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expansions for the excited state functions (4). The second and most severe shortcoming of this method is its inability, thus far, to provide insight into the physical aspects of bonding or suggestions for treatment of more complex molecules. A complete review of the literature concerning computations on the hydrogen molecule will not be given here since recent and complete reviews on the subject are available elsewhere (5) and (6). In addition, reviews by Löwdin (7) and (8) consider recent advances in the theory of molecular quantum mechanics and applications of these theories to the hydrogen molecule problem.

Since the work of James and Coolidge one of the most significant developments has been the proof, largely by numerical calculation, that correlated electron distributions are essential in order to account theoretically for binding energies of even the simplest molecules, including hydrogen. In order to explain the significance of electron correlation, it seems essential to describe the work from which this conclusion emerges and to define an uncorrelated distribution in mathematical terms.

The principal tool in calculating the energy for complex systems from approximate eigenfunctions has been the variation principle. This principle is as follows. Let $H$ be the Hamiltonian operator for a given system and let $\phi$ be a normalized function depending on the same independent variables and satisfying the same boundary conditions as an eigenfunction of $H$. 
APPENDIX A

The digital computer program developed to find the eigenvalues $A$, $p$ is given below in the symbolic language called FORTAN 2, which is commonly used in conjunction with the IBM 704 digital computer. The general scheme of solution is as follows. Using starting values of $A$, $p$ given as data to the computer, the condition that $M$ be symmetric or antisymmetric is applied through equations III. 21 or III. 22. The choice between a symmetric or an antisymmetric solution is made by the computer on the basis of input data. In general this sum will not be zero, as required by the boundary conditions, since $A$, $p$ are not exact eigenparameters. The value of $A$, holding $p$ constant, is then altered until the boundary condition on $M$ is satisfied to a degree of accuracy determined by input data. Next, the boundary condition that $A$ vanish exponentially as $\lambda$ goes to $\infty$ is applied, using equation III. 14. In this branch $A$ is held constant and $p$ is systematically altered until this boundary condition is satisfactorily accurate. With this new value of $p$ the cycle is then repeated, this repetition being continued until successive values of $p$ agree with each other to a specified degree of accuracy.
There are two aspects of the program that demand caution. First, the quantity that determines the maximum amount that A can be altered must contain a sign. This sign is determined by the slope of the curve showing boundary value as a function of A while p is held constant. Rather than determine this slope it is easier to guess. If the guess is incorrect, the program will be unable to find a solution and the final value of A will be unchanged from the initial guess. If this happens, a change in the sign of the increment of A will allow the computer to find a solution. This same phenomenon does not occur with the increment of p, which is undoubtedly connected to the fact that p appears as the square in both the differential equations that are being solved. In all cases the sign on the increment of p was taken to be positive. The second problem is concerned with the demands made on the accuracy of the boundary conditions and how close successive values of p must agree. If these accuracy requirements are not compatible with one another the computer will again be unable to find a solution. A systematic determination of the requirements for compatibility of the accuracy requirements has not been made but a typical set of compatible requirements that were found empirically are given below. If either of the above mentioned difficulties arises, an error message is printed out preceding the usual output data. This error message is usually adequate to determine the exact place where trouble was incurred but, because of the
interdependency of the various branches of the program, no systematic list can be compiled that will not contain numerous exceptions. In these cases, the programmer must rely on his own intuition and ingenuity to correct the situation.

Input Information

Input data consists of two cards with the following information.

The first card contains, all in fixed point notation as determined by the format statement number 2,

$$R = \text{the internuclear distance}$$

$$AO = \text{the initial guess of the value for } A$$

$$DA = \text{the largest increment that is allowed while changing } A$$

$$PO = \text{the initial guess of the value of } p$$

$$DP = \text{the largest increment that is allowed while changing } p.$$ 

The second card contains

$$M = \text{the value of the eigenparameter } m$$

$$MT = \text{the number of terms that are used in the expansion of the eigenfunction } M$$

$$C = \text{the code word determining the symmetry of the solution } M; C = 1 \text{ determines a symmetric solution, } C = 0 \text{ determines an antisymmetric solution}$$

$$W1 = \text{the upper bound allowed to the error in calculating the boundary condition on } M$$

$$W2 = \text{the upper bound allowed to the error in calculating the boundary condition on } \Lambda$$
W3 = the lower bound allowed on DP
W4 = the lower bound allowed on DA
W5 = the upper bound on the difference between successive values of p.

The format of this card is determined by statement number 3. Values of
W1 = 1.0x10^-3, W2 = 1.0x10^-3, W3 = 1.0x10^-7, W4 = 1.0x10^-6 and
W5 = 1.0x10^-3 were found, in the majority of cases, to be a consistent set
of accuracy requirements that gave rather accurate results.

Output Information

The output information consists of the following information. On
the first line the input information on card one is printed plus
A01 = the final value of A
P01 = the final value of p.

The second line prints out the information that was given on the second card
of input data. The remaining information consists of the coefficients of M
as calculated by the recurrence relationship III. 19. If the output information
is preceded by the statement OOF = X, where X may equal 1, 2, 5, 6, 9, 10,
11, or 13, the program was unable to find a solution under the conditions
given in the input data. The value of X indicates the branch in which the
error first appeared.
DIMENSIONAT(100)*ALPHA(100)*BETA(100)*GAMMA(100)

FORMAT(F6.2,F11.7,F5.2,F11.7,F5.3)
FORMAT(I2,I3,I2,5E7.0)
FORMAT(I2,I3,I2,5E7.0)
FORMAT(1H 6F11.7)
FORMAT(5H OOF=I2)
FORMAT(3H S=F12.7)
READ2*R,A0,DA,P0,DP
READ3*M,MT,C,W1,W2,W3,W4,W5
A01=A0
A02=A0
DA1=DA
DP1=DP
PC1=PC
P02=P0
S1=999.
S2=999.
H=M
U=A01-P02**2+(H+1.)*(H+2.*P02)
AT(1)=1.0
AT(2)=-(U-2.*R)/(2.*(H+1.))
DO17K=1,MT
T=K
AT(K+2)=(-0.5*AT(K+1)*(T*(T+2.*H+1.+4.*P02)+U-2.*R)
AT(K)*(P02*H-R+P02*T))/((T+1.)*(T+1.+H))
IF(C)29,30,33
PRINT101,JOOF
GOTO83
S=0.0
DO31K=1,MT
S=S+AT(K)*(-1.)*T
GOTO35
S=0.0
DO34K=1,MT
T=K
S=S+AT(K)*(T-1.-P02)*(-1.)*T
IF(ABS(S)-W1)51,51,36
IF(ABS(S)-ABS(S1))40,18,37
IF(S1)110,50,112
A01=A01+DA1
DA1=0.5*DA1
GOTO113
A01=A01-DA1
DA1=0.5*DA1
GOTO113
97

113 IF(ABSF(DA1)-W4)114,39,39
114 J00F=13
       PRINT101,J00F
       GOT083
0039 GOT013
0018 J00F=2
       PRINT101,J00F
       GOT083
0040 S1=S
0041 IF(ABSF(DA1)-W4)41,44,44
       DA1=DA
       IF(S)45,50,48
       A01=A01-DA1
       DA1=DA1/2
       GOT013
0048 A01=A01+DA1
0049 GOT046
0050 J00F=5
       PRINT101,J00F
       GOT083
0051 A02=A01
S1=999.
0052 SG=-H-1.+R/P01
0053 DO54 K=1,12
      T=K
      ALPHA(K)=T*(T+H)
0054 DO56 K=1,12
      T=K
      BETA(K)=2.*((T-1.)**2+(T-1.)*(4.*P01-2.*SG)-A02+P01**2
      C-2.*P01*SG-(H+1.)*(H+SG)
0056 C-2.*P01*SG-(H+1.)*(H+SG)
0057 DO58 K=1,12
      T=K
      GAMMA(K)=(T-2.-SG-H)*(T-2.-SG)
      L=12-K
0060 BETA(L)=BETA(L)-ALPHA(L)*GAMMA(L+1)/BETA(L+1)
51 CF=GAMMA(2)/BETA(2)
62 B1=BETA(1)/ALPHA(1)
0063 IF(ABSF(S1-CF)-W2)64,64,67
0064 IF(ABSF(P01-P02)-W5)83,83,65
0065 P02=P01
S2=999.
S2=999.
0066 GOT013
      67 IF(ABSF(B1-CF)-ABS(S2))72,68,69
0068 J00F=6
PRINT101,JO0F
GOT083

0069 IF(S2)105,106,107
105 P01=P01-DP1
  DP1=0.5*DP1
  GOT0108
106 JO0F=10
    PRINT101,JO0F
    GOT083
107 P01=P01+DP1
  DP1=0.5*DP1
  GOT0108
108 IF(ABS(DP1)-W3)109,71,71
109 JO0F=11
    PRINT101,JO0F
    GOT083
0071 GOT052
0072 S2=B1-CF
    IF(ABS(DP1)-W3)73,76,76
0073 DP1=DP
0076 IF(B1-CF)78,77,81
0077 JO0F=9
    PRINT101,JO0F
    GOT083
0078 P01=P01+DP1
0079 DP1=DP1/2.
0080 GOT052
0081 P01=P01-DP1
0082 GOT079
0083 PRINT4,R,A0,DA,P0,DP,A01,P01
0084 PRINT5,M,MT,C,W1,W2,W3,W4,W5
0085 PRINT6,(AT(K),K=1,MT)
0086 GOT07
END(0,1,1,1,1)
APPENDIX B

The problem of averaging the Hamiltonian over functions expressed as a linear combination of hydrogen like functions is well documented. Preuss (13) gives pertinent references and a concise discussion of this literature. One difference in this problem and the one discussed by Preuss is that the functions used here are solutions to differential equations. Hence, instead of using the techniques in Preuss, use was made of the differential equations to find the average of the kinetic energy operator.

The integral involving \(1/r_{12}\) was treated in the following manner. Assuming the expansion in spheroidal coordinates

\[
\frac{1}{r_{12}} = \frac{1}{R} \sum_{\tau=0}^{\infty} \sum_{\nu=0}^{\tau} C_{\tau}^{\nu} \left( \frac{Q_{\tau}^{\nu}(\lambda_{1}) P_{\tau}^{\nu}(\lambda_{2})}{Q_{\tau}^{\nu}(\lambda_{2}) P_{\tau}^{\nu}(\lambda_{1})} \right) P_{\tau}^{\nu}(\mu_{1}) P_{\tau}^{\nu}(\mu_{2}) \cos^{\nu}(d_{1} - d_{2})
\]

where

\[
C_{\tau}^{\nu} = \epsilon_{\nu} (-1)^{\nu}(2\tau + 1) \left[ \frac{(\tau - \nu)!}{(\tau + \nu)!} \right]^{2}, \quad \epsilon_{0} = 1; \epsilon_{\nu} = 2; \nu > 1;
\]
it is evident that the integration over $\phi$ reduces this to a single sum over $\tau$, since no function used depends on the independent variable $\phi$. Next, by integrating over $\mu$, the integral reduces to a sum of integrals of the type

$$
H_{\tau}(m, \alpha; n, \beta) = \int_1^\infty \int_1^\infty Q_\tau \left( \begin{array}{c} \lambda_1 \\ \lambda_2 \\ \end{array} \right) P_\tau \left( \begin{array}{c} \lambda_2 \\ \lambda_1 \\ \end{array} \right) e^{-\alpha \lambda_1 - \beta \lambda_2} \lambda_1^m \lambda_2^n \ d\lambda_1 \ d\lambda_2.
$$

B. 2

These integrals have been extensively tabulated, so rather than go through the tedious problem of performing this integration, use was made of these tables. In this case, $\alpha = \beta$, but only by accident will $\alpha$ be a value that has already been tabulated. Hence some form of interpolation is necessary. Interpolation formulae has been developed for this purpose (13) but, in spite of this technique's superior and better understood error limits, the following convenient scheme was developed. Over the range of interest, $1.0 = \alpha = 2.25$, logarithms of the integral B. 2 were taken. A table of differences for these logarithms was then formed and interpolated using an appropriate central difference scheme. Taking the anti-log of this result then produced the value of interest. Empirical testing of this scheme gave evidence that the error was small in the fifth significant figure near the center of the table and for low values of $m, n$. As $n, m$ increases the interpolation error increases but, since the coefficients of the expansion decrease even more rapidly, no increase in error is introduced into the average value. Near the end of the table for small values of $\alpha$, again the error increases but, since
this part of the table comes into use only for terms involving \( k \) and \( k^2 \) of function IV. 2, this has very little affect on the overall accuracy of the average of the Hamiltonian. Preuss (18) gives a somewhat more detailed study of the logarithmic interpolation of B. 2 but, as in this case, is unable to give an accurate upper bound for the error. He gives the expected percentage error as a function of the various parameters but fails to mention the interpolation scheme used on the logs. If the interpolation were linear, as one must assume, his limits on the error are indeed impressive when one notices the large intervals that are being used.

Two short programs were written for a digital computer in FORTRAN that performed the above logarithmic interpolation and then summed these results. The data for the interpolation were taken from Miller et al. (19) and the coefficients used in summing these integrals were developed from the integration of \( \mu \) and a combination of the coefficients of the solutions given in Tables 3 and 4.
Then the mean value of $H$, designated by $E$, exceeds the lowest eigenvalue of $H$ whatever $\phi$ may be and equals the lowest eigenvalue only when $\phi$ is the corresponding eigenfunction. Stated otherwise, the quantity

$$E = \int \phi^* H \phi \, d\tau$$

is an extreme with respect to variation of $\phi$ and this extreme is a minimum for the lowest energy state.

If one chooses a trial function in the form of a simple product of functions each depending on the coordinates of a single electron, Slater (39) and Fock (38) have demonstrated the following result. When the individual one-electron functions make the mean energy an extreme, $E$ of equation I. 1, they must also satisfy a set of simultaneous second order differential equations. These differential equations are identical in form to Schrödinger equations where the potential is that for an electron in the field of the nuclei and the mean field of the remaining electrons. This potential for one electron is independent of the position of any of the remaining electrons and in addition corresponds to an uncorrelated distribution of electrons. It follows that a product function, constructed as stated above, defines an average for equation I. 1 that does not include correlation of electron motion. The equations obtained are identical with those of Hartree (40).
APPENDIX C

For any potential function $V(R, x)$ that is homogeneous and of degree $-1$ where

$$[T(R, x) + V(R, x)] \phi(R, x) = E(R)\phi(R, x), \quad \text{C. 1}$$

it follows that

$$[(1/k^2)T(R, x) + (1/k^2)V(R, x)] \phi(kR, kx) = E(kR)\phi(kR, kx). \quad \text{C. 2}$$

Taking the partial derivative with respect to $k$

$$[-(2/k^3)T(R, x) + (1/k^2)V(R, x)] \phi(kR, kx)$$

$$+ [(1/k^2)T(R, x) + (1/k) V(R, x)] \frac{\partial \phi(kR, kx)}{\partial k} = \frac{\partial E(kR)}{\partial k} \phi(kR, kx)$$

$$+ E(kR) \frac{\partial \phi(kR, kx)}{\partial k}. \quad \text{C. 3}$$

Multiplying through by $\phi(kR, kx)/\int |\phi(kR, kx)|^2 \, dx$, and integrating with respect to $dx$,

$$-2/k^2 T(kR) - 1/k V(kR) + \int \phi(kR, kx) [1/k^2 T(R, x) + 1/k V(R, x)] R \frac{\partial \phi(kR, kx)}{\partial k} \, d(kx)$$

$$= R \frac{\partial E(kR)}{\partial (kR)} + E(kR)R \int \phi(kR, kx) \frac{\partial \phi(kR, kx)}{\partial (kR)} \, d(kx) \quad \text{C. 4}$$

is found if $\phi(R, x)$ is normalized, where $T(kR)$, $V(kR)$ are averages of the kinetic energy operator and potential function respectively. From the fact
that \( \phi(R, x) \) is normalized, it also follows that

\[
\int \frac{\partial \phi(R, x)}{\partial R} \phi^*(R, x) \, dx = 0. \tag{C. 5}
\]

From the fact that the Hamiltonian is a Hermitian operator and using equation C. 2, the integral in equation C. 4 becomes

\[
R \int \frac{\partial \phi(kR, kx)}{\partial (kR)} \left[ \frac{1}{k^2} T(R, x) + \frac{1}{k} V(R, x) \right] \phi^*(kR, kx) \, d(kx)
\]

\[
= R \, E(kR) \int \frac{\partial \phi(kR, kx)}{\partial (kR)} \phi^*(kR, kx) \, d(kx) = 0. \tag{C. 6}
\]

It follows that equation C. 4 becomes, on setting \( k = 1 \)

\[
-2T(R) - V(R) = R \frac{\partial E(R)}{\partial R} = R \frac{dE(R)}{dR}, \tag{C. 7}
\]

or, using equation C. 1 after averaging over \( \phi(R, x) \),

\[
2E(R) + R \frac{dE(R)}{dR} = V(R). \tag{C. 8}
\]

Equation C. 8 constitutes the analogue of the virial theorem in quantum mechanics.
APPENDIX D

We define $\phi_n^\circ$ as an eigenfunction of the Hamiltonian

$$H\phi_n^\circ = \left[ \frac{-\hbar^2}{8\pi^2 m} \left( \nabla_1^2 + \nabla_2^2 \right) + (1+\alpha')U + V \right] \phi_n^\circ$$  \hspace{1cm} D. 1

with eigenvalues $E_n''$, where

$$U = 1/r_{12} - 1/r_{ab1} - 1/r_{ab2}$$ \hspace{1cm} D. 2

$$V = -1/r_{ba1} - 1/r_{ba2}.$$ \hspace{1cm} D. 3

Replacing $\alpha'$ by $\alpha' + \delta\alpha'$, the perturbed Hamiltonian

$$(H + \delta\alpha' U)\phi_n = E_n^\prime \phi_n$$ \hspace{1cm} D. 4

is obtained. From non-degenerate perturbation theory, the energy $E_n$ is given by

$$E_n = E_n'' + \langle \phi_n^\circ | U | \phi_n^\circ \rangle \delta\alpha' + o(\delta\alpha'')$$ \hspace{1cm} D. 5

or alternately, when we take $\phi_n^\circ$ to be the wave function for the lowest state having an eigenvalue $E_n''$ of equation D. 1

$$\frac{E-E''}{\delta\alpha'} = -\mu' + o(\delta\alpha')$$ \hspace{1cm} D. 6

where $\mu'$ is defined by equation V. 5. Now

$$\lim_{\delta\alpha' \to 0} \left[ \frac{E-E''}{\delta\alpha'} \right] = \frac{\partial E''}{\partial \alpha'}.$$ \hspace{1cm} D. 7
so it follows that

\[ \frac{\partial E''}{\partial \alpha'} = -\mu' \]

and if \( E'' = E' - \alpha' \mu \), then

\[ \frac{\partial E'}{\partial \alpha'} = \mu - \mu' \]

where \( \mu \) is defined by equation V. 4.
APPENDIX E

First, the one-electron potential will be defined in a general way so that the constrained Hamiltonian will have the same interpretation as given in Section V. Next, this general definition will be applied to the one-electron potential function defined by equation IV. 7.

Writing the assumed one-electron potential function as the sum

\[ V(1) = V_a(1) + V_r(1), \]  

where \( V_a \) is the attraction for the nuclei and \( V_r \) is the electron-electron repulsion term, by the same argument given in Section II it follows that the electron repulsion term which is consistent with the assumed one-electron potential is

\[ V_r(1) = V(1) + 1/r_a + 1/r_b \]  

since \( V_a(1) \) is exactly the last two terms of equation E. 2. The exact potential function for \( H_2 \) can be written as

\[ 1/r_{12} - 1/r_{a1} - 1/r_{a2} - 1/r_{b1} - 1/r_{b2} = U + Q. \]  

Defining

\[ U = 1/r_{12} - V_r(1) - V_r(2) \]  

and

\[ Q = V(1) + V(2), \]
we see from equations E. 1, E. 2 that $U + Q$ is the exact electronic potential for the hydrogen molecule.

The constraint defined by equation V. 3 now becomes

$$\mu' = (\Psi |-U|\Psi) \quad \text{E. 6}$$

$$\mu = (u|V_r|u) \quad \text{E. 7}$$

where $u$ is now a solution to a one-electron Schrödinger equation with a potential defined by equation E. 1 and $\Psi$ is an extreme for the integral

$$E'' = \left(\Psi \left| -\frac{\hbar^2}{8\pi^2 m} \left(\nabla^2 + \nabla^2_2\right) + (1+\alpha')U + Q \right|\Psi\right). \quad \text{E. 8}$$

With these definitions it follows that $\alpha'$ has exactly the same interpretation as before and this fact will be demonstrated below for a specific case.

Remembering that the one-electron potential containing an effective atomic number or screening constant was defined in this case by

$$V(1) = -\frac{k}{r_{ba}}, \quad \text{E. 9}$$

it follows from equation E. 2 that

$$V_r(1) = (1-k)/r_{ba} + 1/r_{ab}, \quad \text{E. 10}$$

from equation E. 4 that

$$U = 1/r_{12} - (1-k)/r_{ba1} - (1-k)/r_{ba2} - 1/r_{ab1} - 1/r_{ab2} \quad \text{E. 11}$$

and from equation E. 5 that

$$Q = -k/r_{ba1} - k/r_{ba2}. \quad \text{E. 12}$$
The analogues to equations E. 6 and E. 7 for this case are

\[ \mu_k' = (\Psi | -U| \Psi), \quad \text{E. 13} \]

\[ \mu_k = (u|V_r|u) \quad \text{E. 14} \]

where \( U \) and \( V_r \) are defined by equations E. 11 and E. 10, respectively.

We also define

\[ \gamma_k = (\Psi |-Q|\Psi), \quad \text{E. 15} \]

where \( Q \) is defined in this case by equation E. 12.

Assuming that \( \alpha' \) and \( k \) are constant, the virial theorem for equation E. 8 is

\[ 2E'' + R \frac{dE''}{dR} = -(1 + \alpha')\mu_k' - \gamma_k' \quad \text{E. 16} \]

since the potential is homogeneous and of degree -1 for these assumptions.

A treatment analogous to that in Appendix D gives

\[ \frac{\partial E''}{\partial \alpha'} = -\mu_k' \quad \text{E. 17} \]

and

\[ \frac{\partial E''}{\partial k} = \frac{\alpha'}{k} \gamma_k' \quad \text{E. 18} \]

Allowing \( \alpha' \) and \( k \) to become arbitrary functions of \( R \), it follows that

\[ \frac{\partial E''}{\partial R} = \frac{dE''}{dR} + \mu_k' \frac{d\alpha'}{dR} - \frac{\alpha'}{k} \gamma_k' \frac{dk}{dR} \quad \text{E. 19} \]

hence the virial theorem becomes

\[ 2E'' + R \frac{dE''}{dR} = -(1 + \alpha')\mu_k' - \gamma_k' \left(1 - \frac{\alpha'}{k} \frac{dk}{dR}\right) - R\mu_k' \frac{d\alpha'}{dR}. \quad \text{E. 20} \]
If we define

$$\gamma_k' \left(1 - \frac{\alpha'}{k} \frac{dk}{d\rho}\right) = \xi_k'$$  \hspace{1cm} E. 21

and, as before, if $E'' = E' - \alpha' \mu_k$ and $\phi = R\mu_k$, equation E. 20 becomes

$$2E' + R \frac{dE'}{dR} = \alpha' (\mu_k - \mu_k') + \alpha' \frac{d\phi_k}{dR} + R(\mu_k - \mu_k') \frac{d\alpha'}{dR} - \mu_k' - \xi_k'$$  \hspace{1cm} E. 22

For $\alpha' = -1$, $E'$ is equal to $E_{t-1/2R}$ as before. This follows from equations E. 7 and E. 8. For this value of $\alpha'$, $\mu_k'$ will be called $\mu_k^*$ and $\xi_k'$ will be designated by $\xi_k^*$. For $\alpha' = \alpha$, the value for which the constraint is satisfied, we define $E' = E = (\Psi|H|\Psi)$, $\xi_k'$ becomes $\xi_k$ and $\mu_k' = \mu_k$ by definition. If $\alpha'$ is set equal to zero, it can be seen from equation E. 8 that $E'' = E' = W$. This is exactly the interpretation of $\alpha'$ that was obtained in Section V except the terms $\mu_k'$, $\mu_k'$ and $\xi_k'$ have meanings altered by the presence of the term $k$.

Let $\alpha' = \alpha$ in equation E. 22, and from the above discussion it follows that

$$2E + R \frac{dE}{dR} = \alpha \frac{d\phi_k}{dR} - \mu_k - \xi_k.$$  \hspace{1cm} E. 23

Subtracting equation E. 22 from equation E. 23

$$2(E-E')+R \frac{d(E-E')}{dR} = (\xi_k' - \xi_k) + (\alpha - \alpha') \frac{d\phi_k}{dR} - (\mu_k - \mu_k') \frac{dR(\alpha' - \alpha)}{dR} - (\mu_k - \mu_k') \frac{dR(1+\alpha)}{dR}$$  \hspace{1cm} E. 24

is found after some rearranging. As before, an attempt to find a solution to equation E. 24 in terms of power series expansions will be made. By the same
argument given in Section V, the following expansions can be defined:

\[ R^2 (E' - E) = \sum_{n=2}^{\infty} \frac{\theta_n}{n!} \left[(\alpha' - \alpha)R\right]^n \]

\[ R(\mu_k - \mu_k') = \sum_{n=1}^{\infty} \frac{n\theta_n}{n!} \left[(\alpha' - \alpha)R\right]^n \] \hspace{1cm} E. 25

\[ (\xi_k - \xi_k') = \sum_{n=1}^{\infty} \frac{\beta_n}{n!} \left[(\alpha' - \alpha)\right]^n. \]

The coefficients \( \beta_n \) have a slightly different meaning than they did in Section V but their formal mathematical properties are the same. On substituting these expansions into equation E. 24

\[ \frac{d\theta_n}{dR} = \theta \frac{dR(1+\alpha)}{dR} + \frac{\beta_n}{R^{n-1}} \hspace{1cm} n > 1 \] \hspace{1cm} E. 26

and, for \( n = 1 \),

\[ \theta_2 \frac{dy}{dR} + \theta_1 + \frac{d\theta_k}{dR} = 0, \quad y = R(1+\alpha) \] \hspace{1cm} E. 27

are found which are equivalent to equations V. 35 and V. 36. Truncating the expansions in equation E. 25 to the first non-vanishing term, we find

\[ R^2 (E' - E) = \frac{\theta_2}{2} \left[R(\alpha' - \alpha)\right]^2 \] \hspace{1cm} E. 28

\[ (\mu_k - \mu_k') = \theta_2 (\alpha' - \alpha) \]

\[ (\xi_k - \xi_k') = \beta_1 (\alpha' - \alpha). \]

Setting \( \alpha' = -1 \) in equation E. 24

\[ \frac{df}{dR} = R(\xi_k^* - \xi_k) + y \frac{d\theta_k}{dR} \] \hspace{1cm} E. 29
is obtained where \( f \) is defined by equation V. 38 and equation E. 29 is equivalent to equation V. 41. For this value of \( \alpha' \), equation E. 28 becomes

\[
f = -\frac{\theta}{2} y^2
\]

\[
R(\mu_k - \mu_k^*) = -\theta_2 y \quad \text{E. 30}
\]

\[
R(\xi_k^* - \xi_k) = \beta_1 y.
\]

The set of equations E. 27, E. 29, E. 30 is equivalent to the set of equations V. 36, V. 41, V. 42, V. 43, V. 44 and, in fact, because of their identical form, this set of equations will result in an analogue to equations V. 48.

That is,

\[
\frac{d\theta_2}{dR} = 0. \quad \text{E. 31}
\]

This formal treatment is correct as long as the truncation made to obtain equation E. 28 is correct. This is known to be a good approximation when \( y \) is small. It can be shown that \( y \) actually becomes zero by the following argument. Equation V. 54 gave \( E_u - E_t = \mu - \mu' = \mu - \mu^* \), since it applies to the case \( \alpha' = -1 \), and investigation of Tables 7 and 10 shows that \( E_u - E_t \), hence \( \mu - \mu^* \), vanishes between \( R = 0.5 \) and \( R = 0.6 \). It follows from the second formula of equation E. 30 that \( y \) must vanish at this point and, hence, in this region of \( R \) the truncations must be accurate. In the following steps, where \( \alpha' \) is set equal to zero to obtain the analogue to equation V. 55, it follows that the validity of these truncations is open to question. In the present
A many electron function defined as a product of one-electron functions does not satisfy the Pauli Exclusion Principle. Fock (38) pointed out that if one employs a trial function expressed as a determinant

\[
\Phi = \frac{1}{\sqrt{n!}} \begin{vmatrix}
\phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_n) \\
\phi_2(x_1) & \cdots & \cdots & \cdots \\
\vdots & \ddots & \ddots & \ddots \\
\phi_n(x_1) & \cdots & \cdots & \phi_n(x_n)
\end{vmatrix}
\]

where \(\phi_i(x_k)\) is a function depending on both position and spin coordinates of the \(k^{\text{th}}\) electron, symbolized by \(x_k\), the Pauli Exclusion Principle is satisfied.

Since the determinant of equation I. 2 can be expressed as a sum of products of functions depending on the coordinates of one electron only, a function in the form of equation I. 2 also defines an electron distribution with minimum correlation compatible with the exclusion principle. The correlation energy is defined as the difference between the exact electronic energy of a system and the extreme of equation I. 1 provided by a function in the form given by equation I. 2.

Kolos and Roothaan (22) conclude that the best binding energy for the hydrogen molecule that can be obtained from a function in the form of equation I. 2 is 3.63 eV. Coulson (41), using an approximate function containing five terms, was the first to predict this limit accurately. This is to
treatment this question will be answered, as well as possible, by testing the accuracy of the predictions when this assumption is made.

Taking \( \alpha' \) equal to zero, the value for which the constraint is automatically satisfied, the first formula in equation E. 28 gives the analogue to equation V. 50 for this case, and by the same argument given in Section V

\[
W - E_u = \frac{9}{2} E. 32
\]

is found. Equations E. 31 and E. 32 mean that the correlation energy defined by equation E. 32 must be a constant no matter what function of \( R \) the parameter \( k \) may be. There is, however, a practical limit on this function for the following reason. \( E_u \) depends on \( k \) since it is the average of the exact Hamiltonian for \( H_2 \) over a product of one-electron eigenfunctions of the Schrödinger equation with a potential defined by equation E. 9. It is known, however, that the exact energy of the hydrogen molecule does not depend on a one-electron potential function in any way. Hence, if equation E. 32 is to accurately represent a relation between the exact energy \( W \) and \( E_u \), \( E_u \) must be made as insensitive as possible to a variation of the parameter \( k \) and, ideally \( E_u \) should not depend on \( k \) at all. The function of \( k \) for which \( E_u \) is the most insensitive to change in \( k \) is known to be that function of \( k \) which makes \( E_u \) a minimum. Hence, it follows that the prediction of equation E. 32 will be the most accurate when \( k \) is taken to be such a function of \( R \).
The test of equation E. 32 made in Section V verifies this reasoning. It is found that, when $k = 1$ for all $R$, $\theta^2/2$ is a fair approximation to a constant and when $k$ is so adjusted to make $E_u$ a minimum, equation E. 32 is even more accurately obeyed. It follows that the approximate solution to the virial equation, equation E. 24, given here is fairly accurate over the range of internuclear distance that has been tested by the methods given above. It should be mentioned, however, that extreme care must be used in extending the theory and a great deal of information is yet to be obtained before the validity of these approximations is well understood.
APPENDIX F

Assume that
\[ \alpha' - \alpha = b\beta(R) \]  \hspace{1cm} F. 1

where \( b \) is some constant and \( \beta(R) \) is an arbitrary function of \( R \). Replacing \( \alpha' - \alpha \) in each of the equations V. 21, V. 23, V. 30 by \( b\beta(R) \), it follows that, on substituting these series expansions into equation V. 20, no requirements can be placed on the function \( \beta(R) \) if it is to be arbitrary as assumed. When equating coefficients of \( (b)^n \) in equation V. 20, \( \beta(R) \) does indeed turn out to be a completely arbitrary function of \( R \). With this being the case, the recurrence relationship given by equation V. 31 and the terminal condition of equation V. 32 are required by equation V. 20.
BIBLIOGRAPHY


31. ____________, ibid., p. 401.


I, James Mack Peek, was born in Unionville, Missouri, September 5, 1933. I received my secondary-school education in public schools and my undergraduate training at Western Illinois State College, which granted me the Bachelor of Science degree in 1955. From The Ohio State University, with Professor Quentin Van Winkle of the Department of Chemistry acting as my adviser, I received the Master of Science degree in 1958. I was appointed Kettering Foundation Fellow for the year 1958-1959. Since that time, I have been a Research Assistant in the Department of Chemistry at The Ohio State University, under the supervision of Professor Edwin N. Lassettre, while completing the requirements for the Doctor of Philosophy degree.
be compared with the experimental binding energy at the equilibrium internuclear distance, which is 4.75 eV (8). The correlation energy at this point is then 1.11 eV. It is found that the correlation energy increases to a limit of 7.74 eV (8) at infinite internuclear distance. These comparatively large correlation energies establish that accurate energy calculations are not possible when these one-electron functions (molecular orbitals) are employed in trial functions of the type of equation I.2. It may still be the case, however, that molecular orbitals can be employed in some different way which will permit more accurate calculations than those described above.

In this case the molecular orbitals must, however, be defined in some other manner than as solutions to the equations of Hartree or the modified equations of Fock. Slater (11) has suggested that the potential function for a single electron in a complex atom or molecule be calculated by an extension of the intuitive method employed by Hartree and has given a formula which is applicable to any type of wave function, correlated or not. In this way a molecular orbital can at least be defined and the deduction of molecular energies carried out in some appropriate manner to be developed later. With this in mind a rather simple potential function has been studied which approaches, at large internuclear distances, the correct potential function and which apparently provides a fair approximation near the equilibrium internuclear distance. This potential function may be explained as follows.
Assuming correlated motion of the electron in the hydrogen molecule, it follows that one electron would most probably be found in the neighborhood of one of the nuclei while the second electron is near the remaining nucleus. In the limit of infinite internuclear distance, this is certainly so and the potential for each electron becomes a coulomb potential centered on the nearest nucleus. In this model, it will be assumed that a coulomb potential prevails for the individual electrons at all internuclear distances. This assumption of a single electron coulomb potential carries with it an implication in addition to the assumption of extreme correlated motion. That is, for one electron to have a coulomb potential centered on the near nucleus, the remaining electron must screen the far nucleus completely. This is exact at very large internuclear distances but is certainly less accurate at small internuclear distances. A quantitative test of this potential will be given in Section II for the equilibrium internuclear distance.

With this potential it is now possible to write down the one-electron Hamiltonian for the hydrogen molecule. This Hamiltonian is a sum of a kinetic energy operator and the potential function. In treating the resulting differential equation, a departure from the usual technique is made. The hydrogen molecule has $D_2h$ symmetry, which means that an eigenfunction of the one electron Hamiltonian must either be symmetric or antisymmetric with respect to reflection through a plane perpendicular to and bisecting the line connecting the two nuclei. For this to be so, the component of the
gradient of this function normal to this plane must vanish, or the function itself must vanish on this plane, for a symmetric or antisymmetric function, respectively. Using one or the other of the above conditions as a condition on the symmetry plane allows one to consider the space on the one side of the symmetry plane only, with the function in the remaining half-space being generated by reflection through the symmetry plane.

It should be pointed out that this model is a natural adaptation of the Wigner-Seitz (9) treatment of solids to the homopolar two-electron bond. In their model, it is assumed that the electronic potential is that appropriate for the isolated atom. The resulting Schrödinger equation is solved using boundary conditions derived in the following way. Lines are drawn from the nucleus of the atom under consideration to the nucleus of each of its nearest neighbors. Planes perpendicular to and bisecting these lines are then used to construct a cell around the central nucleus. Boundary conditions, derived from symmetry, appropriate to the system under consideration are then applied on the surface of this cell which surrounds the central atom. This theory has had considerable success in predicting the binding energy of alkali metal crystals such as sodium (10), even when approximating to the cell with a sphere.

Because of the success of the Wigner-Seitz cell model in treating metallic solids, it seems of considerable interest to see if an extension to a homopolar diatomic bond has merit. If the model proves successful in this
application to the hydrogen molecule, it should also provide some physical insight into this type of bond. In addition it is hoped that, because of the relatively simple potential, extension to more complicated systems will prove possible, although this problem will not be considered here.

It will be shown that the molecular energy can be obtained from the model in a self-consistent way. This analysis is given in the first four parts of Section III (see also (37)). The results of this calculation provide a test of the ability of the model to describe bonding in the hydrogen molecule but, since the exact Hamiltonian was not averaged, the results cannot be directly compared with the work of others. This comparison is provided in Section IV by averaging the exact Hamiltonian for the hydrogen molecule over various forms of two-electron functions constructed from one-electron functions provided by the model. It is evident that, no matter what one-electron function is used, a product function can do no better than the SCF result. Rather than continue along the same lines and construct more complicated molecular wave functions, a theory is presented that, in principle, allows one to proceed directly to the total electronic energy without considering any average of the Hamiltonian other than that for the simple product of one-electron functions from the model. This theory and an application to the hydrogen molecule is given in Section V.
II. A ONE-ELECTRON POTENTIAL FOR THE
HYDROGEN MOLECULE

As stated in the Introduction, an approximate calculation of the
one-electron potential for the hydrogen molecule has been made in an effort
to test the accuracy of a coulomb potential. Because the model incorporates
the property of electron correlation, it is important for reasons of com-
parison that this calculation include correlation effects in the electron-
electron repulsion term. Slater (11) has considered this problem and sug-
gests that the potential of one electron in the field of the remaining electrons,
$V_e(1)$, can be obtained from

$$V_e(1) = \frac{\int u^*(1\ldots n; s_1 \ldots s_n) \left( \sum_{i=2}^{n} \frac{e^2}{r_{1i}} \right) u(1\ldots n; s_1 \ldots s_n) dv_2 dv_3 \ldots dv_n}{\int u^*(1\ldots n; s_1 \ldots s_n) u(1\ldots n; s_1 \ldots s_n) dv_2 dv_3 \ldots dv_n}. \quad \text{II. 1}$$

The integration is to be carried out over all spin coordinates and all spatial
coordinates except for those of the first electron. Each number, $n$, in paren-
theses refers to all spatial coordinates and $s_n$ represents the spin coordinates
of the $n^{\text{th}}$ electron. The symbol $dv_n$ designates the volume element for the $n^{\text{th}}$
electron. This equation is valid for any type of electron distribution and, in
fact, the type of distribution is determined by the function $u$. 


Ideally, the exact function for the hydrogen molecule should be used for \( u \), but practical considerations force one to consider the use of an approximate function. The simplest function having the character of a correlated electron distribution and going to the correct limit at large internuclear distance is the unscaled Heitler-London function, its form being

\[
\psi(1, 2) = a(1) b(2) + a(2) b(1)
\]

where \( a, b \) are hydrogen 1s atom orbitals centered around nuclei \( a, b \), respectively, and containing the coordinates of either electron one or two as indicated in the parentheses (see Figure 1). In this case the spin function is omitted since the spin and spatial parts of the wave function are factorable for a two electron system. Introducing this function into equation II.1

\[
V_e(1) = \frac{a^2(1) \int b^2(2)/r_{12}^2 \, dv_2 + 2a(1)b(1) \int a(2)b(2)/r_{12}^2 \, dv_2 + b^2(1) \int a^2(2)/r_{12}^2 \, dv_2}{a^2(1) + b^2(1) + 2a(1)b(1) \int a(2)b(2) \, dv_2}
\]

is obtained where \( V_e(1) \) is in atomic units. It is to be noted that \( V_e(1) \) is a function of the coordinates of electron one only, as indicated by the number in parentheses. If this electron is restricted to the neighborhood of, say, nucleus \( a \) and the internuclear distance is made large, \( b(1) \) will approach zero. Hence all terms but the first become negligible and this term approaches \( 1/r_b \). Now, the total one-electron potential in atomic units is defined as

\[
V(1) = -1/r_a -1/r_b + V_e(1)
\]
FIGURE 1. --The coordinate system for the hydrogen molecule

The nuclei are represented by a, b and the two electrons are designated by 1, 2. The distances between the respective particles are given by r with the appropriate subscripts.
A NEW THEORY OF MOLECULAR ORBITALS AND CORRELATION ENERGY OF MOLECULAR HYDROGEN

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

JAMES MACK PEEK, B. S., M. Sc.

The Ohio State University
1962

Approved by:

Alvin M. Lassette
Adviser
Department of Chemistry
where the first two terms on the right represent the electron-nuclear attraction and the last term is the nuclear repulsion term. Taking $V_e(1)$ as $1/r_b$ with $R$ large, it follows that $V(1)$ becomes $-1/r_a$. This is the isolated atom potential, the correct potential for two hydrogen atoms at large distances, which confirms the statement that the Heitler-London function gives the correct potential at large internuclear distances.

Equation II. 3 was evaluated in the following manner. First, it is convenient to introduce elliptical coordinates, defined as

$$\lambda_i = \frac{r_{ai} + r_{bi}}{2R} \quad 1 \leq \lambda_i \leq \infty$$

$$\mu_i = \frac{r_{ai} - r_{bi}}{2R} \quad -1 \leq \mu_i \leq 1 \quad \text{II. 5}$$

$$0 \leq \phi \leq 2\pi$$

where the angle $\phi$ is measured from the xz plane. The denominator of II. 3 integrates immediately to give

$$\exp(-2r_{ai}) + \exp(-2r_{bi}) + \exp(2R\mu) \left[ H_2(2R, \infty) - \frac{(2R)^3}{3} H_0(2R, \infty) \right] \quad \text{II. 6}$$

where

$$H_n(a, b) = \int_a^b \exp(-t)t^n dt \quad \text{II. 7}$$

The evaluation of the integral in equation II. 7 is elementary and this provides all the information necessary to compute the normalization term. To evaluate
the first and third integrals appearing in the numerator of equation II. 3 it is necessary to consider the expansion of $1/r_{12}$ in spherical polar coordinates (12). When this expansion is introduced into the first and third integrals of equation II. 3

$$\pi \left[ \frac{H_2(0, 2r_{bl})}{2r_{bl}} + H_1(2r_{bl}, \infty) \right]$$  \text{II. 8}

results for the first integral and

$$\pi \left[ \frac{H_2(0, 2r_{al})}{2r_{al}} + H_1(2r_{al}, \infty) \right]$$  \text{II. 9}

results for the third integral. Evaluation of the second integral is somewhat more cumbersome in that the expansion of $1/r_{12}$ must be used in elliptical coordinates. The expansion used is given by Preuss (13) where his $R$ is twice that used in this analysis. The second integral in equation II. 3 becomes

$$4\pi R^2 \left\{ \left[ Q_0(\lambda_1) - P_2(\mu_1)Q_2(\lambda_1) \right] \left[ R_2 - K_0/3 \right] + \left[ I_2 - I_0/3 \right] \left[ 1 - P_2(\mu_1)P_2(\lambda_1) \right] + P_2(\lambda_1)P_2(\mu_1)K_1 \right\}$$  \text{II. 10}

where $P_n$, $Q_n$ are Legendre functions of the first and second kind, respectively. The remaining terms are integrals defined as follows:

$$K_n = \int_{\lambda_1}^{\infty} \exp(-2Rt)t^n dt$$  \text{II. 11}

$$K_\lambda = \int_{\lambda_1}^{\infty} \exp(-2Rt)t^n dt$$  \text{II. 12}

$$I_n = \int_{\lambda_1}^{\infty} \exp(-2Rt)t^n Q_0(t) dt$$  \text{II. 13}
All terms, with the exception of those involving $I_n$, can be integrated immediately, so these terms were computed at each desired point on the potential surface. Changes of the independent variable and integration by parts reduces the term $-I_0/3$ to a sum of known functions and integral logarithms. In order to make maximum use of the existing tables of integral logarithms (42), this term was calculated at a series of closely spaced points corresponding to tabulated values of the integral logarithm and then interpolated to obtain the required values to complete the calculation of $V_e(1)$.

The quantity $+V(1)$ is given in Table 1 as a function of the Cartesian coordinates $z$, $x$ where $z$ is shown horizontally and $x$ vertically. The origin of the coordinate system is taken as the midpoint of the line connecting the two nuclei (Figure 1) and the quantities $+V(1)$ and distance are in atomic units. It is necessary to show only a cross-section containing the $z$ axis since the potential does not depend on the angle $\phi$. The resulting potential is illustrated in Figure 2 by a series of equipotential lines. This figure shows the potential surface for one electron in the hydrogen molecule under the assumption that the electron-electron repulsion is given by Slater's formula using the Heitler-London function as an approximation to the exact function.

We are now in a position to compare the assumed potential, $-1/r_b$, with that computed from equation II. 4. If the potential were $-1/r_b$, on the left side of the symmetry plane in Figure 2, the equipotential lines would be circles. This is a fair approximation except in the vicinity of the symmetry
**TABLE 1.** An approximate one-electron potential for the hydrogen molecule at the equilibrium internuclear distance

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FIGURE 2. - Equipotential lines for the hydrogen molecule at the equilibrium internuclear distance
plane. A more accurate estimation of the deviations from the Coulomb law is provided by Figure 3. The potential \(-V(l)\) is shown as a function of \(1/r_b\) along each of three directions radiating from nucleus \(b\); the first (curve A) along the line \(be\) of Figure 1, the second (B) along \(bd\) perpendicular to the line of centers, and the third line (C) along \(bc\). If the Coulomb law were an accurate approximation, the curves should be straight lines with a slope of 45 degrees. This is accurate for curve B and curve A deviates only slightly from such a line. Curve C deviates more markedly from a straight line although it approaches this line asymptotically at small values of \(r_b\). It can be concluded that this simple potential agrees quite well with the one computed from an approximation based on the Heitler-London wave function except in the vicinity of the symmetry plane. Hence, a Coulomb potential centered on the near nucleus will be employed as an approximation to the actual potential in the investigation of the model described in the Introduction.
FIGURE 3. $-V$ vs. $1/r_b$. Curves A, B and C refer to the respective lines be, bd, and bc of Figure 2.
III. ANALYSIS OF THE MODEL

A. Mathematical Formulation

In more specific terms the coulomb potential for a single electron is given by $-1/r_b$ on the left side of the symmetry plane, that is $r_a > r_b$, and $-1/r_a$ on the right side of the symmetry plane, $r_b < r_a$ (see Figure 2). Throughout this work, the convention of treating the left side of the symmetry plane will be adopted. Also all terms will be given in atomic units unless otherwise stated and the term $1/2R$, the nuclear repulsion term, will be omitted from all potential terms. With this convention, it follows that $\mu$ is confined to the interval $(0, 1)^*$ while $\lambda$ is confined to $(1, \infty)$. The potential for the left side becomes

$$V = \frac{-1}{R(\lambda - \mu)} \quad \text{III. 1}$$

in elliptic coordinates. In certain instances it may be worthwhile to consider a formula which applies to both sides of the dividing plane, that is, over the complete interval $(-1, 1)$ for $\mu$. Such a formula is as follows

$$V = \frac{-1}{R(\lambda - |\mu|)} \quad \text{III. 2}$$

*The notation used means that if $(a, b)$ is a closed interval for $x$, then $a \leq x \leq b$ and the open interval $(a, b)$ for $x$ implies $a < x < b$. It is also stipulated that $b > a$.  

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where $|\mu|$ denotes the absolute value of $\mu$. An additional pair of symbols $r_{ba}$ and $r_{ab}$, denoting respectively the distances of a point from the nearest and furthest nuclei, will be found useful later. In elliptic coordinates these quantities are given by the following formulae:

$$r_{ba} = R(\lambda - |\mu|)$$  \hspace{1cm} III. 3

$$r_{ab} = R(\lambda + |\mu|).$$  \hspace{1cm} III. 4

In terms of this notation equation III. 2 becomes

$$V = \frac{-1}{R(\lambda - |\mu|)} = \frac{-1}{r_{ba}}.$$  \hspace{1cm} III. 5

The assumption of a coulomb potential on either side of the symmetry plane has an interesting consequence. If the potential on one side were to be coulombic, $V(1)$ of equation II. 4 would become $-1/r_b$. Solving for $V_e(1)$, the electron-electron repulsion term is found to be $1/r_a$. It follows, as a result of the assumed coulombic potential, that $1/r_a$ replaces $V_e(1)$ of equation II. 1 or II. 4.

Remembering the conventions introduced, the one-electron Schrödinger equation for the model is

$$-1/2 \nabla^2 \Psi - 1/r_b \Psi = \epsilon \Psi$$  \hspace{1cm} III. 6
where \( \varepsilon \) is the one-electron energy. Introducing \( \psi = M(\mu) \Lambda(\lambda) e^{i m \phi} \) the equation is separable into the two ordinary differential equations

\[
\frac{d}{d\lambda} \left[ (\lambda^2 - 1) \frac{d\Lambda}{d\lambda} \right] + \left[ -p^2 \lambda^2 + 2R \lambda - \frac{m^2}{\lambda^2 - 1} + A \right] \Lambda = 0 \tag{III.7}
\]

\[
\frac{d}{d\mu} \left[ (1 - \mu^2) \frac{dM}{d\mu} \right] + \left[ \frac{2}{p} \mu^2 + 2R \mu - \frac{m^2}{1 - \mu^2} - A \right] M = 0 \tag{III.8}
\]

where \( A \) is a separation parameter, and \( p^2 = -2R^2 \varepsilon \). The boundary conditions are: (i) \( M \) or its first derivative with respect to \( \mu \) vanish on the symmetry plane, \( \mu = 0 \), and is bounded at \( \mu = 1 \); (ii) \( \Lambda \) must be bounded at \( \lambda = 1 \) and vanish at \( \lambda = \infty \).

Equation III.7 has been studied by Jaffe (14), and equation III.8 has been treated by Wilson (15). The boundary conditions employed by Wilson are different from the above but the analysis is otherwise applicable. For the sake of completeness the analyses and the necessary modifications to our equations are outlined below.

The new independent variable \( w = \frac{\lambda - 1}{\lambda + 1} \) and the new dependent variable

\[
\Lambda = (\lambda^2 - 1)^{m/2}(\lambda + 1)^{\sigma} e^{-p\lambda} y, \quad \sigma = \frac{R}{p} - m - 1 \tag{III.9}
\]
ACKNOWLEDGMENTS

I wish to thank my adviser, Professor Edwin N. Lassettre, for suggesting this problem, for his many contributions to its solution, and for his continuous encouragement throughout the period of the investigation.

Contributions by many others were also invaluable in the completion of this investigation. I shall mention Dr. James M. Stewart for aid in digital computer programming, the faculty members and graduate students who contributed through many informal discussions and my family and personal friends, whose understanding can never be repaid.
are introduced into equation III. 7. The resulting equation for $Y$ is

$$w(1-w^2) \frac{d^2Y}{dw^2} + \left[ -(m+2\sigma-1)w^2 + 2(\sigma-2p-1)w + m + 1 \right] \frac{dY}{dw} \quad \text{III. 10}$$

$$+ \left[ \sigma(\sigma+m)w + \sigma(1+2p) + m(m+1+\sigma) + A - p^2 \right] Y = 0.$$  

$Y$ must be bounded at $\lambda = 1$ in order that $\Lambda$ be bounded. Introducing the series $Y = \sum_{t=0}^{\infty} g_t w^t$, which is necessarily bounded at $\lambda = 1$, leads to the recurrence formula

$$\alpha_t g_{t+1} - \beta_t g_t + \gamma_t g_{t-1} = 0 \quad \text{III. 11}$$

with the terminal condition $\alpha_1 g_1 - \beta_0 g_0 = 0$, where

$$\alpha_t = (t+1)(t+1+m) \quad \beta_t = 2t^2 + (4p-2\sigma) t - A + p^2 - 2p\sigma - (m+1)(m+\sigma) \quad \text{III. 12}$$

$$\gamma_t = (t-\sigma)(t-1+m-\sigma).$$

The second solution to equation III. 10 is not bounded at $\lambda = 1$ and is not representable as a series of positive powers of $w$ (25). The ratio $T_t = g_t / g_{t-1}$ was shown by Jaffe to be obtainable from the continued fraction

$$T_t = \frac{\gamma_t}{\beta_t} \frac{\alpha_t \gamma_{t+1}}{-\beta_{t+1}} \frac{\alpha_{t+1} \gamma_{t+2}}{-\beta_{t+2}} \ldots \quad \text{III. 13}$$
which converges for a solution of equation III. 10 bounded at \( w = 1 \). From equation III. 9 it follows that \( \Lambda \) vanishes at \( \lambda = \infty \). When \( t = 1 \), then 
\[
T_1 = \frac{\beta_0}{\alpha_0}, \quad \text{and the continued fraction becomes}
\]
\[
\frac{\beta_0}{\alpha_0} = \frac{\gamma_1}{\beta_1} \frac{\alpha_1}{-\beta_2} \frac{\gamma_2}{-\beta_3} \frac{\alpha_2}{-\beta_4} \frac{\gamma_3}{-\beta_5} \ldots
\]  
III. 14

This equation has as its roots the eigenvalues of \( p \) for a given \( \Lambda \) or vice versa.

Introducing, following Wilson, the new dependent variable \( F \) through
\[
M = (1 - \mu^2)^{m/2} e^{+p(\mu-1)} F
\]  
III. 15
and the new independent variable \( x = \mu - 1 \), equation III. 8 becomes
\[
x(x+2) \frac{d^2 F}{dx^2} + 2 \left[ m + 1 + (m + 1 + 2p) x + px^2 \right] \frac{dF}{dx} \\
+ \{ q - 2[R - p(m+1)] x \} F = 0
\]  
III. 16
where
\[
q = A - p^2 + (m+1)(m+2p) - 2R.
\]  
III. 17

Substituting the power series expansion
\[
F = \sum_{t=0}^{\infty} a_t x^t
\]  
III. 18
into equation III. 16, the following recurrence formula is obtained;

\[ 2(t+1)(t+1+m)a_{t+1} + [t(t+2m+1+4p)+q]a_t + 2(pt-R+pm)a_{t-1} = 0. \]  

III. 19

The terminal condition for \( t = 0 \) is

\[ 2(m+1)a_1 + qa_0 = 0. \]  

III. 20

This series expansion assures that \( F \), hence \( M \), is analytic at \( \mu = 1 \). By imposing the remaining boundary condition, the one on the symmetry plane, a second equation in \( A \) and \( p \) is found. In one case, for a solution symmetric with respect to reflection through the symmetry plane, \( dM/d\mu = 0 \) at \( \mu = 0 \) gives

\[ \sum_{t=0}^{\infty} (-1)^t(p-1)a_t = 0 \]  

III. 21

and in the second case, for a solution antisymmetric with respect to reflection through the symmetry plane, \( M = 0 \) at \( \mu = 0 \) gives

\[ \sum_{t=0}^{\infty} (-1)^t a_t = 0. \]  

III. 22

Since equation III. 8 contains no odd powers of \( p \), \( p \) can be replaced with \(-p\) without altering the equation. Introducing this change into equation III. 15 gives a different representation of the same solution to equation III. 8, which is characterized by replacing \( p \) by \(-p\) in equations III. 16, III. 17, III. 19, III. 21 and III. 22. Both forms of the solution to equation III. 8 were studied and gave, as required, identical eigenvalues. It was found that the first
form of solution, corresponding to the equations listed above, converged much faster at large R and therefore was the one most generally employed.

The two equations III. 14 and III. 21 or III. 22 give two relationships between A and p, where simultaneous solution for a given R and m constitutes a pair of eigenvalues for the system. Although these equations determine, in principle, the eigenvalues for A and p, no simple formula is available for numerical calculation. For this reason, a program for a digital computer was written which, given starting values for A, p, would systematically vary one and then the other of the parameters until a pair of eigenvalues of predetermined accuracy is found. The details concerning this program are given in Appendix A.

These relationships are adequate for calculating eigenvalues but the expression for A has a decided disadvantage in calculating matrix elements since complicated integrals arise. This difficulty can be avoided entirely by expanding A in an appropriate series of Laguerre polynomials. Making the substitution

$$
\Lambda = \left[ \left( \frac{r^2}{4p^2} \right) + \frac{r}{p} \right]^{m/2} e^{-r/2} \sum_{n=0}^{\infty} b_n L_n^{(m)}(r)
$$

III. 23

into equation III. 7, where $$r = 2p(\lambda - 1)$$ and $$L_n^{(m)}(r)$$ is an associated Laguerre polynomial as defined by Szegö (16), we find the following three-term
recurrence formula for the coefficients:

\[ n(\sigma-n+1)b_{n-1} - \left[ q+4R+(m+1-4p)n+(\sigma-n)(2n+m+1) \right] b_n \]
\[ + (n+m+1)(\sigma-n+m) b_{n+1} = 0 \]

with the terminal condition

\[ (m+1)(\sigma+m)b_0 - (q+4R+\sigma+m\sigma)b_0 = 0. \]

This solution is bounded at \( \lambda = 1 \) and also goes to zero exponentially as \( \lambda \) goes to \( \infty \), as required. It is of interest that the coefficients \( g_n \) of equation III. 11 are related to the above coefficients \( b_n \), when \( m = 0 \), by

\[ b_n = \frac{\Gamma(n+1)}{\Gamma(n-\sigma)} g_n \]

where \( \Gamma \) is a gamma function. No proof will be given for this relationship since it is not used in any of the remaining analyses.

Although equation III. 23 is useful for many purposes, yet another representation of the solution to equation III. 7 will be found to be useful, especially when dealing with excited state functions. Designating \( p, A \) as the eigenparameters for the ground state and \( m, p', A' \) as the eigenparameters for a certain excited state, the solution to the excited state differential equation can be found in the following way. Introducing into equation III. 7

\[ \Lambda = (\lambda^2-1)^{m/2} e^{-r/2} \sum_{n=0}^{\infty} c_n L_n^{(m)}(r) \]

III. 27
where \( r \) has the definition given above, the following recurrence relationship is found for the coefficients:

\[
\begin{align*}
\alpha (n+m+2)(n+m+1)c_{n+2} & - (n+m+1) \left[ \sigma - n + m + 2\alpha (2n+m+2p+2) \right] c_{n+1} \\
+ \left\{ q'' + 2R - 4pn + \sigma (m+1) + 2n(\sigma - n) + \alpha \left[ 4p(2n+m+1) + 6n(n+m+1) + (m+1)(m+2) \right] \right\} c_n \\
- n[\sigma - n + 2\alpha + 2p + 2n + m] c_{n-1} + \alpha n(n-1)c_{n-2} &= 0,
\end{align*}
\]

where \( q'' = A'' + (m+1)(m-2p) - p''^2 \), \( \sigma = (R/p) - m - 1 \), \( 4\alpha = 1 - (p''/p)^2 \).

Although this expansion is not as convenient as equation III. 23 and the coefficients, \( c_n \), may not decrease as rapidly as the expansion in the variable corresponding to the excited state being studied, this expansion has one decided advantage. That is, when dealing with integrals involving a product of two functions for different states, by representing one of the functions as the expansion defined by equation III. 23, the orthogonality relationship between Laguerre polynomials of different degree is preserved. The only added complexity arises from having to deal with the five term recurrence relationship, equation III. 28. This is manifest in the increased amount of arithmetic in handling the five terms and in the terminal conditions. However, the arithmetic is a minor matter when a digital computer is employed. Also, since the solution in terms of the excited state \( p'' \) is known, the following special technique can be used to handle the terminal conditions.

Terminal relationships between the coefficients \( c_0, c_1, c_2 \) and \( c_0, c_1, c_2, c_3 \) follow automatically from equation III. 28 for \( n = 0 \) and \( n = 1 \). Ordinarily the
third terminal condition necessary to determine the coefficients of equation III. 28 is found by truncating the expansion in equation III. 27 at some maximum value of \( n \) (26). The following derivation gives a more appropriate condition on the coefficients and, at the same time, is numerically easier to use than this third terminal condition. The following technique is also used to determine a value for the arbitrary coefficient \( c_0 \) which insures that solutions represented by equations III. 23 and III. 27 are normalized to the same value. Hence the normalization constant can be calculated from equation III. 23 rather than from the more slowly convergent expansion of equation III. 27. For \( m = 0 \), equating equation III. 23 to III. 27, multiplying through by \( \exp(-r/2)L_n(r) \) and integrating with respect to \( r \), the relationship

\[
C_k = \sum_{n=0}^{\infty} \left( \int_0^\infty b_n \exp\left(-\frac{r^2+r}{2}\right) L_n(r) L_k(r) \, dr \right) = \sum_{n=0}^{\infty} \frac{k}{n} b_n ^n
\]

is required for the coefficient \( c_k \). Utilizing the generating function for the Laguerre polynomials (16) it is easily shown that

\[
I_n^0 = \frac{2p^n}{p + p'} \beta^n
\]

\[
I_n^1 = \frac{-4}{(1-p''/p)^2} [(n+1)\beta^n - npn^{-1}] + I_n^0
\]

where \( \beta = (p''/p'')(p + p') \). Now, with the condition on \( c_0 \)

\[
c_0 = \sum_{n=0}^{\infty} I_n^0 b_n
\]
equation III. 27 will have the same normalization constant as the expansion in equation III. 23. With $c_1$ determined by

$$c_1 = \sum_{n=0}^{\infty} \frac{1}{n} b_n \quad \text{III. 32}$$

along with the two starting terminal conditions, equation III. 28 can be used to generate the coefficients of equation III. 27 without recourse to the terminal condition at large $n$.

In discussing the differential equation for $M$ it is convenient to introduce the potential as defined in equation III. 5, which is defined over the range $(-1, 1)$ for the variable $\mu$. In this instance, the differential equation for $M$ (III. 8) becomes

$$\frac{d}{d\mu} \left[ (1-\mu^2) \frac{dM}{d\mu} \right] + (p^2 \mu^2 + 2R |\mu| - \frac{m^2}{1-\mu^2} - A) M = 0. \quad \text{III. 33}$$

This differs from equation III. 8 only in the term $|\mu|$. To find a solution for equation III. 33 in terms of the associated Legendre functions, we first introduce

$$|\mu| P_{2n} = \sum_{l=0}^{\infty} g_{2n, 2l} P_{2l}^{(2)}(\mu) \quad \text{III. 34}$$

and then substitute

$$M = \sum_{n=0}^{\infty} h_{2n, 2n} P_{2n}^{(m)}(\mu) \quad \text{III. 35}$$
into equation III. 33. We obtain

\[ [A_{2n-2} + 2R g_{2n-2, 2n}] h_{2n-2} + [B_{2n} + 2R g_{2n, 2n}] h_{2n} \]

\[ + [C_{2n+2} + 2R g_{2n-2, 2n}] h_{2n+2} = -2R \sum_{l=1}^{n-1} g_{2l+1, 2n}, \quad l \neq n-1, n, n+1 \]

as the recurrence formula for the coefficients, where the quantities are defined as follows:

\[ A_{2n-2} = p^2 \gamma_{2n-2} \]

\[ \gamma_n = \frac{(n+1)(n+2)}{(2n+1)(2n+3)} \]

\[ B_{2n} = \beta_{2n} p^2 A - 2n(2n+1) \]

\[ \beta_n = \frac{4n^3 + 6n^2 - 1}{(2n+1)(2n-1)(2n+3)} \]

\[ C_{2n+2} = p^2 \epsilon_{2n+2} \]

\[ \epsilon_n = \frac{n(n-1)}{(2n+1)(2n-1)} \]

\[ g_{2k, 2l} = (2l+1) \int_0^1 P_{2l+1} P_{2k} d\mu + 1 \int_0^1 P_{2l-1} P_{2k} d\mu. \]

It will be noted that equation III. 36 involves every coefficient that is not assumed to be zero; hence this representation is not useful for the calculation of eigenvalues but has utility in developing a solution convenient for computing average values. Also, equation III. 36 is written in a form that will generate even solutions to equation III. 33 only. To obtain the analogous formula for the odd solutions, substitute everywhere \( n-1 \) for \( n \).

It is also of interest to note that if the absolute value of \( \mu \) is expanded in a Legendre series and only the first two terms are retained, on substituting this truncated series into equation III. 33 a differential equation is obtained
which has been treated extensively by Stratton, et al. (17). This approximation will be excellent as \( R \) becomes small, and hence, Stratton's results give a good indication how the solutions to equation III. 33 behave in this region.

Let the linear differential operators on the left side of equations III. 7 and III. 8, excluding the term \( A \) be designated by \( Q \) and \( S \), respectively. Then the requirement that the following integrals be extremes with respect to variation in \( f \) and \( g \)

\[
J = \frac{\int_{-\infty}^{\infty} fQf \, dv}{\int_{-\infty}^{\infty} f^2 \, dv} \tag{III. 38}
\]

\[
K = \frac{\int_{0}^{1} gSg \, dv}{\int_{0}^{1} g^2 \, dv} \tag{III. 39}
\]
gives the differential equations III. 7 and III. 8 if \( f, g \) are functions satisfying the same boundary conditions as \( A \) and \( M \) respectively. These conditions are exact and follow immediately from the calculus of variations as applied to Sturm-Liouville problems (27). The integrals are given explicitly, for future reference, since approximate values of the eigenvalue \( A \), and approximate eigenfunctions, are obtained by this method in subsequent chapters. We note that \( K = A \) when \( g = M \), the solution to equation III. 8, and \( J = -A \) when \( f = A \), the solution to equation III. 7.
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Since preliminary values of $A, p$ are necessary to start the successive approximation method employed with the digital computer it will be useful to obtain approximate relationships between the eigenparameters which will generate these starting values. These starting values do not have to be of high accuracy but very little is known about how $p$ behaves and even less is known about $A$. We do know that $p$ goes to $R/n$ as $R$ becomes both large and small. This follows from the fact that $\varepsilon$ must go to the hydrogen atom energy $-1/2n^2$, where $n$ is the principal quantum number, at these extremes in $R$.

One approximate relation between $A$ and $p$ is obtained from equation III. 39, with $m = 0$, by setting $g$ equal to a constant. This function satisfies the boundary condition $(dM/d\mu)_{\mu=0} = 0$ and gives the relationship

$$A = p^{2/3} + R$$

as an approximation to the largest eigenvalue, $A$, of equation III. 8. It is to be noted in passing that, no matter what solution of equation III. 7 is involved, the wave function in this case has symmetry $\sigma^g_u$ using the conventional notation for diatomic molecules (28). If, with $m = 0$, we let $g = \mu$, which satisfies the boundary condition $(M)_{\mu=0} = 0$, it follows from equation III. 39 $A$ is given approximately by

$$A = p^{2/2} + 2R/3 - 2.$$
This is an approximation to the highest eigenvalue, \( A_n \), of equation III. 8 corresponding to a function antisymmetric with respect to reflection through the dividing plane. The total wave function, \( \Psi \), has the symmetry described by the term symbol \( \sigma_u \).

A further relation between \( R \) and \( \varepsilon \), hence \( p \), can be obtained from averaging the Hamiltonian operator of equation III. 6 over the variation function \( \exp(-R\lambda)\cosh\mu \). This function has symmetry appropriate to \( \sigma_g \). From these values of the energy, approximate values of \( p \) can be obtained which will serve well as starting values. This method provides an approximation only to the lowest energy state.

For higher energy states, adequate starting values were found from the following simple scheme. At small \( R \), the terms linear in \( \lambda, \mu \) in equations III. 7 and III. 8 become negligible, hence approximating to the equations whose solutions and eigenvalues are tabulated by Stratton, et al. (17). Hence from these tables approximate values of \( p \) and \( A \) were obtained at small \( R \) for all states of interest. These starting values were then used in the digital computer program to obtain the exact eigenvalues \( A, p \) for these various states. Rough extrapolation to larger \( R \) provides another series of starting values. The eigenvalues \( A, p \) for any given state can be built up in this way for the complete range of \( R, (0, \infty) \). Admittedly this is a very rough scheme for finding starting values; however, it proved adequate. This fact points out some measure of flexibility in the digital computer program.
B. A One-Electron Correlation Diagram

Solving the set of differential equations generated by the model, equations III. 7, III. 8, the energy for one electron $\epsilon$ (or its equivalent; p) and the eigenparameter $A$ has been found as a function of $R$ and at the various values of $m$. A one-electron correlation diagram, showing $\epsilon$ as a function of $R$ for all states correlating to the separated atom with $n = 1, 2, 3$, is shown in Figure 4. Following that, in Table 2, the eigenparameters for these states are listed as a function of $R$. The accuracy of these eigenparameters is indicated by the number of figures listed. It is to be noted that the last figure quoted is somewhat uncertain. The program from which these values were obtained has a provision for varying the accuracy and hence the number of significant figures will vary. States of more interest, such as the ground state near the equilibrium internuclear distance, were studied with greater accuracy than states of less immediate interest.

In order to better distinguish the various states, the following notation has been devised. After each state the two numbers $(j, k)$ have been added. The second number $k$, for a given molecular state gives 1, the total orbital angular momentum of the combined atom subshell to which this state
correlates. The first number, $j$, gives $n-1-1$ for the combined atom to which
the molecular state correlates. Obviously $j+k = n-1$, hence the molecular
state must correlate to a combined atom with a major quantum number of $n$,
or $j+k+1$.

One advantage of this notation is that it makes it possible to
recognize the similarity between certain states. Note that states having the
same value of $m^2$ and $k$ behave in the same way whatever value $j$ may take.
For example, consider the states $\sigma_g (j, 0)$, where $j = 0, 1, 2$. In each case
correlation is between combined atom and separated atom states with the
same value of $n$. Their behavior for intermediate values of $R$ is also quite
similar. Other examples are obvious from the consideration of Figure 4.
This regular behavior is useful in predicting the character of higher states.
For instance, if one wished to correlate states going to separated atoms with
$n = 4$, one could arrive at the qualitative behavior of these states just by con-
sidering the lower states.

Table 2 affords some general information on the behavior of $A$.
At small $R$ it is seen that this quantity goes to $-1(1-1)$. This is expected be-
havior when one considers the results obtained by Stratton, et al. (17).
This analogy, at small $R$, was pointed out earlier. In the case of the $\sigma_g (0, 0)$
and $\sigma_u (0, 1)$ states, $A$ is found from a variation treatment to behave as $R^2$
in the limit of large $R$. No further investigation of the significance or be-
havior of $A$ has been made.
FIGURE 4. -- The one-electron correlation diagram for the hydrogen molecule
TABLE 2.—The eigenvalues, $p$ and $A$, tabulated as a function of $R$ for various states

<table>
<thead>
<tr>
<th>$R$</th>
<th>$A$</th>
<th>$p$</th>
<th>$A$</th>
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The one-electron correlation diagram serves, in many ways, to justify the assumptions made in constructing the model. To emphasize this point, several of these observations are listed below, along with some comments on the application of these results to more complicated systems.

1) Figure 4 shows that the argument given concerning the correct limiting behavior of the one-electron energy at large $R$ is correct. For the cases $n = 1, 2, 3$ it is seen that $\epsilon$ approaches $-1/2n^2$ for the separated atoms.

2) It should be pointed out that the model reduces to the hydrogen atom rather than the helium atom in the limit of small $R$. However, as $n$ increases for the combined atom, it can be seen from Slater's rules for nuclear screening (28) that the actual one-electron potential for the helium atom quickly becomes that assumed in the model. For one electron in the helium atom excited to a state $n = 2$, the remaining $1s$ electron is 85% effective in screening the nucleus and for higher states, the $1s$ electron screens the nucleus completely.

3) Because of the incorrect limit of the model at small $R$, the minimum for the one-electron energy for the ground state is probably spurious. The correct limit is $-0.92$ a.u. (29) where the model goes to the $1s$ hydrogen atom energy, $-0.5$ a.u. This minimum occurs at such small $R$, however, that it seems reasonable that this will not seriously affect the results near the equilibrium internuclear distance for the hydrogen molecule. From the argument given above it can be seen that this error will become less important
as $n$ increases for the combined atom. This is also confirmed by the fact that the first ionization potentials of the states $n(s, p, \ldots)$ for helium approach rapidly to the ionization potential of the $n^{th}$ excited state of the hydrogen atom (see (30)).

4) When interpreted in the light of molecular orbital or valence bond methods, the correct limits, especially at large $R$, have an added significance. Without appeal to the concepts of electronic exchange, as in the valence bond case, or admitting to an incorrect limit, as in the case of the usual single configuration molecular orbital method, the model gives molecular orbitals that behave correctly at large $R$.

5) The behavior at intermediate internuclear distance is at least qualitatively correct. Note that the orbitals become bonding or anti-bonding as one proceeds toward smaller $R$ from the separated atom case. For example, for the separated atom with $n = 1$, it is known that a bonding and an anti-bonding orbital will occur. This is also predicted by the model. The states are designated by $\sigma_g (0,0)$, $\sigma_u (0,1)$ respectively and have, as indicated, the expected symmetry. This same behavior is observed for the higher states, although their dependence on $R$ becomes more complex. These results show that the model incorporates many of the properties of a homo-polar bond. This seems even more remarkable when one notices that the Schrödinger equation is identical with that of the hydrogen atom. The only difference between this treatment of the molecule and the atom is in the boundary conditions, and this is sufficient to lead to bonding and anti-bonding orbitals.
6) It will be noted that the non-crossing rule is violated in many instances, as it is in the case of the hydrogen molecule ion correlation diagram (31). This is due to the fact that the model has more symmetry than is actually possessed by the hydrogen molecule. If one were to take into account the inter-electron repulsion term, a perturbation term would arise that would probably have the effect of separating these forbidden crossings. If this effect were small, the states $\sigma_g^*(1,0)$ and $\sigma_g^*(0,2)$ would combine to give a lower state with two minima and an upper state with one minimum. This is interesting when one considers the result recently obtained by Davidson (24) in which the potential function of the first excited state $\Sigma^+_g$ for the hydrogen molecule has a double minimum.

7) These one-electron orbitals have another interesting characteristic. For example, the state $\sigma_g^*(0,2)$ has a minimum and then crosses over the energy corresponding to the atomic state from which it arose and continues to a higher state of the combined atom. Several other states, such as $\sigma_g^*(1,2)$ and $\pi_u^*(0,3)$ behave similarly. Using a qualitative argument, one could say that these orbitals are bonding until they reach the critical energy, equal to the corresponding atomic energy, where they then become anti-bonding. At these unique points enough information is available to calculate $R$, $A$, and $p$ from the model without further assumption. At one of these points $\varepsilon = -(1/2)(R/p)^2 = -(1/2n^2)$, providing one relationship between $R$ and $p$. This eigenvalue also assures that the functions $\Lambda$, $M$ are identical,
in the half plane considered, with hydrogen atom orbitals and are, therefore, expressible as exponentials multiplied by polynomials. Two more relations between $R$, $A$ and $p$ result from imposing the boundary conditions on these polynomials. This constitutes a system of three equations in three unknowns and, hence can be solved. This procedure was carried out for a few of the simpler cases. For the $\sigma_g^{(0,2)}$ state the cross-over point was found to be $R = 2.82842$, for $\sigma_g^{(1,2)} R = 2.91807$, for $\pi_u^{(0,3)} R = 5.19615$ and for $\sigma_g^{(0,4)} R = 9.274$.

8) It is possible, in a qualitative way, to use these results to build up orbitals for more complicated homo-polar systems. In these cases an effective atomic number must be introduced. The one-electron potential becomes $-z/r_b$. If in Figure 4, $R$ is replaced by $zR$ and $\varepsilon$ is replaced by $\varepsilon/z^2$, the figure remains valid. Although no specific arguments of this nature will be considered, a few general observations can be made. Note that the $\sigma_g^{(j,0)}$, $\sigma_u^{(j,1)}$ states converge to the united atom energy at relatively small $R$. This means that electrons in these orbitals, even if they are in the valence shell, will contribute little to bonding when $R$ is large. Also at these larger values of $R$ the $\sigma_g$, $\sigma_u$ states correlating with combined atom states having the largest orbital angular momentum quantum numbers are the orbitals that contribute, respectively, the most to bonding and anti-bonding. At smaller values of $R$, it should be noticed that, especially in the case correlating to separated atoms with $n = 2$, the $\pi_u^{(j,1)}$ state becomes more bonding while the bonding
\( \sigma_{(j,2)} \) state becomes less bonding and is finally promoted to an anti-bonding state. This predicts that, as \( R \) decreases, a bond of \( \pi_u \) type will contribute more to bonding, while a bond of \( \sigma_g \) type will contribute less, until very small values of \( R \) are reached.
C. Construction of Wave Functions

Now that the eigenparameters $A$, $p$ are known we are in a position to construct the wave functions in such a way as to be most convenient for the calculation of average values. The wave functions for the state $\sigma_g(0, 0)$ will be the state studied in greatest detail since this state is the best understood for the hydrogen molecule. Also, this detailed analysis will be given for the equilibrium internuclear distance, $R = 0.7$, for several excited states, while the ground state will be investigated at a number of internuclear distances including the equilibrium internuclear distance.

As pointed out earlier, the most convenient representation for the wave function, which is to be used in the calculation of average values, is as an expansion of orthogonal polynomials. An expression for $A$ in terms of Laguerre polynomials is given in equation III. 23. Once $A$ has been calculated at a given $p$ and numerical values inserted into equation III. 23, the ratio $a_n/a_0$ can be calculated as a function of $n$. Any number of coefficients can be calculated but it is found that the coefficients go through a minimum and then increase. This behavior is due to the fact that the eigenparameters are known with only finite accuracy. It would take parameters known with
infinite accuracy to provide accurate coefficients at large $n$. Since this is not practical, the following scheme was used to circumvent this difficulty. It is assumed that the series in equation III. 23 can be terminated at some value, say $k$. This assumption leads to a set of linear homogeneous equations for the coefficients. Hence, the determinant of the coefficients must vanish. If the previously calculated $p$ is employed, then this relationship determines an $A$, say $A'$, which is self-consistent with the assumed truncation of the solution. If this $A'$ turns out to be in good agreement with the one resulting from the initial eigenvalue calculation; the solution truncated at $k$ is assumed to be a sufficiently accurate representation of the solution. Practical experience also justifies the truncations that were made in that, when calculating various matrix elements, the last terms retained invariably contributed little to the results of this calculation. This technique is equivalent to assuming a variation function in the form of equation III. 23 truncated at $k$ and finding the coefficients of this expansion by making $J$ of equation III. 38 an extreme. The extreme of $J$ becomes $A'$. For several cases, wave functions were found by both methods and, as required, identical results were obtained. For the ground state, it was found that three terms in the series were sufficient to produce a self-consistent $A'$ in good agreement with the $A$ calculated originally (see Table 3). More terms were required for the excited states. The results for these states are shown in Table 5.
The development of solutions to equation III. 8, or its equivalent equation III. 33, follows the same outline. A truncated solution of the form of equation III. 35 is assumed, and an $A''$ is found which is consistent with this truncation for the given $p$. The recurrence relationship of equation III. 36, along with the condition imposed by the truncation was used in most cases, although a variation method exists. This variation method is based on equation III. 39, in which case $K$ becomes $A''$. The results for $M$ are shown in Table 4 for the ground state and Table 6 for the various excited states at $R = 0.7$.

Note that the number of significant figures given for the parameters $A$, $p$ and $A'$ in Table 3 exceeds the accuracy listed for $A$, $p$ in Table 2. These values listed for $A$, $p$ are the results found from computations made with the digital computer which have not been rounded off to their expected accuracy. These values of $p$ were the ones used in the condition imposed by truncation and the $A'$ given are the values necessary to satisfy this condition. Hence, if the values listed for $p$ and $A'$ were used, along with the condition imposed by the truncated expansion, the coefficients given would be found. If the values for $A'$ or $p$ were rounded off, this calculation would give different coefficients and the condition imposed by truncation would no longer be as accurately satisfied. The $A$ given in Table 3 is listed with this many significant figures for the sake of comparison. Note that $A$ and $A'$ agree, in general, to the same number of significant figures given for $A$ in Table 2. These remarks also apply for the $A''$ and $A'$ listed in Tables 4, 5 and 6.
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TABLE 3. —The coefficients of the $\Lambda$ expansion, equation III. 28, the parameters $A$, $p$ and the self-consistent $A'$ as a function of $R$ for the $\sigma_g(0,0)$ state

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<td>1.2124921</td>
<td>1.7867174</td>
<td>1.7866296</td>
<td>0.017102</td>
<td>0.0016580</td>
</tr>
<tr>
<td>1.3</td>
<td>1.4069386</td>
<td>2.2694758</td>
<td>2.2685956</td>
<td>0.0100752</td>
<td>0.0011084</td>
</tr>
<tr>
<td>1.5</td>
<td>1.5982504</td>
<td>2.8121903</td>
<td>2.8119235</td>
<td>0.0074047</td>
<td>0.0007474</td>
</tr>
</tbody>
</table>

TABLE 4. —The coefficients of the $M$ expansion, equation III. 35, and the self-consistent $A''$ as a function of $R$ for the $\sigma_g(0,0)$ state

<table>
<thead>
<tr>
<th>R</th>
<th>$A''$</th>
<th>$a_2$</th>
<th>$a_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.3473752</td>
<td>0.0770009</td>
<td>-0.0047839</td>
</tr>
<tr>
<td>0.5</td>
<td>0.6376210</td>
<td>0.1454888</td>
<td>-0.0063680</td>
</tr>
<tr>
<td>0.6</td>
<td>0.8000935</td>
<td>0.1843740</td>
<td>-0.0064232</td>
</tr>
<tr>
<td>0.7</td>
<td>0.9738656</td>
<td>0.2260423</td>
<td>-0.0058778</td>
</tr>
<tr>
<td>0.71</td>
<td>0.9918485</td>
<td>0.2303502</td>
<td>-0.0057874</td>
</tr>
<tr>
<td>0.72</td>
<td>1.0099683</td>
<td>0.2346912</td>
<td>-0.0056896</td>
</tr>
<tr>
<td>0.73</td>
<td>1.0281910</td>
<td>0.2390548</td>
<td>-0.0055851</td>
</tr>
<tr>
<td>0.8</td>
<td>1.1590793</td>
<td>0.2703479</td>
<td>-0.0046484</td>
</tr>
<tr>
<td>0.9</td>
<td>1.3559048</td>
<td>0.3171353</td>
<td>-0.0026541</td>
</tr>
<tr>
<td>1.1</td>
<td>1.7867060</td>
<td>0.4179091</td>
<td>+0.0016580</td>
</tr>
<tr>
<td>1.3</td>
<td>2.2695437</td>
<td>0.5272498</td>
<td>+0.0146784</td>
</tr>
<tr>
<td>1.5</td>
<td>2.8107976</td>
<td>0.6445231</td>
<td>+0.0301298</td>
</tr>
</tbody>
</table>
TABLE 5. -- The coefficients of the $\Lambda$ expansion, equation III. 28, the parameters $A$, $p$ and the self-consistent $A'$ for various states at $R = 0.7$

<table>
<thead>
<tr>
<th>State</th>
<th>$p$</th>
<th>$A$</th>
<th>$A'$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_3$</th>
<th>$b_4$</th>
<th>$b_5$</th>
<th>$b_6$</th>
<th>$b_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_u(0,1)$</td>
<td>0.4707326</td>
<td>-0.8066</td>
<td>-0.8065500</td>
<td>-0.16951</td>
<td>-0.01952</td>
<td>-0.00426</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\sigma_u(1,1)$</td>
<td>0.27970</td>
<td>-0.8938</td>
<td>-0.892518</td>
<td>0.91339</td>
<td>-0.35076</td>
<td>-0.05557</td>
<td>-0.01438</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\sigma_u(2,1)$</td>
<td>0.19960</td>
<td>-0.9187</td>
<td>-0.9146937</td>
<td>1.01845</td>
<td>0.77966</td>
<td>-0.48831</td>
<td>-0.09194</td>
<td>-0.02600</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\sigma_u(3,1)$</td>
<td>0.15528</td>
<td>-0.9250</td>
<td>-0.9199062</td>
<td>1.04145</td>
<td>0.97168</td>
<td>0.65873</td>
<td>-0.59495</td>
<td>-0.12513</td>
<td>-0.03740</td>
<td>--</td>
</tr>
<tr>
<td>$\sigma_u(0,3)$</td>
<td>0.18120</td>
<td>-11.0625</td>
<td>-11.067643</td>
<td>-2.51464</td>
<td>2.06480</td>
<td>-0.52527</td>
<td>-0.01591</td>
<td>-0.00313</td>
<td>-0.00082</td>
<td>--</td>
</tr>
<tr>
<td>$\sigma_u(1,3)$</td>
<td>0.14394</td>
<td>-11.075</td>
<td>-11.073866</td>
<td>-1.58403</td>
<td>-0.40664</td>
<td>1.60960</td>
<td>-0.58542</td>
<td>-0.02105</td>
<td>-0.00411</td>
<td>--</td>
</tr>
<tr>
<td>$\sigma_u(0,5)$</td>
<td>0.11830</td>
<td>-29.100</td>
<td>-29.097205</td>
<td>-4.68373</td>
<td>8.74034</td>
<td>-8.09986</td>
<td>3.70082</td>
<td>-0.64730</td>
<td>-0.00860</td>
<td>-0.00167</td>
</tr>
<tr>
<td>$\tau_u(0,1)$</td>
<td>0.37470</td>
<td>-1.4330</td>
<td>-1.433899</td>
<td>0.03641</td>
<td>0.00723</td>
<td>0.00009</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
TABLE 6.--The coefficients of the M expansion, equation III. 35, and the self-consistent $A''$ for several states at $R = 0.7$

<table>
<thead>
<tr>
<th>State</th>
<th>$A''$</th>
<th>$a_3$</th>
<th>$a_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_u(0,1)$</td>
<td>-0.8066418</td>
<td>0.04893</td>
<td>0.00075</td>
</tr>
<tr>
<td>$\sigma_u(1,1)$</td>
<td>-0.8948969</td>
<td>0.04334</td>
<td>0.00049</td>
</tr>
<tr>
<td>$\sigma_u(2,1)$</td>
<td>-0.9185147</td>
<td>0.04183</td>
<td>-0.00009</td>
</tr>
<tr>
<td>$\sigma_u(3,1)$</td>
<td>-0.9281497</td>
<td>0.04121</td>
<td>-0.00005</td>
</tr>
<tr>
<td>$\sigma_u(0,3)$</td>
<td>-11.071978</td>
<td>-56.14657</td>
<td>+0.00063</td>
</tr>
<tr>
<td>$\sigma_u(1,3)$</td>
<td>-11.077997</td>
<td>-56.79264</td>
<td>+0.00004</td>
</tr>
<tr>
<td>$\sigma_u(0,5)^*$</td>
<td>-29.095313</td>
<td>-1.00000</td>
<td>+77.50488</td>
</tr>
</tbody>
</table>

*For this state $a_3$ is adjusted to 1 and $a_1$ is then negligible ($a_1 < 0.0001$).
One state for \( m = 1 \), the \( (0, 1) \) state, was studied. The self-consistent \( A \)'s were found to be \( A' = 1.4338990 \) and \( A'' = 1.43376 \). The resulting wave functions are

\[
\begin{align*}
\Lambda &= (\lambda^2 - 1)^{1/2} \exp(-r/2)[L_0^{(1)} + 0.03641L_1^{(1)} + 0.00732L_2^{(1)} + 0.00009L_3^{(1)}] \\
M &= P_1^{(1)} + 0.03681P_3^{(1)}.
\end{align*}
\]
D. Molecular Energy from the Model

We are now in a position to calculate the total energy of the hydrogen molecule as predicted by the model without introducing any further approximations. The one-electron Hamiltonian defined by equation III. 6 includes the kinetic energy of the electron plus the total potential energy of this electron. It follows that the total energy of the molecule would be twice the one-electron energy, $\varepsilon$, except for the fact that this would be counting the assumed electron-electron repulsion term twice. As pointed out in Section II this term is $(u|1/r_{ab}|u)$. Hence, the total energy $E_t$ is

$$E_t = 2\varepsilon - (u|1/r_{ab}|u) + 1/2R,$$

III. 42

remembering that the internuclear repulsion term was not included in the Hamiltonian and correcting for counting the interelectron repulsion term twice. The quantity $\varepsilon$ can be obtained from the values of $p$ in Table 2. The average value, $(u|1/r_{ab}|u)$, can be calculated using the expression $u = \Lambda M$ where $\Lambda$ is given in Table 3 and $M$ in Table 4. The calculated values of $E_t$ are given in Table 7. The average values $(u|1/r_{ab}|u)$ and $(u|1/r_{ba}|u)$ are also given for future reference. $E_t$ is shown as a function of $R$ in Figure 5.
TABLE 7. -- The quantities \( (u|1/r_{ab}|u) \), \( (u|1/r_{ba}|u) \) and \( E_t \) tabulated as a function of \( R \) for the \( \sigma_g(0,0) \) state

| \( R \) | \( (u|1/r_{ab}|u) \)  | \( (u|1/r_{ba}|u) \)  | \(-E_t\)  |
|-------|-----------------|-----------------|--------|
| 0.3   | 0.88052         | 1.38897         | 0.55713|
| 0.5   | 0.71598         | 1.32255         | 1.06887|
| 0.6   | 0.64933         | 1.27599         | 1.15303|
| 0.7   | 0.59223         | 1.23013         | 1.19257|
| 0.71  | 0.58702         | 1.22558         | 1.19496|
| 0.72  | 0.58186         | 1.22120         | 1.19706|
| 0.73  | 0.57677         | 1.21682         | 1.19898|
| 0.8   | 0.54322         | 1.18756         | 1.20777|
| 0.9   | 0.50076         | 1.14936         | 1.20880|
| 1.1   | 0.43137         | 1.08717         | 1.19182|
| 1.3   | 0.37706         | 1.04123         | 1.16374|
| 1.5   | 0.33356         | 1.00950         | 1.13552|
FIGURE 5.—The total electronic energy of the hydrogen molecule as predicted by the model, $E_T$, shown as a function of $R$. 
The curve of Figure 5 has a minimum at $2R = 1.7$ au and leads to a dissociation energy of 5.65 eV. These are to be compared with the observed equilibrium internuclear distance of 1.4 au and the dissociation energy of 4.75 eV. These results are a self-consistent deduction from the model, hence include no approximations other than the approximation to the potential function made in constructing the model. In view of the rather crude potential function assumed, these results agree rather well with experiment and compare remarkably well with the results of more complicated calculations. For example, although it predicts the correct equilibrium internuclear distance, the best self-consistent field (SCF) calculation predicts a dissociation energy of 3.63 eV which is not in as good agreement with experiment as the prediction by the model. It is felt that these facts justify a more intensive investigation of the theoretical and practical aspects of the model. This investigation has been undertaken and the results are given in the remaining sections.
E. Theoretical Oscillator Strengths for the Hydrogen Molecule

Theoretical oscillator strengths, based on the model, have been calculated for various transitions from the ground state. The formulae for the oscillator strength \( f \) of a single narrow adsorption band, are (33)

\[
f = \frac{8\pi^2 \frac{m c \nu}{3 \hbar}}{D = 1.085 \times 10^{11} \nu D}
\]

for the frequency of the adsorption band, \( \nu \), in \( \text{cm}^{-1} \) and \( D \) in \( \text{cm}^2 \), where

\[
D = GQ^2
\]

III. 43

III. 44

\[
\vec{Q} = \sum_i \int \psi_m^* \vec{r}_i \psi_n \, d\tau_i
\]

III. 45

and \( \psi_m \), \( \psi_n \) are taken as normalized. The quantity \( \vec{r}_i \) is the radius vector to the \( i \)th electron and \( G \) is the degeneracy of the final state. There are two alternate expressions for the so-called dipole length operator defined by equation III. 45. These are

\[
\vec{Q} = \frac{1}{E_n - E_m} \sum_i \psi_m^* \nabla_i \psi_n \, d\tau
\]

III. 46

defining the dipole velocity operator, and

\[
\vec{Q} = \frac{1}{(E_n - E_m)^2} \sum_i \int \psi_m^* (\nabla_i V_i) \psi_n \, d\tau
\]

III. 47
which defines the dipole accelerator operator. Further details concerning these formulae are available in the review by Mulliken and Rieke (33).

When evaluating these integrals using approximate functions for the states involved, usually obtained from a variation calculation, it is found that the three equivalent operators shown above give different results for \( \vec{Q} \).

A physical interpretation of this phenomenon has been given by Chandrasekhar (36) and it can be illustrated mathematically in the following way. Assume that \( \psi_n \) and \( \psi_m \) satisfy Schrödinger equations of the form

\[
H\psi = \left( -\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V \right) \psi = \frac{i\hbar}{2\pi} \frac{\partial\psi}{\partial t}.
\]

It can readily be shown that

\[
\nabla^2(\vec{r}\psi) = 2 \nabla \psi + \vec{r} \nabla^2 \psi,
\]

it can readily be shown that

\[
\frac{\partial}{\partial t} \int_m^n \psi^* \vec{r} \psi \, d\tau = \frac{\hbar}{2\pi i m} \int_m^n \psi^* \nabla \psi_n \, d\tau = \frac{-\hbar}{2\pi i m} \int_n^m \psi \nabla \psi^* \, d\tau.
\]

We can now write, because of our initial assumption, that

\[
\psi_m = \exp \left( \frac{-2\pi i E_m t}{\hbar} \right) U_m(x)
\]

\[
\psi_n = \exp \left( \frac{-2\pi i E_n t}{\hbar} \right) U_n(x)
\]
TABLES (Continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.</td>
<td>The quantities $d\Theta'(kR)/d\eta(kR)$, $k$, $R$ and $-E_u'(kR)$ as a function of $kR$.</td>
<td>75</td>
</tr>
<tr>
<td>12.</td>
<td>The quantities $k$ and $-E_u(R)$ as a function of $R$.</td>
<td>75</td>
</tr>
<tr>
<td>13.</td>
<td>The equilibrium internuclear distance, $r_{eq}$, and $\omega_e$ predicted from the $E_u$ curve for $k = 1$ and $k \neq 1$.</td>
<td>77</td>
</tr>
<tr>
<td>14.</td>
<td>The correlation energy $\theta_{2/2}$ from both the screened and unscreened one-electron potential cases.</td>
<td>91</td>
</tr>
</tbody>
</table>
where \( U \) is a solution of a time independent Schrödinger equation with eigenvalues \( E_m, E_n \), respectively. It follows that

\[
\frac{\partial}{\partial t} \int \psi_m^* \psi_n \, d\tau = \frac{2\pi i}{\hbar} (E_m - E_n) \int \psi_m^* \psi_n \, d\tau. \tag{III. 52}
\]

Expressing \( E \) in atomic units, equations III. 50, III. 52 give

\[
\int \psi_m^* \psi_n \, d\tau = \frac{-1}{E_m - E_n} \int \psi_m^* \nabla \psi_n \, d\tau = \frac{1}{E_m - E_n} \int \psi_n \nabla \psi_m^* \, d\tau, \tag{III. 53}
\]

which proves the equivalence of equations III. 45 and III. 46. To complete this proof, it is necessary to take account of the fact that \( \psi \) has the form of equation III. 51. This is certainly so for the model, hence it is known in advance that this calculation will yield the same results for the two methods of calculating \( \mathbf{Q}_i \). It does not, however, remove the fact that this calculation involves the use of approximate one-electron wave functions for the hydrogen molecule.

The results of this calculation are given in Table 8. The first four entries correspond to transitions between \( \sigma \) states that correlate to a combined atom with \( l = 1 \), for the next two, \( l = 3 \) and for the next to last \( l = 5 \). Since \( \Delta l = \pm 1 \) is the selection rule for atomic transitions, it appears that the model predicts behavior somewhat similar to the combined atom. This conclusion follows from the large changes in the transition probabilities found for the different values of orbital angular momentum of the combined atom that correlates to the corresponding molecular state.
TABLE 8. --Theoretical oscillator strengths for the hydrogen molecule

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\Delta \epsilon$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma(0,0) \rightarrow \sigma(0,1)$</td>
<td>11.73 eV</td>
<td>0.280</td>
</tr>
<tr>
<td>$\sigma(0,0) \rightarrow \sigma(1,1)$</td>
<td>15.71 eV</td>
<td>0.0154</td>
</tr>
<tr>
<td>$\sigma(0,0) \rightarrow \sigma(2,1)$</td>
<td>16.78 eV</td>
<td>0.00416</td>
</tr>
<tr>
<td>$\sigma(0,0) \rightarrow \sigma(3,1)$</td>
<td>17.21 eV</td>
<td>0.00172</td>
</tr>
<tr>
<td>$\sigma(0,0) \rightarrow \sigma(0,3)$</td>
<td>16.97 eV</td>
<td>$1.038 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\sigma(0,0) \rightarrow \sigma(1,3)$</td>
<td>17.31 eV</td>
<td>$0.788 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\sigma(0,0) \rightarrow \sigma(0,5)$</td>
<td>17.49 eV</td>
<td>$3.99 \times 10^{-13}$</td>
</tr>
<tr>
<td>$\sigma(0,0) \rightarrow \pi(0,1)$</td>
<td>13.99 eV</td>
<td>0.276</td>
</tr>
</tbody>
</table>

There are only two transitions that have been studied (by other investigators) in great detail. They are the $1\Sigma_g^+ - 1\Sigma_u^+$ (Lyman bands) and the $1\Sigma_g^+ - 1\Pi_u$ (Werner bands) transitions. It has been estimated (34) that the best value for the Lyman band is $f = 0.27$. Mulliken and Rieke (33) suggest, from experimental results, that the sum of these two oscillator strengths for these two states is about 0.65. The first value in Table 8 corresponds to the Lyman bands, and is in quite good agreement with the best estimated value for this transition. The last value in Table 8 corresponds to the Werner bands, hence the sum is somewhat less than the experimental estimate. Unfortunately,
there are no theoretical or experimental estimates that can be compared with the remaining oscillator strengths given in Table 8.

Shull (35) reviews much of the existing work on these two bands, while Ehrenson and Phillipson (34) discuss the Lyman band system. By comparison with the results given in these papers, two things become evident. First, these transition probabilities are not known to a high degree of accuracy. The range of values obtained from various approximate functions is much greater than 100%. In view of this fact, it is felt that the values obtained here are of great interest since they agree rather well with the best estimates available. Second, this calculation will give identical results for the dipole length and dipole velocity methods. Examination of the references cited above shows that this is far from being true for the majority of calculations now available in the literature.
IV. AVERAGE OF THE EXACT HAMILTONIAN FOR THE HYDROGEN MOLECULE

A. Average of the Hamiltonian over Functions from the One-Electron Model

The greatest volume of theoretical work being done today in molecular structure involves assuming some sort of wave function containing adjustable parameters and then averaging the exact Hamiltonian for the system over this function. The variation theorem is used to adjust these parameters so that the lowest energy possible for a function of this form is obtained. Examination of the reviews by Yoshizumi (6) and McLean et al. (5) gives one an idea of the amount of effort being put into this type of calculation. In order to compare the present model with this work, the average of the exact Hamiltonian operator for the hydrogen molecule must be calculated.

Since there is no way in which the eigenfunction for a two-electron system can be obtained from one-electron eigenfunctions without making some explicit assumption about correlation, the course followed has been to average the Hamiltonian using trial functions of the following three types:

\[ u(1)u(2) \]  
\[ u(1)u(2) + kv(1)v(2) \]  
\[ u(1)u(2)[1 - c_1 \mu_1 - c_2 \mu_2] \]
In these equations u is the solution to equation III. 6 designated by \( \sigma_g(0,0) \) while v is that designated by \( \sigma_u(0,1) \). The numbers 1, 2 in parentheses designate coordinates of electrons 1 and 2 while \( \mu_1, \mu_2 \) are the elliptic coordinates of electrons 1 and 2 (see equation II. 5). The function IV. 1 is an uncorrelated distribution while IV. 2 is a correlated distribution of the type to which the exact eigenfunction approaches at large internuclear distance. Function IV. 3 is a modification of IV. 2 in which the added terms \( u(1) \mu_1 \), \( u(2) \mu_2 \) have symmetry \( \sigma_u \) but which differs from IV. 2 in an important way which can best be explained by references to equation III. 23. In function III. 2 the function u involves an exponent p for the ground state while v involves an exponent p for an excited state. The latter value of p (excited state) is much smaller than the former (ground state) near the equilibrium internuclear distance, although the two approach each other at large internuclear distances. The function IV. 3 is one in which the exponents for both terms are the same.

The mathematical problems in averaging the Hamiltonian have been investigated in great detail elsewhere (18) (13). However, in Appendix B some notes are given on the techniques that were used to find \( (1/r_{12})_{av} \).

The results are shown in Table 9. In addition to the average Hamiltonian (last row) the average values of several additional quantities calculated from function IV. 1, IV. 2, IV. 3 are given in columns three, four and five respectively. For comparison the averages (where available)
calculated by Kolos and Roothaan (22) from a self-consistent field (SCF) treatment are given in column six and those calculated by the same authors from a 40 term variation function of the James and Coolidge type are given in column two. The constants \( k \) and \( c \) were obtained by imposing the condition that the energy be a minimum. These values are \( k^2 = 0.00512 \) and \( c^2 = 0.30804 \), when the functions \( u, v \) are properly normalized.

TABLE 9. --Average of the exact Hamiltonian and other quantities over various two-electron functions

<table>
<thead>
<tr>
<th></th>
<th>( \Psi ) (exact)</th>
<th>( \Psi ) (equation IV. 1)</th>
<th>( \Psi ) (equation IV. 2)</th>
<th>( \Psi ) (equation IV. 3)</th>
<th>( \Psi ) (SCF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Psi \ r_{12} )</td>
<td>0.59737</td>
<td>0.65716</td>
<td>0.65011</td>
<td>0.61969</td>
<td>0.6586</td>
</tr>
<tr>
<td>( \Psi \ V )</td>
<td>-2.34928</td>
<td>-2.27326</td>
<td>-2.27503</td>
<td>-2.31545</td>
<td>-2.2672</td>
</tr>
<tr>
<td>( \Psi \ T )</td>
<td>1.17484</td>
<td>1.14562</td>
<td>1.14194</td>
<td>1.16867</td>
<td>1.1336</td>
</tr>
<tr>
<td>( \Psi \ r_{ab} )</td>
<td>---</td>
<td>0.59223</td>
<td>0.59092</td>
<td>0.59132</td>
<td>---</td>
</tr>
<tr>
<td>( \Psi \ V_{model} )</td>
<td>---</td>
<td>-2.33818</td>
<td>-2.33081</td>
<td>-2.34381</td>
<td>---</td>
</tr>
<tr>
<td>( \Psi \ r_{ba} )</td>
<td>---</td>
<td>1.23012</td>
<td>1.22709</td>
<td>1.23339</td>
<td>---</td>
</tr>
<tr>
<td>( \Psi \ H )</td>
<td>-1.17444</td>
<td>-1.12764</td>
<td>-1.13309</td>
<td>-1.14678</td>
<td>-1.1336</td>
</tr>
</tbody>
</table>

The energy obtained using IV. 1 should be compared to the SCF energy since the latter is the best possible with a product type function. Comparing columns three and six, we see that agreement is generally good, not only for the total energy, but for the kinetic and potential energies as well.
It is a matter of considerable interest that energies so close to SCF can be obtained from a product function of type IV. 1 in which \( u \) is obtained by solving a Schrödinger equation with a predetermined potential. Note that the function IV. 1 contains no adjustable parameter. The calculations of Table 9 refer to \( R = 0.7 \) only. The average Hamiltonian has also been calculated using IV. 1 at other values of \( R \) and these results are given in Table 10. The average Hamiltonian in Table 10 is designated by \( E_u \).

<table>
<thead>
<tr>
<th>( R )</th>
<th>( \langle \psi \mid 1/r_{12} \mid \psi \rangle )</th>
<th>( -E_u )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.71066</td>
<td>1.07419</td>
</tr>
<tr>
<td>0.6</td>
<td>0.68348</td>
<td>1.11888</td>
</tr>
<tr>
<td>0.7</td>
<td>0.65716</td>
<td>1.12764</td>
</tr>
<tr>
<td>0.8</td>
<td>0.63130</td>
<td>1.11969</td>
</tr>
<tr>
<td>0.9</td>
<td>0.60580</td>
<td>1.10376</td>
</tr>
<tr>
<td>1.1</td>
<td>0.57033</td>
<td>1.05286</td>
</tr>
</tbody>
</table>

Note that use of IV. 2 improves the energy only very slightly (see Table 9 column four). The improvement is much greater when IV. 3 is used (see column five). However, it is notable that even the best of these functions, IV. 3, gives an average repulsion between electrons \( \langle \psi \mid 1/r_{12} \mid \psi \rangle = 0.61969 \) au which differs from the exact, 0.59737 au, by considerably more than the
average repulsion \( (u|1/r_{ab}|u) = 0.59223 \text{ au} \) predicted by the model itself. Note also that the average potential energy calculated from the model

\[
(u|V_{\text{model}}|u) = -2(u|1/r_{ba}|u) - (u|1/r_{ab}|u) + 1/2R \quad \text{IV. 4}
\]

(the second term on the right compensating for counting electron-electron repulsion twice in the first term) is equal to \(-2.33818 \text{ au}\) which agrees fairly well with the exact value, \(-2.34928\). The average kinetic energy calculated from the model, \(1.14562 \text{ au}\), does not agree well with the exact average, \(1.17484 \text{ au}\).

These observations lead one to conclude that the model predicts the potential energy rather accurately while not doing as well with the kinetic energy. With this fact, it would seem ideal if it were possible to calculate the total energy of the molecule without using the less accurate kinetic energy value. This calculation can be done by using the virial theorem, its form being (32)

\[
2E + R \frac{dE}{dR} = V. \quad \text{IV. 5}
\]

Equation IV. 5 is valid when the potential employed in the Schrödinger equation is homogeneous and of degree \(-1\). Assuming the average of \(V_{\text{model}}\) (equation IV. 4) is equal to the exact potential energy for the hydrogen molecule, the total electronic energy at the equilibrium internuclear distance can be calculated as follows. If \(E\) of equation IV. 5 is a minimum at \(R = 0.7\), i.e., \((dE/dR)_{R = 0.7} = 0\), then

\[
2E = V_{\text{model}} \quad \text{IV. 6}
\]
for the assumptions stated above. From the appropriate value listed in Table 9, it follows that \( E = -1.169 \text{ au} \). This agrees well with the exact energy. However, this good agreement at \( R = 0.7 \) is not obtained when equation IV. 5 is used to calculate \( E \) at other internuclear distances. The results, none the less, of this type of reasoning are encouraging and lead one to hope that a more refined theory will provide accurate energies. Obviously, it would be of great value to be able to construct a potential curve from average values found in the above manner because of the relative simplicity of the calculation as compared to an extended variational treatment of the problem. A theory designed to take advantage of the above mentioned results will be presented in Section V.
B. Average of the Hamiltonian over Functions from the Model with a Modified Potential

The average of the Hamiltonian presented in the preceding section contained no appeal to the variation theorem except in adjusting expansion coefficients of the trial wave functions. As pointed out in Part B of Section III, the model goes to a hydrogen atom rather than to the helium atom at zero internuclear distance. For this reason it is to be expected that functions at small \( R \) will contain a considerable error. By introducing a screening factor for nuclear charge into the potential

\[
kV_1 = -k/r_{ab1},
\]

IV. 7

where \( k \) is an effective nuclear charge, this situation can be remedied to a certain degree. Rather than attempt to solve the one-electron Hamiltonian containing the variable factor \( k \), it is possible to relate these solutions to those that have already been found for \( k = 1 \). After that has been done, the value of \( k \) will be found that will make the product average of the exact Hamiltonian for the hydrogen molecule a minimum.

Solutions for the one-electron Hamiltonian containing a variable \( k \) can be found in terms of the solutions for \( k = 1 \) in the following way. For the one-electron Hamiltonian operator

\[
H(R, x_1)u(R, x_1) = [T(R, x_1) + V_1(R, x_1)]u(R, x_1) = \epsilon(R)u(R, x_1),
\]

IV. 8

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## FIGURES

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<th>Description</th>
<th>Page</th>
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<td>Coordinate system for the hydrogen molecule</td>
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<td>2.</td>
<td>Equipotential lines for the hydrogen molecule at the equilibrium internuclear distance</td>
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<td>$-V$ vs. $1/r_b$. Curves A, B and C refer to the respective lines be, bd, and bc of Figure 2</td>
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</tbody>
</table>
where $R$ is the internuclear distance and $x_1$ represents the spatial coordinates of electron one, we introduce an expansion of all coordinates by the factor $k$,

$$[T(kR, kx_1) + V_1(kR, kx_1)] u(kR, kx_1) = \epsilon (kR) u(kR, kx_1). \quad \text{IV. 9}$$

Since $T, V_1$ are homogeneous and of degree $-2, -1$ respectively,

$$[T(R, x_1) + kV_1(R, x_1)] u(kR, kx_1) = k^2 \epsilon (kR, kx_1). \quad \text{IV. 10}$$

The following definition is now made,

$$\phi(R, x) = u(R, x_1)u(R, x_2) \quad \text{IV. 11}$$

where $x$ represents all spatial coordinates of the function on the right. We require

$$\int \phi^*(R, x)\phi(R, x)dx = 1. \quad \text{IV. 12}$$

Then

$$\int \phi^*(kR, kx)\phi(kR, kx)dx = k^{-n} \int \phi^*(kR, kx)\phi(kR, kx)d(kx) = k^{-n} \quad \text{IV. 13}$$

where $n$ is the total number of electronic coordinates, from which it follows that the function $k^{+(n/2)}\phi(kR, kx)$ is normalized. Then,

$$T(R) = \int \phi^*(R, x)T(R, x_1)\phi(R, x)dx = \int u(R, x_1)T(R, x_1)u(R, x_1)dx_1, \quad \text{IV. 14}$$

since equation IV. 12 also requires $u(R, x_2)$ to be normalized. In addition,

$$\gamma(R) = -2 \int u(R, x_1)V_1(R, x_1)u(R, x_1)dx_1 = -\int \phi^*(R, x)[V_1(R, x_1) + V_2(R, x_2)]\phi(R, x)dx. \quad \text{IV. 15}$$
For any operator, \( Q(R, x) \), which is homogeneous and of degree \( c \)

\[
Q(R) = \int \phi^*(R, x)Q(R, x)\phi(R, x)dx,
\]

it follows that

\[
k^n \int \phi^*(kR, kx)Q(R, x)\phi(kR, kx)dx = k^{-c} \int \phi^*(kR, kx)Q(kR, kx)\phi(kR, kx)d(kx) = k^{-c} Q(kR)
\]

since

\[
k^c Q(R, x) = Q(kR, kx).
\]

From equation IV. 10 and the above conditions it follows that

\[
T(kR) - \gamma(kR)/2 = \varepsilon(kR).
\]

This completes the definition of the one-electron energy, \( \varepsilon(kR) \), for the potential given by equation IV. 7.

The exact Hamiltonian for the hydrogen molecule is

\[
H(R, x) = T_1 + T_2 + \frac{1}{r_{12}} - \frac{1}{r_{ab_1}} - \frac{1}{r_{ab_2}} - \frac{1}{r_{ba_1}} - \frac{1}{r_{ba_2}} + \frac{1}{2R},
\]

where \( T_1 = -(\hbar^2/8\pi^2 m)\nabla_1^2 \). Now, averaging this operator over \( k^n \phi(kR, kx) \)

\[
E_u(kR) = \int \phi^*(kR, kx)H(R, x)\phi(kR, kx)d(kx)
\]

\[
= k^2 T_1(kR) + k^2 T_2(kR) - k\mu'(kR) - k\gamma(kR) + k/2kR,
\]

where

\[
\mu'(R) = -\int \phi^*(R, x)[\frac{1}{r_{12}} - \frac{1}{r_{ab_1}} - \frac{1}{r_{ab_2}}] \phi(R, x)dx.
\]

From equation IV. 19, IV. 21 becomes

\[
E_u(kR) = 2k^2 \varepsilon(kR) - (1-k)\gamma(kR) - k\mu'(kR) + k/2kR.
\]
In order to complete the calculation, \( k \) must be determined from the condition that \( E_u(kR) \) be an extreme with respect to variation of \( k \)

\[
\frac{\partial E_u(kR)}{\partial k} = 0. \quad \text{IV. 24}
\]

Imposing this condition on equation IV. 23, and noting that

\[
\frac{\partial}{\partial k} = R \frac{\partial}{\partial (kR)} \quad \text{IV. 25}
\]

\[
k \left[ 4\varepsilon (kR) + 2k\varepsilon (kR) \frac{\partial \varepsilon (kR)}{\partial (kR)} \right] - (1-2k)\gamma(kR) - (1-k)kR \frac{\partial \gamma(kR)}{\partial (kR)} - \mu'(kR)
\]

\[
- kR \frac{\partial \mu'(kR)}{\partial (kR)} = 0 \quad \text{IV. 26}
\]

is required. The proof that

\[
2\varepsilon(R) + R \frac{\partial \varepsilon(R)}{\partial R} = \frac{\gamma(R)}{2} \quad \text{IV. 27}
\]

is given in Appendix C. Expanding the coordinates in equation IV. 27 by \( k \), and substituting into equation IV. 26

\[
k \gamma(kR) - (1-2k)\gamma(kR) - (1-k)kR \frac{\partial \gamma(kR)}{\partial (kR)} - \mu'(kR) - kR \frac{\partial \mu'(kR)}{\partial (kR)}
\]

\[
= -(1-k) \frac{\partial \pi(kR)}{\partial (kR)} - \frac{\partial \theta'(kR)}{\partial (kR)} = 0 \quad \text{IV. 28}
\]

is obtained, where

\[
\theta'(R) = R\mu'(R) \quad \text{IV. 29}
\]

\[
\pi(R) = R\gamma(R)
\]

or

\[
k = \frac{\partial \theta'(kR)}{\partial \pi(kR)} + 1 \quad \text{IV. 30}
\]
is the condition that $k$ makes $E_u(kR)$ an extreme. All the quantities necessary to determine $k$ are given in Tables 7 and 10. The resulting values of $k$ and the necessary derivatives are given in Table 11 along with the corresponding values of $R$ and $E_u(kR)$. In order to obtain $E_u(kR)$ at the usual values of $R$, it is necessary to extrapolate backwards to the desired internuclear distances. The result of this extrapolation is listed in Table 12.

**TABLE 11.** --The quantities $d\varphi'(kR)/d\pi(kR)$, $k$, $R$ and $-E_u(kR)$ as a function of $kR$

<table>
<thead>
<tr>
<th>$kR$</th>
<th>$d\varphi'(kR)/d\pi(kR)$</th>
<th>$k$</th>
<th>$R$</th>
<th>$-E_u(kR)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.06480</td>
<td>1.06480</td>
<td>0.46957</td>
<td>1.05464</td>
</tr>
<tr>
<td>0.6</td>
<td>0.01781</td>
<td>1.01781</td>
<td>0.59850</td>
<td>1.11677</td>
</tr>
<tr>
<td>0.7</td>
<td>-0.01614</td>
<td>0.98368</td>
<td>0.71148</td>
<td>1.12759</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.03871</td>
<td>0.96129</td>
<td>0.83221</td>
<td>1.11675</td>
</tr>
<tr>
<td>0.9</td>
<td>-0.05617</td>
<td>0.94383</td>
<td>0.95356</td>
<td>1.09664</td>
</tr>
</tbody>
</table>

**TABLE 12.** --The quantities $k$ and $-E_u(R)$ as a function of $R$

<table>
<thead>
<tr>
<th>$R$</th>
<th>$k$</th>
<th>$-E_u(R)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.05106</td>
<td>1.07767</td>
</tr>
<tr>
<td>0.6</td>
<td>1.01435</td>
<td>1.11929</td>
</tr>
<tr>
<td>0.7</td>
<td>0.98650</td>
<td>1.12780</td>
</tr>
<tr>
<td>0.8</td>
<td>0.96664</td>
<td>1.12120</td>
</tr>
<tr>
<td>0.9</td>
<td>0.95114</td>
<td>1.10654</td>
</tr>
</tbody>
</table>
Examination of the uncorrelated average of the Hamiltonian for one-electron functions arising from the screened potential shows very little improvement over the results from the unscreened potential. This is not unexpected since the unscreened function gave an energy in good agreement with the SCF results at the equilibrium internuclear distance. The greatest change occurs at small R. This again was to be expected because of the failure of the model at small R explained above.

As another measure of the accuracy of this energy, \( \omega_e \), the fundamental frequency of nuclear vibration, will be calculated. The assumption is made that this frequency is given adequately by the harmonic oscillator expression

\[
\omega_e = \frac{1}{2\pi} \sqrt{k/\mu} \quad \text{IV. 31}
\]

where \( \mu \) is the reduced mass for the system and \( k \) is the force constant related to the harmonic oscillator potential by

\[
V_{osc} = 1/2 k(x-x_0)^2. \quad \text{IV. 32}
\]

Postulating that the total electron energy curve, \( E_u \), serves as the potential for nuclear vibration, it follows that, expanding around the equilibrium internuclear distance \( x_0 \) where \( x = 2R \)

\[
V_{osc} = E_u(R) - E_u(R_0) = \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{\partial E_u(R)}{\partial x} \right)_{R=R_0} (x-x_0)^n. \quad \text{IV. 33}
\]
However, under the assumptions made above, the only non-vanishing term in equation IV. 33 is for $n = 2$, and by comparison to equation IV. 32 we see that

$$k = \left( \frac{\partial^2 E_u}{\partial x^2} \right)_{x=x_0} = \frac{1}{4} \left( \frac{\partial^2 E_u}{\partial R^2} \right)_{R=R_0}. \quad \text{IV. 34}$$

Converting $\omega_e$ to cm$^{-1}$ we find

$$\omega_e = 3.6216 \times 10^3 \sqrt{\left( \frac{\partial^2 E_u}{\partial R^2} \right)_{R=R_0}}. \quad \text{IV. 35}$$

The equilibrium internuclear distance, $r_{eq}$, and $\omega_e$ are given in Table 13 as predicted from the $E_u$ curve for both the screened and unscreened one-electron potential cases. As expected, the influence of the screening factor is most noticeable in $\omega_e$ since this quantity depends on the second derivative of the $E_u$ curve. There is also some improvement in the equilibrium internuclear distance. In each case, the model predicts the equilibrium internuclear distance to be somewhat too small. This indicates that the functions are not yet appropriately scaled, although the error is not large.

**TABLE 13.**--The equilibrium internuclear distance, $r_{eq}$ and $\omega_e$ predicted from the $E_u$ curve for $k=1$ and $k\neq1$

<table>
<thead>
<tr>
<th></th>
<th>$k=1$</th>
<th>$k\neq1$</th>
<th>Experimental (43)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{eq}$</td>
<td>0.7240 Å</td>
<td>0.7327 Å</td>
<td>0.74116 Å</td>
</tr>
<tr>
<td>$\omega_e$</td>
<td>5,588 cm$^{-1}$</td>
<td>4,466 cm$^{-1}$</td>
<td>4400.39 cm$^{-1}$</td>
</tr>
</tbody>
</table>
The values of $\omega_e$ are too large. This is expected since the $E_u$ curve must lie above the exact potential curve, and, as a result, the second derivative in equation IV. 35 will probably be too large.

Porto and Lambert (23) calculated $\omega_e$ from the results of Kolos and Roothaan based on 40 and 50 term variation functions. They found that $\omega_e = 4410.04 \text{ cm}^{-1}$ when a 15th degree polynomial was used to fit the potential curve. Using the data of Kolos and Roothaan, the calculation was repeated in the same way that was used to find the values in Table 13. This calculation indicated that the numerical method used here gives results accurate to less than 0.5% with respect to the best value obtainable from the data given here.
V. A THEORY FOR CONSTRUCTING THE TOTAL ENERGY FROM A MODIFIED VIRIAL THEOREM

The point has been made that a product wave function, when used to average the exact Hamiltonian for a system, gives a mean value for the energy that, at best, exceeds the exact energy by a finite amount known as the correlation energy. The usual method of improving this calculation is to assume a more complicated function that incorporates electron correlation. In this section a theory will be developed for the hydrogen molecule which, in principle, will determine the difference between a product average of the Hamiltonian and the exact electronic energy. This product average is defined as being an average over the function, assumed to be normalized

\[ \Phi = u(1)u(2) \]

V. 1

where \( u \) is defined as an eigenfunction of equation III. 6. Hence, this theory is based on the approximation to the potential made in the model.

The development of the theory will consist of the following steps:

1) the introduction of a constraint on the average of the exact Hamiltonian;
2) derivation of the appropriate virial equation; and 3) investigating an approximate solution for the resulting equation. The theory was developed as the result of an indirect argument which would be awkward to explain in advance.
Hence the constraint imposed will merely be stated in the following paragraphs and the mathematics developed without attempting to explain the original motivation. This procedure has the disadvantage that the entire development seems highly formalized and devoid of physical content. The final results, however, will justify the treatment and the course adopted gets quickly to the final results.

Using the definitions given in Part A of Section III, it is easily shown that the Hamiltonian operator for the hydrogen molecule can be written as

\[
H = \frac{-\hbar^2}{8\pi^2 m} (\nabla_1^2 + \nabla_2^2) + \frac{1}{r_{12}} - \frac{1}{r_{ab1}} - \frac{1}{r_{ab2}} - \frac{1}{r_{ba1}} - \frac{1}{r_{ba2}}. \quad \text{V. 2}
\]

The terms \(1/r_{12}\), \(1/r_{ab1}\), \(1/r_{ab2}\) are all related to each other and to the repulsion between electrons. The term \(1/r_{12}\) is obviously the mutual potential energy of two electrons a distance \(r_{12}\) apart. The term \(1/r_{ab1}\) is the average of \(1/r_{12}\) over the position of electron 2 with the position of electron 1 fixed (see Slater's formula, equation II. 1), at least according to the assumptions of the model. The term \(1/r_{ab2}\) has a similar significance. If the assumptions are correct, then the average values of all three terms should be the same.

A less stringent assumption is the correlated average of the term \(1/r_{ab1} + 1/r_{ab2} - 1/r_{12}\) is the same as the uncorrelated average of \(1/r_{ab}\), that is

\[
\mu = \mu'. \quad \text{V. 3}
\]
where
\[ \mu = (u | 1/r_{ab} | u) \quad \text{V. 4} \]

\[ \mu' = (\Psi | 1/r_{ab1} + 1/r_{ab2} - 1/r_{12} | \Psi). \quad \text{V. 5} \]

The condition of equation V. 3 will not be exactly satisfied, although it is apparently a good approximation at \( R = 0.7 \) for the hydrogen molecule. If however, we impose equation V. 3 as a constraint and then demand that, subject to this constraint, the function \( \Psi \) be so adjusted as to make the energy a minimum, this will provide the best \( \Psi \) compatible with the constraint. We note that \( u \) is a predetermined constant and hence the condition of equation V. 3 is equivalent to demanding that \( \mu' \) be a constant. We can therefore use the Lagrange multiplier method, with multiplier \( \alpha' \), and hence the condition for a constrained extreme is

\[
\frac{-\hbar^2}{8 \pi^2 m} \left( \nabla_1^2 + \nabla_2^2 \right) \Psi + (1 + \alpha') \left( \frac{1}{r_{12}} - \frac{1}{r_{ab1}} - \frac{1}{r_{ab2}} \right) \Psi - \left( \frac{1}{r_{ba1}} + \frac{1}{r_{ba2}} \right) \Psi = E'' \Psi. 
\]

V. 6

Let \( \alpha \) be the values of \( \alpha' \) for which the constraint is satisfied. It is convenient to define a new quantity \( E' \) by the equation

\[ E' = E'' + \alpha' \mu. \quad \text{V. 7} \]

There are three values of \( \alpha' \) which are of particular interest. The first is that \( \alpha' \) for which the constraint is satisfied. For this case, it can be verified from equations V. 3 and V. 6

\[ E'' = (\Psi | H | \Psi) - \alpha \mu \]

V. 8
I. INTRODUCTION

The history of the application of quantum mechanics to the hydrogen molecule is almost as old as modern quantum mechanics itself. In 1927 Heitler and London (1) presented a calculation of the binding energy of the hydrogen molecule. Six years later James and Coolidge (2) reported a binding energy of 4.7210 electron volts (eV) at the internuclear distance of 1.40 atomic units (au) as compared to the experimental values of 4.746 eV for the binding energy and 1.4016 au for the equilibrium internuclear distance. This provided a definitive test of the applicability of quantum mechanics to molecular systems and, in view of the precision of the results, it would appear that the hydrogen molecule problem is essentially solved.

For two reasons, however, intensive research on the comparatively simple system has persisted until the present. The first reason is that extension of the James and Coolidge technique to the study of the complete ground state potential curve or to an investigation of the excited state structure of the hydrogen molecule leads to complications. These complications are slow convergence of the expansion of the ground state wave function at large internuclear distances (3) and the difficulties of constructing appropriate
where $H$ is the Hamiltonian of equation V. 2. It follows from equation V. 7 that $E' = (\Psi \mid H \mid \Psi )$ (when $\alpha = \alpha'$) and, in what follows, we shall designate $E'$ by $E$ in this particular case. The second case is that for which $\alpha' = 0$. In this case $E'' = W$, the exact eigenvalue for hydrogen and, obviously, $E' = W$ as well. Finally, the value $\alpha' = -1$ is of interest. In this case, it follows from equations III. 6, V. 6 that $E'' = 2\varepsilon$ and, from equation III. 57 it is found that

$$E' = 2\varepsilon - \mu = E_t - 1/2R. \quad V. 9$$

Also, when $\alpha' = -1$, it follows that

$$\Psi = u(1)u(2). \quad V. 10$$

Although the condition that $\alpha' = \alpha$ will be used later, it is convenient to consider cases for which $\alpha' \neq \alpha$. In particular, assume for the moment that $\alpha'$ is arbitrary and independent of $R$. For this case the potential energy term of equation V. 6 is homogeneous and of degree $-1$. It follows immediately from the virial theorem that

$$2E'' + R \left( \frac{\partial E''}{\partial R} \right)_{\alpha'} = -(1 + \alpha') \mu' - \gamma' \quad V. 11$$

where

$$\gamma' = (\Psi \mid 1/r_{ba1} + 1/r_{ba2} \mid \Psi ). \quad V. 12$$

Note in equation V. 11 the subscript $\alpha'$ on the derivative which emphasizes that $\alpha'$ must be constant during the differentiation with respect to $R$. This enters because the potential term of equation V. 6 is only homogeneous of
degree -1 when $\alpha'$ does not depend on $R$. We can, however, easily obtain an equation which applies when $\alpha'$ is a function of $R$. That is, considering $E''$ as a function of $R$ and $\alpha'$, it follows that

$$\frac{dE''}{dR} = \left(\frac{\partial E''}{\partial R}\right)_{\alpha'} + \left(\frac{\partial E''}{\partial \alpha'}\right) \frac{d\alpha'}{dR}. \quad V. 13$$

It will be shown in Appendix D that

$$\left(\frac{\partial E''}{\partial \alpha'}\right) = -\mu'. \quad V. 14$$

and hence

$$\left(\frac{\partial E''}{\partial R}\right)_{\alpha'} = \frac{dE''}{dR} + \mu' \frac{d\alpha'}{dR}. \quad V. 15$$

On substituting equation V. 15 into equation V. 13, we obtain

$$2E'' + R \frac{dE''}{dR} = -(1+\alpha')\mu' - \gamma' - \mu' R \frac{d\alpha'}{dR}. \quad V. 16$$

Introducing $E'$, defined by equation V. 7, we see that equation V. 16 becomes

$$2E' + R \frac{dE'}{dR} = (\mu - \mu') \left(\alpha' + R \frac{d\alpha'}{dR}\right) + \alpha' \frac{d\theta}{dR} - \mu' - \gamma'. \quad V. 17$$

where we define

$$\theta = R\mu'. \quad V. 18$$

At this point, we will review the significance of some of the quantities defined above for particular values of $\alpha'$. It was shown above that, when $\alpha' = -1$, $\psi$ is defined by equation V. 10. It follows that $\mu'$, which will be called $\mu^*$ for this value of $\alpha'$, becomes the product average and can be
found from values given in Table 7 and Table 10. The quantity $\mu$, which does not depend on $\alpha'$ or $\alpha$, is given in Table 7. For this particular value of $\alpha'$, the quantity $\gamma'$ will be designated by $\gamma^*$ so that it will not be confused with the $\gamma'$ going with other values of $\alpha'$. The quantity now designated by $\gamma^*$ is a product average defined by equation V. 12 and can also be obtained from Table 7. For values of $\alpha' = \alpha$, which satisfy the constraint, we let $\gamma'$ become $\gamma$, $E'$ become $E$ and, by definition, $\mu'$ is equal to $\mu$. Unless the variational problem for $\Psi$ is solved in some manner, these quantities will not be known. It will not be necessary to distinguish in any special way the quantities defined above for $\alpha'$ when $\alpha' = 0$ except, as was pointed out above, $E'' = E' = W$.

Allowing $\alpha' = \alpha$ and remembering the definitions given above, equation V. 17 becomes

$$2E + R \frac{dE}{dR} = \alpha \frac{d\theta}{dR} - \mu - \gamma.$$  \hspace{1cm} \text{V. 19}

Subtracting equation V. 17 from equation V. 19 and multiplying through by $R$

$$\frac{d}{dR} \left[ R^2 (E-E') \right] = R^2 (\mu' - \mu) \frac{d(\mu' - \alpha)}{dR} + R^2 (\mu' - \mu) \frac{d\alpha}{dR} + (\alpha' - \alpha)(\mu' - \mu)R$$  \hspace{1cm} \text{V. 20}

$$+ \alpha (\mu' - \mu)R + R(\alpha - \alpha') \frac{d\theta}{dR} + R(\mu' - \mu) + R(\gamma' - \gamma)$$

is obtained. We attempt to find a solution to equation V. 20 in the following way. Expanding $E'$ in a power series of $\alpha'$ around $\alpha$.

$$E' - E = \sum_{n=1}^{\infty} \frac{\lambda n}{n!} (\alpha' - \alpha)^n$$  \hspace{1cm} \text{V. 21}
is obtained where

\[ \lambda_n = \left( \frac{\partial^n E'}{\partial \alpha'^n} \right)_{\alpha' = \alpha} \]  

Expanding \(-\gamma'\) in the same manner

\[ \gamma - \gamma' = \sum_{n=1}^{\infty} \frac{\beta_n}{n!} (\alpha' - \alpha)^n \]  

is found, where

\[ \beta_n = \left( \frac{\partial^n (-\gamma')}{\partial \alpha'^n} \right)_{\alpha' = \alpha} \]  

For \(-\mu'\)

\[ \mu - \mu' = \sum_{n=1}^{\infty} \frac{\epsilon_n}{n!} (\alpha' - \alpha)^n \]  

is found, where

\[ \epsilon_n = \left( \frac{\partial^n (-\mu')}{\partial \alpha'^n} \right)_{\alpha' = \alpha} \]  

In Appendix D it is shown that

\[ \frac{\partial E'}{\partial \alpha'} = \mu - \mu' \]  

hence it follows that

\[ \epsilon_n = \lambda_{n+1} \]
Also note that, from the definition of the constraint,
\[ \epsilon_0 = \lambda_1 = (\mu - \mu') \frac{\alpha'}{\alpha} = 0. \] V. 29

Now, equation V. 25 becomes
\[ \mu - \mu' = \sum_{n=1}^{\infty} \frac{n\lambda_n}{n!} (\alpha' - \alpha)^{n-1}. \] V. 30

On substituting equations V. 21, V. 23, V. 30 into equation V. 20
\[ 2\lambda_n + R \frac{d\lambda_n}{dR} = R \lambda_{n+1} \frac{d\alpha}{dR} + n\lambda_n + (1+\alpha) \lambda_{n+1} + \beta_n \quad n > 1 \] V. 31

is obtained as a recurrence relationship between the expansion coefficients
(see Appendix F). The terminal condition, \( n = 1 \), yields
\[ \lambda_n (1+\alpha) + \beta_1 + R \frac{d\alpha}{dR} + \frac{d\theta}{dR} = 0. \] V. 32

If we now make the assumption that the expansions in equations
V. 21, V. 22, V. 23 are valid at \( \alpha' = -1 \), where we define
\[ y = R(1+\alpha) \] V. 33
and
\[ \lambda_n = R^{n-2} \theta_n \]
V. 34

equations V. 31, V. 32 become
\[ \frac{d\theta_n}{dR} = \theta_{n+1} \frac{dy}{dR} + \frac{\beta_n}{R^{n-1}}, \quad n > 1 \] V. 35
and
\[ \theta_2 \frac{dy}{dR} + \beta_1 + \frac{d\theta}{dR} = 0. \] V. 36
Remembering the definitions of equations V. 33, V. 34 and the fact $E' = E_t$
for $\alpha' = -1$, the expansions in equations V. 21, V. 23, V. 30 become

$$-f = \sum_{n=2}^{\infty} \frac{\theta_n}{n!} (-y)^n$$  \hspace{1cm} V. 37

where

$$f = -R^2(E_t - E),$$  \hspace{1cm} V. 38

$$\gamma - \gamma^* = \sum_{n=1}^{\infty} \frac{\beta_n}{n!} \left( \frac{\gamma}{R} \right)^n$$  \hspace{1cm} V. 39

and

$$R(\mu - \mu^*) = \sum_{n=1}^{\infty} \frac{n\theta_n}{n!} (-y)^{n-1}.$$  \hspace{1cm} V. 40

Setting $\alpha' = -1$ in equation V. 20 gives

$$\frac{df}{dR} = R(\gamma^* - \gamma) + y \frac{d\theta}{dR}.$$  \hspace{1cm} V. 41

Now, if we make the further assumption that the expansion of equations V. 37, V. 39, V. 40 can be truncated to the first non-vanishing term, the equations

$$f = -\frac{\theta_2}{2} y^2$$  \hspace{1cm} V. 42

$$R(\gamma^* - \gamma) = \beta, y$$  \hspace{1cm} V. 43

$$R(\mu - \mu^*) = -\frac{\theta_2}{2} y$$  \hspace{1cm} V. 44

are found. Equations V. 36, V. 41, V. 42, V. 43, V. 44 consist of a set of five equations in the unknowns $y, f, \beta_1, \gamma$ and $\theta_2$. 
However, since this set of equations contains derivatives of the variables \( f \) and \( y \), it will not be possible to find a solution unless independent conditions are known that will determine the constants of integration for these equations. Specifically, these conditions involve knowing \( E \) at some \( R \) for which the value of \( \alpha \) is also known. There are specific values of \( \alpha \) for which something is known, but, as yet, no conditions adequate for a complete solution of these equations have been found. At the point \( \alpha = 0 \), the constraint is naturally satisfied and \( E = W \). This provides no information, however, since one would have to have previous knowledge of the exact energy \( W \).

At the point \( \alpha = -1 \), it is known that \( E = E_t \), \( \mu = \mu^* \) and \( \gamma = \gamma^* \), but on inspection of equations V. 36, V. 41, V. 42, V. 43, V. 44 it can be seen that no conditions on \( \theta_2 \) or \( \beta_1 \) arise. This does give the information that \( \left( \frac{df}{dR} \right)_{\alpha=0} = 0 \), but this does not prove to be useful in providing conditions for the necessary integrations. It may be that it will prove possible to solve this set of equations, which represent an approximate solution to equation V. 20, but more information, such as limiting behavior, is necessary.

These equations do provide, however, some information of value. Substituting equation V. 43 into equation V. 41 gives

\[
\frac{df}{dR} = \beta_1 y + y \frac{d\theta}{dR}.
\]

V. 45

Multiplying equation V. 36 by \( y \) and then subtracting from equation V. 45

\[
\frac{df}{dR} = \theta_2 y \frac{dy}{dR}
\]

V. 46
is obtained. Next, differentiating equation V. 42 we find

\[ \frac{df}{dR} = -\theta_2 y \frac{dy}{dR} - \frac{y^2}{2} \frac{d\theta_2}{dR} . \]  

V. 47

However, from equation V. 46 we see that

\[ \frac{d\theta_2}{dR} = 0, \]

V. 48

or \( \theta_2 \) is required to be a constant. It is also possible to give a specific interpretation to the constant \( \theta_2 \). Going back to equation V. 21, truncating the sum to the first non-vanishing term and using the same definitions, it is found that.

\[ E' - E = (\theta_2/2)(\alpha' - \alpha)^2. \]  

V. 49

For \( \alpha' = 0 \), it was shown above that \( E' = W \), hence it follows that

\[ W - E = (\theta_2/2) \alpha^2. \]  

V. 50

Equation V. 42 can be written in the following form,

\[ E_t - E = (\theta_2/2)(1+\alpha)^2. \]  

V. 51

Subtracting equation V. 51 from equation V. 50, it is found that

\[ W - E_t = - (\theta_2/2)(1+2\alpha) \]  

V. 52

and, using equation V. 44,

\[ W - E_t = \theta_2/2 + \mu - \mu'. \]  

V. 53

is found. Definitions in previous sections show that

\[ E_{u_t} - E_t = (2\epsilon - \mu + 1/2R) - (2\epsilon - \mu + 1/2R) = \mu - \mu'. \]  

V. 54
Hence equation V. 53 becomes

\[ W - E_u = \Theta_2 / 2. \]

Equation V. 55 indicates, to the degree of accuracy of this theory, that \( W - E_u \) must be a constant. From the discussion given in the Introduction, equation V. 55 also defines a type of correlation energy since \( W \) is the exact energy and \( E_u \) is an uncorrelated energy. This will not be the usual definition of correlation energy unless \( E_u \) turns out to be equal to the SCF energy (8), although it has been pointed out that the difference between these two uncorrelated energies is small (see Table 9). Because of this, the theoretical result of equation V. 55 seems quite significant since it has been empirically demonstrated by Löwdin (8) that the correlation energy is actually a constant over a rather wide range of \( R \) near the equilibrium internuclear distance.

It is possible to provide a test of equation V. 55 since \( E_u \) has been calculated and \( W \) is known to a high degree of accuracy from the calculations of Kolos and Roothaan (22). From these values, \( \Theta_2 / 2 \) can be calculated as a function of \( R \) and, if this theory is correct, these values should be constants independent of \( R \). In Table 14 it is seen in column 4 that this is not a bad approximation. From an analogous derivation given in Appendix E, it will be shown that the modified one-electron potential function containing an effective atomic number also predicts equation V. 55. Even better agreement is obtained for this case, as can be seen from column 6 of Table 14.
TABLE 14. —The correlation energy \( \Theta_{2/2} \) from both the screened and unscreened one-electron potential cases

<table>
<thead>
<tr>
<th>R</th>
<th>-W</th>
<th>-( E_u(k=1) )</th>
<th>-( \Theta_{2/2} )</th>
<th>-( E_u(k\neq1) )</th>
<th>-( \Theta_{2/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.12452</td>
<td>1.07419</td>
<td>0.05033</td>
<td>1.07767</td>
<td>0.04685</td>
</tr>
<tr>
<td>0.6</td>
<td>1.16493</td>
<td>1.11888</td>
<td>0.04605</td>
<td>1.11929</td>
<td>0.04564</td>
</tr>
<tr>
<td>0.7</td>
<td>1.17444</td>
<td>1.12764</td>
<td>0.04680</td>
<td>1.12780</td>
<td>0.04664</td>
</tr>
<tr>
<td>0.8</td>
<td>1.16854</td>
<td>1.11969</td>
<td>0.04885</td>
<td>1.12120</td>
<td>0.04734</td>
</tr>
<tr>
<td>0.9</td>
<td>1.15498</td>
<td>1.10376</td>
<td>0.05122</td>
<td>1.10654</td>
<td>0.04844</td>
</tr>
</tbody>
</table>

In summary, this theory provides the following information. It predicts that the difference between the exact energy and the uncorrelated average of a Hamiltonian for a system, correlation energy, must be a constant. It has, as yet, not been possible to determine the value of this constant except from a value of the exact energy at one value of R. It is not surprising, however, that this constant is hard to determine for, if it were possible to calculate it in some simple way, this theory would provide not only an approximation to the constrained average of the Hamiltonian but, apparently, a good approximation to \( W \), the exact energy of \( H_2 \). It seems probable that the foregoing theory can be extended to more complicated systems but the details of this extension have not yet been considered.