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QUANTUM THEORY AND ELECTRON PAIR BOND[1]

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Abstract

It is shown for some simple examples that the stable molecular quantum state of a polyatomic system, is nearly identical with a state, by which there are built so many electron pairs between each pair of atoms, as the corresponding chemical formula shows.

1. THE aim of the following note is to point out more definitely the connection between the quantum theory and the Lewis' electron pair idea for some simple examples of poly-atomic molecules. In principle this paper contains nothing new; the principles have all been developed in recent papers published by G. Rumer and the writer[1] and by H. Weyl.[2] It seems to the writer, however, that the results of the following calculations, while indeed very simple, might be of interest.

The quantum theory leads to a full justification of the electron pair conception for diatomic molecules. Let us consider two atoms A and B with n_a and n_b free electrons of parallel spin (spin angular momenta $n_a/2$ and $n_b/2$) and let us assume for simplicity that the orbital angular momenta are zero. For every value of the spin momentum of the whole system s between $(n_a+n_b)/2$ and $|(n_a-n_b)/2|$ there exists just one interaction term with an energy ϵ_s.

Instead of s we can introduce the number of *pairs* p of electrons with *antiparallel spin* between A and B defined by

$$p = \frac{n_a + n_b}{2} - s$$

Lewis' electron pairs are just these pairs of electrons with antiparallel spin. In the chemical picture, p would be the number of valence-dashes between A and B. If we further introduce the number of *free* valences, which go out from the atom A

$$\nu_a = n_a - p$$

then the energy will assume the simple form

$$\epsilon_p = J_E + (p - \nu_a\nu_b)(AB) \quad p = 0, 1, \cdots n_b \text{ if } n_b \leqq n_a \tag{1}$$

where J_E is the Coulomb interaction of the two atoms, (AB) the well-known exchange integral between A and B. By the usual assumptions of the sign of

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[1] W. Heitler and G. Rumer, Zeits. f. Physik 68, 12 (1931).

[2] H. Weyl, Gott. Nachr. 1931, in press.

(AB), $[(AB)$ negative$]$ which are now justified in many cases, ϵ_p assumes the largest negative value (strongest bond) if p has the largest value $(=n_b)$. If p becomes smaller, the bond energy will become smaller and finally negative (if $p=0$) corresponding to repelling atoms.

2. This simple theory cannot be extended to the general case of polyatomic molecules. If we have several atoms A, B, C—with n_a, n_b, n_c—electrons, we get in the general case *several*, say f_s, interaction terms (not only one) belonging to a specified s. One could define for all these f_s terms an entire number of electron pairs

$$p = \frac{n_a + n_b + n_c + \cdots}{2} - s$$

but one cannot say, how these f_s terms differ one from the other (except the interaction energy value of course) and further, one cannot say, how many of these p electron pairs are built between two *specified atoms* A and B. Just this question, however, is answered in Lewis' theory.

In the previously mentioned papers. it has been shown, that one can use for the unperturbed system certain unperturbed wave-functions, such that by each of them is built a certain number of electron pairs (or valence-dashes) p_{ab} between each pair of two atoms A and B etc. If this wave-function belongs to a certain value p the sum of the p_{ab} must be equal to p

$$p_{ab} + p_{ac} + p_{bc} + \cdots = p$$

Such a wave-function we will denote by

$$\psi_1 = [AB]^{p_{ab}}[AC]^{p_{ab}} \cdots .$$

There exist f_s independent wave-functions $\psi_1 \cdots \psi_{f_s}$ which differ by the distribution p_{ab}, $p_{ac} \cdots$ of the valence dashes between the atoms, but all have the same *sum* p of valence dashes. Weyl calls such a function a "*pure valence state*," because the valence dashes are here strictly localized between the atoms.

The wave-functions $\phi_1, \cdots \phi_{f_s}$ belonging to the f_s different energy states $\epsilon_1 \cdots \epsilon_{f_s}$ are, however, *not* identical with these pure valence states. In the zeroth order of approximation they are linear combinations of the ψ's.

$$\phi_i = \sum_k c_{ik}\psi_k. \tag{2}$$

The coefficients c_{ik} in Eq. (2) depend on the ratio of the exchange integrals, and therefore on the distances of the atoms.

A pure energy state is a superposition of some pure valence states, or, in the language of the quantum mechanics the energy is not permutable by the valence-dash-configuration.

It seems, that the valence-dash picture should no longer have a place in the quantum theory. We will now show, that it can again assume a certain meaning.

If the coefficients (2) are determined, one can easily work out the *probabilities* of any pure valence state ψ_k if the system is in a definite energy state ϕ_i and vice versa. This probability is

$$w_{ik} = \left| (\phi_i \psi_k) \right|^2$$

where $(\phi_i\psi_k)$ is the integral $\int \phi_i \psi_k$ integrated over all space and spins (scalar product of ϕ_i and ψ_k).

We will show, for some simple examples, that these probabilities for a definite state ϕ are all *small* except for *one* valence state ψ_k in which case these probabilities are *nearly* equal to unity. To a certain energy state there corresponds therefore *nearly* a certain valence state; for the *stable molecular state* it will be just this valence state, which one expects from the *chemical standpoint.*

It is first necessary to make mention of some properties of the valence states. If one builds all valence states, by giving all possible values to the numbers p_{ab}, p_{ac} (while the sum is the same of course) one gets more than f_s valence states. Some of them are therefore linearly dependent. Further two such valence states will not be orthogonal $(\psi_i \psi_k) \neq 0$. The pure valence states do not exclude one another. There is always a certain probability $|(\psi_i\psi_k)|^2$ for the tate ψ_k if the system is in the state ψ_i.[3]

3. Let now for instance A_1 and A_2 be two atoms with two valence electrons each, H_1 and H_2 be two atoms with one valence electron. We consider the atom configuration

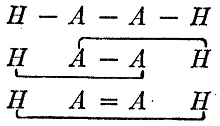
$$H_1A_1A_2H_2$$

and neglect the exchange integrals between non-neighbours. The other exchange integrals will be of the same order of magnitude. Let the distances be chosen so, that they are equal

$$(H_1A_1) = (A_1A_2) = (A_2H_2).$$

One can build three pure valence states

$$\begin{aligned} \psi_1 &= [A_1A_2][A_1H_1][A_2H_2] \\ \psi_2 &= [A_1A_2][A_1H_2][A_2H_1] \\ \psi_3 &= [A_1A_2]^2[H_1H_2] \end{aligned}$$



$$H - A - A - H$$
$$H \quad A - A \quad H$$
$$H \quad A = A \quad H$$

On the right hand side is given the corresponding "chemical formula." ψ_1 alone would, of course, correspond to a usual chemical molecule.

If these three ψ's are normalized the following relation holds[1,2]

$$\psi_1 - \psi_2 - \frac{2}{3^{1/2}}\psi_3 = 0.$$

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[3] It is then possible that for a specified ϕ_i the probabilities for *two* valence states ψ_k, ψ_l are nearly equal to unity. See the second example in the text.

The exact meaning of $|(\phi_i\psi_k)|^2$ is the probability to find the valence state ψ_k and *not* an other state, which is in *contradiction* (*orthogonal*) to ψ_k. In general ψ_l will not be in contradiction to ψ_k.

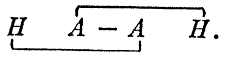
We get therefore two energy states ϕ_1, ϕ_2 one of which, namely ϕ_1, leads to an attraction of the atoms while the other, ϕ_2 leads to a repulsion.[1] For the scalar products have been found the following values.

$$(\phi_1\psi_1) = 0.98 \qquad (\phi_2\psi_1) = 0.19$$
$$(\phi_1\psi_2) = 0.17 \qquad (\phi_2\psi_2) = 0.99$$
$$(\phi_1\psi_3) = 0.72 \qquad (\phi_2\psi_3) = -0.70$$

One sees that $(\phi_1\psi_1)$ is ~ 1 and on the other hand also $(\phi_2\psi_2)$ is ~ 1. One could therefore use for the stable molecular state ϕ_1 *nearly* the chemical formula

$$H - A - A - H$$

in agreement with chemical expectations. For the repelling state one could use the formula



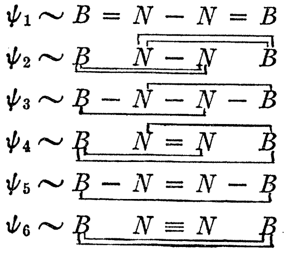
$$H \quad A - A \quad H.$$

The state ψ_3 has, however, for ϕ_1 and ϕ_2 a probability $\sim\frac{1}{2}$. It is a superposition of the two above formulae.[4]

Now let N be an atom with three electrons and B an atom with two electrons, and let us consider the configuration

$$B \quad N \quad N \quad B.$$

One can build six pure valence states corresponding to six valence-dash-configurations:



$$\psi_1 \sim B = N - N = B$$
$$\psi_2 \sim B \quad N - N \quad B$$
$$\psi_3 \sim B - N - N - B$$
$$\psi_4 \sim B \quad N = N \quad B$$
$$\psi_5 \sim B - N = N - B$$
$$\psi_6 \sim B \quad N \equiv N \quad B$$

Of these only three are linearly independent, and there exist therefore three energy states ϕ_1, ϕ_2, ϕ_3, of which ϕ_1 represents a stable molecular state[1] and ϕ_2, ϕ_3 represent repelling states. Of the latter two ϕ_3 has the greater forces of repulsion.

Making the same assumptions about the exchange integrals, the scalar products are:

$$(\phi_1\psi_1) = 0.95 \qquad (\phi_2\psi_1) = -0.33 \qquad (\phi_3\psi_1) = 0.08$$
$$(\phi_1\psi_2) = -0.02 \qquad (\phi_2\psi_2) = -0.33 \qquad (\phi_3\psi_2) = 0.94$$
$$(\phi_1\psi_3) = 0.16 \qquad (\phi_2\psi_3) = -0.98 \qquad (\phi_3\psi_3) = 0.18$$
$$(\phi_1\psi_4) = 0.15 \qquad (\phi_2\psi_4) = -0.37 \qquad (\phi_3\psi_4) = -0.92$$
$$(\phi_1\psi_5) = 0.94 \qquad (\phi_2\psi_5) = 0.37 \qquad (\phi_3\psi_5) = -0.02$$
$$(\phi_1\psi_6) = 0.58 \qquad (\phi_2\psi_6) = 0.55 \qquad (\phi_3\psi_6) = 0.60.$$

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[4] If the exchange integrals are not equal, the above numbers will be changed. If for instance $z = (A_1A_2)/(A_1H_1) + (A_2H_2)$ becomes equal to zero, $(\phi_1\psi_1) = 1$, if $z = \infty$ $(\phi_1\psi_3) = 1$.

It is here remarkable, that one can use for the molecular state ϕ_1 *two* chemical formulae, which are both near to ϕ_1

$$\psi_1 \sim B = N - N = B \text{ or } \psi_5 \sim \underbracket{B - N = N - B}.$$

The first one is to be expected. The second one, however, seems from the chemical standpoint also to be reasonable.

Corresponding to ϕ_2 the formula $\mathrlap{\underbracket{}}B-\overbracket{N-N-B}$ could be used, and to ϕ_3 the formula $\mathrlap{\underbracket{\underbracket{}}}B\quad\overbracket{\overbracket{N-N\quad B}}$ or $\mathrlap{\underbracket{\underbracket{}}}B\quad\overbracket{N=N\quad B}$; it is apparent that these last formulae are quite alien to the chemist, since such states represent states of repulsion.