64-5

OFFICE OF NAVAL RESEARCH

Contract Nonr-1677(01)

Project No. NR-051-362

TECHNICAL REPORT NO. 9

A Statistical Theory of the Hydrogen Molecule-Ion

by

Sidney Golden and Judith G. Chernin

Department of Chemistry

Brandeis University, Waltham, Massachusetts

September 15, 1963

A Statistical Theory of the Hydrogen Molecule-Ion

by

Sidney Golden and Judith G. Chernin
Department of Chemistry
Brandeis University, Waltham, Massachusetts

Abstract

A version of statistical theory is applied to the hydrogen molecule-ion, with good results for the electronic energies of the lowest attractive and repulsive states. For the former, a binding energy of 0.085 a.u. is obtained with an internuclear distance of 2.10 a.u., to be compared with 0.103 a.u. and 2.00 a.u. obtained from the exact solution of Schroedinger's equation. The method employed involves the use of hydrogen atomic orbitals, although when the latter refer to unbound states they are approximated by plane waves.

1. Introduction

The first application of the Thomas-Fermi theory(1,2) to molecular systems occurred soon after its introduction, when Hund(3) used it to approximate the electron-density and the electric field in the nitrogen and fluorine molecules. Since then, the original statistical theory of Thomas and Fermi has been employed to estimate the binding energy of molecular systems(4). The numerical results which have been obtained from the use of the original Thomas-Fermi theory have been, at best, only in fair agreement with experimental values of bond energies and bond distances; at worst, an absence of binding has been indicated. Recently, the limitations of the Thomas-Fermi theory in this connection have been established by Teller(5). He has shown that this theory is incapable, in terms of its original formulation, of yielding energetically stable molecular systems. A similar conclusion is obtained for the version of statistical theory known as Thomas-Fermi-Dirac theory, in which the effect of electron exchange has been incorporated(6) into the original theory.

In the years following its introduction, the theory of Thomas and Fermi has been subjected to a variety of other modifications(7). Of all of these, the one due to von Weizsäcker(8) has produced what seems to provide the most radical and most effective connection of the original theory with quantum mechanics(9). With this modification, Gombás(10) has obtained approximate values for the binding energy and the bond length of the nitrogen molecule which are in good agreement with the experimental values of these quantities. From this result, a sufficiently quantum-mechanical version of statistical theory appears to be essential for a realistic application to molecular systems.

An alternative to the von Weizsäcker theory is one which is the formal analogue of the Thomas-Fermi theory, but employs a basis of eigenfunctions of some suitable approximate Hamiltonian which is more closely related to the physical system of interest rather than the basis of eigenfunctions of momentum implicit in the original theory. Such a version has been shown to yield relatively good results for the energy values and electron densities of helium-like atoms(11). The present paper is concerned with an application of this version of statistical theory to approximate the binding energy of the simplest molecular system -- the hydrogen molecule-ion. Because of the simplicity of this system, the usual complications attending the determination of a self-consistent field can be avoided. As a consequence, the inherent limitations of the theory can be best assessed under the most stringent circumstances.

2. Formalism

In the interest of brevity, we shall simply sketch the formalism to be employed here(12). The properties of a single-particle (i.e., an electron, since we tacitly suppose nuclei of infinite mass) can be determined from the density matrices (representatives) of the system determined by

$$\underset{\sim}{\rho}_M(\vec{x}', \vec{x}) = \sum_{n=1}^{\infty} \psi_n^*(\vec{x}')\, \vartheta(\lambda_M - \underset{\sim}{H})\, \psi_n(\vec{x}), \tag{2.1}$$

where $\vec{x}$ stands for the configurational and spin coordinates of the particle, $\underset{\sim}{H}$ is the Hamiltonian of the system, $\{\psi_n(\vec{x})\}$ is any complete, orthonormal set of functions with the correct boundary conditions. Here, $\vartheta(y)$ is the Heaviside unit function defined by

$$\begin{aligned} \vartheta(y) &= 1, \quad y > 0, \\ &= 0, \quad y < 0; \end{aligned} \tag{2.2}$$

a convenient representation of the ϑ-operator -- the spectral operator of $\underset{\sim}{H}$ -- is

$$\vartheta(\lambda_M - \underset{\sim}{H}) = \frac{1}{2\pi i}\, P \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{dz}{z}\; e^{z\lambda_M}\; e^{-z\underset{\sim}{H}}, \quad \gamma > 0; \tag{2.3}$$

the parameter λ_M, which plays the role of a "chemical potential per state"(12), is chosen so that

$$\mathrm{Tr}(\underset{\sim}{\rho}_M) = \int d\vec{x}\; \underset{\sim}{\rho}_M(\vec{x}, \vec{x}) = M, \text{ a positive integer.} \tag{2.4}$$

With this normalization, M refers to the M lowest eigenstates of $\underset{\sim}{H}$.(13)

In terms of the eigenfunctions of $\underset{\sim}{H}$, $\{\phi_n(\vec{x})\}$, the density matrices assume the form originally introduced by Dirac(6)

$$\begin{aligned} \underset{\sim}{\rho}_M(\vec{x}', \vec{x}) &= \sum_{n=1}^{\infty} \vartheta(\lambda_M - E_n)\, \phi_n^*(\vec{x}')\, \phi_n(\vec{x}) \\ &= \sum_{n=1}^{M} \phi_n^*(\vec{x}')\, \phi_n(\vec{x}), \end{aligned} \tag{2.5}$$

so that for any arbitrary observable $\underset{\sim}{A}$, the quantity

$$\langle A \rangle_M = \mathrm{Tr}(\underset{\sim}{\rho}_M \underset{\sim}{A}) = \sum_{n=1}^{M} \langle \phi_n | A | \phi_n \rangle$$

yields the sum of the expectation values of $\underset{\sim}{A}$ for the M lowest eigenstates of $\underset{\sim}{H}$. In particular, we see that

$$\langle E \rangle_M = \mathrm{Tr}(\underset{\sim}{\rho}_M \underset{\sim}{H}) = \sum_{n=1}^{M} E_n, \tag{2.6}$$

where $E_1 \leqslant E_2 \leqslant E_3$ --- are the eigenvalues of the Hamiltonian. It can be verified(14) that Eq. (2.6) is obtainable from(12)

$$\langle E \rangle_M = \int_0^M \lambda(M)\, dM = \int_0^M \lambda\{\mathrm{Tr}\underset{\sim}{\rho}_M\}\, d\{\mathrm{Tr}\,\underset{\sim}{\rho}_M\} \tag{2.7}$$

which emphasizes the role played by λ , noted earlier.

Equations (2.4) and (2.7) involve the traces of the density matrices and are thus invariant to the choice of basis employed for this evaluation. They are exact. Moreover, in the approximation dealt with here, they will be used to provide an estimate of the electronic energy of the system of interest.

Before considering any approximation, however, we examine the effect of the symmetry of the system upon its density matrices. Since the Hamiltonian of the system is left invariant as a consequence of the application of certain symmetry operations, the density matrices, by Eq. (2.1), likewise must remain invariant to their application. In particular, the inversion symmetry of the hydrogen molecule-ion will be exploited to simplify the density matrices for that system. In this case, we have the Hamiltonian, in atomic units, of electronic motion (see Fig. 1)

$$\underset{\sim}{H} = -\tfrac{1}{2} \nabla_{\vec{r}_2}^{2} - \frac{1}{r_2} - \frac{1}{r_3} . \qquad (2.8)$$

Clearly, the Hamiltonian remains invariant as a result of the application of the unitary transformation $\underset{\sim}{\mathcal{J}} \cdots \underset{\sim}{\mathcal{J}}^{\dagger}$, where

$$\underset{\sim}{\mathcal{J}} : \quad \vec{r}_0 \longrightarrow -\vec{r}_0 , \qquad (2.9)$$

corresponding to inversion through the mid-point on the internuclear axis. Furthermore, since

$$\underset{\sim}{\mathcal{J}}^{2} = \underset{\sim}{I}, \qquad (2.10)$$

the inversion operator also is Hermitian. Hence its eigenfunctions comprise two distinct symmetry species: those which are symmetric (gerade) and those which are antisymmetric (ungerade) with respect to the inversion operation. Because $\underset{\sim}{\mathcal{J}}$ and $\underset{\sim}{H}$ commute, their simultaneous eigenfunctions possess the same symmetry.

In terms of such simultaneous eigenfunctions, we may construct two sorts of density matrices. Their construction is facilitated by the introduction of the orthogonal projections

$$\underset{\sim}{S}_{(\pm)} \equiv \tfrac{1}{2}(\underset{\sim}{I} \pm \underset{\sim}{\mathcal{J}}). \tag{2.11}$$

Since $\underset{\sim}{\mathcal{J}}$ and $\underset{\sim}{H}$ commute, we may obtain

$$\vartheta(\lambda_M - \underset{\sim}{H}) = \underset{\sim}{S}_{(+)}\,\vartheta(\lambda_M - \underset{\sim}{H})\,\underset{\sim}{S}_{(+)} + \underset{\sim}{S}_{(-)}\,\vartheta(\lambda_M - \underset{\sim}{H})\,\underset{\sim}{S}_{(-)}$$

and, ultimately,

$$\underset{\sim}{\rho}_M(\vec{x}', \vec{x}) = \underset{\sim}{\rho}_M^{(+)}(\vec{x}', \vec{x}) + \underset{\sim}{\rho}_M^{(-)}(\vec{x}', \vec{x}), \tag{2.12}$$

where, by Eqs. (2.1) and (2.9) and the introduction of the coordinates of Fig. 1,

$$\underset{\sim}{\rho}_M^{(\pm)}(\vec{x}', \vec{x}) = \frac{1}{4} \sum_{n=1}^{\infty} \left\{\psi_n^*(\vec{r}_o{}') \pm \psi_n^*(-\vec{r}_o{}')\right\} \vartheta(\lambda_M - \underset{\sim}{H}) \left\{\psi_n(\vec{r}_o) \pm \psi_n(-\vec{r}_o)\right\}. \tag{2.13}$$

The two classes of density matrices $\underset{\sim}{\rho}^{(+)}$ and $\underset{\sim}{\rho}^{(-)}$ are demonstrably orthogonal and refer to the inversion-symmetric and inversion-antisymmetric states, respectively, of the hydrogen molecule-ion. It is noteworthy that the resulting basis functions here are of the Pauling type$^{(15)}$, but do not comprise an orthonormal basis.

Analogous to Eqs. (2.4) and (2.7), we obtain

$$M^{(\pm)} = \mathrm{Tr}(\underset{\sim}{\rho}_M^{(\pm)}) = \frac{1}{2} \sum_{n=1}^{\infty} \langle \psi_n(\vec{r}_o) | \vartheta(\lambda_M^{(\pm)} - \underset{\sim}{H}) | \psi_n(\vec{r}_o) \rangle$$

$$\pm \frac{1}{2} \sum_{n=1}^{\infty} \langle \psi_n(-\vec{r}_o) | \vartheta(\lambda_M^{(\pm)} - \underset{\sim}{H}) | \psi_n(\vec{r}_o) \rangle; \tag{2.14}$$

$$\langle E\rangle_M^{(\pm)} = \mathrm{Tr}(\underset{\sim}{\rho}_M^{(\pm)}\,\underset{\sim}{H}) = \tfrac{1}{2}\sum_{n=1}^{\infty}\langle\psi_n(\vec{r}_o)|\,\underset{\sim}{H}\,\vartheta(\lambda_M^{(\pm)}-\underset{\sim}{H})\,|\psi_n(\vec{r}_o)\rangle$$

$$\pm\tfrac{1}{2}\sum_{n=1}^{\infty}\langle\psi_n(-\vec{r}_o)|\,\underset{\sim}{H}\,\vartheta(\lambda_M^{(\pm)}-\underset{\sim}{H})|\,\psi_n(\vec{r}_o)\rangle. \quad (2.15)$$

3. Quasi-classical Approximation -- Discrete States

The approximation to be considered here can be expressed simply as

$$e^{-z\underset{\sim}{H}} \equiv e^{-z(\underset{\sim}{H}_o+V)} \doteq e^{-zV}\,e^{-z\underset{\sim}{H}_o} \quad (3.1)$$

where

$$\underset{\sim}{H}_o = -\tfrac{1}{2}\nabla_{\vec{r}_2}^2 - \frac{1}{r_2} \quad (3.2)$$

and

$$V = -\frac{1}{r_3} \quad (3.3)$$

This warrants taking $\{\psi_n(\vec{r}_o)\}$ to be the complete orthonormal basis of eigenfunctions of the hydrogen atom corresponding to one of the nuclei of the hydrogen molecule-ion. With this identification, we find it convenient to refer to nucleus -2 of Fig. 1 as the origin and obtain

$$\underset{\sim}{H}_o\,\psi_n(\vec{r}_o) \equiv \underset{\sim}{H}_o\,\psi_n(\vec{r}_2) = E_n^{\,o}\,\psi_n(\vec{r}_2), \quad (3.4)$$

where $E_n^{\,o}$ is an appropriate eigenvalue of the hydrogen atom. A corresponding normalized eigenfunction is(16)

$$\psi_n(\vec{r}_2) \equiv R_{n\ell}(r_2)\;\Theta_{\ell m}(\theta_2)\;e^{im\phi_2}/\sqrt{2\pi}, \quad (3.5)$$

and

$$E_n^{\,o} = -\frac{1}{2n^2}\,. \quad (3.6)$$

(The azimuthal angle ϕ_2 measures rotation of the electron about the internuclear axis, but is not included in Fig. 1.) The effect of inversion of the eigenfunctions can be seen to be

$$\begin{aligned} \underset{\sim}{\mathcal{I}}\;\psi_n(\vec{r}_2) &\equiv R_{n\ell}(r_3)\;\Theta_{\ell m}(\theta_3)\;e^{im(\phi_2+\pi)}/\sqrt{2\pi} \\ &= (-1)^m\,R_{n\ell}(r_3)\;\Theta_{\ell m}(\theta_3)\;e^{im\phi_2}/\sqrt{2\pi} \\ &\equiv \psi_n(-\vec{r}_3). \end{aligned} \tag{3.7}$$

Combining these results with Eq. (2.3), we obtain

$$\vartheta(\lambda_M - \underset{\sim}{H})\,\psi_n(\vec{r}_2) \doteq \vartheta(\lambda_M + \frac{1}{2n^2} + \frac{1}{r_3})\,\psi_n(\vec{r}_2). \tag{3.8}$$

The approximations to Eqs. (2.14) and (2.15) can now be effected. With Eq. (3.7), we obtain

$$\begin{aligned} \mathrm{Tr}(\underset{\sim}{\rho}_M{}^{(\pm)}) = \tfrac{1}{2}\sum_{n=1}^{\infty}\sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{+\ell}\Big\{&\langle\psi_n(\vec{r}_2)|\,\vartheta(\lambda_M{}^{(\pm)}+\frac{1}{2n^2}+\frac{1}{r_3})\,|\psi_n(\vec{r}_2)\rangle \\ &\pm\langle\psi_n(\vec{r}_3)|\,\vartheta(\lambda_M{}^{(\pm)}+\frac{1}{2n^2}+\frac{1}{r_3})\,|\psi_n(\vec{r}_2)\rangle\Big\}\;. \end{aligned} \tag{3.9}$$

Making use of the addition theorem for spherical harmonics$^{(17)}$, one can obtain

$$\ell + \tfrac{1}{2} = \sum_{m=-\ell}^{+\ell}\Theta_{\ell m}^{2}(\theta_2),$$

and

$$(\ell + \tfrac{1}{2})\,P_\ell\,(-\cos\alpha) = \sum_{m=-\ell}^{+\ell}\Theta_{\ell m}(\theta_2)\,\Theta_{\ell m}(\theta_3)\,e^{im\phi_2}\;e^{-im(\phi_2+\pi)}\;.$$

With these relations it can be established that Eq. (2.14) is approximated by

$$M_d^{(\pm)} \doteq \frac{1}{4\pi} \sum_{n=1}^{\infty} \sum_{\ell=0}^{n-1} (\ell + \tfrac{1}{2}) \Big\{ \Big\langle R_{n\ell}(r_2) \Big| \vartheta\Big(\lambda_M^{(\pm)} + \frac{1}{2n^2} + \frac{1}{r_3}\Big) \Big| R_{n\ell}(r_2) \Big\rangle$$

$$\pm (-1)^{\ell} \Big\langle R_{n\ell}(r_3) \Big| P_{\ell}(\cos\alpha)\, \vartheta\Big(\lambda_M^{(\pm)} + \frac{1}{2n^2} + \frac{1}{r_3}\Big) \Big| R_{n\ell}(r_2) \Big\rangle \Big\}, \quad (3.10)$$

where use has been made of the relation $P_{\ell}(-x) = (-1)^{\ell} P_{\ell}(x)$. In equivalent terms, Eq. (2.15) is approximated by

$$\langle E_d \rangle_M^{(\pm)} \doteq -\frac{1}{8\pi} \sum_{n=1}^{\infty} \sum_{\ell=0}^{n-1} \frac{(\ell+\frac{1}{2})}{n^2} \Big\{ \Big\langle R_{n\ell}(r_2) \Big| \vartheta\Big(\lambda_M^{(\pm)} + \frac{1}{2n^2} + \frac{1}{r_3}\Big) \Big| R_{n\ell}(r_2) \Big\rangle$$

$$\pm (-1)^{\ell} \Big\langle R_{n\ell}(r_3) \Big| P_{\ell}(\cos\alpha)\, \vartheta\Big(\lambda_M^{(\pm)} + \frac{1}{2n^2} + \frac{1}{r_3}\Big) \Big| R_{n\ell}(r_2) \Big\rangle \Big\}$$

$$- \frac{1}{4\pi} \sum_{n=1}^{\infty} \sum_{\ell=0}^{n-1} (\ell + \tfrac{1}{2}) \Big\{ \Big\langle R_{n\ell}(r_2) \Big| \frac{1}{r_3}\, \vartheta\Big(\lambda_M^{(\pm)} + \frac{1}{2n^2} + \frac{1}{r_3}\Big) \Big| R_{n\ell}(r_2) \Big\rangle$$

$$\pm (-1) \Big\langle R_{n\ell}(r_3) \Big| \frac{P_{\ell}(\cos\alpha)}{r_3}\, \vartheta\Big(\lambda_M^{(\pm)} + \frac{1}{2n^2} + \frac{1}{r_3}\Big) \Big| R_{n\ell}(r_2) \Big\rangle \Big\}. \quad (3.11)$$

Because of Eq. (2.2), the integrands in Eqs. (3.10) and (3.11) have non-zero values in restricted regions of configuration space. In particular, such non-zero values occur for

$$\lambda_M^{(\pm)} + \frac{1}{2n^2} + \frac{1}{r_3} \geqslant 0$$

Hence, defining

$$\zeta_M^{(\pm)} \equiv -\lambda_M^{(\pm)} > 0, \quad (3.12)$$

we must restrict the various integrations to the region

$$0 \leqslant r_3 \leqslant \frac{1}{\zeta_M^{(\pm)} - \frac{1}{2n^2}} . \quad (3.13)$$

4. Approximation for the Continuum

The expressions of the previous Section are formally incomplete transcriptions of the results of Section 2. They include only the eigenfunctions of negative energy of the hydrogen atom. To complete the transcription one requires the inclusion of the eigenfunctions of the continuum of positive energy values. Although these are well-known(18), they are extremely difficult to handle in the present context. As a consequence, an additional approximation will be made here in which the plane-wave basis of the original Thomas-Fermi theory will be used for the continuum. Such usage can be justified only in an asymptotic ($E^o \longrightarrow +\infty$) sense, however. Even so, the use of the original Thomas-Fermi density to approximate the continuum is bound to introduce errors related to the poor values of the binding energy it yields for atoms. For this reason, we have adapted a version of statistical theory(9) which has been shown to yield improved results for atoms. In this theory, the density matrix of the system is developed in a power series in Planck's constant and terms up to and including h^2 are retained.

In essence, the adaptation consists in representing the unbound states of the hydrogen atom centered at nucleus -2 by eigenfunctions of momentum and their corresponding energy by their (asymptotic) kinetic energy. Compared to Eqs. (3.5) - (3.6), we represent (for the continuum)

$$\psi_n(\vec{r}_2) \doteq e^{i\vec{p}\cdot\vec{r}/\hbar} \tag{4.1}$$

and

$$E_n^{\,o} \doteq p^2/2m. \tag{4.2}$$

(These quantities are not expressed in atomic units.) In addition, we take for the continuum(19)

$$\vartheta(\lambda_M - \underset{\sim}{H})\,\psi_n(\vec{r}_2) \doteq e^{i\vec{p}\cdot\vec{r}_2/\hbar}\Big[\vartheta(\lambda_M + \frac{1}{r_3} - p^2/2m)$$

$$+\Big\{\frac{\hbar}{mi}\,\vec{p}\cdot\nabla V - \frac{\hbar^2}{4m}\nabla^2 V\Big\}\vartheta''(\lambda_M + \frac{1}{r_3} - p^2/2m)$$

$$+\frac{\hbar^2}{6m}\Big\{(\vec{p}\cdot\nabla)^2 V + \nabla V\cdot\nabla V\Big\}\,\vartheta'''(\lambda_M + \frac{1}{r_3} - p^2/2m)$$

$$-\frac{\hbar^2}{8m^2}(\vec{p}\cdot\nabla V)^2\,\vartheta'''(\lambda_M + \frac{1}{r_3} - p^2/2m)\quad , \qquad (4.3)$$

with

$$V = -\frac{1}{r_3}\ .$$

With this approximation the continuum contribution to Eqs. (2.14) - (2.15) can be evaluated. For this purpose, we note that the resulting approximation to the first series of both Eqs. (2.14) and (2.15), apart from a factor of $\frac{1}{2}$, then correspond to the expressions which are obtained for a hydrogen atom centered about nucleus-3 in Fig. 1. These have been given in ref. (9) and will only be summarized here. We obtain (in atomic units)

$$M_c^{(1)} = \frac{2^{5/2}}{3\pi}\int_{r_o}^{r_1} dr\, r^2\Big\{(\frac{1}{r} - \zeta_M)^{3/2} - \frac{1}{64r^4}(\frac{1}{r} - \zeta_M)^{-3/2}\Big\}, \qquad (4.4)$$

which can be evaluated in closed form, and

$$\langle E\rangle_c^{(1)} = -3M_c^{(1)}\zeta_M - \frac{2^{3/2}\zeta_M}{3\pi}\Big\{r_1(1-2\zeta_M r_1) - r_o(1-2\zeta_M r_o)\Big\}, \qquad (4.5)$$

where $r_o \leqslant r_1$ are both determined by the condition that

$$r(1 - \zeta_M r)^3 = \frac{1}{64}\ . \qquad (4.6)$$

The approximation for the continuum contribution to the second series of Eqs. (2.14) - (2.15) entails the multiplication of Eq. (4.3) by $e^{i\vec{p}\cdot\vec{r}_3/\hbar}$, by Eq. (3.7), and an integration of the product over available momenta. This has been carried out but, in the interest of brevity, the details will be omitted. We have obtained

$$M_c^{(2)} = \frac{\pi^{\frac{1}{2}}}{4R} \sum_{k=o}^{\infty} \frac{2^{k+1}}{(2k+2)!\,\Gamma(\frac{3}{2}+k+1)} \frac{d^{2k+2}}{d\xi_M^{\;2k+2}} \left(\xi_M^{\;k}\, e^{-\sqrt{2\xi_M}R}\right), \tag{4.7}$$

where R is the internuclear distance (in atomic units). With the aid of Eq. (2.7), we can obtain

$$\langle E_c\rangle_M^{(2)} = -M_c^{(2)}\xi_M + \int_{\infty}^{\xi_M} d\xi\, M_c^{(2)}(\xi). \tag{4.8}$$

The continuum approximations to the normalization and energy are to be halved and added to the discrete contribution according to Eqs. (2.14) and (2.15). That is, we take

$$M^{(\pm)} = M_d^{(\pm)} + \tfrac{1}{2}\left\{M_c^{(1)} \pm M_c^{(2)}\right\} \tag{4.9}$$

and

$$\langle E\rangle_M^{(\pm)} = \langle E_d\rangle_M^{(\pm)} + \tfrac{1}{2}\left\{\langle E_c\rangle_M^{(1)} \pm \langle E_c\rangle_M^{(2)}\right\}. \tag{4.10}$$

5. Computation

The evaluation of Eqs. (4.9) and (4.10) were carried out numerically as follows. For the integrals in Eqs. (3.10) and (3.11), the integrand could be expressed in terms of Bessel functions, following Coulson$^{(20)}$, and reduced to radial integrations on r_3. These integrals were evaluated analytically and expressed in terms of the upper limit given by Eq. (3.13)$^{(21)}$. Different integrals arising from the use of different wave functions are related by a common value of ξ_M. Hence the upper limits of their respective ranges of integration are simply determined and depend, for a given value of ζ_M, only upon the principal quantum number of the wave function. The procedure followed consisted in choosing a value of ζ_M, evaluating the appropriate upper bounds and substituting into the analytical expressions for the integrals. Actually, the discrete contribution was limited to states for which $n \leq 3$. (Estimates of the contribution to the normalization were made for $n = 4$ which led us to believe that their contribution was less than 0.02.)

For a fixed value of ζ_M, the quantities in Eqs. (4.4) - (4.8) were evaluated and combined according to Eqs. (4.9) - (4.10).

These computations were carried out for a fixed value of the internuclear distance, R, until successive trial values of ζ_M gave a value of unity (± 0.005) for the normalization integral.

The procedure was repeated for different values of the internuclear distance.

6. Results

The results which have been obtained are exhibited compactly in Figs. (2) - (5). The approximations inherent in the truncation of the discrete contribution and the plane-wave representation of the continuum contribution warrant no more elaborate presentation. Nevertheless, from Figs. (2) and (3) the computed values for the potential energy of the H_2^+ molecule, in both the ground gerade and ungerade states, are in good agreement with those obtained from the solution of the relevant Schroedinger's equation(22). For the bound state, a binding energy of 0.085 a.u. and an equilibrium distance of 2.10 a.u. have been obtained; these compare favorably with the quantum values of 0.103 a.u. and 2.00 a.u., respectively.

In Figs. (4) and (5) are presented the contributions to the normalization (of unity) made by the various states. The indications are that an important continuum contribution is always present for the range of internuclear distances used in these computations. Moreover, its importance increases for large internuclear distances, becoming equal in value to the discrete contribution when the internuclear distance becomes indefinitely large.

Although the results which have been obtained suggest that a sufficiently quantum-mechanical version of statistical theory can yield results for molecular binding energies and bond distances which are in good agreement with those obtained from precise calculations, the method described in this paper holds little promise of extension to polyelectronic molecules. In the absence of any self-consistent field approximations, the resulting integrals will be even more complicated than those of the present paper. The latter involve integrations over finite regions of configuration space of one electron; in polyelectronic molecules the corresponding regions for each electron will be correlated with those of the others, rendering an analytical evaluation of the pertinent integrals impractical, if not impossible.

References

1. L. H. Thomas, Proc. Camb. Phil. Soc., 23, 542 (1957).
2. E. Fermi, Z. Phys., 48, 73 (1928).
3. F. Hund, Z. Phys., 77, 12 (1932).
4. See, for example, N. H. March, Advances in Physics, Vol. 6 (1957), where numerous references are cited.
5. E. Teller, Rev. Mod. Phys., 34, 627 (1962).
6. P. A. M. Dirac, Proc. Camb. Phil. Soc., 26, 376 (1930).
7. See, for example, P. Gombás, Die Statistische Theorie des Atoms und Ihre Anwendungen (Springer, Vienna, 1949), where these are described in detail.
8. C. F. von Weizsäcker, Z. Phys., 96, 431 (1935).
9. One such connection is given in S. Golden, Phys. Rev., 105, 604 (1957); this correction has been evaluated by R. A. Berg and L. Willets, Proc. Phys. Soc. (London), A68, 229 (1955).
10. P. Gombas, Acta Phys. Hung., 9, 461 (1959).
11. S. Goldén, Phys. Rev., 107, 1283 (1957).
12. S. Golden, Rev. Mod. Phys., 32, 322 (1960).
13. We are tacitly supposing that the energy spectrum is non-degenerate (apart from spin). This is apt to be fulfilled for ground states, our main interest here.
14. Strictly speaking, the integral should be understood as a Stieltje's integral when M assumes only integral values.
15. L. Pauling, Chem., 5, 173 (1928). These functions are, of course, generically related to the Heitler-London functions for the hydrogen molecule; see, for example, W. Heitler and F. London, Z. Physik., 44, 455 (1927).
16. We emphasize that the present section is restricted to the eigenfunctions of the discrete spectrum but formally is applicable to the continuum. The discrete functions are found in L. Pauling and E. B. Wilson, Jr., Introduction to Quantum Mechanics (McGraw-Hill, New York, 1935), p. 138.
17. See, for example, L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Addison-Wesley, Reading, 1958), pp. 87 and 494.
18. See, for example, reference (17), p. 418.
19. The result which follows is readily obtained from reference (9) by taking the limit of the expressions developed there as T ⟶ 0.

20. C. A. Coulson, Proc. Camb. Phil. Soc., 33, 104 (1937).

21. In the interest of brevity, and because they are rather special to the present problem, these integrals are not presented here.

22. See, for example, D. R. Bates, K. Ledsham and A. L. Steward, Phil. Trans. Roy. Soc., 246, 215 (1953).

TECHNICAL REPORT DISTRIBUTION LIST

CONTRACTOR BRANDEIS UNIVERSITY
NR NO. 051-362

CONTRACT NUMBER Nonr 1677(01)

NO. COPIES

Commanding Officer
Office of Naval Research Branch Office
230 N. Michigan Avenue
Chicago 1, Illinois (1)

Commanding Officer
Office of Naval Research Branch Office
207 West 24th Street
New York 11, New York (1)

Commanding Officer
Office of Naval Research Branch Office
1030 East Green Street
Pasadena 1, California (1).

Commanding Officer
Office of Naval Research Branch Office
Box 39, Navy No. 100, F.P.O.
New York, New York (7)

Director, Naval Research Laboratory
Washington 25, D.C.
Attn: Technical Information Officer (6)
Chemistry Division (2)

Chief of Naval Research
Department of the Navy
Washington 25, D. C.
Attn: Code 425 (2)

DDR&E
Technical Library
Room 3C-128, The Pentagon
Washington 25, D.C. (1)

Department of the Army
Supply & Maintenance Command
Maintenance Readiness Division
Washington 25, D.C.
Attn: Technical Director (1)

NO. COPIES

U.S. Army Natick Laboratories
Clothing & Organic Materials Division
Natick, Massachusetts
Attn: Associate Director (1)

Harry Diamond Laboratories
Washington 25, D.C.
Attn: Library (1)

Office, Chief of Research & Development
Department of the Army
Washington 25, D. C.
Attn: Physical Sciences Division (1)

Chief, Bureau of Ships
Department of the Navy
Washington 25, D. C.
Attn: Code 342A (2)

Technical Library, DLI-3
Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C. (4)

Defense Documentation Center
Cameron Station
Alexandria, Virginia (20)

Commanding Officer
U.S. Army Electronics Research and Development Laboratory
Attn: SELRA/DR
Fort Monmouth, New Jersey 07703 (1)

Naval Radiological Defense Laboratory
San Francisco 24, California
Attn: Technical Library (1)

Naval Ordnance Test Station
China Lake, California
Attn: Head, Chemistry Division (1)

TECHNICAL REPORT DISTRIBUTION LIST

CONTRACTOR BRANDEIS UNIVERSITY

NR NO. 051-362

CONTRACT NUMBER Nonr 1677(01)

NO. COPIES

Commanding Officer
Army Research Office
Box CM, Duke Station
Durham, North Carolina
Attn: CRD-AA-IP (1)

Atomic Energy Commission
Division of Research
Chemistry Programs
Washington 25, D. C. (1)

Atomic Energy Commission
Division of Technical Information
Extension
Post Office Box 62
Oak Ridge, Tennessee (1)

Commanding Officer
U. S. Army Chemical Research and
Development Laboratories
Attn: Librarian
Edgewood Arsenal, Maryland (1)

Commanding Officer
ONR Branch Office
495 Summer Street
Boston 10, Massachusetts (2)

Dr. Virginia Griffing
Department of Chemistry
Catholic University of America
Washington, D. C. (1)

Dr. J. O. Hirschfelder
Naval Research Laboratory
University of Wisconsin
Madison 6, Wisconsin (1)

Dr. R. G. Brewer
Department of Chemistry
University of California
Los Angeles, California (1)

NO. COPIES

Dr. J. T. Vanderslice
Institute of Molecular Physics
University of Maryland
College Park, Maryland (1)

Dr. Harrison Shull
Department of Chemistry
Indiana University
Bloomington, Indiana (1)

Dr. G. B. Kistiakowsky
Department of Chemistry
Harvard University
Cambridge 38, Massachusetts (1)

Dr. D. F. Hornig
Department of Chemistry
Princeton University
Princeton, New Jersey (1)

Dr. H. P. Broida
Department of Physics
University of California
Santa Barbara, California (1)

Dr. S. H. Bauer
Department of Chemistry
Cornell University
Ithaca, New York (1)

Mr. W. M. Lee, Director
Contract Research Department
Pennsalt Chemicals Corporation
900 First Avenue
King of Prussia, Pennsylvania (2)

Dr. E. B. Wilson, Jr.
Department of Chemistry
Harvard University
Cambridge 38, Massachusetts (1)

TECHNICAL REPORT DISTRIBUTION LIST

CONTRACTOR BRANDEIS UNIVERSITY
NR NO. 051-362

CONTRACT NUMBER Nonr 1677 (01)

NO. COPIES

Dr. Henry Eyring
Graduate School
University of Utah
Salt Lake City, Utah (1)

Dr. B. L. Crawford, Jr.
Department of Chemistry
University of Minnesota
Minneapolis, Minnesota (1)

Dr. J. H. Goldstein
Department of Chemistry
Emory University
Emory, Georgia (1)

Dr. J. C. Slater
Department of Physics
Massachusetts Institute of Technology
Cambridge 39, Massachusetts (1)

Dr. R. S. Mulliken
Department of Physics
University of Chicago
Chicago 37, Illinois (1)

Dr. Martin L. Sage
Department of Chemistry
University of Oregon
Eugene, Oregon (1)

Dr. I. Amdur
Department of Chemistry
Massachusetts Institute of Technology
Cambridge 39, Massachusetts (1)

Dr. B. G. Anex
Department of Chemistry
Yale University
New Haven, Connecticut (1)

NO. COPIES

Commanding Officer
ONR Branch Office
Box 39 Navy No. 100 Fleet Post Office
New York, New York (7)
FOR TRANSMITTAL TO:

Dr. N. H. March
Department of Physics
Sheffield University
Sheffield, England

Dr. H. C. Longuet-Higgins
Department of Theoretical Chemistry
Cambridge University
Cambridge, England

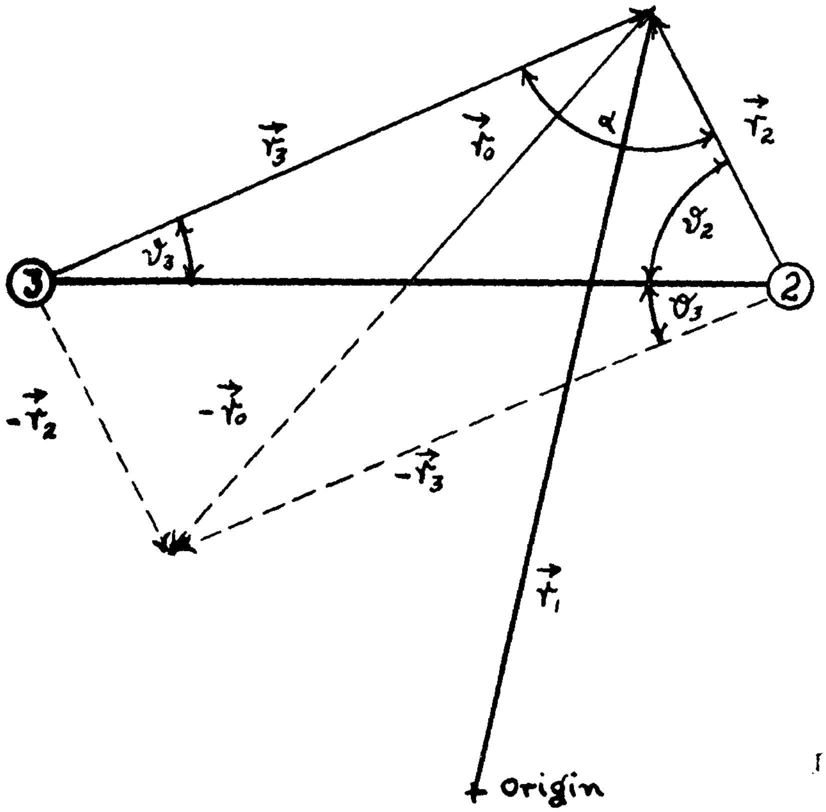
Dr. D. ter Haar
Clarendon Laboratory
Oxford University
Oxford, England

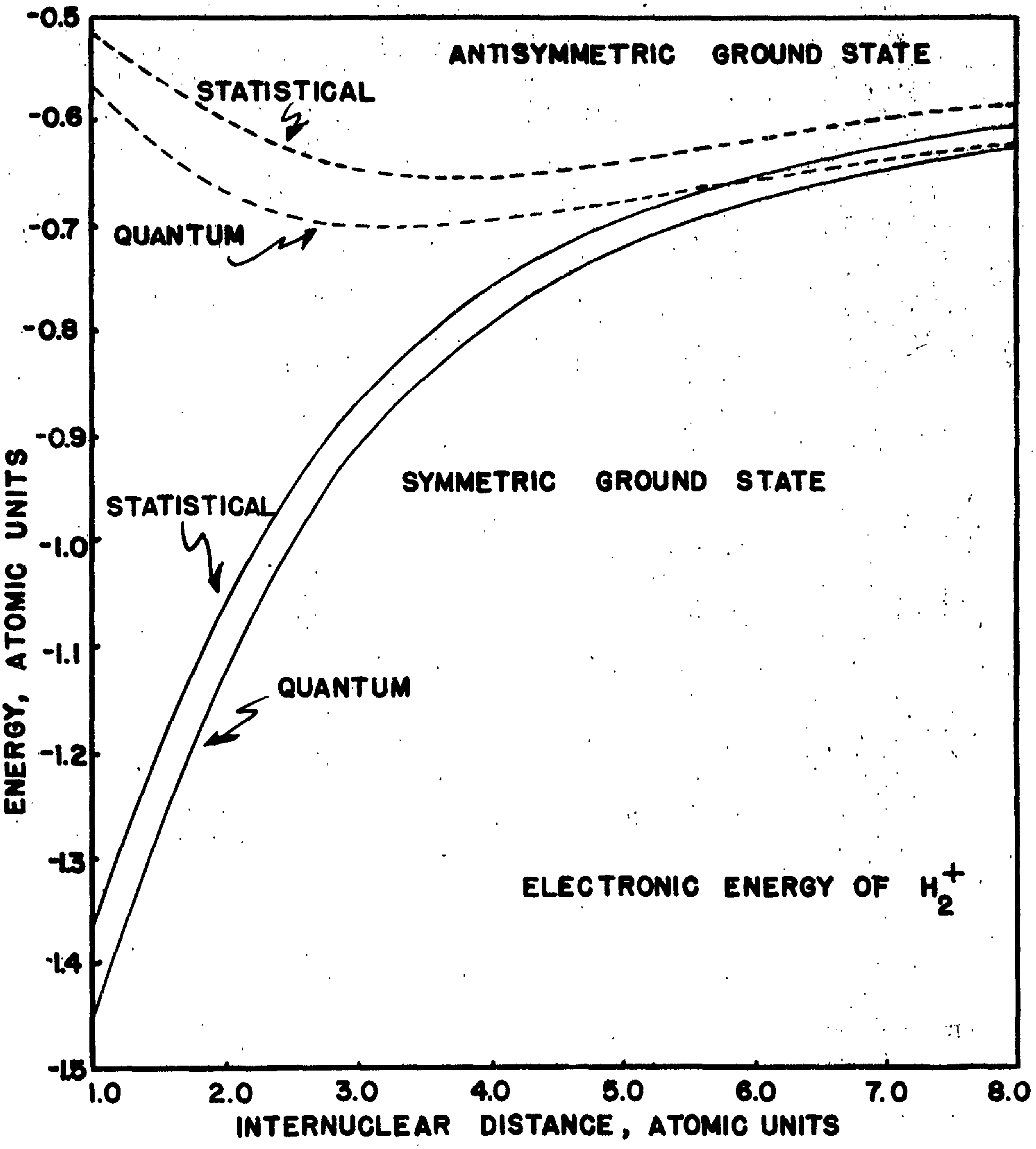
Dr. C. A. Coulson
Mathematical Institute
Oxford University
Oxford, England

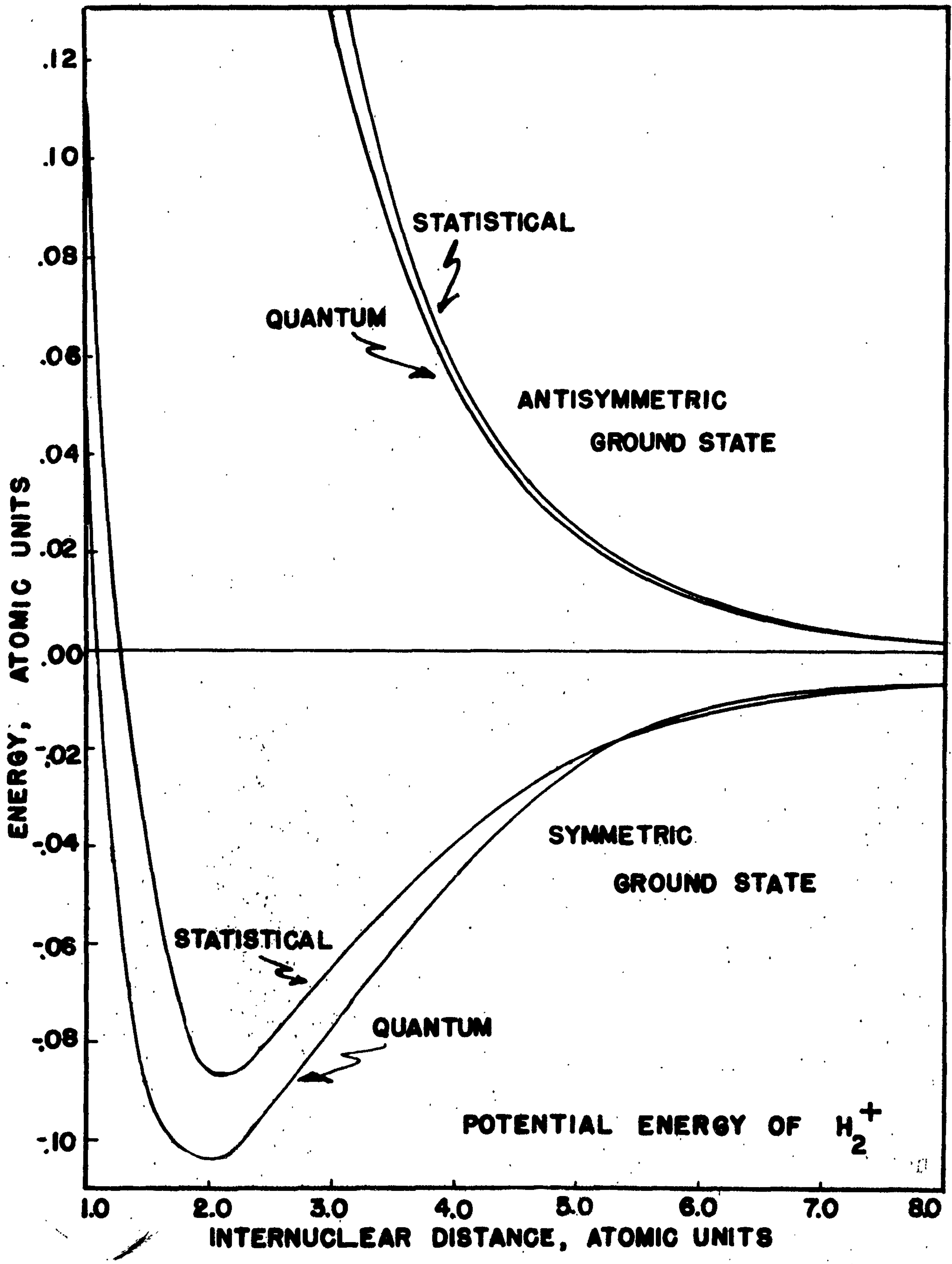
Dr. D. R. Bates
Department of Applied Mathematics
The Queen's University of Belfast
Belfast, N. Ireland

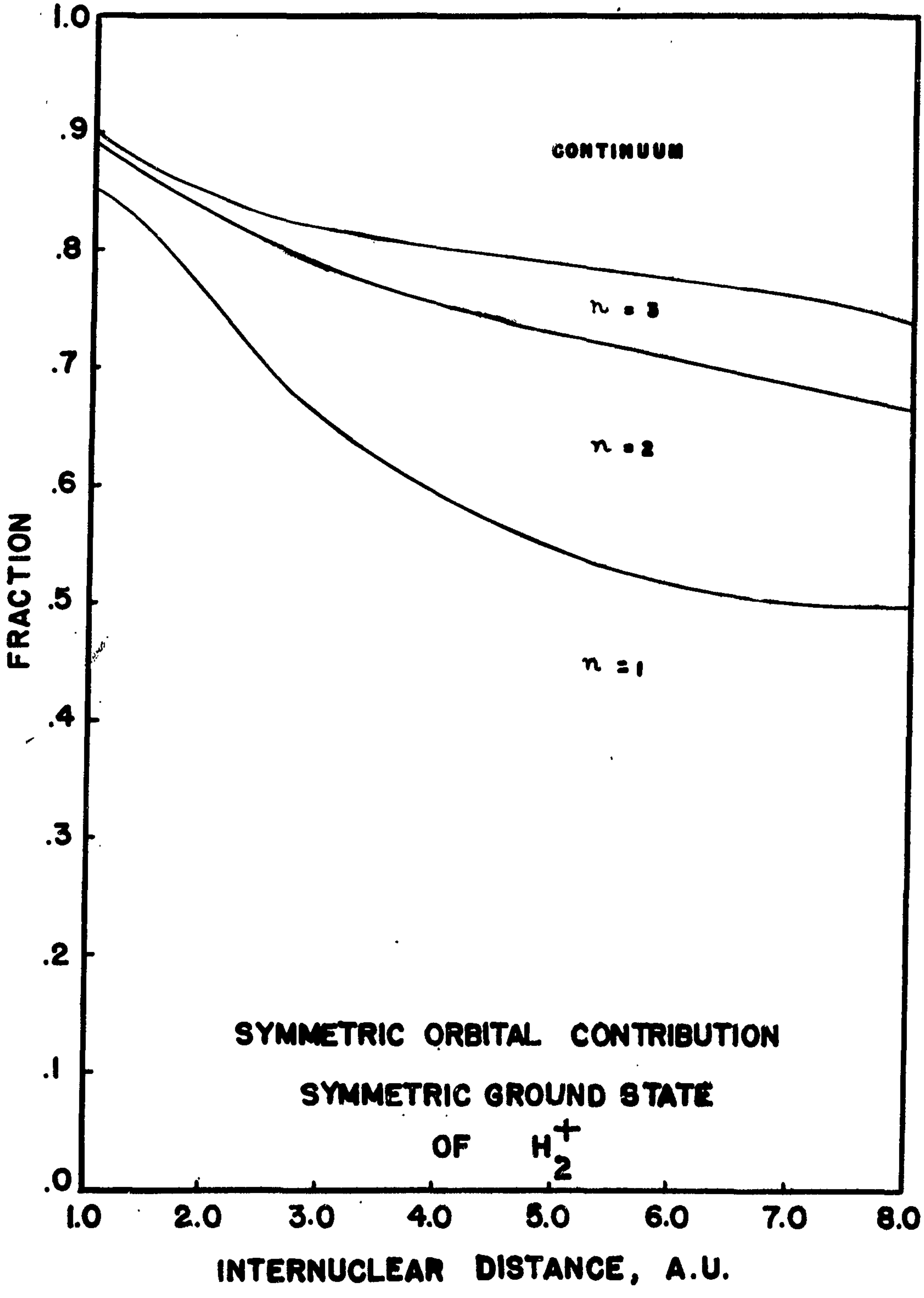
Dr. W. A. Bingel
Max-Planck Institute for Physics
and Astrophysics
Aumeisterstrasse 6, Munich, Germany

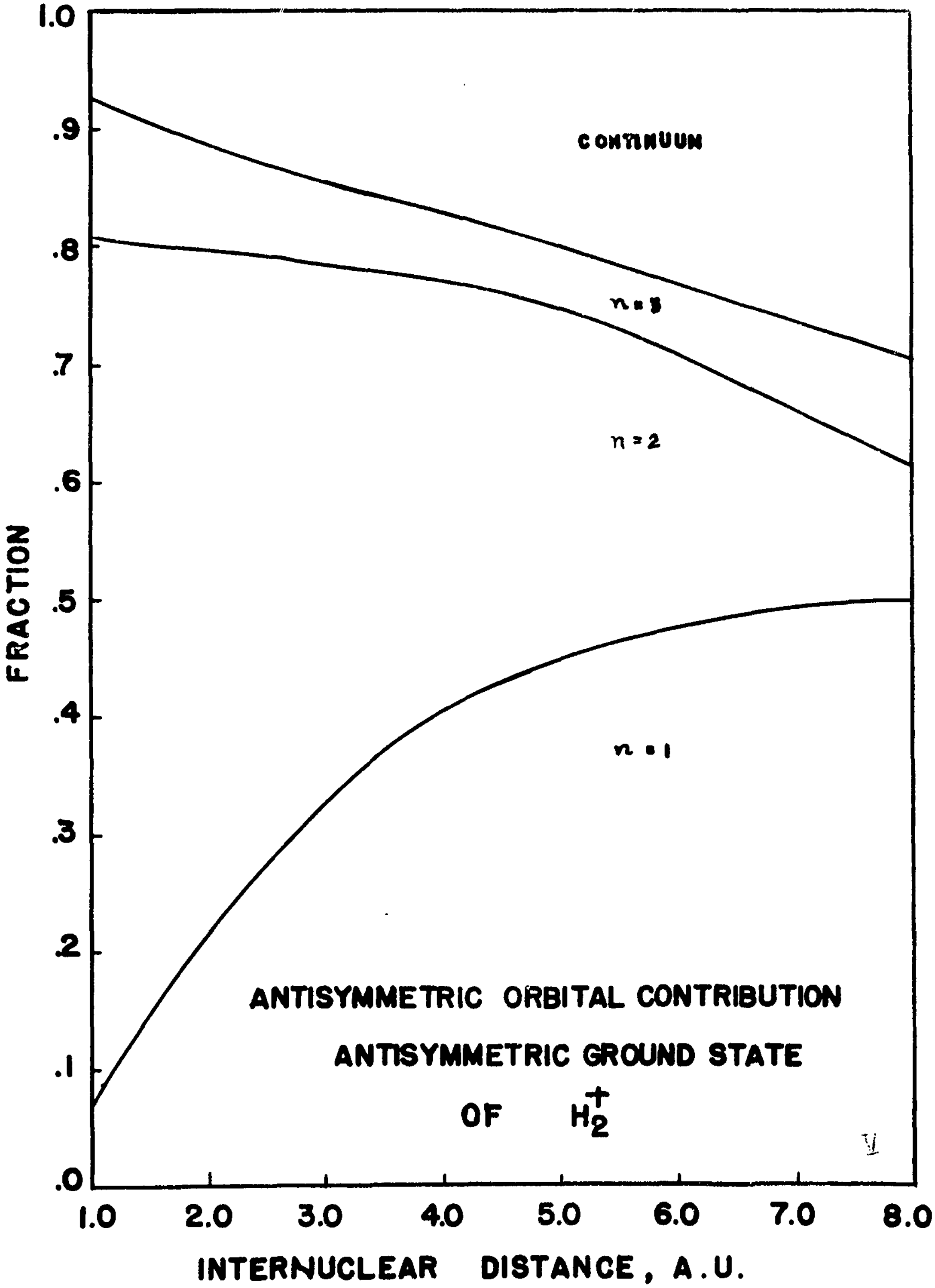
Madame R. Herman
Observatoire de Paris
Section d'Astrophysique
Meudon (S.-et-O.), France


$\vec{r}_3$
$\vec{r}_0$
α
$\vec{r}_2$
ϑ_2
ϑ_3
3
2
ϑ_3
$-\vec{r}_2$
$-\vec{r}_0$
$-\vec{r}_3$
$\vec{r}_1$
Origin


ANTISYMMETRIC GROUND STATE
STATISTICAL
QUANTUM
SYMMETRIC GROUND STATE
STATISTICAL
QUANTUM
ELECTRONIC ENERGY OF H_2^+
ENERGY, ATOMIC UNITS
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
-1.3
-1.4
-1.5
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
INTERNUCLEAR DISTANCE, ATOMIC UNITS


.12
.10
.08
.06
.04
.02
.00
-.02
-.04
-.06
-.08
-.10
ENERGY, ATOMIC UNITS
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
INTERNUCLEAR DISTANCE, ATOMIC UNITS
STATISTICAL
QUANTUM
ANTISYMMETRIC
GROUND STATE
SYMMETRIC
GROUND STATE
STATISTICAL
QUANTUM
POTENTIAL ENERGY OF H_2^+


1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
FRACTION
CONTINUUM
$n = 3$
$n = 2$
$n = 1$
SYMMETRIC ORBITAL CONTRIBUTION
SYMMETRIC GROUND STATE
OF H_2^+
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
INTERNUCLEAR DISTANCE, A.U.



ANTISYMMETRIC ORBITAL CONTRIBUTION

ANTISYMMETRIC GROUND STATE

OF H_2^+