131444	1.6485	1.0960
3.0	.9108962	.9108419	2.0183	1.3270	.9107373	1.8934	1.3475
4.0	.7960849	.7959439	2.5149	1.7600	.7957618	2.2271	1.7884
5.0	.7244203	.7241933	2.9987	2.2340	.7239979	2.5555	2.2670

a. The energies are given in atomic units and do not include nuclear-nuclear repulsion energy $1/R$

b. Ref. 21

c. Equation (28) where value σ is given by equation (25)

d. Equation (28) where value σ is given by equation (37)

where g , a and b are variational parameters and the energy is calculated as before.

Table III gives the energy as a function of R for optimized values of g , a , and b . " σ " is given by equation (25), the boundary condition.

A second possibility uses wavefunction (28) with σ being third variational parameter instead of being a function of a , b and R . The energy is computed and the results are given in Table III.

Surprisingly the three parameter wavefunction (39) gives exactly the same results as the three parameter wavefunction (28), using σ as variational parameter. This means that additional flexibility introduced into the wavefunction (28) by allowing the independent variation of σ accounts for the first two terms

$$\sum_{k=0}^{\infty} g_k \left[\frac{(\mu-1)}{(\mu+1)} \right]^k.$$

The value of the parameter g in wavefunction (39) is found to be negative (Table III), as expected, because g is positive for the exact wavefunction.

Inspection of Tables I and III show that the three parameter wavefunctions give little improvement over the two parameter ones.

TABLE III Energy and parameters for 1Σ ground state of H_2^+ for three parameter wavefunction

R/a_0	$-E^b$ (Exact)	Three-parameter variation				Three-parameter variation			
		$-E^c$	a	b	$-g$	$-E^d$	a	b	σ
0.2	1.9286203	1.9286203	.1964	.1135	.0257	1.9286203	.1964	.1135	.0184
0.4	1.8007540	1.8007540	.3795	.2202	.0957	1.8007540	.3796	.2202	.0548
0.8	1.5544801	1.5544800	.7053	.4137	.3280	1.5544800	.7059	.4137	.1392
1.0	1.4517863	1.4517860	.8519	.5034	.4760	1.4517860	.8530	.5134	.1814
1.2	1.3623078	1.3623070	.9903	.5899	.6393	1.3623070	.9919	.5899	.2224
1.6	1.2159372	1.2159337	1.2475	.7566	1.0001	1.2159337	1.2503	.7566	.2998
2.0	1.1026342	1.1026242	1.4849	.9192	1.3936	1.1026242	1.4890	.9192	.3706
2.4	1.0132203	1.0131982	1.7082	1.0800	1.8092	1.0131982	1.7136	1.0800	.4352
3.0	.9108962	.9108423	2.0245	1.3270	2.4582	.9108423	2.0317	1.3270	.5206
4.0	.7960849	.7959442	2.5234	1.7600	3.5697	.7959442	2.5331	1.7600	.6350
5.0	.7244203	.7241935	3.0087	2.2340	4.6788	.7241935	3.0202	2.2340	.7183

- a. The energies are in atomic units and do not include nuclear-nuclear repulsion energy $1/R$
b. Ref. 21
c. Equation (39)
d. Equation (28) where a, b and σ are treated as variational parameters.

4. One parameter variational wavefunction

To take into account the "Cusp Condition" (37) and "boundary condition" (25) on σ , we may introduce a one parameter wavefunction (42).

From equations (37) and (25)

$$\sigma = R/a - 1 = 2 \left\{ -R + a + b \tanh(b) \right\} \quad (40)$$

or

$$a = .5 \left(\left[R - b \tanh(b) - \frac{1}{2} \right] \pm \left[\left[R - b \tanh(b) - \frac{1}{2} \right]^2 + 2R \right]^{1/2} \right) \quad (41)$$

We can neglect the minus sign in (41) so that a is positive.

Using equations (40) and (41) in the following wavefunction,

$$\psi = (1+\mu) e^{\sigma - a\mu} \cos R(b\mathcal{D}) \left\{ \begin{array}{l} \sigma = \sigma(b) \\ a = a(b) \end{array} \right\} \quad (42)$$

the calculated energy is listed in Table IV. We emphasize that a is a function of b in equation (42).

From Table IV it can be seen that for low and moderate internuclear separation, one parameter wavefunction (42) gives better results than Hirschfelder's¹⁹ two parameter wavefunction (43).

$$\psi = N_A e^{-a\mu} \cos R(b\mathcal{D}) \quad (43)$$

It is also found that at higher values of R the two parameter geometric mean wavefunction²⁰ gives better

TABLE IV Energy and parameter for 1σ ground state of H_2^{+a} for one parameter wavefunction (42).

R/a_0	<u>One parameter variation</u>			<u>Two parameter variation</u> (Hirschfelder)	<u>Two parameter variation</u> (Geometric mean)
	$-E^b$ (Exact)	$-E^c$	b	$-E^d$	$-E^e$
0.2	1.9286203	1.9286203	.1134	1.92854	
0.4	1.8007540	1.8007540	.2199	1.80053	
0.8	1.5544801	1.5544796	.4147		
1.0	1.4517863	1.4517849	.5060	1.45149	1.451485
1.2	1.3623078	1.3623041	.5946		
1.6	1.2159372	1.2159199	.7672	1.21571	
2.0	1.1026342	1.1025835	.9372	1.10244	1.102447
2.4	1.0132203	1.0131090	1.1075		
3.0	.9108962	.9106434	1.3673	0.91074	0.910765
4.0	.7960849	.7955527	1.8213	0.79588	0.795967
5.0	.7244203	.7237576	2.3086	0.72415	0.724298

a. The energies are given in atomic units and do not include nuclear-nuclear repulsion energy $1/R$

b. Ref. 21

c. Equation (42)

d. Ref. 19

e. Ref. 20

results whereas at low values of R a one parameter wavefunction (41) gives better results.

5. Summary and Conclusions

Let us now conclude this chapter with a short summary.

In this chapter we have learned that a clever two parameter wavefunction can give better results than some three parameter wavefunctions. For example, two parameter wavefunction (28) gives better results than most of the three parameter wavefunctions, and the (two parameter) geometric mean wavefunction gives the best results at higher values of R . As the molecule dissociates, it becomes more important to take into account the probability density at moderate electron distance. This fact is taken into account by geometric mean function with the result of that it gives better results as R increases, in fact it gives better results at large R than any other variational wavefunction.

We expect that the results could be further improved if we introduce more flexibility by putting an additional parameter into angular dependent part of the wavefunction (28).

To the best of our knowledge wavefunction (28) gives lower variational energies than any wavefunction published to date for small and moderate internuclear separation.

In order to extend this work further, we dealt with the two electron problem, H_2 molecule, which involves correlation.

Chapter III

H_2 MOLECULE

In the previous chapter, we dealt with H_2^+ , a single electron moving about two protons. If we want to consider any molecule or ion with more than one electron, we come across the many electron problem and it is necessary to handle it by approximate methods. In this chapter we will be dealing with hydrogen molecule H_2 , with two electrons which is the next most complicated problem after H_2^+ . Furthermore the two electron systems provide a bridge between comparatively simple one electron systems and those with many electrons.

This problem has been studied in great detail by many workers. When we deal with this problem in detail, we meet most of the methods which are applied in many more complicated cases of molecular structure. It will be worth mentioning that this problem is a celebrated one in the field of molecular theory as well as in the understanding and the development of many electron wave mechanics.

A. Two parameter unrestricted closed shell wavefunction (3)

Now we will construct the simple two parameter variational wavefunction.

Consider the behavior of a system consisting of two electrons. If we describe one of them by a wavefunction

$f(\mu_1, \nu_1)$ a function of spheroidal coordinates of this particle and the other one by a wavefunction $f(\mu_2, \nu_2)$, the product of these two will represent a wavefunction for the system. (We assume a σ state where f is independent of ϕ .)

In order to see if the term $(1 + \mu)^\sigma$ plays an important role in the wavefunction of the H_2 molecule the $f(\mu, \nu)$ is taken to be of the form

$$f(\mu, \nu) = (1 + \mu)^\sigma e^{-a\mu} \cosh(b\nu) \quad (1)$$

where μ and ν are the usual spheroidal coordinates, a and b are the variational parameters and the value of σ is given by the following expression

$$\sigma = R/a - 1 \quad (2)$$

where R is internuclear separation.

From the above discussion the wavefunction ψ for the hydrogen molecule is given by

$$\psi = \psi_1 \psi_2 \quad (3)$$

where $\psi_1 = (1 + \mu_1)^\sigma e^{-a\mu_1} \cosh(b\nu_1)$

and $\psi_2 = (1 + \mu_2)^\sigma e^{-a\mu_2} \cosh(b\nu_2)$

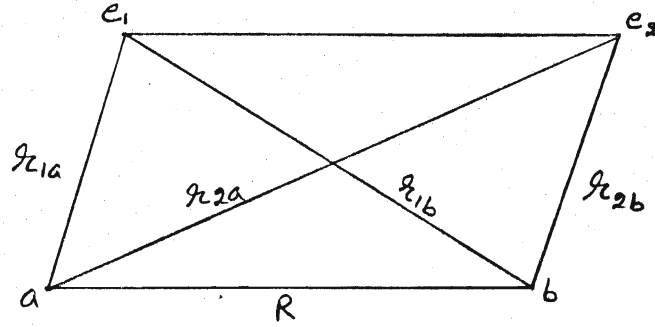
The symbols have the same meaning as described above.

For hydrogen molecule, the Hamiltonian operator, in atomic units, is

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_{1a}} - \frac{1}{r_{2a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}} + \frac{1}{R} \quad (4)$$

where the subscripts 1 and 2 refer to the electrons and the subscripts a and b refer to the nuclei as shown in the figure(3).

Figure 3

Coordinate system of H₂ Molecule

In the equation (4) ∇_1^2 and ∇_2^2 are the Laplacian operators and their value in spheroidal coordinates is given by the following expression.²³

$$\nabla_1^2 = \frac{4}{R^2(\mu_1^2 - \nu_1^2)} \left[\frac{\partial}{\partial \mu_1} \left\{ (\mu_1^2 - 1) \frac{\partial}{\partial \mu_1} \right\} + \frac{\partial}{\partial \nu_1} \left\{ (1 - \nu_1^2) \frac{\partial}{\partial \nu_1} \right\} + \frac{(\mu_1^2 - \nu_1^2)}{(\mu_1^2 - 1)(1 - \nu_1^2)} \frac{\partial^2}{\partial \phi_1^2} \right] \quad (5)$$

Similarly ∇_2^2 can be obtained by changing the subscript from 1 to 2. Further r_{1a} , r_{1b} , r_{2a} , r_{2b} are related to usual spheroidal coordinates by the following expressions.

$$\mu_{1R} = r_{1a} + r_{1b} \quad (6)$$

$$\nu_{1R} = r_{1a} - r_{1b} \quad (7)$$

In the same way if we replace the subscript 1 by 2, we can obtain relations between \mathcal{H}_{2b} and μ_2, \mathcal{D}_2 .

The hamiltonian H given by equation (4) can also be written as

$$H = H_1 + H_2 + \frac{1}{\mathcal{H}_{12}} \quad (8)$$

neglecting $1/R$, where

$$H_1 = -\frac{1}{2} \nabla_1^2 - \frac{1}{\mathcal{H}_{1a}} - \frac{1}{\mathcal{H}_{1b}} \quad (9)$$

and similarly

$$H_2 = -\frac{1}{2} \nabla_2^2 - \frac{1}{\mathcal{H}_{2a}} - \frac{1}{\mathcal{H}_{2b}} \quad (10)$$

In equation (8) H_1 and H_2 are simply hamiltonian operators for the hydrogen molecular ion.

Consider a variational wavefunction $\psi = \psi_1 \psi_2$ given by equation (3) and minimize the corresponding expectation value of the energy, which is given by

$$E = \int \psi^* H \psi d\tau / \int \psi^2 d\tau \quad (11)$$

In the above equation (11) the term $\int \psi^2 d\tau$ in the denominator accounts for the normalization of ψ .

The value of energy E is found to be

$$E = \frac{2E_1 + \int \psi_1 \psi_2 \frac{1}{\mathcal{H}_{12}} \psi_1 \psi_2 d\tau_1 d\tau_2}{\int \psi_1^2 \psi_2^2 d\tau_1 d\tau_2} \quad (12)$$

where E_1 is the expectation value of the energy for H_2^+ .

The Coulomb integral $\int \psi_1 \psi_2 \frac{1}{r_{12}} \psi_1 \psi_2 d\tau_1 d\tau_2$ accounts for the Coulomb repulsion between the two electronic distributions. The computation of this two centred integral will be discussed in Appendix IV.

The energy is minimized by varying the variational parameters "a" and "b". The values of energy and the optimized values of the variational parameters are given in Table V and VI.

B. Two parameter Cusp-Condition closed shell wavefunction (14)

Instead of using the value of σ given by equation (2), we can use the value of σ given to satisfy the "Cusp Condition" described in the last chapter. The value of σ satisfying the Cusp Condition is given by the following expression (13).

$$\sigma = 2 \left[-R + a + b \tanh(b) \right] \quad (13)$$

Consider the Cusp Condition closed shell wavefunction

$$\Psi = \psi_1 \psi_2 \quad (14)$$

where $\psi = (1 + \mu^\sigma) e^{-a\mu} \cosh(b\mu)$

and value of σ is given by equation (13).

The value of energy for the two parameter cusp condition wavefunction (14) as a function of internuclear distance R is given in Table V.

It can be seen from the Table V that the values of energy obtained from Cusp Condition wavefunction are better than the wavefunction (3), which clearly shows that Cusp Condition is more important in the case of hydrogen molecule which is in contrast to H_2^+ where the results obtained from boundary condition σ are better.

The most ready explanation for this is the presence of the $\frac{1}{r_{12}}$ term in the H_2 Hamiltonian, which is not found in H_2^+ . This term prevents the separation of the μ and ν variables, and hence the H_2^+ boundary condition on σ is, strictly speaking, not valid.

We further discuss the closed shell results at the end of this chapter.

C. Open Shell Wavefunction

Now we will consider the H_2 problem in more detail. As we know that in many cases the numbers to be calculated by quantum mechanical calculations are already known from experiment. In order to gain more, the results should lead to physical insight which may lead to new and more powerful calculational methods.

In order to get reasonable agreement with the experimental numbers, many quantum mechanical calculations in molecules make use of large number of configuration interactions.

The concept of configuration interaction arises from the fact that there are several electronic states with energies close to those of the states which are under consideration. Moreover, some of these states have the same symmetry, so that they can interact. This means that in order to get a good approximation to the ground state, one must make use of an improved variational treatment which mixes together these configurations. Such an approach is known as configuration interaction.

As the number of configurations increases, the results become better but at the same time the understanding of the true nature of the wavefunction becomes more difficult. In order to avoid this difficulty, one can instead make use of the open shell technique coupled with extensive variation of non linear parameters in a highly flexible molecular orbital.

In open shell technique, the two electrons in the hydrogen molecule are assigned different orbitals in order to separate their charge distribution to some extent. This is perhaps the simplest method of describing electron repulsion.

The method described above has the advantage of giving results comparable to a number of configuration interactions and hence the physical interpretation becomes much simpler.

It is worth mentioning at this point that the amount of calculation needed for open shell technique is much greater than that of closed shell method.

In order to make use of the variational method, we choose the following open shell wavefunction (15).

$$\begin{aligned}\Psi &= \psi(1) \phi(2) + \phi(1) \psi(2) \\ &= \psi_1 \phi_2 + \phi_1 \psi_2\end{aligned}\quad (15)$$

where

$$\psi = (1+\mu)^{\sigma} e^{-a\mu} \cosh(b\varpi) \quad (16)$$

and

$$\phi = (1+\mu)^{\sigma'} e^{-a'\mu} \cosh(b'\varpi) \quad (17)$$

In the above equations (16) and (17) μ and ϖ are usual spheroidal coordinates. a , a' , b and b' are variational parameters and value of σ is given by equation (13). Similarly, the value of σ' will be given by the right hand side of the equation (13) if we replace a by a' and b by b' .

In order to simplify the work, we assumed that the wavefunction (15) is based on a sum of products of one electron functions.

The quality of the results expected from wavefunction (15) depends upon the degree to which this wavefunction can be made to approximate the actual molecular wavefunction. Therefore in order to get better results the wavefunction should have enough flexibility. In particular, we avoid all unnecessary restrictions on the wavefunction and allow the

computer to find the collection of orbitals which represent the best possible wavefunction of the chosen parametric form by varying the variational parameters a , a' , b and b' .

D. Electron Correlation Problem

Another distinction between a closed shell wavefunction (14) and an open shell wavefunction (15) comes from the phenomena of correlation. In the case of H_2 , there can be three kinds of correlation: in-out correlation, left-right correlation and angular correlation.

In the case of in-out correlation the electrons tend to repel each other in such a way that one electron is near to the axis (nuclei) and the other is further out radially.

The open shell wavefunction (15) has enough flexibility in order to account for in-out correlation partly by making the function ψ_1 corresponding to an orbital concentrated near to the axis where as the function ψ_2 corresponding to more spread out orbital. In this way, this part of the wavefunction is large when one electron is near to the axis and the other is further out radially.

In the case of left-right correlation, one electron tends to be on the left hand atom when the other electron is at the right hand atom. Unfortunately, the wavefunction (15) does not take into account this kind of correlation, because it does not have a nodal plane between the nuclei.²²

Finally we have to consider angular correlation in

which both the electrons tend to keep the opposite sides of an axial plane. If both the electrons have the same values of μ and φ , which means that both of the electrons are confined to the same circle in a plane normal to the nuclear axis, then they can move in such a way that they are touching, or at opposite ends of a diameter, or anywhere between. Obviously, we require the electrons to be at opposite ends of the diameter. To do this, thereby taking into account this angular correlation, we must use a correlated wavefunction¹⁸ which involves the term \mathcal{R}_{12} explicitly into the wavefunction or a configuration interaction involving ϕ dependence.²²

It has been found that the wavefunctions involving direct dependence on \mathcal{R}_{12} are more successful as compared to the configuration interaction method, because in the case of configuration interaction we are trying to expand this cusp-like behavior in Fourier series, which is a relatively slowly convergent expansion. On the other hand, the correlated wavefunctions have the disadvantage that it is extremely difficult to give them any simple physical interpretation. In addition, it is more difficult to generalize this approach to many electron systems.

To summarize, the open shell wavefunction (15) takes into account in-out correlation, but not left-right or angular correlation.

TABLE V Energy for $1S^f$ Ground State of H_2^f

R/a ₀	<u>closed shell wavefunctions</u>			<u>open shell wavefunction</u>	
	-E ^a	-E ^b	-E ^c (Hoyland)	-E ^d (Hoyland)	-E ^e
1.30		1.13165		1.13201	1.13711
1.35		1.13297		1.13338	1.13817
1.40	1.12777	1.13316	1.13209	1.13361	1.13827
1.45		1.13238		1.13288	1.13708
1.50		1.13078		1.13134	1.13526

a. Equation 3

b. Equation 14

c. Hoyland's closed shell results with integral n values, Ref. 11.

d. SCF energy from Hoyland, Ref. 11

e. Equation 15

f. All numbers are in atomic units.

TABLE VI Parameters for $1S\sigma^-$ Ground State of H_2^f

R/a_0	a^c	b^c	a^d	b^d	a^e	b^e	a'^e	b'^e
1.30			.6703	.6884	.9313	.4691	.6460	.9779
1.35			.6859	.7115	.9500	.4913	.6619	1.0008
1.40	.9865	.7037	.7009	.7345	.9858	.5344	.6561	1.0051
1.45			.7152	.7572	.9829	.5341	.6928	1.0465
1.50			.7290	.7797	.9971	.5549	.7078	1.0692

c. Wavefunction (3)

d. Wavefunction (14)

e. Wavefunction (15)

f. All numbers are in atomic units.

Open shell results

Consider the open shell wavefunction (15). The expression for expectation value of energy is found to be

$$E = \left\{ \int \phi^2 d\tau \int \psi^2 d\tau \cdot E_1 + \int \psi^2 d\tau \int \phi^2 d\tau E_2 + \right. \\ \left. \int \psi_1 \psi_2 \frac{1}{r_{12}} \phi_1 \phi_2 d\tau_1 d\tau_2 + 2 \int \psi H_1 \phi d\tau \cdot \int \psi \phi d\tau + \right. \\ \left. \int \psi_1 \phi_2 \frac{1}{r_{12}} \psi_1 \phi_2 d\tau_1 d\tau_2 \right\} / \left\{ \int \psi^2 d\tau \int \phi^2 d\tau + \left(\int \psi \phi d\tau \right)^2 \right\} \quad (18)$$

where

$$E_1 = \int \psi^* H_1 \psi d\tau / \int \psi \psi d\tau$$

and

$$E_2 = \int \phi^* H_2 \phi d\tau / \int \phi \phi d\tau$$

The energy is computed only for $R = 1.4$, the equilibrium distance and the value of energy, along with optimized variational parameters a, b, a', b' are listed in Table V. and VI.

Consider the simple molecular orbital wavefunction

(19) for H_2 molecule.

$$\psi = \left\{ \psi_a(1) + \psi_b(1) \right\} \left\{ \psi_a(2) + \psi_b(2) \right\} \quad (19)$$

$$\equiv \psi_a(1) \psi_a(2) + \psi_a(1) \psi_b(2) + \psi_b(1) \psi_a(2) + \psi_b(1) \psi_b(2)$$

where

$$\psi_a(1) = \frac{1}{\sqrt{11}} e^{-\alpha a_1} \quad (20)$$

$$\psi_b(1) = \frac{1}{\sqrt{11}} e^{-\alpha b_1} \quad \text{etc.} \quad (21)$$

Hellman²⁴ found the dissociation energy of the ground

state of hydrogen molecule using the above wavefunction (19) to be ~ 2.65 a.u. and the equilibrium internuclear distance to be $R \sim 1.6$ a.u.

It can be seen that these values are not in agreement with the experimental values $D = 4.72 \text{ e.v.}^{12}$ and $R = 1.4 \text{ a.u.}$ The reason of disagreement is due to the presence of ionic terms which corresponds to unstable ionic states in the wavefunction (19). The better representation of the ground state of hydrogen molecule may be obtained by dropping these ionic terms. This leads to the famous function (22) used by Heitler and London.²⁵

$$\psi = \psi_a^{(1)} \psi_b^{(2)} + \psi_b^{(1)} \psi_a^{(2)} \quad (22)$$

The wavefunction (22) leads to dissociation energy 3.14 e.v.^{12} and internuclear distance $R = 1.64$. It can be seen that the value of dissociation energy obtained from Heitler London wavefunction is slightly better than that obtained from molecular orbital wavefunction (19).

Later on the wavefunction (22) was modified by introducing the variational parameter α , that is

$$\psi_a^{(1)} = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha r_{a1}} \quad (23)$$

where α is the variational parameter.

Using the value of $\alpha = 1.17$, the wavefunction (22) gave the value of $D = 3.76 \text{ e.v.}^{26}$

As early as 1933 James and Coolidge introduced a variational correlated wavefunction which was written as a function of elliptical coordinates including the \mathcal{R}_{12} term explicitly. Their thirteen term function gave $R = 1.40$ and $D = 4.698 \text{ e.v.}$ which is in essentially complete agreement

with experiment.

From the Table V it can be seen that the energy calculated from two parameter closed shell wavefunction (14) is better than Hoyland's¹¹ two parameter closed shell wavefunction (24) with integral values of n .

$$\psi = \mu_1^n e^{-a\mu_1} \cosh(b\mu_1) \mu_2^n e^{-a\mu_2} \cosh(b\mu_2) \quad (24)$$

It is also found that the closed shell wavefunction (14) gives better results than closed shell wavefunction of McLean.²²

The open shell wavefunction (15) does not improve the results much better - about .1 e.v. It will be worth mentioning at this stage that McLean²² and Wallis²⁷ also found that their open shell wavefunction improved the hydrogen molecule energy about .08 e.v. over the closed shell wavefunction. This slight improvement is obtained because the open shell wavefunction (15) takes into account partly in-out correlation which is found to be approximately 0.25 e.v. by McLean.²²

It is found by McLean that the greatest improvement in B.E. comes from left-right correlation ($\sim .5$ e.v.). When they take left-right correlation into account, they get a B.E. of 4.0858 e.v. They also find that the angular correlation accounts for about .3 e.v.

It is found that the open shell wavefunction (15) gives better results than McLeans open shell wavefunction, even the closed shell wavefunction (14) gives better results than McLean's open shell wavefunction.

It can be seen from Table V that the closed shell results obtained from wavefunction (14) as well as from closed shell wavefunction of Hoyland are comparable to S.C.F. results obtained by Hoyland.¹¹ This is probably due to the fact that in both cases the effect of correlation is not taken into account. On the other hand, the results obtained from open shell wavefunction (15) are better than the S.C.F. results, as expected.

E. Summary and Conclusions

Let us now conclude this chapter with a brief summary.

In this chapter we have seen that the two parameter closed shell wavefunction (14) involving the term $(1 + \mu^\sigma)$ gives better results than Hoyland's two parameter closed shell wavefunction. It again shows the importance of $(1 + \mu^\sigma)$ over the term μ^n even for two electron problem.

We have also seen the slight improvement in results obtained by open shell wavefunction due to correlation.

This work may be further extended by performing the S.C.F. calculation and by computing the energy for the system HeH^+ . It may also be extended by performing the configuration interaction calculation, in order to take into account the different types of correlation. This will obviously improve the results to a great extent.

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Appendix I

THE BORN-OPPENHEIMER APPROXIMATION

Consider the Schrodinger equation (1) for a system of n electrons and N Nuclei.

$$H\psi = E\psi \quad (1)$$

where ψ is the wavefunction of the system and H is the exact Hamiltonian given by the following equation (2).

$$H = -\sum \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \sum \frac{\hbar^2}{2m} \nabla_i^2 + V_{nn} + V_{ne} + V_{ee} \quad (2)$$

In equation (2) m is the mass of the electron and M_α is the mass of the α^{th} nucleus. V_{nn} is the potential energy due to nuclear interactions whereas V_{ne} and V_{ee} represent contribution to the potential energy due to nuclear-electronic and electronic interactions respectively. The first two terms in equation (2) correspond to the kinetic energy of nuclei and the kinetic energy of the electrons respectively.

If we make the assumption that the nuclei are fixed, the Hamiltonian, H_e , for electrons is given by

$$H_e = -\sum \frac{\hbar^2}{2m} \nabla_i^2 + V_{ne} + V_{ee} \quad (3)$$

If we represent H_n by

$$H_n = -\sum_{\alpha=1}^N \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + V_{nn} \quad (4)$$

we at once get from (2), (3) and (4)

$$H = H_e + H_n \quad (5)$$

In order to solve the Schrodinger equation (1), the wavefunction, ψ , is approximated by a simple product of an electronic wavefunction and an nuclear wavefunction ψ_n .

$$\psi = \psi_e \cdot \psi_n \quad (6)$$

In equation (6) ψ_e is the electronic wavefunction which is the eigen function of H_e so that

$$H_e \psi_e = E_e \psi_e \quad (7)$$

and ψ_n is the nuclear wavefunction, which is a function of nuclear coordinates only.

Equation (6) is known as Born-Oppenheimer Approximation.¹

From equations (1), (2) and (6)

$$\left\{ -\sum_{\alpha=1}^N \left(\frac{\hbar^2}{2M_\alpha} \right) \nabla_\alpha^2 - \sum_{i=1}^n \left(\frac{\hbar^2}{2m} \right) \nabla_i^2 \right\} \psi_e \psi_n + (V_{nn} + V_{ne} + V_{ee}) \psi_e \psi_n = E \psi_e \psi_n \quad (8)$$

It can be easily shown that

$$\begin{aligned} \nabla_\alpha^2 \psi_e \psi_n &= \nabla_\alpha \nabla_\alpha (\psi_e \psi_n) = \psi_n \nabla_\alpha^2 \psi_e + \\ &+ 2 \overrightarrow{\nabla_\alpha \psi_e} \cdot \overrightarrow{\nabla_\alpha \psi_n} + \psi_e \nabla_\alpha^2 \psi_n \end{aligned} \quad (9)$$

and

$$\nabla_i^2 \psi_e \psi_n = \psi_n \nabla_i^2 \psi_e \quad (10)$$

From equations (8), (9) and (10)

$$\left\{ -\sum_{\alpha=1}^N \left(\frac{\hbar^2}{M_{\alpha}} \right) \nabla_{\alpha}^2 \psi_e \cdot \nabla_{\alpha}^2 \psi_n - \sum_{\alpha=1}^N \left(\frac{\hbar^2}{2M_{\alpha}} \right) \psi_n \nabla_{\alpha}^2 \psi_e \right\} +$$

$$\psi_e \sum_{\alpha=1}^N -\frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 \psi_n + \psi_n \sum_{i=1}^n -\frac{\hbar^2}{2m} \nabla_i^2 \psi_e +$$

$$(V_{nn} + V_{ne} + V_{ee}) \psi_e \psi_n = E \psi_e \psi_n \quad (11)$$

If we neglect the terms in bracket $\left\{ \right\}$, we get

$$\psi_e \sum_{\alpha=1}^N -\frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 \psi_n + \left[\sum_{i=1}^n -\frac{\hbar^2}{2m} \nabla_i^2 \psi_e + \right.$$

$$\left. (V_{ne} + V_{ee}) \psi_{ee} \right] \psi_n = E \psi_n \psi_e - V_{nn} \psi_e \psi_n \quad (12)$$

From equations (3), (7) and (12) it follows that

$$(H_n + E_e) \psi_n = E \psi_n. \quad (13)$$

It should be noted that equation (13) which is a Schrodinger equation for ψ_n is obtained by neglecting the terms in the bracket of equation (11) which represents a coupling of the electronic and nuclear motion.

From the above discussion, it is clear that Born-Oppenheimer Approximation is valid only if the terms in the bracket of equation (11) which are neglected, are small compared to the smallest term outside the bracket, that is,

$$-\sum_{\alpha=1}^N \left(\frac{\hbar^2}{2M_{\alpha}} \right) \psi_e \nabla_{\alpha}^2 \psi_n.$$

This term represents the kinetic energy of the nuclei.

Since $\nabla_d \psi_e$ is usually very small as compared to $\nabla_n \psi_n$, because ψ_e is only a slowly varying function of the nuclear coordinates, the Born-Oppenheimer Approximation is usually valid.

Appendix II

COMPUTATION OF H_2^+ ENERGY FOR $1S\sigma$ STATE

The expectation value of the energy E , for H_2^+ is given by the following expression (1)

$$E = \frac{\int d\tau \psi H \psi}{\int d\tau \psi^2} \quad (1)$$

In the above expression the wavefunction is

$$\psi = (1+\mu)^\sigma e^{-a\mu} \cosh(b\tau) \quad (2)$$

$$\text{having } \sigma = R/a - 1 \quad (3)$$

The hamiltonian is

$$H = -\frac{2}{R^2(\mu^2 - \tau^2)} \left\{ \frac{\partial}{\partial \mu} (\mu^2 - 1) \frac{\partial}{\partial \mu} + \frac{\partial}{\partial \tau} (1 - \tau^2) \frac{\partial}{\partial \tau} + 2R\mu \right\} \quad (4)$$

$$\text{and } \int d\tau = 2\pi \int_{-1}^{+1} d\tau \int_1^\infty d\mu \frac{R^3}{8} (\mu^2 - \tau^2) \quad (5)$$

From the equations (1) - (5), it can be shown that

$$E = -\frac{2}{R^2} \left[\left\{ \int_1^\infty d\mu (1+\mu)^{2\sigma} e^{-2a\mu} \left(\sigma - 2a\mu + \frac{\sigma^2(\mu-1)}{(1+\mu)} - 2a\mu\sigma + 2a\sigma + a^2\mu^2 - a^2 + 2R\mu \right) \int_{-1}^{+1} d\tau \cosh^2(b\tau) \right\} + \right.$$

$$\begin{aligned}
& \left[\frac{2}{b} \int_1^{\infty} d\mu (1+\mu)^{2\sigma} e^{-2a\mu} \int_{-1}^{+1} d\vartheta (1-\vartheta^2) \cosh^2(b\vartheta) - \right. \\
& \left. 2b \int_1^{\infty} d\mu (1+\mu)^{2\sigma} e^{-2a\mu} \int_{-1}^{+1} d\vartheta \vartheta \sinh(b\vartheta) \cosh(b\vartheta) \right] / \\
& \left\{ \int_{-1}^{+1} d\vartheta \vartheta^2 \cosh^2(b\vartheta) \int_1^{\infty} d\mu e^{-2a\mu} (1+\mu)^{2\sigma} - \int_{-1}^{+1} d\vartheta \cosh^2(b\vartheta) \int_1^{\infty} d\mu \mu^2 e^{-2a\mu} (1+\mu)^{2\sigma} \right\} \\
& \text{or} \tag{6}
\end{aligned}$$

$$\begin{aligned}
E = & \text{HCOF}(1) * \text{SUM}(1) + \text{HCOF}(2) * \text{SUM}(2) \\
& + \text{HCOF}(3) * \text{SUM}(3) + \text{HCOF}(4) * \text{SUM}(4) \\
& + \text{HCOF}(5) * \text{SUM}(5) / [\text{SCOF}(1) * \text{SUM}(1) + \text{SCOF}(2) * \text{SUM}(5)] \tag{7}
\end{aligned}$$

In the above equation

$$\text{HCOF}(1) = (\sigma + 2a\sigma + b^2 - a^2) \text{BNU}(1) - b^2 * \text{BNU}(2) - 2b * \text{BNU}(3)$$

$$\text{HCOF}(2) = 2(R - a - a\sigma) * \text{BNU}(1)$$

$$\text{HCOF}(3) = \sigma^2 * \text{BNU}(1)$$

$$\text{HCOF}(4) = -\sigma^2 * \text{BNU}(1)$$

$$\text{HCOF}(5) = a^2 * \text{BNU}(1)$$

$$\text{SCOF}(1) = \text{BNU}(2)$$

$$\text{SCOF}(2) = -\text{BNU}(1)$$

$$\text{BNU}(1) = \int_{-1}^{+1} d\vartheta \cosh^2(b\vartheta) = \frac{\sinh(2b)}{2b}$$

$$\text{BNU}(2) = \int_{-1}^{+1} d\vartheta \vartheta^2 \cosh^2(b\vartheta)$$

$$= \frac{1}{3} + \frac{1}{2b^3} \left\{ \left(b^2 + \frac{1}{2}\right) \sinh(2b) - b \cosh(2b) \right\}$$

$$\begin{aligned}
\text{BNU}(3) &= \int_{-1}^{+1} d\vartheta \, \vartheta \sinh(b\vartheta) \cosh(b\vartheta) \\
&= \frac{1}{2b^2} \left\{ b \cosh(2b) - \frac{1}{2} \sinh(2b) \right\} \\
\text{SUM}(1) &= \int_1^{\infty} d\mu (1+\mu)^{2\sigma} e^{-2a\mu} \\
\text{SUM}(2) &= \int_1^{\infty} d\mu \mu (1+\mu)^{2\sigma} e^{-2a\mu} \\
\text{SUM}(3) &= \int_1^{\infty} d\mu (1+\mu)^{2\sigma-1} \mu e^{-2a\mu} \\
\text{SUM}(4) &= \int_1^{\infty} d\mu (1+\mu)^{2\sigma-1} e^{-2a\mu} \\
\text{SUM}(5) &= \int_1^{\infty} d\mu \mu^2 (1+\mu)^{2\sigma} e^{-2a\mu}
\end{aligned}$$

For computing energy of H_2^+ all angular integrals are calculated analytically as indicated. The radial integrals involved are of the following general form

$$I = \int_1^{\infty} \mu^m e^{-2a\mu} (1+\mu)^b d\mu$$

where b and a are non integers and m is an integer. Because this type of integral can not be evaluated analytically, all radial integrals are evaluated numerically in double precision using a Gaussian quadrature (Appendix III). Since μ varies from one to infinity, the technique of mapping an arbitrary range into $(-1, 1)$ with a side condition involving the use of Gauss-Legendre is used.²

Normally we used 32 points of Gaussian Quadrature data, but to verify the accuracy of the integrals, a few of the integrals were computed by 50 points of Gaussian Quadrature data. They were found to be in complete agreement. Thus all radial integrals calculated numerically are expected to be correct at least up to nine significant figures.

Since the variables are separable in H_2^+ problem, and since Rothstein's³ as well as our wavefunction had the same angular dependence, the value of the parameter b will be the same in both cases. So while computing the variational energy we took the optimized values of b for different values of R and calculated energy as a function of a , b and R . While computing the energy for the wavefunction having different angular dependent term than $\cosh(b\sigma)$, the variational parameter " b " is varied independently. The same procedure is used for computing the energy for the wavefunction having σ as a function of a and b .

To minimize the energy by varying the parameters for the given value of R , the function minimization program, No. 60 of Quantum Chemistry program exchange (Indiana University) is used.

We expect the value of the variational parameters to be correct up to at least four significant figures and the value of energy to be correct to at least seven significant figures.

Appendix III

GAUSSIAN QUADRATURE INTEGRATION

In this appendix we outline briefly the principle of Gauss's Quadrature formula which is used for numerical integration of radial integrals.

If we want to evaluate the definite integral $\int_a^b f(x) dx$ from a given number of values of $f(x)$ we have to see where these values should be taken in order to get the maximum possible accuracy. It is found that the points in interval (a, b) should not be equidistant, but they are symmetrically placed with respect to midpoint of the interval of integration.

According to Gaussian quadrature formula⁴

$$\int_a^b f(x) dx \simeq \sum_{i=1}^n A_i f(x_i).$$

where x_i are called the points of the formula and the A_i are called coefficients or weights.

Quadrature formula is said to have degree of precision m if it is exact whenever $f(x)$ is a polynomial of degree $\leq m$ and it is not exact for $f(x) = x^{m+1}$. It can be shown that⁴ if $f(x)$ is a polynomial of degree not higher than $(2n - 1)$, then x_1, x_2, \dots, x_n are the zeros of the orthogonal polynomials in (a, b) . The value of the coefficients A_i are determined by the integration of these polynomials.

Appendix IV

COMPUTATION OF H_2 ENERGY FOR $1S\sigma$ STATE

In this appendix we describe the calculation of variational energy for H_2 molecule closed shell wavefunction. We also describe the computation which mainly involves the evaluation of the Coulomb Integral.

The expectation value of the energy E is given by expression (1)

$$E = \int \psi H \psi d\tau / \int \psi^2 d\tau \quad (1)$$

In the above equation the closed shell wavefunction is

$$\psi = \phi_1 \phi_2 \quad (2)$$

where

$$\phi = (1+\mu)^\sigma e^{-a\mu} \cosh(b\mu) \quad (3)$$

and

$$\sigma = R/a - 1 \quad (4)$$

The hamiltonian H for H_2 molecule is

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}} + \frac{1}{R} \quad (5)$$

The value of E is then found to be

$$E = 2E_{H_2^+} + \frac{\int \phi_1 \phi_2 \frac{1}{r_{12}} \phi_1 \phi_2 d\tau_1 d\tau_2}{\int \phi_1^2 \phi_2^2 d\tau_1 d\tau_2} \quad (6)$$

where $E_{H_2^+}$ is the hydrogen molecular ion energy.

A. Computation of the Coulomb Integral

In the energy expression (6) the value of $E_{H_2^+}$ (hydrogen molecular ion energy) is computed as described in the previous appendix on H_2^+ .

For evaluating the Coulomb integral

$\int \psi_1 \psi_2 \frac{1}{r_{12}} \psi_1 \psi_2 d\tau_1 d\tau_2$ the following Neumann expansion in spheroidal coordinates⁵ is used.

$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{k=0}^{\infty} \sum_{m=-k}^k (-1)^m (2k+1) \left\{ \frac{(k-|m|!)}{(k+|m|!)} \right\}^2$$

$$P_k^{|m|}(\mu_<) Q_k^{|m|}(\mu_>) P_k^{|m|}(\nu_1) P_k^{|m|}(\nu_2) e^{im(\phi_1 - \phi_2)} \quad (7)$$

where μ_1, ν_1, ϕ_1 and μ_2, ν_2, ϕ_2 are the coordinates of the two electrons and $\mu_<$ is the lesser of μ_1 and μ_2 and $\mu_>$ is the greater of μ_1 and μ_2 . The $P_k^{|m|}$'s are the associated Legendre functions whereas $Q_k^{|m|}$'s are the associated Legendre functions of the second kind.

Finally the calculation of the above Coulomb integral requires the following two general kinds of radial double integrals

$$\int_1^{\infty} d\mu_1 e^{-2a\mu_1} (1+\mu_1)^{2\sigma} \mu_1^n Q_k(\mu_1) \int_1^{\mu_1} d\mu_2 e^{-2a\mu_2} (1+\mu_2)^{2\sigma} \mu_2^m P_k(\mu_2) \quad (8)$$

$$\int_1^{\infty} d\mu_1 e^{-2a\mu_1} (1+\mu_1)^{2\sigma} \mu_1^n P_k(\mu_1) \int_{\mu_1}^{\infty} d\mu_2 e^{-2a\mu_2} (1+\mu_2)^{2\sigma} \mu_2^m Q_k(\mu_2) \quad (9)$$

The above double integrals involve two variables μ_1 and μ_2 in which μ_1 is an independent variable and it varies from 1 to infinity, whereas μ_2 varies from 1 to μ_1 . In order to evaluate this integral we have to evaluate

$$\int_1^{\infty} d\mu_1 e^{-2\sigma\mu_1} (1+\mu_1)^{2\sigma} \mu_1^n Q_K(\mu_1)$$

and for each value of μ_1 , we have to evaluate

$$\int_1^{\mu_1} d\mu_2 e^{-2\sigma\mu_2} (1+\mu_2)^{2\sigma} \mu_2^m P_K(\mu_2)$$

This double integral is evaluated by numerical integration. From the above discussion it is clear that for the evaluation of integral (8) we have to make use of a second DO loop within a DO loop. The second DO loop evaluates the integral $\int_1^{\mu_1} d\mu_2 f(\mu_2)$ numerically for the given value of μ_1 . Now in the first DO loop we vary μ_1 by making use of Gaussian Quadrature data, and we evaluate the $f(\mu_1)$ and $\int_1^{\mu_1} f(\mu_2) d\mu_2$ for the given value of μ_1 . Finally we sum over all values of μ_1 . The exact listing of this procedure may be seen under the heading "Start of radial integration" in Subroutine R1 COUL or R2 COUL (Appendix V).

In the Neumann expansion it can be seen that K varies from 0 to infinity, while it is found that significant contribution to Coulomb integral comes only from small values of K . In order to save some computation time, we computed energy using $K = 0, 2$ and 4 and minimized E by

varying the variational parameters. Once nearly optimal parameters are obtained the energy is computed using $K = 0$ to 8 (even K), and it is minimized again.

To evaluate the Coulomb integral we also have to evaluate angular integrals of the form $\int_0^1 P_K(\vartheta) \vartheta^n d\vartheta$, where n is an integer.

A separate subroutine FINDA is written to evaluate this integral. Although this integral can be evaluated analytically for the given value of K and n , since K changes from 0 to 8 the number of integrals to be evaluated is very large. Hence the method of numerical integration using Gaussian Quadrature data is used.

In order to generate $P_K(X)$ and $Q_K(X)$, a separate subroutine, XLEGRE, is written and the listing of the subroutine may be seen in complete open shell listing. (Appendix V).

B. Open-Shell Computation

The energy expression for the open shell wavefunction is given in Chapter III, equation (18).

This requires modification of the closed-shell computer program by requiring the subroutine FIHPSI and OVR LAP. The former evaluates $\int \phi H \psi d\tau$, where

$$\psi = (1+\mu)^{\sigma} e^{-a\mu} \cosh(b\vartheta)$$

$$\phi = (1+\mu)^{\sigma'} e^{-a'\mu} \cosh(b'\vartheta)$$

The latter evaluates the overlap integral, $\int \psi \phi d\tau$,
for the given value of the parameters.

Otherwise the open-shell calculation is the same
as the closed shell calculation.

APPENDIX V

Listing of Open Shell H_2 Program and Computer Time.

All calculations were carried out on the Brock University B5500 computer.

The computer time required to optimize the four parameter open shell wavefunction for H_2 was 90 min. for a single value of R.

Single precision is used throughout except for some sub-routines which required extended precision.

The above figure should give the reader a feeling for the amount of computer time required for the other calculations described in the thesis.

LABEL 000000000F0RTRAN00171215?USER#####;COMPILE H2PAR22/CSGUPTA

B 5 5 0 0 F O R T R A N C O M P I L A T I O N XII. 3,

```

FILE 5=CARD,UNIT = READER
FILE 6=PRFILE,UNIT = PRINTER
C THIS PROGRAM STUDIES H2 WITH
C.....PST=(1+MU)**SIGMA*EXP(-A*MU)COSH(B*NU)
C WHERE A,B ARE VARIATIONAL PARAMETERS
C.....
C..... START OF SEGMENT ***** 1
COMMON W
COMMON /S/RM,T,U, R, NO2
COMMON /G/ IFLAG
DIMENSION X(5),E(5),W(40),T(30),U(30)
NRD= 5
NWT= 6
READ (NRD,2) NO2, RM
2 FORMAT (I3, F5.1)
C.....2*NO2 IS THE GAUSSIAN INTEGRATION GRID SIZE
C RM IS THE WEIGHTING FACTOR IN THE MC LEAN AND YOSHIMINE SECTION
C..... (SEE T.B.M. JOURNAL, MAY 1965,P203).
READ(NRD,3) (T(I), U(I),I=1,NO2)
3 FORMAT (1X, F20.17, F20.17)
WRITE (NWT,133)
133 FORMAT (1H1, 30X, "GAUSSIAN QUADRATURE DATA")
WRITE(NWT,134)(I,T(I), I=1,NO2 )
134 FORMAT (1H , 2HT(, I4,2H)=, E14.8)
WRITE(NWT,135)(I,U(I), I=1,NO2 )
135 FORMAT (1H , 2HU(, I4,2H)=, E14.8)
WRITE(NWT,1)
1 FORMAT(1H0,30X,"VARIATIONAL CALCULATION ON H2 MOLECULE ")
WRITE(NWT,131) NO2,RM
131 FORMAT( 1H ,47X, "GRID SIZE IS 2*", I3, "-- RM= ",D14.8)
WRITE (6,208)
208 FORMAT(1H ,30X," RQ= 1 + (MU1-1)/3 AND RP = 3*MU1/2")
READ (NRD,5) NR
5 FORMAT (I5)
C NR IS THE NUMBER OF R VALUES REQUIRED
C ICNT IS THE NUMBER OF R VALUES TAKEN
ICNT=0
READ (NRD,205) ESCALE,IPRINT,ICON, MAXIT
205 FORMAT (E10.4, 3I5)
100 CONTINUE
READ (NRD,4) N,R, EXACT
4 FORMAT (I3,2X, (F10.6,5X), F17.11)
READ (NRD,207) (X(I),E(I),I=1,N)
207 FORMAT (2E20.4)
C.....X(1)=A
C.....X(2)=B
WRITE(NWT,202) R, EXACT
202 FORMAT (1H0,30X,22H*****FOR THIS CYCLE R=,D8.2,
1EXACT=,E17.11, 5H***** )
WRITE(NWT,203)
203 FORMAT (1H0,12X,1HA,23X,1HB,23X,8HH2ENERGY,23X,4HCOUL)
IFLAG =0
103 CONTINUE
CALL VA04A (X,E,N,ENCAL,ESCALE,IPRINT, ICON,MAXIT)
WRITE (NWT,201) R,EXACT, ENCAL
201 FORMAT (2024,14, E24,14)

```

```

104 CONTINUE
    WRITE (NWT,206)  X(1),X(2)
206  FORMAT (140,"A(OPTIMAL)=",D24.14,"B(OPTIMAL)=",D24.14)
    WRITE (NWT,209)  X(3),X(4)
209  FORMAT (140,"AP(OPTIMAL)=",D24.14,"BP(OPTIMAL)=",D24.14)
    ICNT= ICNT+1
    IF (ICNT-NR) 100,101,101
101 CONTINUE
    STOP
    END

```

SEGMENT 1 IS 295 LONG

START OF SEGMENT ***** 2

```

SUBROUTINE VA04A (X,E,N,F,ESCALE,IPRINT,ICON,MAXIT)
C .....
C
C   THIS IS PROGRAM = 60 FROM Q.C.P.E.
C
C   THIS SUBROUTINE FINDS THE MINIMUM OF A FUNCTION OF SEVERAL
C   VARIABLES
C
C   THE METHOD USED IS M.J.D. POWELL, COMPUTER JOURNAL 7,303(JAN. 1965)
C
C   THE ARGUMENT LIST IS "
C       N THE NUMBER OF VARIABLES
C       X AND E ARE ONE-DIMENSIONAL ARRAYS. ON ENTRY TO THE
C           SUBROUTINE X(I) MUST BE SET TO AN APPROXIMATION TO
C           THE I-TH VARIABLE AND E(I) TO THE ABSOLUTE VALUE
C           ACCURACY TO WHICH ITS OPTIMUM VALUE IS REQUIRED.
C           ON EXIT X(I) WILL BE SET TO THE CALCULATED OPTIMUM
C           VALUE OF THE I-TH VARIABLE.
C       F WILL BE SET TO THE MINIMUM VALUE OF THE FUNCTION
C       ESCALE LIMITS THE MAXIMUM CHANGE IN THE VARIABLES AT A
C           SINGLE STEP. X(I) WILL NOT BE CHANGED BY MORE THAN
C           ESCALE*E(I)
C       IPRINT CONTROLS PRINTING. IF IT IS SET TO ZERO THERE WILL
C           BE NO PRINTING. IF IT IS EQUAL TO ONE THE VARIABLES
C           AND THE FUNCTION WILL BE PRINTED AFTER EVERY OTHER
C           FUNCTION VALUE. SET TO TWO THEY WILL BE PRINTED AFTER
C           EVERY ITERATION.
C       ICON MUST BE SET TO 1 OR 2 DEPENDING ON CONVERGENCE CRIT.
C
C   SUBROUTINES REQUIRED" CALCFX
C .....
C   COMMON W
C   DIMENSION X(5),E(5),W(40)
C   DOUBLE PRECISION F,ESCALE,SCER,FHOLD,FKEEP,FPREV,DL,SUM,FA,FB,FC
C   DOUBLE PRECISION FP,FI,DMAX,DDMAX,DMAG,DDMAG,DACC,DA,DB,DC,DD,DI
C   DOUBLE PRECISION A,AAA,B,D
C   NWT= 6
C   DDMAG=0.1*ESCALE
C   SCER=0.05/ESCALE
C   JJ=N*N+N
C   JJJ=JJ+N
C   K=N+1
C   NFCC=1
C   IND=1

```

```

      INN=1
      DO 1 I=1,N
      DO 2 J=1,N
      W(K)=0.
      IF(I-J)4,3,4
C   3 W(K)=ABSF(F(I))
      3 W(K)= ABS(F(I))
      W(I)=ESCALE
      4 K=K+1
      2 CONTINUE
      1 CONTINUE
      ITERC=1
      ISGRAD=2
      CALL CALCFX(N,X,F)
C   FKEEP=ABSF(F)+ABSF(F)
      FKEEP= ABS(F) + ABS(F)
      5 ITONE=1
      FP=F
      SUM=0.
      IXP=JJ
      DO 6 I=1,N
      IXP=IXP+1
      W(IXP)=X(I)
      6 CONTINUE
      IDIRN=N+1
      ILINE=1
      7 DMAX=W(ILINE)
      DACC=DMAX*SCER
C   DMAG=MIN1F (DDMAG,0.1*DMAX)
      DMAG=AMIN1(DDMAG,0.1*DMAX)
C   DMAG=MAX1F(DMAG,20.*DACC)
      DMAG=AMAX1(DMAG,20.*DACC)
      DDMAX=10.*DMAG
      GO TO (70,70,71),ITONE
      70 DL=0.
      D = DMAG
      FPREV=F
      IS=5
      FA=F
      DA=DL
      8 DD=D-DL
      DL=D
      58 K=IDIRN
      DO 9 I=1,N
      X(I)=X(I)+DD*W(K)
      K=K+1
      9 CONTINUE
      CALL CALCFX(N,X,F)
      NFCC=NFCC+1
      GO TO (10,11,12,13,14,96),IS
      14 IF(F-FA)15,16,24
C   16 IF (ABSF(D)-DMAX) 17,17,18
      16 IF ( ABS(D)-DMAX) 17,17,18
      17 D=D+D
      GO TO 8
C   18 PRINT 19
      18 WRITE (NWT,19)
      19 FORMAT(5X,44HVA04A MAXIMUM CHANGE DOES NOT ALTER FUNCTION)
      GO TO 20

```

```

15 FB=F
   DB=D
   GO TO 21
24 FB=FA
   DB=DA
   FA=F
   DA=D
21 GO TO (83,23),ISGRAD
23 D=DB+DB-DA
   IS=1
   GO TO 8
83 D=0.5*(DA+DB-(FA-FB)/(DA-DB))
   IS=4
   IF((DA-D)*(D-DB))25,8,8
25 IS=1
C   IF(ABS(F-D-DB)-DDMAX)8,8,26
   IF(ABS(D-DB)-DDMAX)8,8,26
C 26 D=DB+SIGNF(DDMAX,DB-DA)
26 D=DB+ SIGN(DDMAX,DB-DA)
   IS=1
   DDMAX=DDMAX+DDMAX
   DDMAG=DDMAG+DDMAG
   IF(DDMAX=DDMAX)8,8,27
27 DDMAX=DDMAX
   GO TO 8
13 IF(F-FA)28,23,23
28 FC=FB
   DC=DB
29 FB=F
   DB=D
   GO TO 30
12 IF(F-FB)28,28,31
31 FA=F
   DA=D
   GO TO 30
11 IF(F-FB)32,10,10
32 FA=FB
   DA=DB
   GO TO 29
71 DL=1.
   DDMAX=5.
   FA=FP
   DA=-1.
   FB=FHOLD
   DB=0.
   D=1.
10 FC=F
   DC=D
30 A=(DB-DC)*(FA-FC)
   B=(DC-DA)*(FB-FC)
   IF((A+B)*(DA-DC))33,33,34
33 FA=FB
   DA=DB
   FB=FC
   DB=DC
   GO TO 26
34 D=0.5*(A*(DB+DC)+B*(DA+DC))/(A+B)
   DI=DB
   FI=FB
   IF(FB-FC)44,44,43

```

```

43 DI=DC
   FI=FC
44 GO TO (86,86,85),ITONE
85 ITONE=2
   GO TO 45
C 86 IF (ABS(D-DI)-DACC) 41,41,93
   86 IF (ABS(D-DI)-DACC) 41,41,93
C 93 IF (ABS(D-DI)-0.03*ABS(D)) 41,41,45
   93 IF (ABS(D-DI)-0.03*ABS(D)) 41,41,45
45 IF ((DA-DC)*(DC-D)) 47,46,46
46 FA=FB
   DA=DB
   FB=FC
   DB=DC
   GO TO 25

47 IS=2
   IF ((DB-D)*(D-DC)) 48,8,8
48 IS=3
   GO TO 8

41 F=FI
   D=DI-DL
C DD=SQRT((DC-DB)*(DC-DA)*(DA-DB)/(A+B))
   DD=SQRT((DC-DB)*(DC-DA)*(DA-DB)/(A+B))
   DO 49 I=1,N
   X(I)=X(I)+D*W(IDIRN)
   W(IDIRN)=DD*W(IDIRN)
   IDIRN=IDIRN+1

49 CONTINUE
   W(ILINE)=W(ILINE)/DD
   ILINE=ILINE+1
   IF(IPRINT-1)51,50,51
C 50 PRINT 52,ITERC,NFCC,F,(X(I),I=1,N)
   50 WRITE(NWT,52) ITERC,NFCC,F,(X(I),I=1,N)
52 FORMAT (/1X,9HITERATION,I5,I15,16H FUNCTION VALUES,
110X,3HF =,F21.14/(5E24.14))
   GO TO(51,53),IPRINT

51 GO TO (55,38),ITONE
55 IF (FPREV-F-SUM) 94,95,95
95 SUM=FPREV-F
   JIL=ILINE
94 IF (IDIRN-JJ) 7,7,84
84 GO TO (92,72),IND

92 FHOLD=F
   IS=6
   IXP=JJ
   DO 59 I=1,N
   IXP=IXP+1
   W(IXP)=X(I)-W(IXP)

59 CONTINUE
   DD=1.
   GO TO 58

96 GO TO (112,87),IND
C 112 IF (FP-F) 37,91,91
   112 IF (FP-F) 37,37,91
91 D=2.*(FP+F-2.*FHOLD)/(FP-F)**2
   IF (D*(FP-FHOLD-SUM)**2-SUM) 87,37,37
87 J=JIL*N+1
   IF (J-JJ) 60,60,61
60 DO 62 I=J,JJ
   K=I-N

```

```

      W(K)=W(I)
62  CONTINUE
      DO 97 I=JIL,N
      W(I-1)=W(I)
97  CONTINUE
61  IDIRN=IDIRN-N

```

```

      ITONE=3
      K=IDIRN
      IXP=JJ
      AAA=0.
      DO 65 I=1,N
      IXP=IXP+1

```

```

      W(K)=W(IXP)
C    IF (AAA=ABSF(W(K)/E(I))) 66,67,67
      IF (AAA=ABS(W(K)/E(I))) 66,67,67

```

```

C 66 AAA=ABSF(W(K)/E(I))
66 AAA=ABS(W(K)/E(I))
67 K=K+1

```

```

65 CONTINUE
      DD MAG=1.
      W(N)=ESCALE/AAA
      TLINE=N
      GO TO 7

```

```

37 IXP=JJ

```

```

      AAA=0.
      F=FHOLD
      DO 99 I=1,N
      IXP=IXP+1

```

```

      X(I)=X(I)-W(IXP)
C    IF (AAA*ABSF(E(I))-ABSF(W(IXP))) 98,99,99
      IF (AAA*ABS(E(I))-ABS(W(IXP))) 98,99,99

```

```

C 98 AAA=ABSF(W(IXP)/E(I))
98 AAA=ABS(W(IXP)/E(I))

```

```

99 CONTINUE
      GO TO 72

```

```

38 AAA=AAA*(1.+DI)

```

```

      GO TO (72,106),IND

```

```

72 IF (IPRINT=2) 53,50,50

```

```

53 GO TO (109,88),IND

```

```

109 IF (AAA=0.1) 89,89,76

```

```

89 GO TO (20,116),ICON

```

```

116 IND=2

```

```

      GO TO (100,101),INN

```

```

100 INN=2

```

```

      K=JJJ

```

```

      DO 102 I=1,N

```

```

      K=K+1

```

```

      W(K)=X(I)

```

```

      X(I)=X(I)+10.*E(I)

```

```

102 CONTINUE

```

```

      FKEEP=F

```

```

      CALL CALCFX (N,X,F)

```

```

      NFCC=NFCC+1

```

```

      DD MAG=0.

```

```

      GO TO 108

```

```

76 IF (F=FP) 35,78,78

```

```

C 78 PRINT 80

```

```

78 WRITE(NWT,80)

```

```

80 FORMAT (5X,37HVA04A ACCURACY LIMITED BY ERRORS IN F)

```

```

      GO TO 20

```

```

      88 IND=1
C     35 DD MAG=0.4*SQRT(FP-F)
      35 DD MAG= .4* SQRT(FP-F)
          ISGRAD=1
      108 ITERC=ITERC+1
          IF (ITERC=MAXIT) 5,5,81
C     81 PRINT 82,MAXIT
      81 WRITE(NWT,82) MAXIT
      82 FORMAT(15,30H ITERATIONS COMPLETED BY VA04A)
          IF (F=FKEEP) 20,20,110
      110 F=FKEEP
          DO 111 I=1,N
              JJJ=JJJ+1
              X(I)=W(JJJ)
      111 CONTINUE
          GO TO 20
      101 JTL=1
          FP=FKEEP
          IF (F=FKEEP) 105,79,104
      104 JTL=2
          FP=F
          F=FKEEP
      105 IXP=JJ
          DO 113 I=1,N
              IXP=IXP+1
              K=IXP+N
              GO TO (114,115),JTL
      114 W(IXP)=W(K)
          GO TO 113
      115 W(IXP)=X(I)
          X(I)=W(K)
      113 CONTINUE
          JTL=2
          GO TO 92
      106 IF (AAA=0.1) 20,20,107
      20 RETURN
      107 INN=1
          GO TO 35
          END

```

START OF SEGMENT ***** 4

SUBROUTINE CALCFX (N,RX,F)

```

C
C.....
C     THIS SUBROUTINE EVALUATES ENCAL FOR SUBROUTINE VA04A
C
C     ARGUMENT LIST"
C         N IS THE NUMBER OF VARIATIONAL PARAMETERS
C         RX IS THE ARRAY OF VARIATIONAL PARAMETER VALUES
C         ENCAL IS THE RETURNED VALUE OF THE FUNCTION
C
C     SUBROUTINE REQUIRED NONE"
C
C.....
COMMON /S/RM,T,U,      R,  N02
DIMENSION RX(5),T(30),U(30)
NWT =6

```

```

PI=3.14159265
R=RX(1)
BP =RX(2)
A=RX(3)
AP =RX(4)
CALL OVRLAP (A,B,A,B,PSI PSI,0)
CALL OVRLAP (AP,BP,AP,BP,FI FI,0)
CALL FIHPSI (A,B,AP,BP, RIHPSI,PSI FI)
CALL R1COUL (A,B,AP,BP,PF1212)
CALL EH2P (A,B,ENCL1)
CALL EH2P (AP,BP, ENCL2)
CALL R2COUL (A,B,AP,BP,PF1122)
F=((ENCL1*PSI PSI*FI FI)+(ENCL2*PSI PSI*FI FI)+(PF1212)+
1(PSI FI*RIHPSI)+(PSI FI*RIHPSI)+(PF1122))/
2((PSI PSI*FI FI)+((PSI FI)*(PSI FI)))+1./R
WRITE (NWT,202) F,PF1212
202 FORMAT (1H ,"H2 ENERGY= ",E24.14,"COUL INTEGRAL=",E24.14)
WRITE (NWT,700) RX(1),RX(2),RX(3),RX(4)
700 FORMAT (1H ,4(E24.14))
RETURN
END

```

SEGMENT 4 IS 83 LONG

START OF SEGMENT ***** 5

```

SUBROUTINE EH2P (A,B,ENCL)
COMMON /S/RM,T,U, R, N02
DIMENSION RX(5),SUM(30), SCOF(10),BNU(3),T(30),U(30),HCOF(10),
1TERM(10)
NWT =6
PI=3.14159265
B2=B*B
B3=B*B2
C.....THESE ARE THE NU INTEGRALS.....
C      BNU(1) = INTEGRAL OF COSH(B*R*NU/2)COSH(B*R*NU/2)
C      BNU(2) = INTEGRAL OF COSH(B*R*NU/2)COSH(B*R*NU/2)NU2
C      BNU(3) = INTEGRAL OF COSH(B*R*NU/2)SINH(B*R*NU/2)NU
C
COSH2= .5E0*( FXP(2.E0*B) + EXP(-2.E0*B) )
SINH2= .5E0*( EXP(2.E0*B) - EXP(-2.E0*B) )
BNU(1)=(SINH2 + 2.E0*B)/(2.E0*B)
BNU(2)=(1.E0/3.E0)+.5E0*(1.E0/B3)*( (B2+.5E0)*SINH2 - B*COSH2)
BNU(3)= .5E0*(1.E0/B2)*( B*COSH2 -.5E0*SINH2)
SINH3 = (EXP(B)-EXP(-B))/2.
COSH3 = (EXP(B)+EXP(-B))/2.
SIGMA = 2.*(-R+A +B*SINH3/COSH3)
HCOF(1)= (SIGMA+2.E0*A*SIGMA+B2-A*A)*BNU(1)-B2*BNU(2)-2.E0*B*BNU(
13)
HCOF(2)=(2.E0*R-2.E0*A-2.E0*A*SIGMA)*BNU(1)
HCOF(3)= SIGMA*SIGMA*BNU(1)
HCOF(4)=-SIGMA*SIGMA*BNU(1)
HCOF(5)= A*A*BNU(1)
SCOF(1)= BNU(2)
SCOF(2)=-BNU(1)
C      START THE MC LEAN AND YOSHIMINE SECTION
C      THIS ZEROS THE INTEGRAL SUMS
N0=1
SUM(1)=0.
SUM(2)=0.

```

```

SUM(3)=0.
SUM(4)=0.
SUM(5)=0.
10 CONTINUE
DO 7 I=1,N02
TI=T(I)
W=2.E0*U(I)*(RM-1.E0)/((1.E0-TI)*(1.E0+TI))
RMU=(RM*(1.E0+TI)-2.E0*TI)/(1.E0-TI)
TRAP= 2.E0*A*RMU
IF (TRAP-1.00E2)70,70,7
70 FACT=( EXP(-TRAP) ) * W
TERM(1)= FACT*(1.E0+RMU)**(2.E0*SIGMA)
TERM(2)= TERM(1)*RMU
TERM(4)= FACT*(1.E0+RMU)**(2.E0*SIGMA-1.E0)
TERM(3)= TERM(4)*RMU
TERM(5)= TERM(2)*RMU
SUM(1)= SUM(1)+ TERM(1)
SUM(2)= SUM(2)+ TERM(2)
SUM(3)= SUM(3)+ TERM(3)
SUM(4)= SUM(4)+ TERM(4)
SUM(5)= SUM(5)+ TERM(5)
7 T(I)=-T(I)
NO = NO+1
IF(NO-2) 6,10,6
6 CONTINUE
HSUM=0.
DO 15 I=1,5
15 HSUM=HSUM+HCOF(I)*SUM(I)
SSUM=SCOF(1)*SUM(1)+SCOF(2)*SUM(5)
C ENCL IS THE VARIATIONAL ENERGY CALCULATED FOR HI+ EQUAL TO HSUM/SSUM
ENCL = 2.E0*HSUM/(SSUM*R*R)
WRITE (NWT,203)
203 FORMAT (1H,5X,"ENCAL", 24X,"B",24X,"HSUM",22X,"SSUM")
WRITE (NWT,201) ENCL,B,HSUM,SSUM
201 FORMAT (4D24.14)
WRITE (NWT,204) BNU(1),BNU(2),BNU(3)
204 FORMAT (3E24.14)
RETURN
END

```

SEGMENT 5 IS 283 LONG

START OF SEGMENT ***** 6

```

SUBROUTINE FIHPSI (A, B, AP, BP, HSUM,SSUM )
C THIS SUBROUTINE EVALUATES FIHPSI INTEGRAL FOR SUBROUTINE CALCFX
C ARGUMENT LIST
C A,B,AP,BP, ARE THE VARIATIONAL PARAMETERS
C SUBROUTINE REQUIRED NONE
COMMON /S/RM,T,U, R, NO2
DIMENSION RX(5),SUM(30), TERM(10),BNU(3),T(30),U(30),HCOF(10),
1 SCOF(10)
NWT =6
PI=3.14159265
D=AP
G =BP
B2=B*B
B3=B*B2
C.....THESE ARE THE NU INTEGRALS.....
C BNU(1) =INTEGRAL OF (COSH(

```

```

C      BNU(2) = INTEGRAL
C      BNU(3) = INTEGRAL OF
      COSH2 = .5E0*( EXP(B+G) + EXP (-B-G))
      SINH2 = .5E0*( EXP(B+G) - EXP (-B-G))
      COSH3 = .5E0*( EXP(B-G) + EXP (-B+G))
      SINH3 = .5E0*( EXP(B-G) - EXP (-B+G))

      BNU(1) = (SINH2/(B+G)) + (SINH3/(B-G))
      BNU(2) = (SINH2/(B+G)) - (2.*COSH2/((B+G)*(B+G))) + (2.*SINH2
1/((B+G)**3)) + (SINH3/(B-G)) - (2.*COSH3/((B-G)*(B-G)))
1+(2.*SINH3/((B-G)**3))
      BNU(3) = (COSH2/(B+G)) + (COSH3/(B-G)) - (SINH2/((B+G)**2))
1-(SINH3/(B-G)**2))

      SINHR = (EXP(B)-EXP(-B))/2.
      COSHR = (EXP(B)+EXP(-B))/2.
      SIGMA = 2.*(-R+A +R*SINH3/COSHR)
      SINHG = (EXP(G)-EXP(-G))/2.
      COSHG = (EXP(G)+EXP(-G))/2.
      SIGMAP = 2.*(-R+D +G*SINHG/COSHG)

      HCOF(1) = (SIGMA+2.E0*A*SIGMA+B2-A*A)*BNU(1)-B2*BNU(2)-2.E0*B*BNU(
13)
      HCOF(2) = (2.E0*R-2.E0*A-2.E0*A*SIGMA)*BNU(1)
      HCOF(3) = SIGMA*SIGMA*BNU(1)
      HCOF(4) = -SIGMA*SIGMA*BNU(1)
      HCOF(5) = A*A*BNU(1)

      SCOF(1) = -BNU(2)
      SCOF(2) = BNU(1)
C      START THE MC LEAN AND YOSHIMINE SECTION
C      THIS ZEROS THE INTEGRAL SUMS

      NO=1
      SUM(1)=0.
      SUM(2)=0.
      SUM(3)=0.
      SUM(4)=0.
      SUM(5)=0.
10  CONTINUE
      DO 7 I=1,NO2
        TI=T(I)
        W=2.E0*U(I)*(RM-1.E0)/((1.E0-TI)*(1.E0-TI))
        RMU=(RM*(1.E0+TI)-2.E0*TI)/(1.E0-TI)
        TRAP=(A+D)*RMU
        IF (TRAP-1.00E2)70,70,7
70  FACT=( EXP(-TRAP))*W
        TERM(1)= FACT*(1.E0+RMU)**(SIGMA+SIGMAP)
        TERM(2)= TERM(1)*RMU
        TERM(4)= FACT*(1.E0+RMU)**(SIGMA+ SIGMAP-1.E0)
        TERM(3)= TERM(4)*RMU
        TERM(5)= TERM(2)*RMU
        SUM(1)= SUM(1)+ TERM(1)
        SUM(3)= SUM(3)+ TERM(3)
        SUM(2)= SUM(2)+ TERM(2)
        SUM(4)= SUM(4)+ TERM(4)
        SUM(5)= SUM(5)+ TERM(5)
7  T(I)=-T(I)
      NO = NO+1
      IF(NO-2) 6,10,6
6  CONTINUE
      HSUM=0.
      DO 15 I=1,5
15  HSUM=HSUM+HCOF(I)*SUM(I)
      SSUM=SCOF(1)*SUM(1)+SCOF(2)*SUM(5)

```

```

      SSUM =SSUM *PI*2.E0 *((R/2.E0)**3)
      WRITE (6,201) BNU(1), BNU(2),BNU(3), HSUM
201  FORMAT (4E24.14)
      HSUM = - (P[*R *HSUM) /2.
      WRITE (6,202) HSUM
202  FORMAT (E24.14)
      WRITE (6,204) SSUM
204  FORMAT (E24.14)
      RETURN
      END

```

SEGMENT 6 IS 293 LONG

START OF SEGMENT ***** 7

```

C      SUBROUTINE RICOUL (A, B, AP, BP, RESULT )
      THIS SUBROUTINE CALCULATES COULOMB INTEGRALS
      COMMON /S/RM,T,V,      R, NO2
      COMMON /G/ IFLAG
      DIMENSION ANUC(52),Z(60), IFACT(4),T(30),U(60),SUM(8),V(30)
      REAL      IFACT
      C=A
      D=AP
      G =BP
      SINHR = (EXP(B)-EXP(-B))/2.
      COSHR = (EXP(B)+EXP(-B))/2.
      SIGMA = 2.*(-R+C +B*SINHR/COSHR)
      SINHG = (EXP(G)-EXP(-G))/2.
      COSHG = (EXP(G)+EXP(-G))/2.
      SIGMAP= 2.*(-R+D +G*SINHG/COSHG)
      PI=3.14159265
      RESULT=0.
      DO 180 J=1,NO2
        U(J) = V(J)
180    T(J)=T(J)
        DO181 J= 1,NO2
          U(J+NO2) = V(J)
181    Z(J+NO2) =-T(J)
          NO2P=2*NO2
          IF(IFLAG .EQ.0) KP =0
          IF(IFLAG .EQ.1) KP =0
          DO 102 K=0,KP,2
            BNU      =0.
            CNU=0.
            DNU=0.
            ENU=0.
C          FIND BNU AND CNU FOR GIVEN VALUE OF K
          DO 120 L=0,19 .1
            CALL FINDA(K,2*L,X)
C.....AND ISNUINTEGRAL WHICH WE DENOTED A(K,N)
C          ANU(1) IS A(K,0)
C          ANU(2) IS A(K,2)
C          ANU(L0+1) IS A(K,2L0)
C          ETC
          ANU(L+1)=X
120    CONTINUE
          DO 30 L=0,18,1
            RL=L
            X=2.0*RL+1.
            CALL GAMMA (X,FACT)

```

```

TERM=((2.*R)**(2*L))/FACT
BNU  =BNU  +TERM*ANU(L+1)
CNU  =CNU+TERM*ANU(L+2)
TERM=((2.*G)**(2*L))/FACT
DNU  =DNU  +TERM*ANU(L+1)
ENU  =ENU+TERM*ANU(L+2)

```

```

30 CONTINUE

```

```

GO TO 802

```

```

WRITE (6,116) L

```

```

116 FORMAT (1H0," BNU AND CNU NOT CALCULATED TO PREVENT UNDERFLOW

```

```

1AT L=",I5)

```

```

WRITE (6,117) TERM,ANU(L+2)

```

```

117 FORMAT (1H ,30X, "TERM=",E24.14,"ANU(L+2)=",E24.14)

```

```

802 CONTINUE

```

```

WRITE (6,111) ANU(1),ANU(2),BNU ,CNU

```

```

111 FORMAT (1H ,"ANU0= ", E24.14,"ANU2=", E24.14, "BNU =", E24.14,"

```

```

1CNU=", E24.14)

```

```

WRITE (6,118) DNU,ENU

```

```

118 FORMAT(2E24.14)

```

```

C NOW THE VALUE OF BNU AND CNU IS KNOWN

```

```

SUM1=0.

```

```

SUM2=0.

```

```

SUM3=0.

```

```

SUM4=0.

```

```

SUM5=0.

```

```

SUM6=0.

```

```

SUM7=0.

```

```

SUM8=0.

```

```

C START OF RADIAL (MU) INTEGRAL SECTION

```

```

DO 40 J=1,N02P

```

```

UJ=U(J)

```

```

ZJ=Z(J)

```

```

XMU1=(RM*(1.E0+ZJ )-2.E0*ZJ )/(1.E0-ZJ )

```

```

W1=2.E0 *UJ *(RM-1.E0)/((1.E0-ZJ )*(1.E0-ZJ ))

```

```

TRAP = 2.*C*XMU1

```

```

IF (TRAP-1.00E2)70,70,71

```

```

70 FNX=EXP(-TRAP) *(1.+XMU1)**(2.*SIGMA))*W1

```

```

CALL XLEGRE (XMU1,K,2,VALQ)

```

```

XTEMP2=FNX*VALQ

```

```

XTEMP1= XTEMP2*XMU1*XMU1

```

```

CALL XLEGRE (XMU1,K,1,VALP)

```

```

XTEMP4=FNX*VALP

```

```

XTEMP3= XTEMP4*XMU1*XMU1

```

```

DO 50 L =1,N02P

```

```

C XMU2 FOR INTEGRALS WITH LIMITS 1 TO XMU1

```

```

RQ = 1.+ (XMU1-1.)/3.

```

```

BETA =((XMU1+1.)-2.*RQ)/(XMU1-1.)

```

```

BETA2=BETA*BETA

```

```

ZL=Z(L)

```

```

UL=U(L)

```

```

XMU2 =(1./(2.*BETA))*((1.-XMU1)+BETA*(XMU1+1.)+(XMU1-1.)

```

```

1*(1-BETA2)/(1.-BETA*ZL ))

```

```

W2 =UL *(XMU1-1.)*(1.-BETA2)/(2.*(1.-BETA*ZL )**2)

```

```

FNY=EXP(-2.*D*XMU2)*((1.+XMU2)**(2.*SIGMAP))* W2

```

```

CALL XLEGRE (XMU2,K,1,VALP)

```

```

YTEMP1=FN*VALP

```

```

TEMP =XTEMP1*YTEMP1

```

```

SUM1 =SUM1 + TEMP *XMU2*XMU2

```

```

SUM3 =SUM3 +XTEMP2*YTEMP1

```

```

SUM5 =SUM5 + TEMP

```

```

TEMP =XTEMP2*YTEMP1*XMU2*XMU2
SUM7 =SUM7 + TEMP
C   XMU3 FOR INTEGRALS WITH LIMITS XMU1 TO INFINITY
RP = 3.*XMU1/2.
XMU3 = (RP*(1.+ZL )-2.*XMU1*ZL )/(1.-ZL )
W3 = 2.*UL *(RP-XMU1)/((1.-ZL )**2)
TRAP = 2.*D*XMU3
IF (TRAP-1.00E2) 170,170,171
170 FNY2= EXP(-TRAP) *((1.+ XMU3)**(2.*SIGMAP))*W3
CALL XLEGRE (XMU3,K,2,VALQ)
YTEMP3= FNY2*VALQ
TEMP =XTEMP3*YTEMP3
SUM2 =SUM2 + TEMP *XMU3*XMU3
SUM4 =SUM4 +XTEMP4*YTEMP3
SUM6 =SUM6 + TEMP
TEMP =XTEMP4*YTEMP3*XMU3*XMU3
SUM8 =SUM8 + TEMP
171 CONTINUE
50 CONTINUE
71 CONTINUE
40 CONTINUE
SUM (1) =SUM1
SUM (2) =SUM2
SUM (3) =SUM3
SUM (4) =SUM4
SUM (5) =SUM5
SUM (6) =SUM6
SUM (7) =SUM7
SUM (8) =SUM8
WRITE (6,112) SUM
112 FORMAT (1H , " SUM1= ", E24.14, "SUM2=", E24.14, " SUM3=", E24.14/
11H ,1X, "SUM4=", E24.14, "SUM5=", E24.14, "SUM6=", E24.14/
11H ,1X, "SUM7=", E24.14, "SUM8=", E24.14/)
C   ANU2 IS ANU(2)
C   ANU0 IS ANU(1)
SEGMENT 8 IS 117 LONG
IFACT(1) = ((ANU(1) +BNU) *(ANU(1) +DNU) *(SUM(1)+SUM(2)))
IFACT(2) = ((ANU(2) +CNU) *(ANU(2) +ENU) *(SUM(3)+SUM(4)))
IFACT(3) = ((ANU(1) +BNU) *(ANU(2) +ENU) *(SUM(5)+SUM(6)))*(-1.)
IFACT(4) = ((ANU(1) +DNU) *(ANU(2) +CNU) *(SUM(7)+SUM(8)))*(-1.)
WRITE (6,114) IFACT
114 FORMAT (1H , "IFACT1=", E24.14, "IFACT2=", E24.14, "IFACT3=",
1E24.14, "IFACT4=", E24.14)
RK=K
RESULT=RESULT+(2.*RK+1.)*(IFACT(1)+IFACT(2)+IFACT(3)+IFACT(4))
WRITE(6,113) K,RESULT
113 FORMAT(1H , "RESULT(", I3, ") = ", E24.14)
102 CONTINUE
RESULT=RESULT*PI*PI*(R**5)/8.
RETURN
END

```

SEGMENT 7 IS 424 LONG

START OF SEGMENT ***** 9

```

SUBROUTINE R2COUL (A, B, AP, BP, RESULT )
C   THIS SUBROUTINE CALCULATES COULOMB INTEGRALS
COMMON /S/RM,T,V, R, NO2
COMMON /G/ IFLAG

```

```

DIMENSION ANU( 52),7(60), IFACT(3),T(30),U(60),SUM(6),V(30)
REAL IFACT
C=A
D=AP
G =BP
SINH B = (EXP(B)-EXP(-B))/2.
COSHB = (EXP(B)+EXP(-B))/2.
SIGMA = 2.*(-R+C +B*SINHB/COSHB)
SINH G = (EXP(G)-EXP(-G))/2.
COSHG = (EXP(G)+EXP(-G))/2.
SIGMAP= 2.*(-R+D +G*SINHG/COSH G)
PI=3.14159265
RESULT=0.
DO 180 J=1,N02
U(J) = V(J)
180 Z(J)=T(J)
DO181 J= 1,N02
U(J+N02) = V(J)
181 Z(J+N02) =-T(J)
N02P=2*N02
IF(IFLAG .EQ.0) KP =0
IF(IFLAG .EQ.1) KP =0
DO 102 K=0,KP,2
BNU =0.
CNU=0.
DNU=0.
ENU=0.
3 FIND BNU AND CNU FOR GIVEN VALUE OF K
DO 120 L=0,19 ,1
CALL FINDA(K,2*L,X)
3.....AND ISNUIINTEGRAL WHICH WE DENOTED A(K,N)
3 ANU(1) IS A(K,0)
3 ANU(2) IS A(K,2)
3 ANU(L0+1) IS A(K,2L0)
3 ETC
ANU(L+1)=X
120 CONTINUE
DO 30 L=0,18,1
RL=L
X=2.0*RL+1.
CALL GAMMA (X,FACT)
TERM=((B+G )**(2*L))/FACT
BNU =BNU +TERM*ANU(L+1)
CNU =CNU+TERM*ANU(L+2)
TERM=((B-G )**(2*L))/FACT
DNU =DNU +TERM*ANU(L+1)
ENU =ENU+TERM*ANU(L+2)
30 CONTINUE
GO TO 802
WRITE (6,116) L
116 FOPMAT (1H0," BNU AND CNU NOT CALCULATED TO PREVENT UNDERFLOW
1AT L=",15)
WRITE (6,117) TERM,ANU(L+2)
117 FORMAT (1H ,30X, "TERM=",E24.14,"ANU(L+2)=",E24.14)
802 CONTINUE
WRITE (6,111) ANU(1),ANU(2),BNU ,CNU
111 FORMAT (1H ,"ANU0= ", E24.14,"ANU2=", E24.14, "BNU =", E24.14,"
1CNU=", E24.14)
WRITE (6,118) DNU,ENU
118 FORMAT(2E24.14)

```

```

C      NOW THE VALUE OF BNU AND CNU IS KNOWN
      SUM1=0.
      SUM2=0.
      SUM3=0.
      SUM4=0.
      SUM5=0.
      SUM6=0.
C      START OF RADIAL (MU) INTEGRAL SECTION
      DO 40 J=1,N02P
      UJ=U(J)
      ZJ=Z(J)
      XMU1=(RM*(1.F0+ZJ )-2.E0*ZJ )/(1.E0-ZJ )
      W1=2.E0 *UJ *(RM-1.E0)/((1.E0-ZJ )*(1.E0-ZJ ))
      TRAP = (C+D)*XMU1
      IF (TRAP-1.00E2) 70,70,71
70     FNX=EXP(-TRAP)      *((1.+XMU1)**(SIGMA +SIGMAP)) *W1
      CALL XLEGRE (XMU1,K,2,VALQ)
      XTEMP2=FNX*VALQ
      XTEMP1= XTEMP2*XMU1*XMU1
      CALL XLEGRE (XMU1,K,1,VALP)
      XTEMP4=FNX*VALP
      XTEMP3= XTEMP4*XMU1*XMU1
      DO 50 L =1,N02P
C      XMU2 FOR INTEGRALS WITH LIMITS 1 TO XMU1
      RQ = 1.+(XMU1-1.)/3.
      BETA=((XMU1+1.)-2.*RQ)/(XMU1-1.)
      BETA2=BETA*BETA
      ZL=Z(L)
      UL=U(L)
      XMU2 =(1./(2.*BETA))*((1.-XMU1)+BETA*(XMU1+1.)+(XMU1-1.))
1 * (1-BETA2)/(1.-BETA*ZL )
      W2 =UL *(XMU1-1.)*(1.-BETA2)/(2.*(1.-BETA*ZL )**2)
      TRAP = (C+D)*XMU2
      FNY=EXP(-TRAP)      *((1.+XMU2)**(SIGMA +SIGMAP)) *W2
      CALL XLEGRE (XMU2,K,1,VALP)
      YTEMP1=FNX*VALP
      TFMP =XTEMP1*YTEMP1
      SUM1 =SUM1 + TEMP *XMU2*XMU2
      SUM3 =SUM3 +XTEMP2*YTEMP1
      SUM5 =SUM5 + TEMP
C      XMU3 FOR INTEGRALS WITH LIMITS XMU1 TO INFINITY
      RP = 3.*XMU1/2.
      XMU3 = (RP*(1.+ZL )-2.*XMU1*ZL )/(1.-ZL )
      W3 = 2.*UL *(RP-XMU1)/((1.-ZL )**2)
      TRAP = (C+D)*XMU3
      IF (TRAP-1.00E2) 170,170,171
170    FNY2=EXP(-TRAP)      *((1.+XMU3)**(SIGMA +SIGMAP)) *W3
      CALL XLEGRE (XMU3,K,2,VALQ)
      YTEMP3= FNY2*VALQ
      TEMP =XTEMP3*YTEMP3
      SUM2 =SUM2 + TEMP *XMU3*XMU3
      SUM4 =SUM4 +XTEMP4*YTEMP3
      SUM6 =SUM6 + TEMP
171    CONTINUE
50    CONTINUE
71    CONTINUE
40    CONTINUE
      SUM (1) =SUM1
      SUM (2) =SUM2
      SUM (3) =SUM3

```

```

SUM (4) =SUM4
SUM (5) =SUM5
SUM (6) =SUM6
WRITE (6,112) SUM
112 FORMAT (1H , " SUM1= ", E24.14, "SUM2=", F24.14, " SUM3=", E24.14/
11H ,1X, "SUM4=", E24.14, "SUM5=", E24.14, "SUM6=", E24.14/)
C ANU2 IS ANU(2)
C ANU0 IS ANU(1)
IFACT(1)=((DNU +RNU )**2)*(SUM(1)+SUM(2))
IFACT(2)=((ENU +CNU)**2)*(SUM(4)+SUM(3))
IFACT(3)=((DNU +RNU )*(ENU +CNU )*2.)*(SUM(5) +SUM(6))
1*(-1.)
WRITE (6,114) IFACT
114 FORMAT (1H , "IFACT1=", E24.14, "IFACT2=", E24.14, "IFACT3=",
1E24.14)
RK=K
RESULT=RESULT+(2.*RK+1.)*(IFACT(1)+IFACT(2)+IFACT(3))
WRITE(6,113) K,RESULT
113 FORMAT(1H , "RESULT(", I3, ") = ",E24.14)
102 CONTINUE
RESULT=RESULT*PI*PI*(R**5)/8.
RETURN
END

```

SEGMENT 9 IS 403 LONG

START OF SEGMENT ***** 10

```

SUBROUTINE XLEGRE (X,N,INDEX,VAL)
C X IS THE VALUE OF ARGUMENT
C N IS THE DEGREE OF POLYNOMIAL
C VAL IS PN(X) OR QN(X) , DEPENDING IF INDEX IS 1 OR 2 RESPECTIVELY
DIMENSION P(80)
IF (N.EQ.0) GO TO 40
P(1)=X
P(2)=1.5E0*X*X-.5E0
DO 10 K=3,N
RK=K
10 P(K) =X*P(K-1)-P(K-2)+X*P(K-1)-(X*P(K-1)-P(K-2))/(RK)
IF (INDEX.EQ.2) GO TO 20
VAL=P(N)
RETURN
20 CONTINUE
TEMP = ABS((1.E0+X)/(1.E0-X))
TERM1=.5E0*P(N)*ALOG(TEMP)
IF (N.EQ.1) GO TO 70
IF (N.EQ.2) GO TO 60
TERM2=P(N-1)
NM=N-1
RN=N
DO 30 M=2,NM
RM=M
30 TERM2=TERM2+(1.E0/RM)*P(M-1)*P(N-M)
VAL=TERM1-TERM2-(1.E0/RN)*P(N-1)
RETURN
40 IF(INDEX.EQ.2) GO TO 50
VAL=1.
RETURN
50 TEMP = ABS((1.E0+X)/(1.E0-X))
VAL=.5*ALOG(TEMP)

```

```

RETURN
60 CONTINUE
TERM2 =(3./2.)*P(N-1)
VAL = TERM1-TERM2
RETURN
70 VAL=TERM1-1.

```

```

RETURN
END

```

SEGMENT 10 IS 126 LONG

START OF SEGMENT ***** 11

```

SUBROUTINE GAMMA (XTEMP,VALUEP)
C THIS ROUTINE CALCULATES THE GAMMA FUNCTION OF X IN DOUBLE PRECISION
C VIA THE CHEBYSHEV EXPANSION GIVEN IN MATH.COMP.15,195(1961)
C VALUE IS THE VALUE OF GAMMA(X)
DOUBLE PRECISION X,Y,F1,A(18),P,VALUE
DATA A/0.4227843350984672,0.4118403304264306,0.08157691924752885
1 ,0.07424901074209492,-.0002669818887403832,0.01115404382906992
2 ,-.002852631864702119,0.002103857920672205,-.0009192675950399503
3 ,0.0004894361069981446,-.0002386428337526365
4 ,0.0001173283102240940,-.00005431838628013509
5 ,0.00002281404115366023,-.000008052343363483095
6 ,0.000002174177495455326,-.0000003889700573876955
7 ,.0000000339818010181043/
X= XTEMP
F1=1.000
Y=X
1 CONTINUE
IF(Y.LE.1.000)GO TO 2
Y=Y-1.000
F1=F1*Y
GO TO 1
2 CONTINUE
IF(Y.LT.0.000)GO TO 4
P=0.000
DO3I=1,18
II=19-I
3 P=(P+A(II))*Y
P=1.000+P
P=P/(Y*(Y+1.000))
VALUE =F1*P
VALUEP=VALUE
RETURN
4 CONTINUE
WRITE(6,5)X
5 FORMAT(46H ERROR IN DGAMMA ROUTINE, VALUE OF ARGUMENT IS ,D24.16)
VALUEP=VALUE
RETURN
END

```

SEGMENT 12 IS 123 LONG

SEGMENT 11 IS 111 LONG

START OF SEGMENT ***** 13

```

SUBROUTINE FINDA(K,N,VAL)
COMMON /S/RM,T,U, R, NO2
DIMENSION U(30),T(30),UP(30),TP(30)

```

```

      REAL NU
      DO 20 I =1,N02
      UP(I) =U(I)
20    TP(I) =T(I)
      N0=1
      VAL=0.
10    CONTINUE
      DO 7 I=1,N02
      NU= (1.E0 +TP(I))/2.E0
      W =UP(I)/2.E0
      CALL XLEGRE (NU,K,1,PK)
      VAL =VAL +W*PK*(NU**N)
7    TP(I)= -TP(I)
      N0 = N0+1
      IF(N0-2) 6,10,6
6    CONTINUE
      RETURN
      END

```

SEGMENT 13 IS 60 LONG

START OF SEGMENT ***** 14

SUBROUTINE OVRLAP (A, B, AP, BP, SSUM,ITAG)

```

C
C
C    THIS SUBROUTINE EVALUATES OVERLAP INTEGRAL FOR SUBROUTINE CALCFX
C    ARGUMENT LIST
C    A,B,AP,BP, ARE THE VARIATIONAL PARAMETERS
C    SUBROUTINE REQUIRED NONE
      COMMON /S/RM,T,U,      R,  N02
      DIMENSION RX(5),SUM(30),      BNU(4),T(30),U(30),TERM(10)
      NWT =6
      PI=3.14159265
      D=AP
      G =BP
      B2=B*B
      B3=B*B2
C.....THESE ARE THE NU INTEGRALS.....
C    BNU(1) =INTEGRAL OF (COSH(B+BP)*NU)
C    BNU(2) =INTEGRAL OF (COSH(B+BP)*NU)*NU*NU
C    BNU(3) =INTEGRAL OF (COSH(B-BP)*NU)
C    BNU(4) =INTEGRAL OF (COSH(B-BP)*NU)*NU*NU
      COSH2= .5E0*( EXP(B+G) + EXP (-B-G))
      SINH2= .5E0*( EXP(B+G) - EXP (-B-G))
      COSH3= .5E0*( EXP(B-G) + EXP (-B+G))
      SINH3= .5E0*( EXP(B-G) - EXP (-B+G))
      BNU(1) =(SINH2)/(B+G)
      BNU(2) =(SINH2/(B+G)) - (2.*COSH2/((B+G) *(B+G))) +(2. *SINH2
1/((B+G) **3))
      IF(ITAG .EQ. 0)GO TO 15
      BNU(3) =(SINH3)/(B-G)
      BNU(4) =(SINH3/(B-G)) - (2.*COSH3/((B-G) *(B-G))) +(2. *SINH3
1/((B-G) **3))
      GO TO 16
15    CONTINUE
      BNU(3) =1.
      BNU(4) =1./3.
      GO TO 16
16    CONTINUE

```

```

SINH8 = (EXP(B)-EXP(-B))/2.
COSH8 = (EXP(B)+EXP(-B))/2.
SIGMA = 2.*(-R+A +R*SINH8/COSH8)
SINH9 = (EXP(G)-EXP(-G))/2.
COSH9 = (EXP(G)+EXP(-G))/2.
SIGMAP = 2.*(-R+D +G*SINH9/COSH9)
C      START THE MC LEAN AND YOSHIMINE SECTION
C      THIS ZEROS THE INTEGRAL SUMS
      NO=1
      SUM(1)=0.
      SUM(2)=0.
10     CONTINUE
      DO 7 I=1,NO2
      TI=T(I)
      W=2.E0*U(I)*(RM-1.E0)/((1.E0-TI )*(1.E0-TI ))
      RMU=(RM*(1.E0+TI )-2.E0*TI )/(1.E0-TI )
      TRAP =(A+D) *RMU
      IF (TRAP-1.00E2)/0,70,7
70     FACT=( EXP(-TRAP      ))*W
      TERM(1)= FACT*(1.E0+RMU)**(SIGMA+SIGMAP)
      TERM (2)= TERM(1)*RMU*RMU
      SUM(1)= SUM(1)+ TERM(1)
      SUM(2)= SUM(2)+ TERM(2)
7      T(I)=-T(I)
      NO = NO+1
      IF(NO-2) 6,10,6
6      CONTINUE
      SSUM =((BNU(1) +BNU(3) ) *SUM(2) -(BNU(2) + BNU(4))*SUM(1))
1*(PI *R*R*R/4.)
      WRITE (6,201) BNU(1), BNU(2),SSUM
201  FORMAT (3E24.14)
      RETURN
      END

```

SEGMENT 14 IS 193 LONG

SEGMENT	15 IS	13 LONG
SEGMENT	16 IS	138 LONG
SEGMENT	17 IS	55 LONG
START OF SEGMENT	*****	18
SEGMENT	30 IS	7 LONG
SEGMENT	18 IS	18 LONG

NUMBER OF SYNTAX ERRORS DETECTED = 0.

PRT SIZE = 116; TOTAL SEGMENT SIZE = 3508 WORDS;

ESTIMATED CORE STORAGE REQUIREMENT = 7232 WORDS;

REFERENCES FOR THE APPENDICES

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5. J. C. Slater, Quantum Theory of Molecules and Solids Vol. 1, McGraw-Hill Book Company, Inc., New York. (1963), page 266.