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LCAO MO Theory Illustrated by Its Application to H₂

A few years ago *ab initio* calculations, i.e., ones involving rigorous solution of some approximate formulation of the Schrödinger equation, could be carried out only for the simplest molecules, and even these taxed the capabilities of existing digital computers. Recently, however, this kind of approach has been extended to molecules large enough to be of chemical interest, partly through the development of more powerful computers (e.g., the CDC 6600) and partly through technical improvements in computational procedures.

These calculations are based on the Roothaan method, an approximation to the Hartree-Fock self-consistent field (SCF) treatment in which the individual orbitals ψ_μ are approximated by linear combinations of a set of assumed functions ϕ_i :

$$\psi_\mu = \sum_i a_{\mu i} \phi_i \quad (1)$$

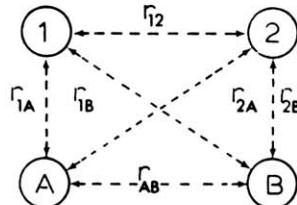
The coefficients $a_{\mu i}$ are found by solving a set of simultaneous algebraic equations (Roothaan's equations), derived by the variation method. The basis set functions ϕ_i are usually a set of AO's of the component atoms (LCAO approximation). By using a sufficiently large basis set, this approach can apparently be made to give results virtually identical with those that would be given by a rigorous Hartree-Fock treatment.

While the results of such calculations are subject to large errors, due to the neglect of electron correlation inherent in the SCF approach, they are already proving of interest in a number of connections and there is also reason to believe that the correlation problem may be solved in due course. In the meantime semiempirical treatments, based on the Roothaan approach, are proving very promising. It therefore seems clear that an understanding of these procedures will soon become essential to anyone concerned with the progress or application of chemical theory.

Several good accounts of the Roothaan method are now available in book form (1); these, however, have usually been formal in nature and have lacked illustration by sufficient specific examples. The purpose of this paper is to remedy this deficiency by a detailed discussion of the hydrogen molecule, using the SCF LCAO MO formalism.

LCAO MO Formalism for H₂

The hydrogen molecule is composed of two protons (A and B) and two electrons (1 and 2); we use the following notation for the interparticle distances. The total wave function Φ of H₂ is an implicit function of the twelve coordinates ($x_A, y_A, z_A; x_B, y_B, z_B; x_1, y_1, z_1; x_2, y_2, z_2$) of the four particles. The total energy is a sum of the kinetic energies of the particles and the



potential energy due to their coulombic interaction; the Hamiltonian operator (\mathbf{H}) is therefore a sum of the corresponding operators, i.e.

$$\mathbf{H} = \mathbf{T}^N + \mathbf{T}^E + \mathbf{G}^{NN} + \mathbf{G}^{NE} + \mathbf{G}^{EE} \quad (2)$$

where the kinetic energy operators for nuclei (\mathbf{T}^N) and electrons (\mathbf{T}^E) are given by

$$\mathbf{T}^N = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2); \quad \mathbf{T}^E = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) \quad (3)$$

M and m being the masses of a proton and an electron, respectively. The internuclear (\mathbf{G}^{NN}), nuclear-electronic (\mathbf{G}^{NE}), and interelectronic (\mathbf{G}^{EE}) potential energies are given by

$$\begin{aligned} \mathbf{G}^{NN} &= \frac{e^2}{r_{AB}} \\ \mathbf{G}^{NE} &= -e^2\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}}\right) \\ \mathbf{G}^{EE} &= \frac{e^2}{r_{12}} \end{aligned} \quad (4)$$

We now assume that the motion of the electrons can be represented by an electronic wavefunction Ψ that depends on the positions of the nuclei but not on their velocities (Born-Oppenheimer approximation); this is equivalent to the assumption that Ψ commutes with \mathbf{T}^N , or that $\mathbf{T}^N\Psi$ is negligible.

In that case

$$\Phi = \Psi \Xi \quad (5)$$

where the electronic wavefunction Ψ is a function of the electronic coordinates, the nuclei being fixed, and the nuclear wave function Ξ is a function of the positions of the nuclei. The total energy E^T for a given fixed position of the nuclei is then

$$E^T = E^E + \frac{e^2}{r_{AB}} \quad (6)$$

where E^E is the total energy of the electrons moving in a fixed potential field due to the fixed nuclei. Thus

$$E^E = \int \Psi \mathbf{H}^E \Psi d\tau \quad (7)$$

where the electronic Hamiltonian \mathbf{H}^E is given by

$$\mathbf{H}^E = \mathbf{T}^E + \mathbf{G}^{NE} + \mathbf{G}^{EE} \quad (8)$$

we can write this in the form

$$\mathbf{H}^E = \mathbf{H}_1^C + \mathbf{H}_2^C + \frac{e^2}{r_{12}} \quad (9)$$

where the *core Hamiltonians* \mathbf{H}_1^C and \mathbf{H}_2^C are given by

$$\mathbf{H}_1^C = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} \quad (10)$$

$$\mathbf{H}_2^C = -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} \quad (11)$$

The core Hamiltonian \mathbf{H}^C represents the sum of the kinetic energy of an electron and its potential energy due to attraction by the nuclei; it is therefore a function of the coordinates of one electron only.

Next we make the *orbital approximation*, which assumes that the motion of each electron i can be represented by an individual one-electron wave function ψ_i . The probability of finding the electron in a given volume element $d\tau_i$ is then $\psi_i^2 d\tau_i$. This approximation thus involves neglect of *electron correlation*, i.e., the tendency of electrons to correlate their motions in such a way as to minimize their mutual repulsions. The one-electron functions must also include a description of the spin of electrons; we write them as spin orbitals $\psi_i \sigma_i$ where ψ_i is a function of the space coordinates (x_i, y_i, z_i) and the spin function σ_i has one of two values (α or β). The electronic wave function for \mathbf{H}_2 is then written as a Slater determinant

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} (\psi_1 \sigma_1)^1 & (\psi_1 \sigma_1)^2 \\ (\psi_2 \sigma_2)^1 & (\psi_2 \sigma_2)^2 \end{vmatrix} \quad (12)$$

The superscript denotes the electron occupying the spin orbital in question.

The final approximation is to write the orbitals ψ_μ as linear combinations of basis set functions ϕ_i (eqn. (1)) which are usually taken to be SCF AO's of the individual atoms. The coefficients $a_{\mu i}$ are normally found by solving a set of simultaneous algebraic equations (Roothaan equations). In the case of \mathbf{H}_2 , the problem is simplified by the presence of a plane of symmetry bisecting the line joining the nuclei; the MO's ψ_1 and ψ_2 must be symmetric, or antisymmetric, for reflection in this plane.

Electronic Wave Functions of \mathbf{H}_2

We will use a *minimum basis set*, i.e., a set of AO's corresponding to the naive conventional picture of inner and valence shell AO's; in \mathbf{H}_2 this corresponds to the 1s AO's of two atoms, given by

$$\begin{aligned} \phi_1 &= \frac{1}{\sqrt{\pi}} e^{-r_A} \\ \phi_2 &= \frac{1}{\sqrt{\pi}} e^{-r_B} \end{aligned} \quad (13)$$

where r_A and r_B are the distances of the electrons from their respective nuclei, measured in *atomic units* (a.u.)

$$1 \text{ a.u.} = a_0 = \frac{\hbar^2}{me^2} = 0.5292 \text{ \AA} \quad (14)$$

where a_0 is the radius of the smallest Bohr orbit for hydrogen. In this system of units, which we will use henceforth, the mass of the electron and the electronic charge are taken to be unity.

From symmetry (see above), the only MO's that can be constructed from ϕ_1 and ϕ_2 are

$$\psi_1 = N_1(\phi_1 + \phi_2) \quad (15)$$

$$\psi_2 = N_2(\phi_1 - \phi_2) \quad (16)$$

The normalization factors N_1 and N_2 are given by

$$N_1 = (\int \psi_1^2 d\tau)^{-1/2} = (2 + 2S_{12})^{-1/2} \quad (17)$$

$$N_2 = (\int \psi_2^2 d\tau)^{-1/2} = (2 - 2S_{12})^{-1/2} \quad (18)$$

where the *overlap integral* S_{12} is given by

$$S_{12} = \int \phi_1 \phi_2 d\tau \quad (19)$$

The unit of energy in a.u. is the *Hartree*

$$1 \text{ a.u. (Hartree)} = \frac{e^2}{a_0} = 27.210 \text{ eV} = 627.71 \text{ kcal/mole} \quad (20)$$

This is twice the ionization potential of a hydrogen atom. In a.u. the core operator \mathbf{H}^C (eqns. (10) and (11)) and the operator \mathbf{G}^{EE} (eqn. (4)) become

$$\mathbf{H}^C = -\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} \quad (21)$$

$$\mathbf{G}^{EE} = \frac{1}{r_{12}} \quad (22)$$

The two electrons in \mathbf{H}_2 can occupy the MO's ψ_1 and ψ_2 in six different ways

$$\begin{array}{ccccccc} \psi_2 & - & \uparrow & \downarrow & \downarrow & \uparrow & \uparrow \\ \psi_1 & \uparrow & \uparrow & \downarrow & \uparrow & \uparrow & - \\ {}^1\chi_1 & {}^3\chi_2 & {}^3\chi_3 & x_4 & x_5 & {}^1\chi_6 \end{array} \quad (23)$$

Each of these *configurations* is represented by a Slater determinant (eqn. (12))

$${}^1\chi_1 = ||\psi_1 \bar{\psi}_1|| = \frac{1}{\sqrt{2}} \left| \begin{matrix} (\psi_1 \alpha)^1 & (\psi_1 \alpha)^2 \\ (\psi_1 \beta)^1 & (\psi_1 \beta)^2 \end{matrix} \right| = \frac{1}{\sqrt{2}} \psi_1^1 \psi_2^2 (\alpha^1 \beta^2 - \alpha^2 \beta^1) \quad (24)$$

$${}^3\chi_2 = ||\psi_1 \psi_2|| = \frac{1}{\sqrt{2}} \left| \begin{matrix} (\psi_1 \alpha)^1 & (\psi_1 \alpha)^2 \\ (\psi_2 \alpha)^1 & (\psi_2 \alpha)^2 \end{matrix} \right| = \frac{1}{\sqrt{2}} \alpha^1 \alpha^2 (\psi_1^1 \psi_2^2 - \psi_2^1 \psi_1^2) \quad (25)$$

$${}^3\chi_3 = ||\bar{\psi}_1 \bar{\psi}_2|| = \frac{1}{\sqrt{2}} \left| \begin{matrix} (\psi_1 \beta)^1 & (\psi_1 \beta)^2 \\ (\psi_2 \beta)^1 & (\psi_2 \beta)^2 \end{matrix} \right| = \frac{1}{\sqrt{2}} \beta^1 \beta^2 (\psi_1^1 \psi_2^2 - \psi_2^1 \psi_1^2) \quad (26)$$

$$x_4 = ||\psi_1 \bar{\psi}_2|| = \frac{1}{\sqrt{2}} \left| \begin{matrix} (\psi_1 \alpha)^1 & (\psi_1 \alpha)^2 \\ (\psi_2 \beta)^1 & (\psi_2 \beta)^2 \end{matrix} \right| \quad (27)$$

$$x_5 = ||\bar{\psi}_1 \psi_2|| = \frac{1}{\sqrt{2}} \left| \begin{matrix} (\psi_1 \beta)^1 & (\psi_1 \beta)^2 \\ (\psi_2 \alpha)^1 & (\psi_2 \alpha)^2 \end{matrix} \right| \quad (28)$$

$${}^1\chi_6 = ||\bar{\psi}_1 \bar{\psi}_2|| = \frac{1}{\sqrt{2}} \left| \begin{matrix} (\psi_2 \alpha)^1 & (\psi_2 \alpha)^2 \\ (\psi_2 \beta)^1 & (\psi_2 \beta)^2 \end{matrix} \right| = \frac{1}{\sqrt{2}} \psi_2^1 \psi_2^2 (\alpha^1 \beta^2 - \alpha^2 \beta^1) \quad (29)$$

The shorthand notation, e.g., $||\psi_1 \bar{\psi}_1||$ is self-explanatory; here the overbar denotes β spin, lack of it α spin.

Four of the determinants (${}^1\chi_1$, ${}^3\chi_2$, ${}^3\chi_3$, ${}^1\chi_6$) can, as indicated, be factored into products of a *space* part and a *spin* part; these are all eigenfunctions of the operators \mathbf{S}_z (representing the component of spin momentum along the z axis) and \mathbf{S}^2 (representing the square of the total spin) and so can serve as representation of \mathbf{H}_2 (for details see reference (1c)). Thus

$$\mathbf{S}^2({}^1\chi_1) = \mathbf{S}^2({}^1\chi_6) = \mathbf{S}_z({}^1\chi_1) = \mathbf{S}_z({}^1\chi_6) = 0 \quad (30)$$

$$\mathbf{S}^2({}^3\chi_2) = {}^3/4\hbar^2({}^3\chi_2)$$

$$\mathbf{S}_z({}^3\chi_2) = \hbar({}^3\chi_2) \quad (31)$$

$$\begin{aligned}\mathbf{S}^2(^3\chi_3) &= \frac{3}{4}\hbar^2(^3\chi_3) \\ \mathbf{S}_z(^3\chi_3) &= -\hbar(^3\chi_3)\end{aligned}\quad (32)$$

Obviously ${}^1\chi_1$ and ${}^1\chi_6$ correspond to singlet states with the electrons paired; ${}^3\chi_2$ and ${}^3\chi_3$ represent substates of a triplet (total spin \hbar) with the spin vector parallel, or antiparallel, to the z axis.

The remaining two determinants (χ_4 and χ_5) are eigenfunctions of \mathbf{S}_z , with eigenvalue zero, but not of \mathbf{S}^2 . However we can construct linear combination of them that are

$${}^3\chi_4 = \frac{1}{\sqrt{2}}(\chi_4 - \chi_5) = \frac{1}{\sqrt{2}}(\psi_1^1\psi_2^2 - \psi_2^1\psi_1^2)(\alpha^1\beta^2 + \alpha^2\beta^1) \quad (33)$$

$${}^1\chi_5 = \frac{1}{\sqrt{2}}(\chi_4 + \chi_5) = \frac{1}{\sqrt{2}}(\psi_1^1\psi_2^2 + \psi_2^1\psi_1^2)(\alpha^1\beta^2 - \alpha^2\beta^1) \quad (34)$$

It is easily seen that

$$\mathbf{S}^2({}^3\chi_4) = \frac{3}{4}\hbar^2({}^3\chi_4) \quad (35)$$

$$\mathbf{S}_z({}^3\chi_4) = 0$$

$$\mathbf{S}^2({}^1\chi_5) = \mathbf{S}_z({}^1\chi_5) = 0 \quad (36)$$

Thus ${}^1\chi_5$ represents a third singlet state, in which the electrons are in different MO's but with paired spins, while ${}^3\chi_4$ represents the third substate of the triplet, with total spin \hbar but with the spin vector perpendicular to the z axis (so that the component of spin along the z axis is zero).

The hydrogen molecule belongs to the $D_{\infty h}$ point group. Since the AO's ϕ_1 and ϕ_2 are totally symmetric for rotation about the internuclear axis, configurations constructed from them must belong to the irreducible representations Σ_g^+ or Σ_u^+ (symmetric for rotation about the axis, symmetric (g) or antisymmetric (u) for reflection in the point bisecting the line joining the nuclei). The configurations X_{1-6} are classified as follows

$$\Sigma_g^+ : {}^1\chi_1, {}^1\chi_6 \quad (37)$$

$$\Sigma_u^+ : {}^3\chi_2, {}^3\chi_3, {}^3\chi_4, {}^1\chi_5 \quad (38)$$

The six configurations are derived from only four spatial wave functions θ_{1-4}

$$\theta_1 = \psi_1^1\psi_1^2 \text{ (ground state singlet, } {}^1\chi_1) \quad (39)$$

$$\theta_2 = \frac{1}{\sqrt{2}}(\psi_1\psi_2^2 - \psi_2\psi_1^2) \text{ (triplet, } {}^3\chi_2, {}^3\chi_3, {}^3\chi_4) \quad (40)$$

$$\theta_3 = \frac{1}{\sqrt{2}}(\psi_1^1\psi_2^2 + \psi_2^1\psi_1^2) \text{ (singly excited singlet, } {}^1\chi_5) \quad (41)$$

$$\theta_4 = \psi_2^1\psi_2^2 \text{ (doubly excited singlet, } {}^1\chi_6) \quad (42)$$

These spatial functions can be denoted graphically by contour maps in two dimensions by taking the distances of the electrons along the AB line as the two coordinates x and y , the contours denoting equal values of the function θ . Figure 1 shows such a plot for θ_1 . Note that there are four points of maximum (and equal) orbital density, corresponding to situations where both electrons are near nucleus A, or both near nucleus B, or one near nucleus A while the other is near nucleus B. A better graphical representation is provided by an analogous plot of θ^2 , this indicating the probability of finding the electrons in various pairs of locations, and an even better one by a three-dimensional plot with θ^2 as the z coordinate. Figure 2 represents such plots for θ_{1-4} ; the peaks correspond to situations

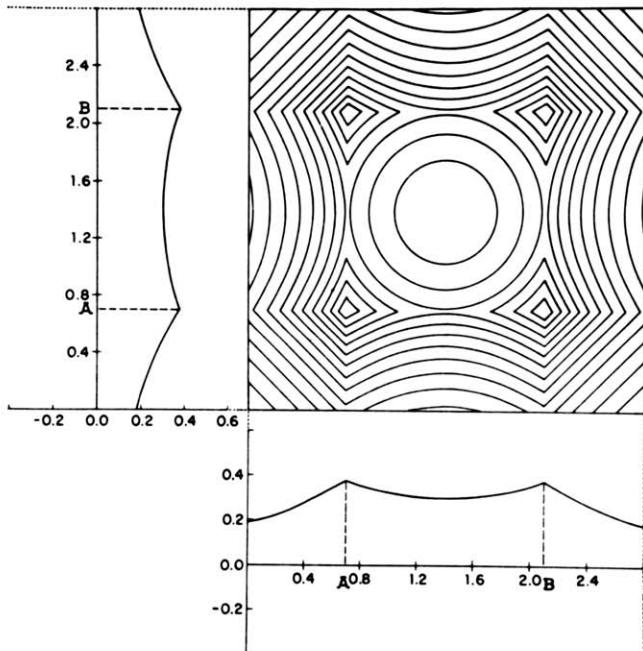


Figure 1. Contour map indicating the variation of θ_1 with distances (x, y) of the two electrons along the line AB.

of high probability. In this and the other three-dimensional plots shown in this paper the spacing of the grid lines is in each case 0.1 a.u.

Various deductions can be made immediately from these diagrams concerning the mode of distribution of the electrons between the two hydrogen atoms. Thus the regions of high orbital density in θ_2 correspond to situations where when electron 1 is near nucleus A, electron 2 is near nucleus B, and conversely, there is very little chance of finding the electrons simultaneously at the same end of the molecule. This of course is a consequence of the Pauli exclusion principle; electrons of the same spin cannot occupy the same point in space, so the probability of finding them close together is also reduced. The singly excited state of θ_3 corresponds on the other hand to a "hybrid" of "ionic" structures, $H^+H^- \leftrightarrow H^-H^+$; here the electrons are most likely to be found near the same nucleus. Finally, in the ground state θ_1 , or in the doubly excited state θ_4 , the electrons are as likely to be found near different nuclei as near the same nucleus; this of course follows because in our simple orbital approximation no account is taken of the tendency of electrons to keep apart, due to their mutual electrostatic repulsion; the weighting of "covalent" structures in θ_2 , or "ionic" structures in θ_3 is due to "exchange" correlation, not to electrostatic repulsions.

Energy and Bond Length

The ground state of H_2 corresponds to the configuration ${}^1\chi_1$ (eqn. (24)). The corresponding electronic energy E_1^E is given (eqns. (7)-(11), (21), and (22))

$$E_1^E = \iiint \frac{1}{\sqrt{2}} \psi_1^1\psi_1^2(\alpha^1\beta^2 - \alpha^2\beta^1) (\mathbf{H}_1^C + \mathbf{H}_2^C + \frac{1}{r_{12}}) \times \frac{1}{\sqrt{2}} \psi_1^1\psi_1^2(\alpha^1\beta^2 - \alpha^2\beta^1) d\tau_1 d\tau_2 d\sigma_1 d\sigma_2 \quad (43)$$

where the integrations are over the space and spin parts of each spin orbital, $\psi_1\alpha$ and $\psi_1\beta$. Since the wave func-

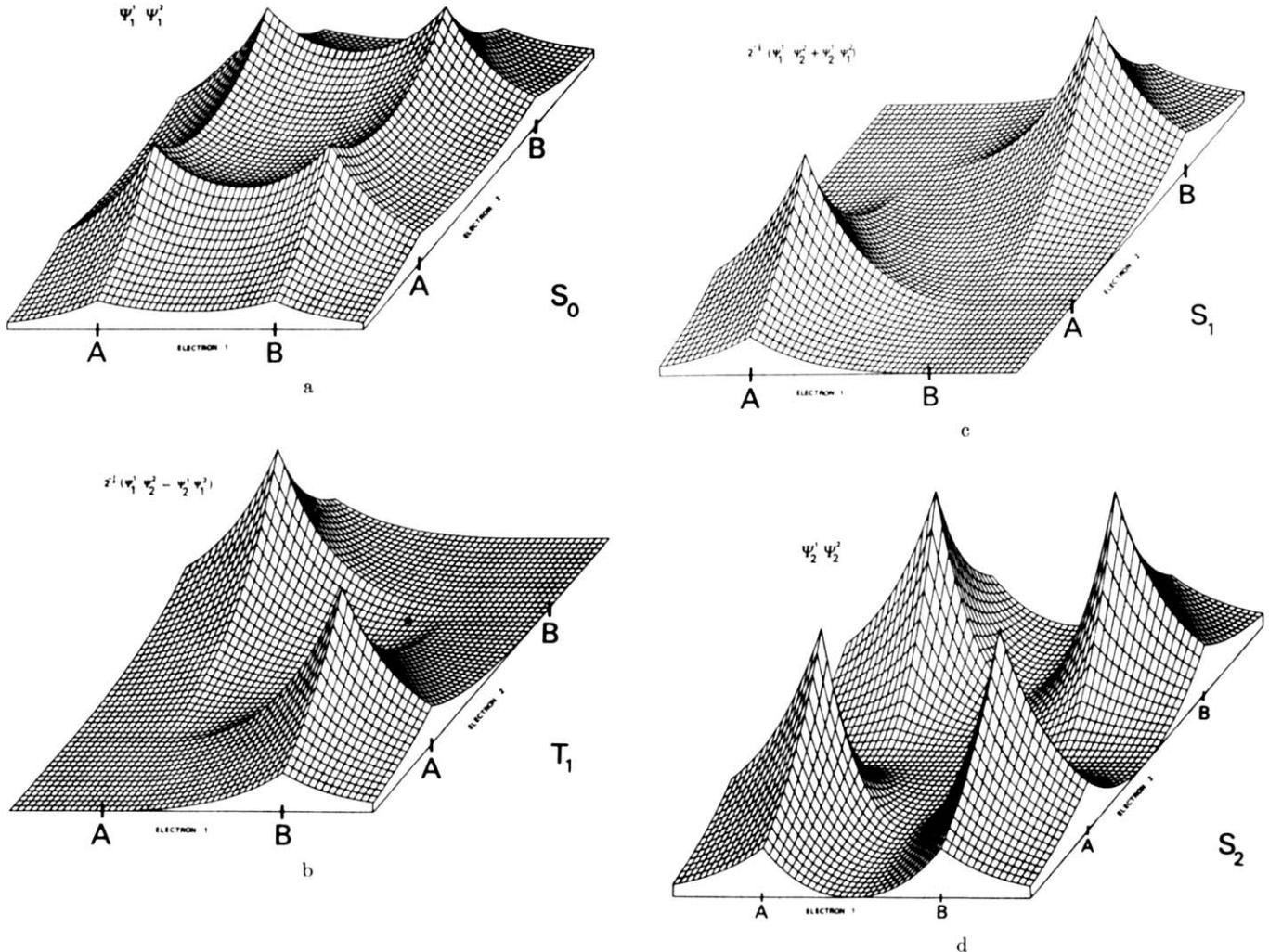


Figure 2. Three dimensional plots of θ^2 versus x and y for a , θ_1 ; b , θ_2 ; c , θ_3 ; d , θ_4 .

tion ${}^1\chi_1$ factors into a product of a space part and a spin part, and since the electronic operator contains no spin terms, the integral can also be factored

$$E_1^E = \frac{1}{2} \iint \psi_1^1 \psi_1^2 \left(\mathbf{H}_1^C + \mathbf{H}_2^C + \frac{1}{r_{12}} \right) \times \iint (\alpha^1 \beta^2 - \alpha^2 \beta^1)^2 d\sigma_1 d\sigma_2 \quad (44)$$

The integral over the spin functions on expansion gives

$$\int (\alpha^1)^2 d\sigma_1 \int (\beta^2)^2 d\sigma_2 - 2 \int (\alpha^1 \beta^1) d\sigma_1 \int (\alpha^2 \beta^2) d\sigma_2 + \int (\beta^1)^2 d\sigma_1 \int (\alpha^2)^2 d\sigma_2$$

Since the spin functions are orthogonal, the middle term vanishes; if α and β are normalized, the other terms are each equal to unity. Hence

$$E_1^E = \iint \psi_1^1 \psi_1^2 \left(\mathbf{H}_1^C + \mathbf{H}_2^C + \frac{1}{r_{12}} \right) \psi_1^1 \psi_1^2 d\tau_1 d\tau_2 \quad (45)$$

Since \mathbf{H}_1^C is a function of the coordinates of electron 1 only, and \mathbf{H}_2^C of electron 2 only

$$E_1^E = \int \psi_1^1 \mathbf{H}_1^C \psi_1^1 d\tau_1 \int (\psi_1^2)^2 d\tau_2 + \int (\psi_1^1)^2 d\tau_1 \int \psi_1^2 \mathbf{H}_2^C \psi_1^2 d\tau_1 + J_{11} \quad (46)$$

$$= 2E_1^C + J_{11} \quad (47)$$

where the coulomb integral J_{11} is given by

$$J_{11} = \iint \psi_1^1 \psi_1^2 \frac{1}{r_{12}} \psi_1^1 \psi_1^2 d\tau_1 d\tau_2 \quad (48)$$

and where E_1^C is the core energy of an electron occupying the MO ψ_1 .

Substituting for ψ_1 from eqns. (15) and (16)

$$\begin{aligned} \mathbf{H}_1^C &= \int \frac{\phi_1 + \phi_2}{\sqrt{2 + 2S_{12}}} (\mathbf{H}^C) \frac{\phi_1 + \phi_2}{\sqrt{2 + 2S_{12}}} d\tau \\ &= \frac{1}{2 + 2S_{12}} [H_{11}^C + H_{22}^C + H_{12}^C + H_{21}^C] \end{aligned} \quad (49)$$

Where

$$\begin{aligned} H_{11}^C &= \int \phi_1 \mathbf{H}^C \phi_1 d\tau \\ H_{22}^C &= \int \phi_2 \mathbf{H}^C \phi_2 d\tau \\ H_{12}^C &= \int \phi_1 \mathbf{H}^C \phi_2 d\tau \\ H_{21}^C &= \int \phi_2 \mathbf{H}^C \phi_1 d\tau \end{aligned} \quad (50)$$

from symmetry

$$\begin{aligned} H_{11}^C &= H_{22}^C \\ H_{12}^C &= H_{21}^C \end{aligned} \quad (51)$$

Substituting for \mathbf{H}^C from eqn. (21)

$$H_{11}^C = \int \phi_1 \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} \right) \phi_1 d\tau \quad (52)$$

$$\begin{aligned}
H_{11}^C &= \int \phi_1(-1/2\nabla_1^2)\phi_1 d\tau \text{ (one-center kinetic energy integral, } T_{11}) \\
&+ \int \phi_1\left(-\frac{1}{r_{1A}}\right)\phi_1 d\tau \text{ (one-center nuclear attraction integral, } V_{11}^A) \\
&+ \int \phi_1\left(-\frac{1}{r_{1B}}\right)\phi_1 d\tau \text{ (two-center nuclear attraction integral, } V_{11}^B)
\end{aligned} \quad (53)$$

Likewise

$$\begin{aligned}
H_{12}^C &= \int \phi_1\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}}\right)\phi_2 d\tau \\
&= \int \phi_1(-1/2\nabla_1^2)\phi_2 d\tau \text{ (two-center kinetic energy integral, } T_{12}) \\
&+ \int \phi_1\left(-\frac{1}{r_{1A}}\right)\phi_2 d\tau \\
&+ \int \phi_1\left(-\frac{1}{r_{1B}}\right)\phi_2 d\tau \text{ (two-center nuclear attraction integrals } V_{12}^A, V_{12}^B)
\end{aligned} \quad (54)$$

All these integrals can be expressed in analytical form, using 1s AO's for ϕ_1 and ϕ_2 (eqn. (13))

$$T_{11} = 1/2 \quad (55)$$

$$T_{12} = -1/[S_{12} - 2(1 + r_{AB})e^{-r_{AB}}] \quad (56)$$

$$V_{11}^A = -1 \quad (57)$$

$$V_{11}^B = -\frac{1}{r_{AB}} + \left(1 + \frac{1}{r_{AB}}\right)e^{-2r_{AB}} \quad (58)$$

$$V_{12}^A = V_{12}^B = -(1 + r_{AB})e^{-r_{AB}} \quad (59)$$

$$S_{12} = (1 + r_{AB} + 1/3r_{AB}^2)e^{-r_{AB}} \quad (60)$$

Expanding J_{11} likewise in terms of AO's

$$\begin{aligned}
J_{11} &= \iint \frac{(\phi_1^1 + \phi_2^1)^2(\phi_1^2 + \phi_2^2)^2}{(2 + 2S_{12})^2} \left(\frac{1}{r_{12}}\right) d\tau_1 d\tau_2 \\
&= \frac{1}{4(1 + S_{12})^2} [(11,11) + (22,22) + (11,22) + \\
&\quad (22,11) + (11,12) + (11,21) + (22,12) + \\
&\quad (22,21) + (12,11) + (21,11) + (12,22) + \\
&\quad (21,22) + (12,12) + (21,12) + (12,21) + (21,21)]
\end{aligned} \quad (61)$$

where

$$(ij,kl) = \iint \phi_i^1 \phi_j^1 \left(\frac{1}{r_{12}}\right) \phi_k^2 \phi_l^2 d\tau_1 d\tau_2 \quad (62)$$

From the definition of the integrals

$$\begin{aligned}
(11,22) &= (22,11) \\
(11,12) &= (11,21) = (12,11) = (21,11) \\
(22,12) &= (22,21) = (21,22) = (12,22)
\end{aligned} \quad (63)$$

Also from symmetry

$$\begin{aligned}
(11,11) &= (22,22) \\
(11,12) &= (22,21)
\end{aligned} \quad (64)$$

From eqns. (61)–(64)

$$\begin{aligned}
J_{11} &= \frac{1}{(1 + S_{12})^2} [1/2(11,11) + 1/2(11,22) + \\
&\quad (12,12) + 2(11,12)]
\end{aligned} \quad (65)$$

Electron repulsion integrals (ij,kl) usually have to be evaluated by numerical integration; however in this simple case they can be expressed analytically

$$(11,11) = 5/8 \quad (66)$$

$$(11,22) = \frac{1}{r_{AB}} \left[1 - \left(1 + \frac{11}{8} r_{AB} + \frac{3}{4} r_{AB}^2 + \frac{1}{6} r_{AB}^3 \right) e^{-2r_{AB}} \right] \quad (67)$$

$$(11,12) = [r_{AB} + 1/8 + 5/16r_{AB} - (1/8 + 5/16r_{AB})e^{-3r_{AB}}] e^{-r_{AB}} \quad (68)$$

$$\begin{aligned}
(12,12) &= \frac{1}{5} \left[\left(\frac{25}{8} - \frac{23}{4} r_{AB} - 3r_{AB}^2 - \frac{1}{3} r_{AB}^3 \right) e^{-2r_{AB}} \right. \\
&\quad \left. + \frac{6}{r_{AB}} \{ (0.57722 + \ln r_{AB}) S_{12}^2 + A^2 f(-4r_{AB}) \right. \\
&\quad \left. - 2AS_{12}f(-2r_{AB}) \} \right]
\end{aligned} \quad (69)$$

In the last expression, 0.57722 is the approximate value of an integral while

$$A = (1 - r_{AB} + 1/3r_{AB}^2)e^{r_{AB}} \quad (70)$$

$$f(a) = \int_a^\infty \frac{1}{x} e^{-x} dx \quad (71)$$

The total electronic energies for the other configurations (eqns. (25)–(34)) can be found in a precisely similar way; the derivations are left to the reader

Triplet state, ${}^3\chi_2, {}^3\chi_3, {}^3\chi_4$

$$E^E = \frac{H_{11}^C + H_{12}^C}{1 + S_{12}} + \frac{H_{11}^C - H_{12}^C}{1 - S_{12}} + J_{12} - K_{12} \quad (72)$$

where

$$\begin{aligned}
J_{12} &= \iint (\psi_1^1)^2 (\psi_2^2)^2 \frac{1}{r_{12}} d\tau_1 d\tau_2 \\
&= \frac{1}{1 - S_{12}^2} [1/2(11,11) + 1/2(11,22) - (12,12)]
\end{aligned} \quad (73)$$

and the *exchange integral* K_{12} is given by

$$\begin{aligned}
K_{12} &= \iint (\psi_1^1 \psi_2^1)(\psi_1^2 \psi_2^2) \frac{1}{r_{12}} d\tau_1 d\tau_2 \\
&= \frac{1}{2(1 - S_{12}^2)} [(11,11) - (11,22)]
\end{aligned} \quad (74)$$

Singly excited singlet state, ${}^1\chi_5$

$$E^E = \frac{H_{11}^C + H_{12}^C}{1 + S_{12}} + \frac{H_{11}^C - H_{12}^C}{1 - S_{12}} + J_{12} + K_{12} \quad (75)$$

Doubly excited state, ${}^1\chi_6$

$$E^E = \frac{2(H_{11}^C - H_{12}^C)}{1 - S_{12}} + J_{22} \quad (76)$$

where

$$\begin{aligned}
J_{22} &= \iint (\psi_2^1)^2 (\psi_2^2)^2 \frac{1}{r_{12}} d\tau_1 d\tau_2 \\
&= \frac{1}{(1 - S_{12})^2} [1/2(11,11) + 1/2(11,22) + (12,12) - 2(11,12)]
\end{aligned} \quad (77)$$

The total energy (E^T) of each of these states is given (eqn. (6)) by adding the internuclear repulsion to the total electronic energy; in a.u.

$$E^T = E^E + \frac{1}{r_{AB}} \quad (78)$$

Table 1 gives values for the basic integrals for various values of r_{AB} , and Table 2 values for the quantities $E_1^C, E_2^C, J_{11}, J_{12}, K_{12}$, and $1/r_{AB}$. Table 3 shows corresponding values of the total energy for the various

Table 1. Basic Integrals for H₂ for Various Internuclear Distances^a

r _{AB}	S ₁₂	T ₁₂	-V _{11B}	-V _{12A}	(11,22)	(11,12)	(12,12)
0	1.000000	0.500000	1.000000	1.000000	0.625000	0.625000	0.625000
1	0.858385	0.306567	0.729329	0.735759	0.554521	0.507045	0.436651
1.5	0.725173	0.195239	0.583688	0.557826	0.490338	0.405369	0.296835
2.0	0.586453	0.112779	0.472527	0.406006	0.425974	0.308036	0.184156
2.5	0.458308	0.058144	0.390567	0.287298	0.368388	0.225595	0.106622
3.0	0.348509	0.024894	0.330028	0.199148	0.319804	0.160742	0.058508
3.5	0.259194	0.006289	0.284542	0.135888	0.279944	0.112156	0.030766
5.0	0.096577	-0.007848	0.199945	0.040428	0.199569	0.034953	0.003717
7.0	0.022189	-0.003805	0.142856	0.007295	0.142845	0.006538	0.000168

^a All values in a.u.

Table 2. Molecular Integrals for H₂ for Various Internuclear Distances^a

r _{AB}	E _{1C}	E _{2C}	J ₁₁	J ₁₂	J ₂₂	K ₁₂	r _{AB} ⁻¹
1.0	-1.288366	-0.454599	0.590834	0.581778	0.614391	0.133901	1
1.5	-1.161681	-0.594101	0.559515	0.550139	0.579453	0.142011	0.666667
2.0	-1.053772	-0.660854	0.526739	0.520284	0.547131	0.151680	0.5
2.5	-0.964830	-0.690642	0.495850	0.493791	0.518440	0.162422	0.4
3.0	-0.892415	-0.700894	0.468741	0.471115	0.493417	0.173695	0.333333
3.5	-0.833890	-0.700663	0.446243	0.452077	0.471809	0.184953	0.285714
5.0	-0.719192	-0.676583	0.404087	0.412414	0.424047	0.214718	0.2
7.0	-0.646897	-0.638632	0.380111	0.383944	0.388044	0.241196	0.142857

^a All values in a.u.

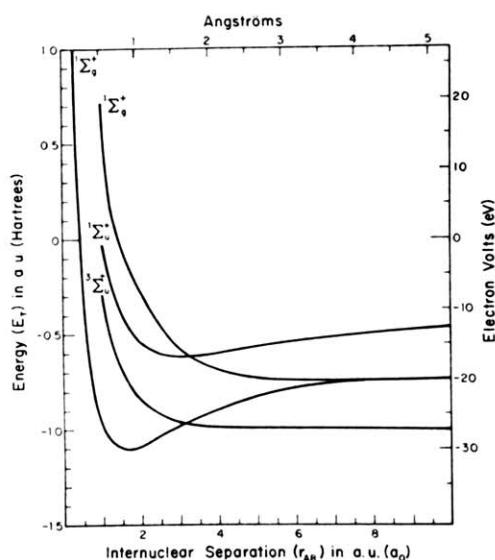


Figure 3. Plot of total energy (E^T) of H₂ versus internuclear distance (r_{AB}) for the ground state (1 Σ_g^+), triplet state (3 Σ_u^+), singly excited singlet state (1 Σ_u^+), and doubly excited state (1 Σ_g^+).

states, while Figure 3 shows a plot of the total energies versus the internuclear distance.

It will be seen that $^1\chi_1$ does correspond, as we have assumed, to the ground state of H₂; the minimum in the curve should correspond to the equilibrium internuclear distance and the depth of the line below the limit (H_A + H_B) to the bond energy. The values estimated in this way (0.84 Å, 2.65 eV) are in fair agreement with experiment (0.74 Å, 4.74 eV).

The curve for the singly excited state (1 Σ_u^+) also has a minimum, implying that it should be a bound state; H₂ has an absorption band at 109 nm corresponding to the transition (1 Σ_u^+ \rightarrow 1 Σ_g^+). The observed excitation energy (11.4 eV) for the zero-zero transition is in good agreement with that estimated from Figure 1 (13.2 eV). The other two states have no minima and so correspond to dissociation into hydrogen atoms.

It will be noticed that the curve for the ground state does not converge to the correct limit (H_A + H_B) for large r_{AB}; this is because we have represented the system

Table 3. Total Energies of Various States of H₂ at Various Internuclear Distances^a

r _{AB}	1 Σ_g^+	1 Σ_u^+	3 Σ_u^+	1 Σ_g^+
1.0	-0.9859	-0.0273	-0.2951	0.7052
1.5	-1.0972	-0.3970	-0.6810	0.0579
2.0	-1.0808	-0.5427	-0.8460	-0.2746
2.5	-1.0338	-0.5993	-0.9241	-0.4628
3.0	-0.9828	-0.6152	-0.9626	-0.5750
3.5	-0.9358	-0.6118	-0.9817	-0.6438
5.0	-0.8343	-0.5686	-0.9981	-0.7291
7.0	-0.7708	-0.5175	-0.9999	-0.7464

^a All values in a.u.

throughout by the single Slater determinant $^1\chi_1$. Expansion of the space part $\psi_1^1\psi_1^2$ of $^1\chi_1$ (eqn. (24) gives)

$$\begin{aligned} \psi_1^1\psi_1^2 &= \frac{1}{2}(\phi_1^1 + \phi_2^1)(\phi_1^2 + \phi_2^2) \\ &= \frac{1}{2}(\phi_1^1\phi_1^2 + \phi_2^1\phi_2^2 + \phi_1^1\phi_2^2 + \phi_2^1\phi_1^2) \end{aligned} \quad (79)$$

Thus the wave function $\psi_1^1\psi_1^2$ can be partitioned into four equal parts, corresponding to situations where both electrons occupy the AO ϕ_1 (i.e., $\phi_1^1\phi_1^2$), or both ϕ_2 (i.e., $\phi_2^1\phi_2^2$), or where they occupy different AO's ($\phi_1^1\phi_2^2$ or $\phi_2^1\phi_1^2$). This can be seen very clearly from the plots of θ_1 and θ_1^2 in Figures 1 and 2a; the general form of these plots is independent of r_{AB}. Obviously this cannot be a satisfactory representation because dissociation of H₂ must give either (H_A + H_B) or (H⁺ + H⁻), not a "hybrid" of the two. Note that dissociation of the triplet 3 Σ_u^+ , and of the singly excited singlet 1 Σ_u^+ , is correctly predicted to give a "pure" state (H_A + H_B) or (H⁺ + H⁻), while dissociation of the doubly excited state again gives a hybrid. The reason for this difference will appear presently.

The total energy (E^T) of H₂ can be written (eqns. (45)–(71)) in the form

$$E^T = \frac{T_{11} + T_{22} + V_{11A} + V_{22B}}{1 + S_{12}} + \frac{\left[\frac{V_{11B} + V_{22A}}{1 + S_{12}} + J_{11} + \frac{1}{r_{AB}} \right]}{A} + \frac{\frac{2(V_{12A} + V_{12B} + T_{12})}{1 + S_{12}}}{B} + \frac{C}{C} \quad (80)$$

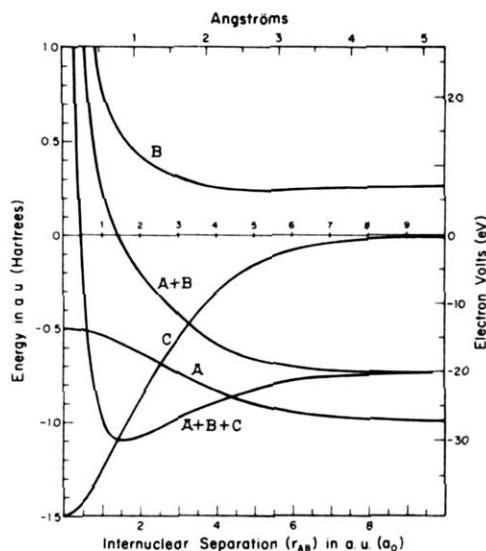


Figure 4. Plot of quantities in eqn. (80) versus r_{AB} .

The numerator of the first term (A) represents the (constant) energy of two hydrogen atoms; A increases with decreasing r_{AB} due to crowding of the electrons. The second term (B) in eqn. (80) represents the mutual interaction of the two atoms, due to classical electrostatic forces; this term does show an energy minimum with decreasing r_{AB} . Figure 4 shows a plot of A , B , and $(A + B)$ versus r_{AB} ; the composite curve shows no minimum whatsoever. These terms collectively represent the situation that would hold if the electron distribution $(\psi_1)^2$ of the occupied MO in H_2 were a simple superposition $[(\phi_1)^2 + (\phi_2)^2]$ of those for the component AO's. In fact there is an additional term $2\phi_1\phi_2$, corresponding to the interference of electron waves when the atoms approach; the last term (C) in eqn. (80) represents the corresponding correction to the "classical" energy. The plots of C , and $(A + B + C)$, in Figure 4 show that this nonclassical term accounts for the whole of the binding in H_2 . This is a special case of a general result; chemical binding, in an orbital description, arises mainly from terms involving one-electron resonance integrals.

Configuration Interaction

Allowance for electron correlation can be introduced into the SCF treatment of a molecule by writing the wave function Θ as a linear combination of configurations χ_m derived by distributing the electrons various possible ways among the various MO's

$$\Theta = \sum_m A_m \chi_m \quad (81)$$

If the molecule has symmetry, the wave function must have corresponding symmetry; Θ must then be written as a combination of configurations χ_m that behave in the same way under the symmetry operation in question. In the case of H_2 , only configurations which are either all gerade (g), or all ungerade (u), can mix, and they must also have similar multiplicities in order that Θ can represent a real spin state. Of our four configurations for H_2 , ${}^1\chi_1$ and ${}^1\chi_6$ can mix, being both ${}^1\Sigma_g$; the other two configurations are both ${}^3\Sigma_u$, and they cannot mix with one another since they are of different multiplicity.

This configuration interaction between ${}^1\chi_1$ and ${}^1\chi_6$

leads to two states whose energies (E_m) are the roots of the secular equation

$$\begin{vmatrix} H_{11} - E & H_{16} \\ H_{16} & H_{66} - E \end{vmatrix} = 0 \quad (82)$$

The corresponding coefficients A_{mi} (eqn. (81)) are given by

$$(H_{11} - E_m)A_{m1} + H_{16}A_{m6} = 0 \quad (83)$$

Here

$$H_{11} = \int ({}^1\chi_1) \mathbf{H} ({}^1\chi_1) d\tau = E_1^E \quad (84)$$

where E_1^E is the total electronic energy of the configuration ${}^1\chi_1$; likewise

$$H_{66} = E_6^E \quad (85)$$

Also

$$\begin{aligned} H_{16} &= \int ({}^1\chi_1) \mathbf{H} ({}^1\chi_6) d\tau \\ &= \iint (\psi_1^1 \psi_1^2) \left(\mathbf{H}_1^C + \mathbf{H}_2^C + \frac{1}{r_{12}} \right) (\psi_2^1 \psi_2^2) d\tau_1 d\tau_2 \\ &= \int \psi_1^1 \mathbf{H}_1^C \psi_2^1 d\tau \int \psi_1^2 \psi_2^2 d\tau_2 + \int \psi_1^1 \mathbf{H}_2^C \psi_2^2 d\tau_2 \int \psi_1^1 \psi_2^1 d\tau_1 \\ &\quad + \iint (\psi_1^1 \psi_2^1) (\psi_1^2 \psi_2^2) \frac{1}{r_{12}} d\tau_1 d\tau_2 \\ &= K_{12} \end{aligned} \quad (86)$$

The first two integrals vanish because ψ_1 and ψ_2 are orthogonal while the third is equal to K_{12} (eqn. (74)). Using the expressions for E_1^E and E_6^E above, and the integrals from Tables 1 and 2, one can calculate the energies of the two states (Θ_a and Θ_b) resulting from mixing of ${}^1\chi_1$ and ${}^1\chi_6$ and also the coefficients A_1 and A_6 (eqn. (83)). Figure 5 shows plots of the total energies of Θ_a , Θ_b , ${}^1\chi_5$, and the triplet state versus r_{AB} . Note that the g state χ_a now correctly dissociates into $(H \cdot + \cdot H)$, while the doubly excited state, like the singly excited one, now dissociates into $(H^+ + H^-)$. The minimum in the ground state case leads to estimates of 0.88 Å and 3.23 eV for the equilibrium bond length and bond energy. The calculated excitation energy remains almost unchanged (13.6 eV).

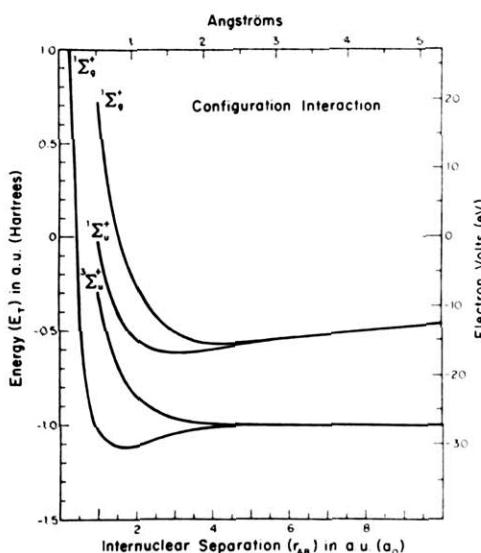


Figure 5. Plots of energies of states, with inclusions of configuration interaction, versus r_{AB} .

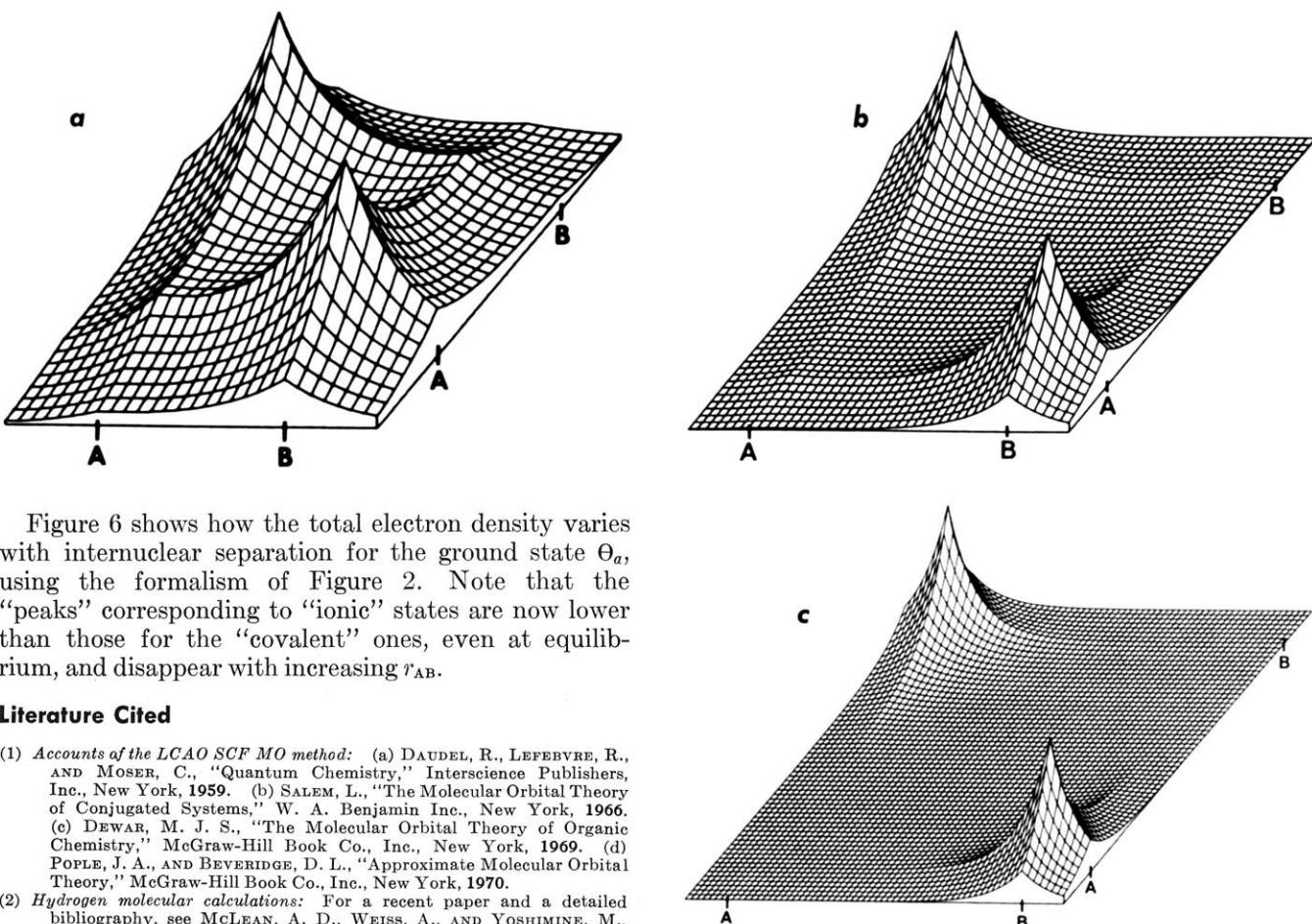


Figure 6 shows how the total electron density varies with internuclear separation for the ground state Θ_a , using the formalism of Figure 2. Note that the "peaks" corresponding to "ionic" states are now lower than those for the "covalent" ones, even at equilibrium, and disappear with increasing r_{AB} .

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Figure 6. Electron density functions for the ground state Θ_a : a, for $r_{AB} = 1.4$ a.u.; b, for $r_{AB} = 3$ a.u.; c, for $r_{AB} = 5$ a.u.