

Diatomic Molecular Orbitals for Small Internuclear Separations*

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An approximate method is presented for the determination of the wave functions and the energy eigenvalues of the molecular orbitals of a homonuclear diatomic molecule at small internuclear separations. Solutions of the wave equation in spheroidal coordinates are derived in simple analytic form under the assumption of a screened two-center Coulomb field, the screening function being given by a certain analytic expression. This can be made to closely approximate the screening function which follows from the Thomas-Fermi statistical model for small internuclear separations. It is shown that with the screening function here set down, the solutions of the Schrödinger equation for an N -electron molecule are readily derived from the known exact solutions for the hydrogen molecular ion. Changes result only in the analogs of the radial parts of the latter solutions, and one obtains approximately self-consistent solutions for the general case at any small internuclear separation. To exemplify the method, computations have been carried out for the states of N_2 which are occupied in the ground state of this molecule, and for separations of 0.1, 0.2, 0.4, and 1.1 Bohr radii. The predicted energies are found to lie in the correct region of the energy correlation diagram.

I. INTRODUCTION

THE method of molecular orbitals has been widely used for the treatment of the electronic structure of molecules. In this method, each electron in the molecule is described by a suitable one-electron wave function, or orbital, possessing quantum numbers which determine its energy and shape. The total wave function for the molecule is then built up by taking properly antisymmetrized products of the individual orbitals.

Of the methods currently available for the determination of the molecular orbitals, the LCAO (linear combination of atomic orbitals) method is perhaps the simplest. Also, with the self-consistency introduced in the recently developed procedure of Roothaan,¹ this method is able to predict ionization energies and other molecular properties which are in quite good agreement with the experimental values. In the latter theory, designated SCF LCAO MO (self-consistent field, linear combination of atomic orbitals, molecular orbitals) self-consistency is introduced at the outset, since the electronic repulsion terms are incorporated directly into the Hamiltonian. A linear combination of atomic orbitals is then taken, and the coefficients are varied in order to minimize the ground-state energy. Aside from the initial choice of the Slater atomic orbitals used in the theory, various other degrees of approximation have also been introduced to reduce the computational labor. Among these has been the omission of the contribution to the potential from the inner shell orbitals, or the substitution of a smooth core potential to represent the effect of the inner shell orbitals. Exact applications of the SCF LCAO MO theory have, however, been undertaken by Ellison and Shull² for H_2O and by Scherr³ for N_2 . It is clear from the work of the above authors that a considerable amount of computational work is to be expected in any application

of this theory. Moreover, if one wishes to know the way in which the wave functions and energies behave as the internuclear separation is varied, then he must carry through the computations at each separation.

Now, in the study of slow collisions between atoms, the molecular orbitals must be known as functions of the internuclear separation, and it is likely that little progress can be made in the study of slow collisions, unless the molecular orbital wave functions are simple analytic expressions which are easily obtainable. The purpose of the present work is here directed toward that goal, although the method to be described here is limited to small internuclear separations (of the order of one Bohr radius and smaller). This region of separations is, however, especially interesting in collisions which result in an appreciable angle of scattering (see, e.g., Everhart *et al.*⁴). In particular, the method here presented is designed for the evaluation of bicentric wave functions and it is easily applied, with a relatively small amount of computation. It yields quite good results for small internuclear separations.

The theory considers each electron as moving in a screened Coulomb field representing the two nuclei and the remaining electrons. The screening used is an approximation to that which comes from the statistical field method of Thomas and Fermi, and it is therefore possible to obtain approximately self-consistent wave functions. In this respect the method is similar to the one used by Brudner and Borowitz⁵ for the atomic case. The wave equation is separated, subject to certain restrictions on the form of the screening function, in spheroidal coordinates. The solutions of the separated equations are then derived in simple analytic form from the known exact solutions of the H_2^+ molecule, as obtained by Bates, Ledsham, and Stewart.⁶ Computational work is facilitated by the fact that the analog

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¹ C. C. J. Roothaan, *Revs. Modern Phys.* **23**, 69 (1951).

² F. O. Ellison and H. Shull, *J. Chem. Phys.* **21**, 1420 (1953).

³ C. W. Scherr, *J. Chem. Phys.* **23**, 569 (1955).

⁴ E. Everhart, R. J. Carbone, and G. Stone, *Phys. Rev.* **98**, 1045 (1955).

⁵ H. J. Brudner and S. Borowitz, *Phys. Rev.* **120**, 2053 (1960).

⁶ D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. Roy. Soc. (London)* **246**, 215 (1953).

of the radial part of the wave functions is the only part which differs from the wave functions for H_2^+ .

The method is applied directly to N_2 , and analytic expressions for the respective states are given at several separations between 0.1 and 1.1 Bohr radii. Energies of the states are drawn in a correlation diagram for these states and the relevant united atom and separated atom energies are also shown. The analogs of the radial part of the wave functions have also been plotted for the separation 1.1 Bohr radii. Some are also drawn at the separations 0.4 and 1.1, for comparison purposes. It should again be emphasized that the other factors, i.e., those involving the angular variables, for any given state are readily obtained from the paper of Bates *et al.*⁶

In the present paper the analytic solutions for H_2^+ are discussed in Sec. II. Such a discussion is necessary since the wave functions for a general diatomic molecule are derived from those for the hydrogen molecular ion. The method is presented in Sec. III, and the results of the application of the method to N_2 are discussed in Sec. IV.

II. WAVE FUNCTIONS FOR THE HYDROGEN MOLECULAR ION

The exact solution of the Schrödinger equation for the hydrogen molecular ion was carried out by Bates, Ledsham, and Stewart.⁶ In that paper the solutions were obtained by separation of the wave equation in spheroidal coordinates, and a total of ten states was investigated. For these states, they were able to obtain a tabulation of several basic parameters, which are functions of the internuclear separation and which serve to determine completely the eigenfunctions and the energy eigenvalues.

The coordinates are defined by families of confocal ellipsoids and hyperboloids. In parametric representation these surfaces are given by

$$\lambda = (r_1 + r_2)/R, \quad \mu = (r_1 - r_2)/R, \quad (1)$$

where r_1 and r_2 are the distances from the two nuclei, and R is the internuclear separation. The third coordinate is the azimuthal angle φ . It should be noted that λ is the analog of the radius r , but it takes on values from 1 to infinity, and that μ is the analog of $\cos\theta$ in spherical coordinates, taking on values from -1 to $+1$.

The potential energy of the electron is

$$V = -e^2(1/r_1 + 1/r_2),$$

which becomes

$$V = -4e^2\lambda/R(\lambda^2 - \mu^2). \quad (2)$$

In these coordinates the Schrödinger equation separates into

$$\frac{1}{\Phi(\varphi)} \frac{d^2}{d\varphi^2} \Phi(\varphi) = -m^2 = \text{const}, \quad (3)$$

$$\frac{d}{d\lambda} \left[(\lambda^2 - 1) \frac{d\Lambda(\lambda)}{d\lambda} \right] + \left[A + 2R\lambda - p^2\lambda^2 - \frac{m^2}{(\lambda^2 - 1)} \right] \Lambda(\lambda) = 0, \quad (4)$$

$$\frac{d}{d\mu} \left[(1 - \mu^2) \frac{dM(\mu)}{d\mu} \right] + \left[-A + p^2\mu^2 - \frac{m^2}{(1 - \mu^2)} \right] M(\mu) = 0, \quad (5)$$

where A is a separation constant and $p^2 = -\frac{1}{4}R^2E$. Here, R is measured in Bohr radii, \hbar^2/me^2 , and the energy E is measured in Rydbergs, $me^4/2\hbar^2$.

The total solution of the wave equation can then be written:

$$\Psi(\lambda, \mu, \varphi; R) = (\lambda^2 - 1)^{\frac{1}{2}m} (\lambda + 1)^{\sigma} e^{-p\lambda} \times \sum_{t=0}^{\infty} g_t [(\lambda - 1)/(\lambda + 1)]^t \sum_s' f_s P_{m+s}^m(\mu) e^{im\varphi}. \quad (6)$$

The parameters σ and p , and the expansion coefficients g_t and f_s , are tabulated by Bates *et al.* as functions of the internuclear separation. The prime on the summation signifies that it is taken over even values of s if the sum of the quantum numbers $(l+m)$ is even, and over odd values if $(l+m)$ is odd.

Since there are several methods currently in use for the designation of molecular states, we shall briefly review the nomenclature used in the present paper and its relationship to the quantum numbers.

Aside from the electron spin, the electronic states of the diatomic molecule are specified by the three quantum numbers n , l , and m_l . Of these only m_l is well defined for all internuclear separations, the remaining two being only approximate except for vanishingly small or very large separations. When the nuclei coalesce R vanishes, and the resulting "united atom" is characterized by the usual quantum numbers n and l . For very small separations of the nuclei n and l are only approximately defined, the system corresponding to the united atom in an axially symmetric electric field. The orbital angular momentum, given by l , is space-quantized in this field with a component $m_l\hbar$ in the field direction. Thus, m_l gives the component of the orbital angular momentum of the electron about the internuclear axis. Since states which have different $|m_l|$ differ slightly in energy, it is convenient to set $|m_l| = m$ and to specify the states by their m values.

It can be shown rigorously (Herzberg⁷) that if the potential energy is independent of the azimuthal angle φ the quantum number m_l is exactly defined for all separations. This follows from the fact that when the potential energy is independent of φ , the wave equation

⁷ G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed., Vol. 1.

will separate at least into parts involving $\Phi(\varphi)$ and a part involving the remaining two coordinates. The values which m can take on are $m=l, l-1, l-2, \dots, 0$.

When the molecule consists of two identical nuclei, the wave functions possess symmetry with respect to reflection in the midpoint of the molecule. Those states which are even under reflection are designated by the symbol g ; those which are odd under reflection are designated by u . Thus, from the united atom viewpoint the electronic states are characterized by n, l, m , and the reflection symmetry of the eigenfunctions.

Symbolically, electrons with m values 0, 1, 2, \dots are designated $\sigma, \pi, \delta \dots$, respectively. To this symbol is added the usual n and l designations and the letter g or u . Using this nomenclature an electron orbital might be given, for example, as $1s\sigma_g, 2s\sigma_g, 2p\pi_u$, etc.

For identical nuclei, and for very large separations, the electronic states must go over into states of the atom from which the molecule is derived. Here again n and l values are assigned, referring in this case to states of the isolated atom, and are symbolized $1s, 2s, 2p$, etc. The symbols indicating the m value and the symmetry customarily precede the n and l symbols, e.g., $\Pi_u 2p, \Pi_g 2p$. It is not generally true that states of given n and l for large separations of the nuclei will go over into states of the united atom with the same n and l values. However, from what was said earlier it will be clear that the m value and the symmetry designations will be conserved as one goes from very large to very small nuclear separations. There is therefore a correlation between the states of the united atom and those of the isolated atoms; in particular, the electronic energy will be a continuous function of the internuclear separation.

III. A METHOD FOR THE GENERAL HOMO-NUCLEAR DIATOMIC MOLECULE

The present work is essentially an attempt to modify the analysis of Bates *et al.* for H_2^+ , in order to derive the wave functions and energy levels for a many-electron diatomic molecule. The method involves the selection of a suitable potential energy function for an electron in the neighborhood of screened nuclei. That is, any given electron in the molecule is to be considered in the combined potential of the nuclei and an approximate potential representing the effect of the remaining $2Z-1$ electrons. The screening function chosen here is an approximation to that which follows from the Thomas-Fermi potential for the molecule in question.

The approximation to the screening function is made in such a way that the wave equation remains separable, and in addition, that the $M(\mu)$ and $\Phi(\varphi)$ equations are identical with those for H_2^+ . The present work therefore leads to new $\Lambda(\lambda)$ functions only, and the theory predicts immediately the energy levels.

A. Separation of the Wave Equation

For an electron in the vicinity of two nuclei of atomic number Z and $2Z-1$ orbital electrons, the potential

energy is approximated by:

$$V = -Ze^2(1/r_1 + 1/r_2)f(\lambda), \quad (7)$$

where again r_1 and r_2 are the distances from the nuclei to the electron, and $f(\lambda)$ is the screening function. The latter will be determined by making the best fit to the Thomas-Fermi screening. In spheroidal coordinates Eq. (7) becomes

$$V = -4Ze^2\lambda f(\lambda)/R'(\lambda^2 - \mu^2), \quad (8)$$

which may be compared with Eq. (2) for H_2^+ . The wave equation is therefore

$$\begin{aligned} \frac{\partial}{\partial \lambda} \left[(\lambda^2 - 1) \frac{\partial \Psi}{\partial \lambda} \right] + \frac{\partial}{\partial \mu} \left[(1 - \mu^2) \frac{\partial \Psi}{\partial \mu} \right] \\ + \left[\frac{1}{(\lambda^2 - 1)} + \frac{1}{(1 - \mu^2)} \right] \frac{\partial^2 \Psi}{\partial \varphi^2} \\ + \left[\frac{1}{4} E' R'^2 (\lambda^2 - \mu^2) + 2ZR'\lambda f(\lambda) \right] \Psi = 0, \end{aligned} \quad (9)$$

where E' is the energy in Rydbergs and R' is the internuclear separation in Bohr radii.

Setting $\Psi(\lambda, \mu, \varphi; R') = F(\lambda)M(\mu)\Phi(\varphi)$, Eq. (9) separates and we have

$$\frac{1}{\Phi(\varphi)} \frac{d^2}{d\varphi^2} \Phi(\varphi) = -m^2 = \text{const.} \quad (10)$$

$$\begin{aligned} \frac{d}{d\mu} \left[(1 - \mu^2) \frac{dM(\mu)}{d\mu} \right] \\ + \left[-A + p'^2 \mu^2 - \frac{m^2}{(1 - \mu^2)} \right] M(\mu) = 0, \end{aligned} \quad (11)$$

$$\begin{aligned} \frac{d}{d\lambda} \left[(\lambda^2 - 1) \frac{dF(\lambda)}{d\lambda} \right] \\ + \left[A - p'^2 \lambda^2 - \frac{m^2}{(\lambda^2 - 1)} + 2ZR'\lambda f(\lambda) \right] F(\lambda) = 0, \end{aligned} \quad (12)$$

where $p'^2 = -\frac{1}{4}R'^2 E'$, and A is again the separation constant. Equations (10) and (11) are identical with the corresponding equations for H_2^+ , i.e., Eqs. (3) and (5), so that our solutions have the same μ and φ dependence as those for H_2^+ .

B. Transformation of the $F(\lambda)$ Equation

The work of Bates and his co-workers has provided solutions of the equation:

$$\begin{aligned} \frac{d}{d\lambda} \left[(\lambda^2 - 1) \frac{d\Lambda(\lambda)}{d\lambda} \right] \\ + \left[A - p'^2 \lambda^2 - \frac{m^2}{(\lambda^2 - 1)} + 2R\lambda \right] \Lambda(\lambda) = 0. \end{aligned} \quad (4)$$

We shall now carry out a transformation of our Eq. (12) (which is the analog of Eq. (4) above) and bring it into precisely the same form as that of Eq. (4). This will be done by assuming a functional relationship between the solutions of Eq. (12), which we wish to find, and the solutions of Eq. (4) which are given by Bates *et al.* and contained in Eq. (6).

The solutions $F(\lambda)$ will be determined in terms of $\Lambda(u)$, where u is a new coordinate whose relationship to λ will be fixed by the screening. The method adopted

here is closely similar to that used by Russek, Sherman, and Flinchbaugh,⁸ for the atomic case.

With the transformation,

$$F(\lambda) = \Lambda(u) \left[\frac{(\lambda^2 - 1) du}{(u^2 - 1) d\lambda} \right]^{-\frac{1}{2}}, \quad (13)$$

where u is a function of λ , to be determined, Eq. (12) then becomes

$$\begin{aligned} \frac{d}{du} \left[(u^2 - 1) \frac{d\Lambda(u)}{du} \right] + \left\{ \frac{-(u^2 - 1)}{2} \left(\frac{du}{d\lambda} \right)^{-\frac{3}{2}} \frac{d}{d\lambda} \left[\frac{d^2 u}{d\lambda^2} \left(\frac{du}{d\lambda} \right)^{-\frac{3}{2}} \right] - \left(\frac{du}{d\lambda} \right)^{-2} \frac{(u^2 - 1)}{(\lambda^2 - 1)} + \left(\frac{du}{d\lambda} \right)^{-2} \frac{(u^2 - 1)}{(\lambda^2 - 1)^2} \lambda^2 \right. \\ \left. - \frac{1}{(u^2 - 1)} + \frac{(u^2 - 1)}{(\lambda^2 - 1)} \left(\frac{du}{d\lambda} \right)^{-2} \left[A - \frac{m^2}{(\lambda^2 - 1)} - p'^2 \lambda^2 + 2ZR' \lambda f(\lambda) \right] \right\} \Lambda(u) = 0. \quad (14) \end{aligned}$$

For identity in form between Eqs. (4) and (14), we now get, upon comparing these equations:

$$\begin{aligned} - \frac{(u^2 - 1)}{2} \left(\frac{du}{d\lambda} \right)^{-\frac{3}{2}} \frac{d}{d\lambda} \left[\frac{d^2 u}{d\lambda^2} \left(\frac{du}{d\lambda} \right)^{-\frac{3}{2}} \right] - \left(\frac{du}{d\lambda} \right)^{-2} \frac{(u^2 - 1)}{(\lambda^2 - 1)} + \left(\frac{du}{d\lambda} \right)^{-2} \frac{(u^2 - 1)}{(\lambda^2 - 1)^2} \lambda^2 - \frac{1}{(u^2 - 1)} \\ + \frac{(u^2 - 1)}{(\lambda^2 - 1)} \left(\frac{du}{d\lambda} \right)^{-2} \left[A - \frac{m^2}{(\lambda^2 - 1)} + p'^2 \lambda^2 + 2ZR' \lambda f(\lambda) \right] = A - \frac{m^2}{(u^2 - 1)} - p'^2 u^2 + 2Ru. \quad (15) \end{aligned}$$

Upon rearrangement, Eq. (15) becomes

$$\begin{aligned} 2ZR' \lambda f(\lambda) = A \left[\frac{(\lambda^2 - 1)}{(u^2 - 1)} \left(\frac{du}{d\lambda} \right)^2 - 1 \right] - (m^2 - 1) \left[\frac{(\lambda^2 - 1)}{(u^2 - 1)^2} \left(\frac{du}{d\lambda} \right)^2 - \frac{1}{(\lambda^2 - 1)} \right] \\ - p'^2 u^2 \frac{(\lambda^2 - 1)}{(u^2 - 1)} \left(\frac{du}{d\lambda} \right)^2 + p'^2 \lambda^2 + 2Ru \frac{(\lambda^2 - 1)}{(u^2 - 1)} \left(\frac{du}{d\lambda} \right)^2 + \frac{(\lambda^2 - 1)}{2} \left(\frac{du}{d\lambda} \right)^{\frac{1}{2}} \frac{d}{d\lambda} \left[\frac{d^2 u}{d\lambda^2} \left(\frac{du}{d\lambda} \right)^{-\frac{3}{2}} \right]. \quad (16) \end{aligned}$$

This is the result which determines the screening function, $f(\lambda)$, when u is determined as a function of λ . Although Eq. (16) appears to be a complicated expression, it is nevertheless possible, by a proper choice of the functional dependence of u on λ , to make it approximate the screening function given by the Thomas-Fermi theory. This will now be done.

C. Transformation of the Coordinate λ

Since u is perfectly arbitrary, it may be chosen as desired, provided the domains of variation of u and λ are the same. The transformation which has been found to give the correct shape to the screening function is

$$u = \beta^{-1}(1 - \alpha) \ln[1 + \beta(\lambda - 1)] + \alpha(\lambda - 1) + 1, \quad (17)$$

where α and β are adjustable parameters.

Hence,

$$du/d\lambda = (1 - \alpha)[1 + \beta(\lambda - 1)]^{-1} + \alpha. \quad (18)$$

We note that this transformation is such that $u = 1$ and $(du/d\lambda) = 1$ when $\lambda = 1$, and that $u \rightarrow \infty$ and $(du/d\lambda) \rightarrow \alpha$ as $\lambda \rightarrow \infty$.

It is now necessary to examine the behavior of $f(\lambda)$ at $\lambda = 1$ and as $\lambda \rightarrow \infty$. The screening function will be found to possess a maximum value at $\lambda = 1$, corresponding to minimum shielding of the nuclear charges by the orbital electrons, and to decrease smoothly to $1/2Z$ at very large values of λ .

1. $\lambda \rightarrow \infty$

With the electron under consideration at large distances from both the nuclei and the remaining $2Z - 1$ electrons, it is effectively in the field of a single positive charge. It follows, moreover, that since $\lambda \gg \mu$ we have $r_1 = r_2 = r = R'/2$. At large distances the potential energy V will then be given approximately by

$$V \xrightarrow{\lambda \rightarrow \infty} -e^2/r = -2e^2/R'. \quad (19)$$

This must equal the asymptotic value of V as given by Eq. (8), i.e.,

$$V = -4Ze^2 \lambda f(\lambda) / R'(\lambda^2 - \mu^2). \quad (8)$$

⁸ A. Russek, C. Sherman, and D. E. Flinchbaugh, Phys. Rev. 126, 573 (1962).

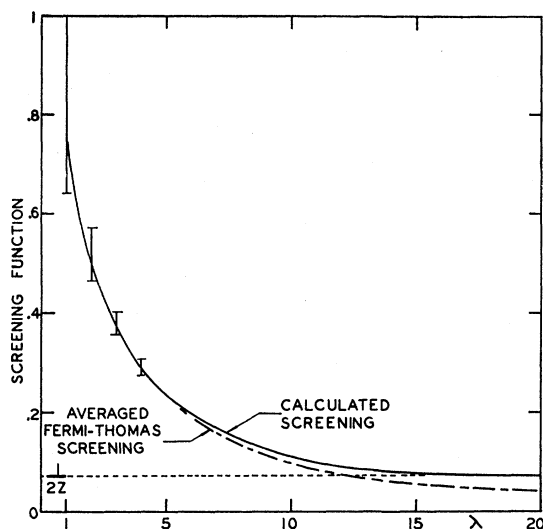


FIG. 1. Matching of the screening function to the averaged Thomas-Fermi screening for the state $2s\sigma_g$ of N_2 at the separation 0.4 Bohr radii. The vertical bars show the total extent of the variation of the screening function as a function of μ for four values of λ .

As λ approaches infinity, we get

$$V \xrightarrow{\lambda \rightarrow \infty} -4Ze^2 f(\infty)/R'\lambda, \quad (20)$$

and a comparison of Eqs. (19) and (20) shows that

$$f(\infty) = 1/2Z. \quad (21)$$

We now examine the asymptotic value of $f(\lambda)$ as given by Eq. (16). The result is

$$2ZR'f(\lambda)|_{\lambda \rightarrow \infty} = -p^2[2\alpha\beta^{-1}(1-\alpha) + \alpha^2\lambda] + p'^2\lambda + 2R\alpha, \quad (22)$$

which becomes, using Eq. (21),

$$R' = -p^2[2\alpha\beta^{-1}(1-\alpha) + \alpha^2\lambda] + p'^2\lambda + 2R\alpha. \quad (23)$$

Clearly this implies two conditions on the parameters α and β . These are

$$p'^2 = \alpha^2 p^2 \quad (24)$$

and

$$R' = 2R\alpha - 2p^2\alpha\beta^{-1}(1-\alpha). \quad (25)$$

The first of these conditions gives the energy eigenvalues once α is determined. The second, together with Eq. (26) below, fixes α and β .

2. $\lambda = 1$

For the case $\lambda = 1$ the electron is actually on the line joining the two nuclei. One might ordinarily expect that the shielding would be negligibly small, i.e., $f(1) = 1$. However, as will become clear, the value of $f(1)$ determined from the Thomas-Fermi theory is not independent of μ , and an average over μ has to be taken. It is therefore convenient to set $f(1) = \delta$, where $\delta \leq 1$ and is to be determined from the Thomas-Fermi theory.

Using this value for $f(1)$, we get from Eq. (16)

$$2ZR'\delta = 2R - p^2(1 - \alpha^2). \quad (26)$$

D. Approximation to the Thomas-Fermi Theory

In the statistical field theory of Thomas⁹ and Fermi¹⁰ for atoms, the potential at any point r , $V(r)$, is given by $V(r) = Ze\chi(r)/r$, where $\chi(x)$ is the solution of the differential equation $x^3 d^2\chi/dx^2 = [\chi]^3$ with appropriate boundary conditions, and $x = 2Z^{1/3}(4/3\pi)^{1/3}r$.

The work of Hund¹¹ on N_2 and F_2 , together with the more recent papers by Firsov¹² and Sheldon,¹³ shows that, aside from a relatively small correction term, the total charge distribution and the total potential at any point can be written as the sum of the charge densities and potentials, respectively, for the individual atoms in the molecule. We therefore proceed in a similar fashion and set for the total potential V :

$$V = V(r_1) + V(r_2) = Ze[\chi(r_1)/r_1 + \chi(r_2)/r_2]. \quad (27)$$

Inserting $r_1 = R'(\lambda + \mu)/2$ and $r_2 = R'(\lambda - \mu)/2$, this becomes

$$V = 2Ze[(\lambda - \mu)\chi(r_1) + (\lambda + \mu)\chi(r_2)]/R'(\lambda^2 - \mu^2). \quad (28)$$

We now compare this result with the form of potential we have used:

$$V = 4Ze\lambda f(\lambda)/R'(\lambda^2 - \mu^2). \quad (8)$$

It is clear from Eq. (28) that the screening predicted by this approximation to the Thomas-Fermi theory for the molecule depends on both λ and μ . However, the screening which we have used in Eq. (8), which permits separation of the wave equation, depends on λ only. We must therefore average Eq. (28) over μ . Actually, for small separations of the nuclei the dependence of V on μ is relatively small, so that the inaccuracy introduced by such an averaging procedure is not too serious at separations ≤ 1 Bohr radius. A typical case is illustrated in Fig. 1. The averaged Thomas-Fermi screening is shown plotted against λ for the $2s\sigma_g$ state of N_2 at the separation 0.4. The total extent of the variation at each λ value is indicated by the horizontal bars, the upper corresponding to $\mu = \pm 1$ and the lower to $\mu = 0$. The largest variation occurs at $\lambda = 1$, along the internuclear line, and in this example at $\mu = \pm 1$, it amounts to 30% of the average value. At $\mu = 0$ it is about 15% below the average. However, at $\lambda = 4$, which corresponds to a distance of the order of 1 Bohr radius from the nuclei, the total variation is about $\pm 5\%$ of the average.

We now compare Eqs. (8) and (28), after appropriate averages over μ , and get

$$f(\lambda) = \langle \chi(r_1)(1 - \mu/\lambda)/2 + \chi(r_2)(1 + \mu/\lambda)/2 \rangle_{av}. \quad (30)$$

⁹ L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

¹⁰ E. Fermi, Rend. adunanza solenne acad. naz. Lincei **6**, 602 (1927); **7**, 342, 726 (1928); Z. Physik **48**, 73 (1929); **49**, 550 (1928).

¹¹ F. Hund, Z. Physik **77**, 12 (1932).

¹² O. B. Firsov, Soviet Phys.—JETP **5**, 1192 (1957).

¹³ J. W. Sheldon, Phys. Rev. **99**, 1291 (1955).

Hence, in the application of the theory we shall approximate the screening function by the above average.

E. Application of the Theory to N_2

In the present work calculations have been carried out for some of the states of N_2 at separations of 0.1, 0.2, 0.4, and 1.1 Bohr radii. The initial step consisted in calculating the Thomas-Fermi averages at each separation, from Eq. (30). The Thomas-Fermi function $\chi(x)$ is tabulated by several authors, e.g., Bush and Caldwell.¹⁴ These tables give $\chi(x)$ as a function of x , where $x = rZ^{1/3}/0.8853$ and the distance r is in Bohr radii.

In order to make the proper averages, the screening is computed for each λ value over the half-range of μ , that is $0 \leq \mu \leq 1$, there being symmetry about $\mu = 0$. The values of the averages of the screening function are then determined. The actual μ dependence is indicated in the sample Thomas-Fermi plot, Fig. 1, by a vertical line through each point. It will be noted that the μ dependence of the screening function is largest for $\lambda = 1$, decreasing as λ increases. This variation improves generally as one goes to smaller internuclear separations. The data was averaged numerically over μ using equal weights.

We get from Eq. (26) for α^2 ,

$$\alpha^2 = 1 - 2Z(R/Z - R'\delta)/p^2. \quad (31)$$

For each state at the chosen separation a value of α was calculated. One must select a value of R , and the corresponding values of p and A , from the tables of basic parameters for H_2^+ . The parameter β is then calculated from Eq. (25), viz.,

$$\beta = \alpha(1 - \alpha)p^2/(R\alpha - R'/2). \quad (32)$$

Numerical accuracy is limited by δ , which is known to within a few parts in the third significant figure.

With α and β determined, u and $du/d\lambda$ are then computed. When these parameters, together with the values of p and A , are substituted into Eq. (16), the screening is determined. In general, the first choice of R , p , and A will not produce good agreement with the Thomas-Fermi screening. It is then necessary to select another value of R and to repeat the procedure until satisfactory matching is obtained. As a criterion for matching to the Thomas-Fermi screening it was decided to accept parameters which lead to a value for $f(2)$ within a few percent of the Thomas-Fermi average. Values of $f(\lambda)$ for the larger λ values were then found to agree quite well with the Thomas-Fermi averages. It should be noted, however, that there will be a divergence between the two curves as λ increases. This divergence arises because the asymptotic value of the Thomas-Fermi curve (which is derived for a neutral molecule) is zero, whereas the calculated $f(\lambda)$ has been made to approach $1/2Z$ as λ approaches infinity,

¹⁴ V. Bush and S. H. Caldwell, Phys. Rev. **38**, 1898 (1931).

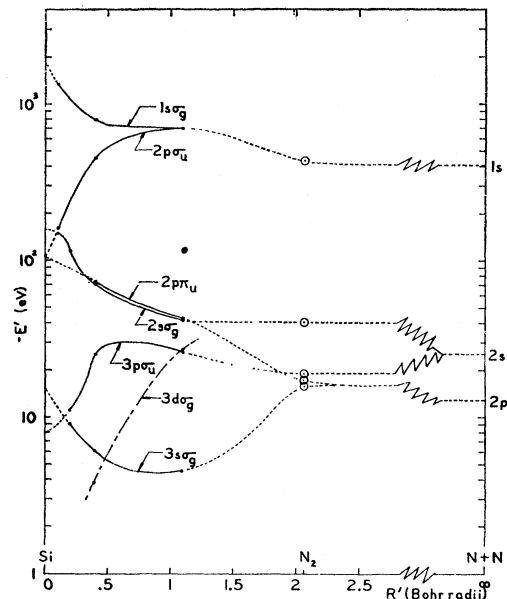


FIG. 2. Energies of the states for N_2 as a function of the internuclear separation. The solid curves are drawn through the points actually calculated in the present work. The dashed lines to the left show the continuation from the calculated curves to the energy levels of the united atom Si, while the dashed lines to the right represent the extension to the energy levels at equilibrium separation as determined experimentally or from the SCF LCAO MO calculations of Scherr (see reference 3) and J. W. Richardson, J. Chem. Phys. **35**, 1829 (1961).

corresponding to the case of a molecular ion appropriate to the present calculation.

Equation (24) gives the energy in terms of α and R , and again the corresponding value of E for H_2^+ . The result is

$$E' = (R/R')^2 \alpha^2 E. \quad (33)$$

Figure 1 shows the matching for the state $2s\sigma_g$, at the separation 0.4, in the present calculations. The value $1/2Z$ is indicated by the horizontal line.

IV. DISCUSSION OF THE RESULTS FOR N_2

N_2 has been discussed at equilibrium separation, 2.068 Bohr radii, by several authors, e.g., Hund¹¹ and Scherr.³ Our numerical computations will be concerned with N_2 at separations up to 1.1 Bohr radii, as an example of the present method. Computational work has largely been directed toward the determination of the energy levels and eigenfunctions of the states which are occupied in the ground state of N_2 . Figure 2 is a plot of the energies of the states as a function of separation. The solid lines are drawn through points actually computed in the present work. To the left, at zero separation, are drawn the energy levels of the united atom, Si. The energy of the lowest lying state is determined from the K absorption edge; the remainder are taken from the paper by Slater.¹⁵ To the

¹⁵ J. C. Slater, Phys. Rev. **98**, 1039 (1955).

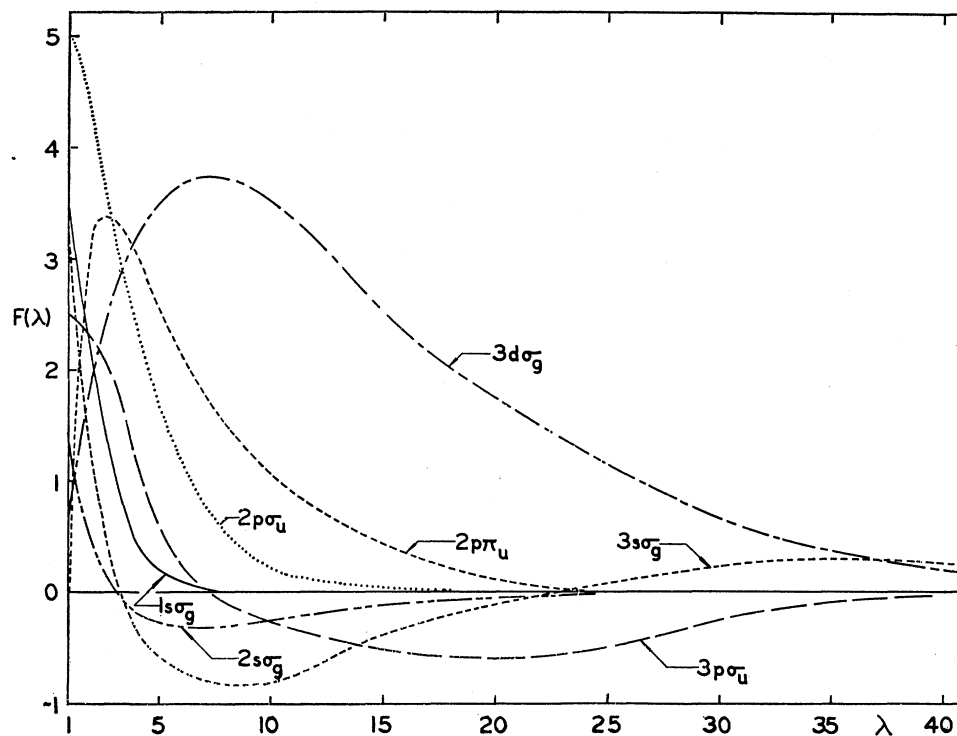


FIG. 3. Unnormalized functions $F(\lambda)$ for N_2 as a function of the parameter λ at the separation 1.1 Bohr radii.

extreme right, at infinite separation, are the levels which are filled or partially filled in the isolated N atom. These data are also taken from Slater. Values corresponding to the equilibrium separation of N_2 are also plotted. Experimental values have been used where available, and those levels for which no experimental confirmation exists have been taken from the SCF LCAO MO calculation of Scherr.³

The computed energy eigenvalues, at separations between 0.1 and 1.1, fall on smooth curves. In view of the fact that these levels certainly approach the correct zero separation values, one would assume that the predictions are reasonable for these intermediate separations. Unfortunately there is no direct experimental confirmation for these small separations. The reason for a probable increase in the reliability of the data as the separation of the nuclei is made to approach zero is indicated below.

With α and β determined, the functions $F(\lambda)$ are readily written down. $\Lambda(u)$ is calculated from Eq. (6) by using the parameters σ and p from the data of Bates *et al.* Figure 3 displays the wave functions obtained from the present data for the separation $R'=1.1$. Figure 4 shows some of the wave functions at the separations 0.4 and 1.1, for comparison. Figures 4(a) and 4(b) show the wave functions for the state $1s\sigma_g$ drawn as a function of the distance from the center of the molecule along the line joining the nuclei, and of the distance measured along the perpendicular bisector of that line, respectively. Figures 4(c) and 4(d) show similar plots at these separations for the

states $2s\sigma_g$ and $3p\sigma_u$. In these cases the abscissas represent distance from the mid-point of the molecule along the perpendicular bisector of the line joining the nuclei, that is, along the line $\mu=0$. The wave functions are not normalized, though this can be done numerically.

In the calculation of the screening functions for the states at $R'=1.1$ from Eq. (16), the initial acceptable values of α and β caused $f(\lambda)$ to fall slightly below $1/2Z$, and then for increasing λ to approach this asymptotic value from below, rather than from above. In order to make the screening function approach $1/2Z$ smoothly from above, the condition at infinity, represented by Eq. (25), was changed. It was found that if the latter condition was such as to make the screening at infinity go to a value in excess of $1/2Z$ equal to the former maximum depth below $1/2Z$, then satisfactory behavior was obtained. Such a correction was not found to be necessary at the smaller separations since it is possible to match the average Thomas-Fermi screening out to large values of λ . Table I gives the values of α and β computed in the present work, together with the values of R and p taken from the tables of Bates *et al.*

In this theory the simplest of assumptions is made concerning the potential energy of the electron under consideration. The screening is assumed to be independent of μ , and this assumption leads to separability of the wave equation and leads to changes in the radial parts of the eigenfunctions only. Clearly, one cannot precisely match this μ -independent screening to the screening predicted by the Thomas-Fermi theory. The

TABLE I. Basic parameters for N_2 .

State	R	p	α	β
(i) $R'=1.1, \delta=0.575$				
$1s\sigma_g$	9.0	4.980	0.795	0.634
$2s\sigma_g$	6.5	2.252	0.427	0.658
$3s\sigma_g$	5.38	1.416	0.224	0.835
$2p\sigma_u$	9.0	4.973	0.794	0.635
$3p\sigma_u$	6.5	2.172	0.349	0.796
$4p\sigma_u$	5.27	1.321	0.196	0.951
$3d\sigma_g$	8.0	3.091	0.502	0.787
$2p\pi_u$	7.3	2.688	0.453	0.760
$3d\pi_g$	7.0	2.342	0.248	1.263
(ii) $R'=0.4, \delta=0.753$				
$1s\sigma_g$	3.0	2.025	0.752	0.372
$2s\sigma_g$	2.55	1.045	0.438	0.294
$3s\sigma_g$	2.33	0.6837	0.22	0.25
$2p\sigma_u$	3.0	1.777	0.660	0.398
$3p\sigma_u$	2.46	0.8796	0.302	0.300
$3d\sigma_g$	2.48	0.8675	0.112	0.954
$2p\pi_u$	2.7	1.205	0.430	0.370
(iii) $R'=0.2, \delta=0.851$				
$1s\sigma_g$	1.5	1.185	0.749	0.258
$2s\sigma_g$	1.32	0.5904	0.512	0.151
$3s\sigma_g$	1.27	0.3922	0.21	0.15
$2p\sigma_u$	1.4	0.7745	0.552	0.221
$3p\sigma_u$	1.29	0.4517	0.25	0.18
$2p\pi_u$	1.35	0.6464	0.491	0.186
(iv) $R'=0.1, \delta=0.916$				
$1s\sigma_g$	0.735	0.6555	0.751	0.160
$2s\sigma_g$	0.680	0.3222	0.51	0.087
$2p\sigma_u$	0.687	0.3542	0.53	0.10
$2p\pi_u$	0.687	0.3388	0.46	0.11

latter is not independent of μ . It is this basic inadequacy which necessitates the calculation of averages over μ of the screening at each λ value. As the separation of the nuclei approaches zero, however, the total variation of the screening function over the entire range of μ also approaches zero. For this reason, the results obtained by this approach are expected to be good at small internuclear separations. The graph of the energy levels, Fig. 2, shows that as R' approaches zero, the levels go into those of the united atom.

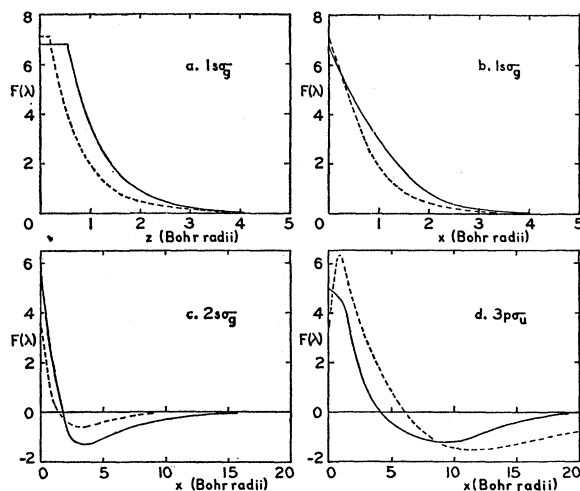


FIG. 4. Some typical wave functions (unnormalized) for N_2 at the separation 0.4 (dashed line) and 1.1 (solid line). The abscissas x and z are distances measured along the bisector of the internuclear line, and along the internuclear line, respectively.

As a further refinement to the theory, one can make the necessary averages of $f(\lambda)$ over μ , by weighting $f(\lambda)$ with $|M(\mu)|^2$, which is directly proportional to the probability of finding the electron under consideration at that value of μ . For the s states $M(\mu)$ is constant, and $f(\lambda)$ will be unaffected by weighting, but $M(\mu)$ for the remaining states depends quite strongly on μ . For $3d\sigma_g$ at $R'=1.1$ the energy predicted when matching to the weighted Thomas-Fermi screening is -27 eV compared with -108 eV computed from the unweighted Thomas-Fermi screening. While this change is an improvement, this level does cross other filled levels, including $3s\sigma_g$. This is, of course, a contradiction of the noncrossing rule (von Neumann and Wigner¹⁶) which forbids the intersecting of states of the same species.

¹⁶ J. von Neumann and E. Wigner, Z. Physik **30**, 467 (1929).