

One-Center Expansion of Molecular Wave Function

Sigeru HUZINAGA

Department of Industrial Chemistry, Kyoto University, Kyoto

(Received February 20, 1956)

The possibility of expanding molecular wave functions into a series of functions with a single center is examined. The calculations are performed for the ground state energies of H_2^+ and H_2 with reasonable results. For example, a simple expansion yields 3.80 e.v. as the binding energy of H_2 . The advantage of this method is, above all, its simplicity in calculations.

§ 1. Introduction

The determination of molecular wave functions is more difficult than that of atomic wave functions because the potential energy of nucleus-electron attraction involves two or more centers in the former case. It is thus a central problem in the molecular theory to overcome many difficulties in calculations caused by this fact and to simplify, wherever possible, the method of calculations. There are two main types of approximation which are most commonly used, known respectively as the valence bond and molecular orbital approximations. The valence bond method is essentially a generalization of the calculation used by Heitler and London for the hydrogen molecule. Here a molecule is regarded as composed of atoms and then the building blocks of the whole wave function are necessarily atomic orbitals. In the molecular orbital theory only the nuclei (or nuclei + inner shells) are first brought into position, and afterwards the valence electrons are allotted to polycentric molecular orbitals. There is no intrinsic connection of this method to atomic orbitals. However it is customary to construct the molecular orbitals as linear combinations of atomic orbitals. There are of course good reasons for the prevailing use of atomic orbitals as building blocks in constructing the whole molecular wave functions. It provides us very effective approximations for many cases.

But the very fact that the electron coordinates have many reference centers creates some obstacles difficult to overcome. Above all, the difficulty in the evaluation of energy integrals concerning the electron-electron interaction is most conspicuous. Two-center integrals are usually evaluated in elliptical coordinates by using the Neumann expansion of the electron-electron interaction. But this procedure is not applicable directly to the multi-center integrals. In all atomic problems we find no grave difficulty like this, where we can use the much simpler Legendre expansion because all electron coordinates are measured from a single center. This leads us very naturally to the idea of expressing the electronic charge cloud in molecules in reference to one appropriate coordinate origin, just as in atoms. Crudely stated, this is nothing but the central idea of the works on multi-center

integrals by Barnett and Coulson,¹⁾ Lundquist and Löwdin.²⁾ They, however, placed their emphasis on the mathematical techniques and they confined themselves to the evaluation of the difficult integrals encountered in the usual theories based on the atomic orbitals. It was a natural consequence that they identified the center of expansion of the wave function with the position of one specially chosen nucleus. We can, however, freely choose the center of the expansion anywhere if it is appropriate physically and mathematically. In this respect we find two very encouraging pioneer works, namely the works of MacDonald³⁾ and Matsen.⁴⁾ MacDonald treated the problem of higher excited states of the hydrogen molecule as a three-center problem. In his treatment the inner unexcited electron occupies the orbit of H_2^+ given by Guillemin and Zener⁵⁾ and the wave function of the outer excited electron is given by the hydrogen-like wave function with the center at the middle point between two nuclei. Of course he had to face a grave difficulty of evaluating three-center integrals, which were performed by means of graphical integrations. The most instructive point in his work is, undoubtedly, that he judged that, in spite of the tedious task of the graphical integrations, the "three-center description" of the whole wave function was superior to the more usual two-center description both with respect to the labors in calculations and the physical interpretations. Matsen tried to calculate the energies of the $1s\sigma$, $2p\sigma$, $2p\pi$, $3d\pi$ and $3d\delta$, states of H_2^+ , by using the hydrogen-like atomic orbitals with the center at the middle point of two nuclei. For $1s\sigma$ state the result was rather poor but for the higher states the results were amazingly good far beyond our first expectation. Being encouraged by these works, we naturally arrive at an idea of describing all the electrons with reference to one single center appropriately chosen in a molecule. We shall begin with two simple examples, the hydrogen molecule ion H_2^+ and the hydrogen molecule H_2 . These may serve as useful means of test and illustration of our procedure: one-center expansion of molecular wave functions.

§ 2. Hydrogen molecule ion

The one-electron problem of H_2^+ can be solved exactly and the very accurate values of energies and wave functions of various states are now available.⁶⁾ Since the higher states were already treated successfully by Matsen as was mentioned in the introduction we restrict ourselves to the calculation of energy of the ground $1s\sigma$ state. We set up the one-center σ -function in the following form:

$$\phi = c_1 s_1(\zeta; r) + c_2 s_n(\zeta'; r) + c_3 d_n(\zeta'; r, \vartheta), \quad (1)$$

$$s_n(\zeta; r) = N(n, \zeta) r^{n-1} e^{-\zeta r} Y_0,$$

$$d_n(\zeta; r, \vartheta) = N(n, \zeta) r^{n-1} e^{-\zeta r} Y_2,$$

$$N(n, \zeta) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2},$$

where ζ , ζ' , c_1 , c_2 and c_3 are variable parameters which should be determined by the variation method and n is also a variable integral number. $N(n, \zeta)$ is the normalization constant for the radial function and Y_l is the normalized axially symmetric spherical surface

Table 1. Nuclear distance $R=1.4$ a.u.

	(1)	(2)	(3)
c_1	1	1	0.761157
c_2	0	0	0.253422
c_3	0	0	0.110674
n	—	—	4
ζ	2	1.095	1.1
ζ'	—	—	4.3
E_{calc}	-0.44016	-1.168	-1.264020
E_{exact}	-1.284265 a.u.		

Table 2. Nuclear distance $R=2.0$ a.u.

	(1)	(2)	(3)
c_1	1	1	0.661432
c_2	0	0	0.339056
c_3	0	0	0.179056
n	—	—	4
ζ	2	0.912	1
ζ'	—	—	3
E_{calc}	+0.10989	-0.967	-1.074755
E_{exact}	-1.102625 a.u.		

Table 3. Nuclear distance $R=2.6$ a.u.

	(1)	(2)	(3)
c_1	1	1	0.626715
c_2	0	0	0.364435
c_3	0	0	0.227291
n	—	—	4
ζ	2	0.787	0.8
ζ'	—	—	2.5
E_{calc}	+0.49209	-0.826	-0.932967
E_{exact}	-0.975475 a.u.		

harmonic of the l -th degree. The essential point is that the origin of coordinates is located at the middle point between two nuclei. The results are listed in Tables 1, 2 and 3.

In each of the above tables the column (1) shows the result obtained by the first order perturbation started from the He atom ground state, the united atom in its strict sense of the word, and (2) the result of Matsen's single-term approximation and (3) the result of the present three-term expansion. The improvement in each stage is quite obvious. The molecule can bind only in the case of (3). Our result seems to be a little bit inferior to the one given by LCAO MO approximation with variable screening but definitely better than LCAO MO without screening. A further comment is that our efforts to find the best values of variational parameters are not exhaustive. Some of them are supplied through rather unconvincing guess works. The situation is the same also in the following section.

§ 3. Hydrogen molecule

In this section we shall calculate the binding energy of the H_2 molecule at the fixed nuclear distance of 1.4 a.u. For the convenience of explanations, let us divide the following description into five stages. We hope this proves to have some heuristic advantage.

Stage (a). As a preliminary step, let us try to calculate the energy of the ground state of the H_2 system by using a wave function, $\Psi = s_1(\zeta; r_1) s_1(\zeta; r_2)$. This may be called a united-atom treatment of H_2 in the sense used by Matsen⁹⁾ for the H_2^+ case. The origin of electron coordinates is of course located at the middle point between two nuclei as before. With $\zeta = 0.935$ the result is -1.7022 a.u. for the electronic energy which means the binding energy of -0.32934 e.v. Thus the molecule cannot bind at all.

Stage (b). The function in the previous stage has an obvious defect. Two electrons concentrate too much at the middle point. Next we shall try to remedy this by spreading the function as $\Psi \sim \phi(1)\phi(2)$, where ϕ is given by (1) without d -term. Although this function is still preserving the complete spherical symmetry around the center of gravity it yields a rather unexpected result that the molecule does bind with the binding energy 0.54289 e.v., the parameter values being $n=4$, $\zeta=1$, $\zeta'=4.3$ and $c_2/c_1=0.2$.

Stage (c). Although we have the stable molecule in the stage (b), the wave function used there cannot be admitted as meaningful because it has a complete spherical symmetry. The hydrogen molecule must have an elongated charge cloud. Then a plausible guess will be to suppose that the inner electron has a wave function similar to the one adopted for H_2^+ at $R=1.4$ a.u. in the preceding section and the outer electron under the influence of the screened nuclear field has an atomic $1s$ -type wave function. The following function is written down along this idea.

$$\Psi \sim \phi_{in}(1)\phi_{out}(2) + \phi_{out}(1)\phi_{in}(2), \quad (2)$$

$$\phi_{in} = s_1(1.1; r) + 0.5s_4(4.3; r) + 0.24406d_4(4.3; r, \vartheta),$$

$$\phi_{out} = s_1(0.8; r),$$

where ϕ_{in} is almost of the same form as the wave function ϕ of H_2^+ at $R=1.4$ a.u. ϕ_{out} is simply an s -type function. This function is the so-called "in-out" type function though in a very primitive fashion. The calculation is quite elementary. It gives 2.5766 e.v. as the binding energy. This result tells us that the single-term approximation for the outer electron is too crude for the ground state. However it is probable that it works well for the higher excited states.

Stage (d). As the next step we try to include the so-called "left-right" correlation by adding to the function of (c) stage a term, $p(1)p(2)$, where $p(r, \vartheta) = N(3, 3)r^2e^{-3r}Y_1$. This leads to a binding energy 2.8837 e.v.

Stage (e). This is the final stage of our calculation so far performed. Of course this does not mean any final stage of the present approximation. Here we use the following wave function.

$$\begin{aligned}\Psi &= c_1\varphi_1(1, 2) + c_2\varphi_2(1, 2) + c_3\varphi_3(1, 2), \\ \varphi_1(1, 2) &= [s_1(\zeta; r_1) + as_4(\zeta'; r_1)][s_1(\zeta; r_2) + as_4(\zeta'; r_2)], \\ \varphi_2(1, 2) &= [s_1(\zeta; r_1) + as_4(\zeta'; r_1)]d_4(\zeta'; r_2, \vartheta_2) \\ &\quad + d_4(\zeta'; r_1, \vartheta_1)[s_1(\zeta; r_2) + as_4(\zeta'; r_2)], \\ \varphi_3(1, 2) &= d_4(\zeta'; r_1, \vartheta_1)d_4(\zeta'; r_2, \vartheta_2),\end{aligned}\tag{3}$$

where the origin of coordinates is located at the middle point between two nuclei. This may be interpreted as follows. In the stage (c) we allotted a sausage type wave function for the inner electron while a simple s -type function for the outer electron. If, however, we allot a sausage type function also for the outer electron, we may be able to obtain a better result. This is the idea which leads us to the above form of the wave function. Another way of explanation may be supplied through the language of the configuration interaction. In this way the in-out correlation may be included more reasonably than in the stage (c).

With the above wave function the calculation is still straight-forward and not tedious. It gives the following result with the parameter values $\zeta=1$, $\zeta'=4.3$, $a=0.25$.

Binding energy: 3.7999 e.v. ($R=1.4$ a.u.)

Coefficients: $c_1=0.66109$, $c_2=0.07881$, $c_3=0.06788$.

This is better than the value 3.60 e.v. obtained by Coulson's best molecular orbital. It may be expected that if we add to the function a left-right correlation term like $p(1)p(2)$ of the stage (d) we have a binding energy of about 4 e.v.

§ 4. Discussion and conclusion

In view of the results of the exploratory applications of the present method to the hydrogen molecule and ion, it seems that the situation is certainly not hopeless. But it is to be noted that we have treated in the preceding sections only two specially simple

examples. The present method must be examined more carefully from the general point of view.

The first advantage of the present method is the easiness of integral calculations. For the sake of convenience, we shall borrow here the notations of Roothaan⁸⁾ without explanations. In his notations all that we need are the following three integrals:

$$(i) \quad (\chi_a | \chi_b), \quad (\rho=0),$$

$$(ii) \quad [a | Q_b],$$

$$(iii) \quad [Q_a | Q_b], \quad (\rho=0).$$

The nuclear distance, ρ , is entered only in the nuclear attraction integral $[a | Q_b]$ and this is easily evaluated by means of the auxiliary function $A_n(\rho)$,

$$A_n(\rho) = \int_1^\infty \xi^n e^{-\rho\xi} d\xi = n! \rho^{-n-1} e^{-\rho} \sum_{k=0}^n \rho^k / k!,$$

$$A_0(\rho) = e^{-\rho} / \rho, \quad A_n(\rho) = (1/\rho) [e^{-\rho} + n A_{n-1}(\rho)].$$

The most troublesome in the molecular theory is the integral of electron-electron interaction energy,

$$[Q_a | Q_b] = \iint [Q_a(1) Q_b(2) / r_{12}] dv_1 dv_2.$$

In the present scheme, however, charge distribution Q_a, Q_b are co-centric and we can easily evaluate the above integral. This is a very favorable situation for the large scale tabulation of the integrals. There exist no difficulties of hetero-nuclear and multi-center integrals.

The second advantage of the present method is its conceptual simplicity especially for higher excited states of molecules. We shall publish in the near future the analytical version of MacDonald's works on H_2 excited states. While we were not so successful in the single-term approximation for the outer electron of the ground state of H_2 as described in the stage (c) of the preceding section, the higher states will be treated more successfully. This conjecture is supported by the encouraging results obtained by Matsen.⁴⁾ This technical possibility may not be limited to the hydrogen molecule only.

Needless to say, the procedure of one-center expansion of molecular wave functions reveals many disadvantages when compared with the prevailing approximations based on atomic orbitals. Expansions of molecular wave functions in one-center functions would be almost impossible for the inner electron still preserving their individual atomic characters in molecules. However it is outer electrons belonging to the whole molecular frame rather than to atom which play the key rôle in determining the physical behavior of molecules. For these outer electrons, the atomic functions form less satisfactory building blocks and conversely the present one-center expansion may increase its suitability both physically and mathematically. Meanwhile the difficulty concerning the inner electrons concentrated on the nuclear positions might be side-stepped by means of certain semi-empirical procedures. In addition the recent advance in computing devices encourages the hope that it may become

possible to expand in good accuracies the molecular wave function into a series of one-center functions by including a large number of terms.

The author wishes to express his sincere thanks to Professor G. Araki for his kind encouragement.

References

- 1) M. P. Barnett and C. A. Coulson, *Phil. Trans. Roy. Soc.* **A243** (1951), 221.
- 2) S. O. Lundquist and P. O. Löwdin, *Arkiv för Physik* **3** (1951), 147.
- 3) J. K. L. MacDonald, *Proc. Roy. Soc.* **A136** (1932), 528.
- 4) F. A. Matsen, *J. Chem. Phys.* **21** (1951), 928.
- 5) V. Guillemin and C. Zener, *Proc. Nat. Acad. Sci.* **15** (1929), 314.
- 6) D. R. Bates, Kathleen Ledsham and A. L. Stewart, *Phil. Trans. Roy. Soc.* **A246** (1953), 215.
- 7) C. A. Coulson, *Proc. Camb. Phil. Soc.* **34** (1938), 204.
- 8) C. C. J. Roothaan, *J. Chem. Phys.* **19** (1951), 1445.