Theoret. chim. Acta (Berl.) 16, 120—125 (1970)

Atom Promotion and Bond Properties in the Hydrogen and the Lithium Molecules

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Received April 28, 1969/August 18, 1969

In the process of forming the hydrogen molecule, the interacting atoms apparently undergo significant "promotion", in the course of which there occurs contraction of each atom's electronic density distribution. Although this step in itself is energetically unfavourable, it appears to be a key factor in building up the charge density in the internuclear region. In forming the lithium molecule, the atoms apparently do not undergo promotion to any significant extent. It is suggested that the difference in the degrees of atom promotion in the formation of these two molecules is an important reason for the great disparity in the strengths of their bonds.

Beim Prozeß der Wasserstoffmolekülbildung unterliegen die wechselwirkenden Atome offensichtlich einer deutlichen „Promovierung", bei deren Verlauf eine Kontraktion der Elektronendichteverteilung von jedem der beiden Atome stattfindet. Obwohl dieser Schritt selbst energetisch ungünstig ist, scheint er ein Hauptfaktor beim Aufbau der Ladungsdichte im Gebiet zwischen den Kernen zu sein. Bei der Bildung des Lithiummoleküls unterliegen die Atome offenbar keiner irgendwie wesentlichen Promovierung. Man vermutet, daß die Verschiedenheit des Grades der Atompromovierung bei der Formation in diesen beiden Molekülen ein wichtiger Grund für die große Diskrepanz ihrer Bindungskräfte ist.

Dans le processus de formation de la molécule d'hydrogène, les atomes qui interagissent subissent apparemment une "promotion" significative, au cours de laquelle il se produit une contraction de la densité électronique sur chaque atome. Quoique cette étape soit en elle même énergétiquement défavorable, elle apparaît comme un facteur clé dans la construction de la densité de charge de la région internucléaire. Lors de la formation de la molécule de lithium, les atomes ne semblent pas subir de promotion significative. On suggère que la différence dans les degrés de promotion atomique pour ces deux molécules est une des raisons importantes de la grande différence dans les énergies de liaison.

It has been proposed by Ruedenberg [1], in a very detailed study of the chemical bond, that one may view the process of bond formation as occurring in two steps: First there is a "promotion" of the valence electrons of the interacting atoms, which consists of a contraction of their charge distributions toward their nuclei and involves an increase in energy, and second there occurs a sharing of these valence electrons by the atoms, with a concomitant decrease in energy. Mathematically the promotion can be represented by an increase of the orbital exponents of the valence electrons over their values in the free atoms.

This promotion step appears to play an important role in the formation of the hydrogen molecule. This is suggested by a consideration of some simple valence-bond wave functions for H_2. The Heitler-London treatment, in which the exponents in the 1*s* atomic orbitals are kept at the free atom values, $\zeta = 1.0$, gives a rather unsatisfactory dissociation energy, $D_e = 3.16$ eV [2], compared to the experimental value, $D_e = 4.747$ eV [3]. The refinement of this function by Wang, in which the only change is that these exponents are allowed to vary, and take the value 1.166, improves the dissociation energy considerably, to $D_e = 3.78$ eV

[4]. The fact that such improvement results from allowing an increase of the orbital exponents strongly suggests that promotion is an important step in the process $H + H \rightarrow H_2$.

The energy of promotion of the hydrogen atoms can be estimated by means of a linear Birge-Sponer extrapolation. It has long been known that if the differences between the vibrational energy levels of a diatomic molecule, ΔG, are plotted against the vibrational quantum numbers, v, the area under this curve will be a good estimate of the dissociation energy, D_0 [5]. Pauling and Sheehan pointed out that if the initial, linear, portion of this curve is extrapolated to $\Delta G = 0$, then the area should give the energy of dissociation into the valence states of the atoms [6]. The difference between the two areas, then, would be the energy of promotion of the atoms into their valence states — which, for atoms of just one valence electron, as H or Li, are the same as their promoted states [1].

Accordingly, such a plot of ΔG vs. v was made for H_2, using the data of Herzberg and Howe [7]. The value obtained for D_0 was 4.48 eV, which agrees very well with the observed $D_0 = 4.477$ eV [3]. The energy of promotion, per hydrogen atom, was estimated to be 0.21 eV (4.8 kcal/mole).

A second estimate of this energy was made by determining what exponents would have to be assigned to the 1*s* orbitals of two hydrogen atoms, placed at the same internuclear distance as in H_2, in order that the sum of their electronic densities at each nucleus would equal the actual density at each nucleus in the molecule. This latter density was obtained from the very accurate Kolos-Roothaan H_2 wave function [8, 9]. The exponent required is $\zeta = 1.1119$, compared to the free atom value of $\zeta = 1.0000$. The energy needed to contract the 1*s* electronic distribution of a hydrogen atom by the amount corresponding to this increase in the orbital exponent is

$$\Delta E = \int \psi^*_{1s,\zeta'} H \, \psi_{1s,\zeta'} \mathrm{d}\tau - \int \psi^*_{1s,\zeta} H \, \psi_{1s,\zeta} \mathrm{d}\tau$$

where $\zeta = 1.00$, $\zeta' = 1.1119$, and $H = -\Delta/2 - 1/r$ (using atomic units). The result is $\Delta E = 0.17$ eV. Thus, if it is assumed that the increase in the orbital exponent from 1.00 to 1.1119 represents the promotion of the atom in the process of forming the molecule, then the energy of promotion is 0.17 eV (3.9 kcal/mole). Two very different methods, then, have yielded estimates of this quantity which are in encouragingly good agreement with each other.

This promotion step has a considerable effect upon the electronic density distribution in the molecule. An indication of this can be obtained from a comparison of the density difference ($\Delta\varrho$) functions computed from the Heitler-London and the Wang H_2 wave functions [10]. ($\Delta\varrho$ functions are obtained by subtracting the free atom densities from the total molecular electronic densities.) It is shown in Ref. [10] that the increase in the orbital exponents results in a significant buildup of charge density in the region between the nuclei.

The bonds in both molecular hydrogen, H_2, and molecular lithium, Li_2, can be described, in simple terms, as involving the sharing of unpaired *s* electrons from the two atoms. The charge distributions in the bonding regions of these two molecules do not, however, show the similarity which might be anticipated. In H_2, the charge density passes through a minimum (or more precisely, a "saddle-point") between the nuclei [11]. In Li_2, however, it goes through a small relative

Table. *Experimentally-determined bond lengths and dissociation energies for group* IA *diatomic molecules* [15]

Molecule	R_e, A	D_0, eV
H_2	0.742	4.48
Li_2	2.672	1.03
Na_2	3.078	0.73
K_2	3.923	0.51
Rb_2	—	0.49
Cs_2	—	0.45

maximum; there is an unusual outward bulge of the constant-density contours near the internuclear axis [12, 13][1]. Looking at the respective density difference diagrams, the $\Delta\varrho$ function for Li_2 is negative near the nuclei, but rises to a positive maximum at the midpoint of the bond [12, 13]; for H_2, however, this function shows the singular behavior of remaining essentially constant along the molecular axis, from one nucleus to the other [10]. So the charge distribution in H_2 is of a significantly different nature from that in Li_2, even though both can be described, roughly, as having *s-s* bonding.

It is not surprising, therefore, that the bond properties of these molecules differ markedly. This is shown in the Table; H_2 has both a shorter bond length and a considerably greater bond energy than would be expected by analogy with the diatomic molecules of the alkali metals.

It will now be suggested that, unlike the case of H_2, promotion of the atoms does *not* play a significant role in the formation of Li_2, and that this is an important reason for the differences between these two molecules.

The vibrational energy levels of Li_2 have been determined experimentally by Loomis and Nusbaum [16]. A ΔG vs. v plot of these data leads to a dissociation energy of $D_0 = 1.14$ eV. Linear extrapolation of only the initial portion of this curve, however, yields a dissociation energy of 1.20 eV. If this can be interpreted as corresponding to dissociation into the valence states of the atoms, then a promotion energy of 0.03 eV per lithium atom is inferred — only about 15% of the promotion energy estimated for each hydrogen atom in forming H_2!

In order to obtain at least a qualitative idea of how promotion of the atoms might affect the charge distribution and the properties of the bond in Li_2, suppose that a simple molecular-orbital wave function is used to represent the Li-Li bond:

$$\Psi = N(\phi_{2s-A} + \phi_{2s-B})$$

in which

$$\phi_{2s-A} = K(\psi_{2s-A} + C_1\psi_{1s-A} + C_2\psi_{1s-B})$$

ψ_{2s} and ψ_{1s} are Slater-type atomic orbitals [17], and C_1 and C_2 are chosen such as to make ϕ_{2s-A} orthogonal to both ψ_{1s-A} and ψ_{1s-B}[2]. N and K are normalization

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[1] The existence of a rather puzzling relative maximum in the electronic density of Li_2 at the midpoint of its bond has previously been pointed out by Roux, Besnainou, and Daudel [14].

[2] The importance of establishing such orthogonality has been discussed by Coulson and Duncanson [18].

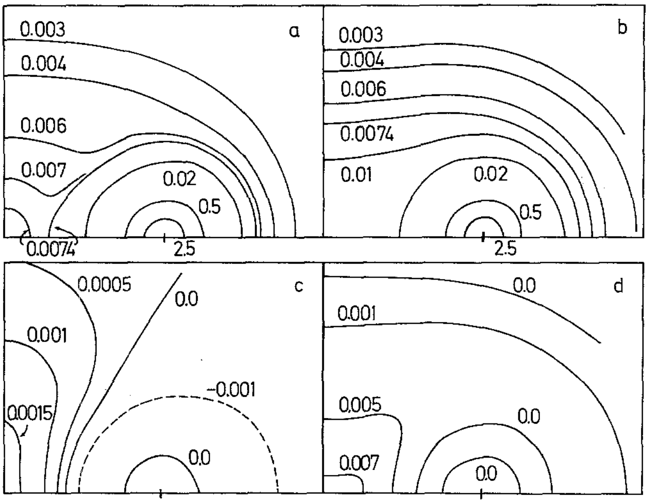

Fig. 1a–d. Calculated total electronic density distributions [a) and b)] and density difference distributions [c) and d)] for the lithium molecule. Plots a) and c) are for $\zeta_{2s} = 0.65$; plots b) and d) are for $\zeta_{2s} = 0.90$

constants. ϕ_{2s-B} is defined analogously to ϕ_{2s-A}. The $1s$ electrons on the two atoms are assumed to be essentially unaffected by the formation of the bond[3].

According to the Slater formula [17], the exponents in ψ_{1s} and ψ_{2s} of a free, unpromoted lithium atom would be $\zeta_{1s} = 2.70$ and $\zeta_{2s} = 0.65$. When the simple molecular-orbital wave function Ψ is written in terms of these unpromoted atomic orbitals, the corresponding molecular charge density distribution,

$$\varrho = 2\Psi^*\Psi + 2\psi^*_{1s-A}\psi_{1s-A} + 2\psi^*_{1s-B}\psi_{1s-B}$$

is as shown in Fig. 1a. The small but intriguing relative maximum in the charge density at the center of the bond is clearly seen. It remains, but to a much lesser extent, if ζ_{2s} is increased to 0.75 — that is, if the atoms are assumed to undergo a certain degree of promotion in the process of forming the molecule. But with a greater degree of promotion, to $\zeta_{2s} = 0.90$, this maximum at the midpoint vanishes completely (Fig. 1b).

On an elementary level, then, the presence of a relative maximum in the computed charge density at the midpoint of the bond in Li_2 is a direct result of writing the molecular wave function in terms of unpromoted atomic orbitals. It seems justified, therefore, to suggest that the relative maximum actually present in Li_2 (according to very good self-consistent-field wave functions [12, 13]) is related to the claimed absence of any significant degree of promotion of the interacting lithium atoms.

The gradual disappearance of the relative maximum with promotion of the lithium atoms does not mean, however, that the charge density between the nuclei is decreasing — exactly the opposite is occurring. Increasing ζ_{2s} leads to a buildup of charge along the internuclear axis, and in the whole region between the nuclei. This is seen in Fig. 1a and 1b; compare, for example, the 0.0074 contour.

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[3] Some support for this approximation can be found in Refs. [18] and [19].

This effect can also be shown by plotting density difference functions; these are presented in Fig. 1c and 1d, corresponding to the total molecular densities in Fig. 1a and 1b, respectively. The density difference plots show clearly that increasing ζ_{2s} results in a much greater buildup of charge in the internuclear region. Thus, an increase of the orbital exponents of the valence electrons, which is interpreted as promotion of the atoms, would lead, just as it did in H_2, to a greater concentration of electronic density in the region between the nuclei, the supposed bonding region of the molecule[4].

It appears then that an initial promotion step, while itself energetically unfavourable, may be very advantageous from the standpoint of eventual molecular stability. The analysis of the simple treatments which have been carried out indicates that such promotion, when it occurs, can have the effect of putting additional charge density into the internuclear region, and thereby presumably making the bond stronger than it would be had the initial promotion not taken place. This apparently does occur in the formation of the hydrogen molecule. It seems that in forming molecular lithium, however, the atoms do not undergo any significant initial promotion. It is suggested that the great disparity in the strengths of the bonds in these two molecules may reflect this difference in the mechanisms of their formation[5].

Acknowledgements. Part of this work was carried out while the author was a member of the Quantum Chemistry Group at Indiana University. He is very grateful to Professor Harrison Shull for stimulating discussions and for his kind support. The suggestion that it might be interesting to determine what free atom orbital exponents would be needed to just balance the electronic density at each nucleus in the hydrogen molecule was made by Professor Shull. The work at Indiana University was supported by the U.S. Air Force Office of Scientific Research and the National Science Foundation. The author also appreciates the financial support of the Computer Research Center at Louisiana State University in New Orleans (NSF Grant No. GP-2964).

References

1. Ruedenberg, K.: Rev. modern Physics **34**, 326 (1962).
2. Heitler, W., London, F.: Z. Physik **44**, 455 (1927). — Sugiura, Y.: Z. Physik **45**, 484 (1927). — Coulson, C. A.: Trans. Faraday Soc. **33**, 1479 (1937).
3. Herzberg, G., Monfils, A.: J. molecular Spectroscopy **5**, 482 (1960).
4. Wang, S. C.: Physic. Rev. **31**, 579 (1928).
5. Birge, R. T., Sponer, H.: Physic. Rev. **28**, 259 (1926).
6. Pauling, L., Sheehan, W. F., Jr.: Proc. nat. Acad. Sci. USA **35**, 359 (1949).
7. Herzberg, G., Howe, L. L.: Canad. J. Physics **37**, 636 (1959).
8. Kolos, W., Roothaan, C. C. J.: Rev. modern Physics **32**, 219 (1960).
9. Davidson, E. R., Jones, L. L.: J. chem. Physics **37**, 2966 (1962).
10. Politzer, P.: J. physic. Chem. **70**, 1174 (1966).
11. — Brown, R. E.: J. chem. Physics **45**, 451 (1966).
12. Bader, R. F. W., Henneker, W. H., Cade, P. E.: J. chem. Physics **46**, 3341 (1967).
13. Ransil, B. J., Sinai, J. J.: J. chem. Physics **46**, 4050 (1967).

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[4] Qualitatively similar changes in the electronic density distribution occur even if $\phi_{2s}-\psi_{1s}$ orthogonality is not established; i.e., $C_1 = C_2 = 0$.

[5] The very interesting and important question of why the formation of Li_2 does not involve significant promotion of the atoms, while the formation of H_2 does, cannot be given a definite answer at present. Tentatively, however, it is suggested that because of the necessity of maintaining inner shell – outer shell orthogonality in the lithium atom, contraction of its electronic density distribution would lead to a relatively large — and unfavourable — increase in kinetic energy. In the hydrogen atom, of course, inner shell-outer shell effects do not arise.

14. Roux, M., Besnainou, S., Daudel, R.: J. Chim. physique **53**, 218, 939 (1956).
15. Herzberg, G.: Spectra of diatomic molecules, 2nd ed. Princeton, New Jersey: D. van Nostrand Co. Inc., 1950.
16. Loomis, F. W., Nusbaum, R. E.: Physic. Rev. **38**, 1447 (1931).
17. Slater, J. C.: Physic. Rev. **36**, 57 (1930).
18. Coulson, C. A., Duncanson, W. E.: Proc. Roy. Soc. (London) A **181**, 378 (1943).
19. Sinanoğlu, O.: Advan. chem. Physics **6**, 315 (1964).

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