SELF-CONSISTENT FIELD FOR MOLECULAR HYDROGEN

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Introduction

The methods of the self-consistent field have been applied with considerable success to study the wave-functions of atoms containing many electrons. Both the original Hartree approximation(7), in which no account is taken of exchange, and the Fock approximation (6), in which this is considered, have been used. (A good discussion of the methods and principles of the self-consistent field approximation may be found in two small monographs by Brillouin (1).) There appears, however, to have been no application of either method to molecules. In part this is explained by the added complication which arises when we have to deal with more than one centre of force. In atomic problems the symmetry is such that one part of the wave-function—the part depending on the angles θ and ϕ—separates out from the rest, which becomes merely a function of the radial distance, so that the problem is that of determining a suitable "central field", in which there is only one variable r present. With molecules, even with the simplest diatomic molecules, this is no longer true; only that part of the wave-function which gives the dependence upon angle round the axis of symmetry separates out, and we are left with two variables in the final equation. With polyatomic molecules, the situation is even more complex. One important result of this is that it is impossible to describe the wave-function in terms of effective nuclear charges in any satisfactory manner, as is done with atoms (3). Nor is it possible to draw the wave-functions graphically, as can be done for the individual electrons in an atom, since in the molecule there are two variables.

There are, however, several purposes—for example, electron scattering and the effects of applied electric and magnetic fields—for which it is desirable to have one-electron wave-functions such as those obtained by a self-consistent field approximation, and accordingly an attempt is made in this paper to obtain such wave-functions for the simplest of all molecules, H_2 in its ground state. In view of the difficulty of representing the wave-functions graphically, even when they have been obtained, analytical forms have been employed, rather than purely numerical solutions of the wave-equation. While solving the general problem, it also seemed desirable to include a simple wave-function, representing a compromise between accuracy and simplicity; the wave-function (B), shortly to be described, is fairly accurate and at the same time very simple.

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The method of the self-consistent field

In the method of the self-consistent field, we consider the motion of each electron alone in the field of the nuclei and of the other electrons present; thus we are compelled to adopt the molecular-orbital (11) rather than the electron-pair viewpoint. To each electron is assigned an orbital ψ, which allows it to move throughout the whole molecule. This description implies a certain limitation, since it is equivalent to taking a time average over all the electron interactions, and it is just this interaction, in the case of H_2, that is responsible for one electron remaining attached to one nucleus and the other electron to the other nucleus, when the two nuclei are separated. Putting it in other words, there is a larger and more diffuse volume available to an electron in a molecular field than in an atomic field, and the electronic repulsion has the effect of keeping the electrons separated from one another and attached to different nuclei. The importance of these r_{12} terms has been shown by Coolidge and James (2) in their detailed study of H_2; it appears that without explicit account of r_{12} in the wave-function there is a limit to the binding energy value attainable, which is 0·43 V. too low. But there is also a further limit if we insist upon both electrons occupying completely equivalent orbitals, and the lowest value of the total energy that we obtain in this paper, while better than that obtained by the simple perturbation method of Heitler and London (12), is worse than in the corresponding variation treatment (13). For this reason it is doubtful if the method of the self-consistent field is ever likely to be as valuable in molecular structure as it has already shown itself to be in calculations of atomic structure.

The principle of the method is very simple; if we assume that each of the electrons is governed by a molecular-orbital ψ, then the complete wave-function for the two electrons is

$$\Psi = \psi(1)\,\psi(2)\,\{\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)\}.$$

Here α and β are the spin wave-functions; these may, however, be omitted from henceforward, since they play no further part in the energy calculations. In this simple case both the Fock and the Hartree methods yield the same result. The wave-function ψ is to be found as the solution of an integral equation, which can be obtained just as in the atomic case. It is

$$H\psi(1) + G(1)\,\psi(1) = E\psi(1).$$

In this equation, E is the total electronic energy of the molecule, H is the operator (a function only of the coordinates of the electron 1)

$$H = 2\left\{-\tfrac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}\right\},$$

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and $G(1)$ is the interaction potential

$$G(1) = \int \frac{\psi^2(2)}{r_{12}} dv_2.$$

We suppose that we are using atomic units (a.u.) throughout; r_a and r_b are the distances of the electron from the two nuclei A and B. This equation is exactly the same in form as that involved in the solution for the ground state of the He atom. The only difference lies in the extra potential term that arises in the Hamiltonian, and in the fact that there is less symmetry in ψ. The first question is, what coordinate system shall be used to determine ψ? Some calculations have already been made by the author (3) in which ψ was represented as the sum of atomic orbitals round the two nuclei; but this is a clumsy approximation and is not easily generalized so as to allow greater flexibility. It seems better to use the spheroidal coordinates λ, μ and ϕ, used by Coolidge and James, which are defined by the relations

$$\lambda = \frac{r_a + r_b}{\rho}, \quad \mu = \frac{r_a - r_b}{\rho},$$

ϕ being the azimuth around the axis AB. ρ is the internuclear distance AB, which we assume to be constant. There is every reason to believe that these coordinates are good ones for our purposes, since, in the case of H_2^+, it has been shown by James (8) that an expression of the type

$$\psi = e^{-\delta\lambda}(1 + a\mu^2)$$

gives an extremely good approximation to the true energy. We may expect the wave-functions to be somewhat less accurate than the energy value, but both are well represented by an expansion of the above type.

The integral equation may be replaced by a variation problem. Thus

$$E = \text{Min}\left[\frac{1}{S}\int \psi(1) H\psi(1)\, dv_1 + \frac{1}{S^2}\int \frac{\psi^2(1)\psi^2(2)}{r_{12}} dv_1 dv_2\right],$$

where

$$S = \int \psi^2(1)\, dv_1.$$

We are to choose ψ so that the energy is a minimum. We find it convenient to express the wave-function as a linear sum of terms similar to those used by Coolidge and James, and we write

$$\psi = \Sigma c_{mn} \lambda^m \mu^n e^{-\delta\lambda}.$$

The problem now becomes merely the choice of the constants c_{mn} and δ which minimize the energy. In the present paper, the wave-functions which are used consist of the terms

$$\psi = e^{-\delta\lambda}(1 + a\mu^2 + b\lambda + c\lambda^2 + d\lambda\mu^2).$$

There is no reason, other than the labour which is already fairly considerable, why more functions should not be included. Thus it has been shown by Coulson

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and Duncanson (4) that terms up to μ^4 are required in heteropolar molecules. It was not considered worth while adding such a term here, since its energy alone is in the continuous spectrum, and the presence of the two terms μ^2 and $\lambda\mu^2$ makes it possible to allow fairly adequately for the variation of ψ along the ellipses λ = constant. Terms with an odd power of μ, such as μ^3, do not appear by reasons of symmetry.

Numerical results

The calculations were only performed for the ground state of the hydrogen molecule, at the equilibrium distance $\rho = 1{\cdot}40$ a.u. $= 0{\cdot}74$ A. The value of the exponent δ was taken to be that used by Coolidge and James, namely 0·75. These authors have shown that this value is very nearly the best one, and the integrals required in this work have almost all been evaluated by these authors. The writer would like to thank Dr A. S. Coolidge for kindly putting at his disposal the numerical values of these integrals. As Coolidge and James remark, even if the chosen value of δ does not happen to be exactly the best one, it is compensated for by the presence of terms in λ and (later) in λ^2, the existence of which is equivalent to a change of δ.

There is no need to describe the detailed calculation or the evaluation of the integrals; they may all be obtained by the methods of Coolidge and James, and although the work is tedious it is perfectly straightforward.

The method of solution of the variational problem was as follows: first of all, only two terms are included, so that

$$\psi = e^{-\delta\lambda}(1 + a\mu^2),$$

and the constant a was chosen so that the energy was a minimum. This gives the simplest two-term function, corresponding to the orbital of H_2^+ given by James. The result, when normalized in atomic units, was

$$\psi = 0{\cdot}68496\, e^{-0{\cdot}75\lambda}(1 + 0{\cdot}23342\mu^2). \qquad \text{(A)}$$

The total electronic energy of this function was $-1{\cdot}82874$ a.u., which gives a binding energy of 3·096 V.

This wave-function is clearly inadequate to govern the detailed variation of ψ, so next a third term was added, so that

$$\psi = e^{-\delta\lambda}(1 + a\mu^2 + b\lambda).$$

The energy was now made a minimum with respect to variations of both a and b. This was done by successively varying a and then b, till a minimum was found by successive approximation. The elegant method of Coolidge and James is not applicable here, since the energy is a polynomial of the fourth degree in a and b. The result in this approximation was

$$\psi = 0{\cdot}83247 e^{-0{\cdot}75\lambda}(1 + 0{\cdot}21948\mu^2 - 0{\cdot}079575\lambda). \qquad \text{(B)}$$

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The minimum electronic energy was $-1{\cdot}84497$ a.u., which gives a binding energy of $0{\cdot}13068$ a.u. $= 3{\cdot}535$ V. (N.B. All the binding energies given in this paper are the differences of the electronic and nuclear energies at equilibrium distance and at infinity, so that no allowance has been made for zero-point vibrational energy; inclusion of this would mean subtracting about $0{\cdot}27$ V. from the binding energies given.) This three-term energy value is a better one than that obtained by the author (3) using linear combinations of atomic orbitals, and probably represents about the best compromise between accuracy and simplicity.

Next the term $c\lambda^2$ was added to the wave-function; this was found to give a lowering of the energy of about $0{\cdot}005$ V., but the precise values of the constants were not determined.

Finally, a full five-term function was used, with a wave-function

$$\psi = e^{-\delta\lambda}(1 + a\mu^2 + b\lambda + c\lambda^2 + d\lambda\mu^2).$$

The energy is a polynomial of the fourth degree in a, b, c and d, and it is clearly impossible to minimize at the same time with respect to all four constants. The process was therefore carried through in stages; for the first stage the values of a and b found in (B) were used to find the best values of c and d. Then these were used, and improved values of a and b were obtained, which in turn were used to obtain better values of c and d. This process could be continued indefinitely, always giving slight improvements, but after four or five such operations, the improvement grows very small and is barely detectable. The final values obtained were, when the wave-function is normalized,

$$\psi = 0{\cdot}87758e^{-0{\cdot}75\lambda}\{1 + 0{\cdot}27787\mu - 0{\cdot}12863\lambda + 0{\cdot}012503\lambda^2 - 0{\cdot}039589\lambda\mu^2\}. \qquad \text{(C)}$$

The lowest energy given by this last function (C) was $E = -1{\cdot}84747$ a.u., so that the binding energy is $3{\cdot}603$ V. The addition of the last two terms has added about $0{\cdot}068$ V. to the binding energy. It seems doubtful if any great gain would now result from adding more functions to ψ, and it seems almost certain that the best self-consistent field energy for the molecule is about $3{\cdot}63$ V. This may be compared with the value of $3{\cdot}470$ V., obtained by the author (3) with combinations of atomic orbitals, with $3{\cdot}761$ V. obtained by Wang (13) in a variational Heitler-London calculation, and with $4{\cdot}27$ V., which is the best value obtained by Coolidge and James by the use of a wave-function without r_{12} terms explicitly included. The observed binding energy is $4{\cdot}72$ V.

It should be added in this connexion that in wave-function (C) the values of the coefficients c and d are small; but they are sensitive to small changes in the assumed values of a and b. Thus a small variation in the value of a, for example, would entail quite a large variation in the values of c and d, although the actual electronic energy would hardly be affected.

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We conclude from this work that the self-consistent field method is only moderately reliable for dealing with molecular problems. It is interesting to compare the percentage deviation of the total electronic energy (not the binding energy) in this case with that in the similar two-electron atomic problem of the He ground state. The table shows the exact and the computed energies and also the percentage errors in the two cases.

	Exact energy	Energy calculated by self-consistent field	Percentage error
He ground state	−2·9037	−2·875	0·99
H_2 ground state	−1·8893	−1·8475	2·21

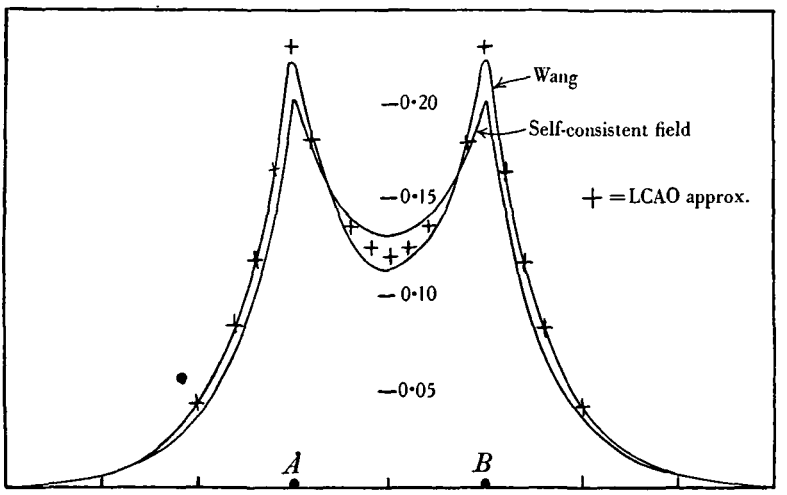


Fig. 1. Curves of $\Psi\Psi^+$. (A and B are nuclei.)

It appears from this table that the molecular energy is about twice as much in error as the corresponding atomic one; this is to be interpreted as due to the greater importance of the r_{12} term, as explained earlier. It has been shown by Eckart (5) that when the errors are small, as here, the discrepancy in the wave-functions may be expected to be of the order of the square of the error in the energy; it therefore follows that the value of the wave-function obtained in the present paper may be expected to have a possible error of about 4 %.

The electron density has been plotted for points along the axis of symmetry, and is shown in Fig. 1. For comparison, the values obtained by the author by the use of atomic orbitals, and those obtained by Wang, are also included. In the latter case, since the wave-function depends explicitly upon the simultaneous positions of both electrons, an averaging process has been necessary over all positions of one of the electrons, to give the expectation value for the other. It

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will be seen from the curves that both the Wang and the LCAO approximations give too low a density in the midpoint of the nuclei, and compensate for this by giving a larger density near the two nuclei and further out still. The charge density dies away very rapidly with the distance, indicating that most of the charge is concentrated between the nuclei. At all points in AB outside the nuclei, there is no significant difference between the values of ψ given by the LCAO approximation and the approximation used by Wang.

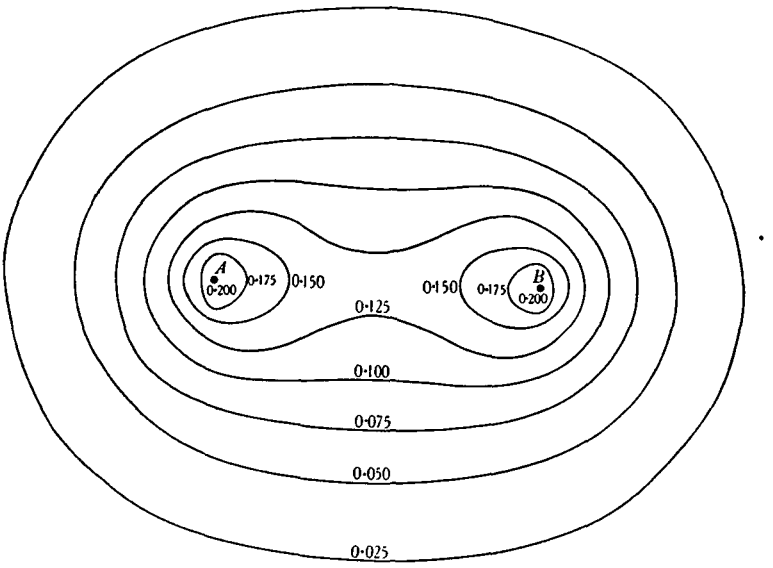


Fig. 2. Contours of $\Psi\Psi^{+}$.

It is interesting to draw contours of the density for various points in a plane through the axis of symmetry; these are drawn in Fig. 2, which may be compared with the contours given by London (10) using the Heitler and London approximation.

One other point is worth investigating further; in the course of the present work using the self-consistent field method, three approximate wave-functions have been obtained (A), (B), (C). In Fig. 3 these are drawn on the same graph to show the convergence of the solutions. First of all the single-term function $e^{-0\cdot75\lambda}$ is drawn. As can be seen, this is quite a fair approximation to the true wave-function. Then the curve (A), labelled "two-term function", has been included, and finally the five-term function (C). The three-term function (B) differs hardly at all from the five-term function, the maximum divergence of the two being 0·005 unit. This gives reason to believe that the approximations have been carried sufficiently far for us to be satisfied with wave-function (C), and also that for most analytical purposes it is good enough to use the simpler wave-function (B).

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Possible further applications

There seems no reason why this method should not be applied to other more complicated molecules; in such cases, the non-bonding electrons of the atoms would be represented by wave-functions similar to those of the isolated atoms, but with allowance for polarization, and the bonding electrons would be given orbitals which embrace the various nuclei. Thus, for a molecule such as LiH, the

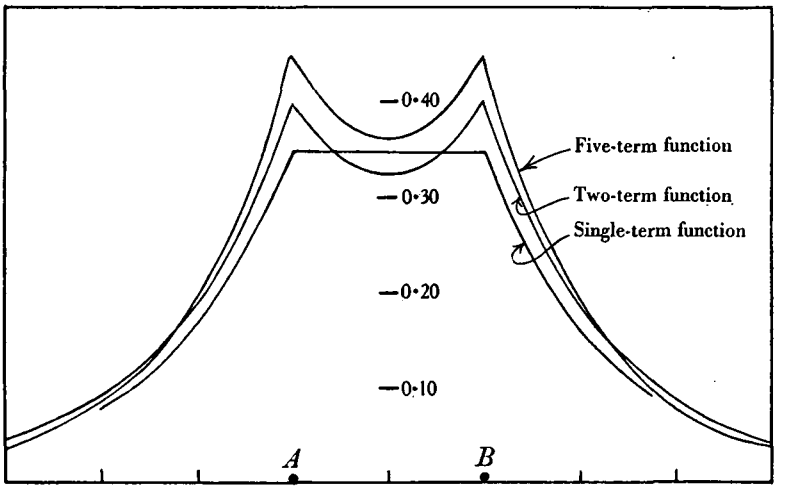


Fig. 3. Curves of Ψ. (A and B are nuclei.)

two electrons of the K shell of lithium would be represented by a wave-function of the type

$$\psi(K\text{ shell}) = f(r) + g(r)\cos\theta,$$

where $f(r)$ and $g(r)$ are functions of the distance from the Li nucleus, and the polarization is allowed for by the presence of the term in $\cos\theta$. Further terms could be added, but it is probable that this would be a good enough approximation. The wave-functions of the bonding electrons, on the other hand, would be expressed as a series in λ and μ. Thus

$$\psi(\text{valence}) = e^{-\delta\lambda}\{1 + a\mu + b\mu^2 + c\lambda + \ldots\}.$$

Unfortunately Knipp (9) and James (8) have shown that there is an appreciable exchange force between the core electrons and the valence electrons, so that it would be necessary to use the more complicated Fock equations, in which account is taken of this exchange, rather than the simpler Hartree ones which neglect it.

In the same way, of course, the higher states of the hydrogen molecule could be determined and also wave-functions for such molecules as Cl_2 and N_2, which are at the moment outside the range of exact solution.

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SUMMARY

The method of the self-consistent field is applied to a discussion of the energy and wave-functions of the ground state of the hydrogen molecule; an analytical expansion of the wave-function is given in terms of spheroidal coordinates, and the distribution of charge is determined. Two simpler, though less accurate, wave-functions for the molecule are also included, and the possibility of using the method for more complex molecules is discussed.

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