

Stabilization and Binding of Quantized Radicals

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electronic shell common to the whole molecule can be assigned. They are discussed in the following letter.

* This is communication IV on "Electronic Structure of Molecules." The other communications in the *J. Chem. Phys.* will be quoted by the following Roman numbers: I. K. Fajans and N. Bauer, **10**, 410 (1942); II. T. Berlin and K. Fajans, **10**, 691, 1942; III. K. Fajans, preceding letter; V. K. Fajans, following letter.

¹ This bonding has to be considered as due to the electron density present between the cores. As has been shown (III, 4) it is possible on this basis to interrelate properties of molecules which do not differ with respect to quantization.

² It should be noted that considering the molecule as the result of the interaction between atoms and not between cores and electrons, it appears to be possible (III, 2b) to correlate the spectroscopic properties of N_2 with the view that eight of the initial electrons of the atoms acted as bonding, two as antibonding, and that in the balance the bond between the atoms is due to six electrons.

³ K. Fajans, *Ber. d. D. Chem. Ges.* **53**, 643 (1920); **55**, 2826 (1922).

⁴ G. N. Lewis, *Chem. Rev.* **1**, 231 (1924).

Stabilization and Binding of Quantized Radicals*

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IN any attempt to reach a uniform point of view concerning the electronic structure of molecules, one has to consider the electric interaction and the quantization.

Using a few characteristic examples we shall combine these two factors into a principle which seems to have broad application to chemical binding.

The oxide MgO can be considered as ionic. However, O^- in the free state is unstable with respect to O^- and e^- (I) and, therefore, the principal quantum number of its eighth electron is $n = \infty$. When combined with Mg^{++} the value of n is reduced, in all probability, to $n = 2$. This process requires energy and, thus, the neon state of O^- has to be stabilized by the binding process.

This point of view can be applied to an electron pair. Left to itself the pair would dissociate. However, it can be stabilized by positive charges, in H^- , He , Li^+ , as well as in H_2 , Li_2 and represents a spacial distribution of negative charge. Depending on the field strength of the positive charges, the pair can be expected to assume a larger or smaller size with unchanged principal quantum number n , but can also differ in quantization as has been concluded (II) for H_2 and Li_2 .

One characteristic example of this analogy between O^- and an electron pair will be given here. The P atoms in P_4O_{10} form a tetrahedron, 6 of the O atoms are situated near the middle of its 6 edges, and each of the remaining 4 is attached directly to one P atom. The P-O distances¹ for the 4 oxygens are shorter than those for the 6 oxygens, which can be easily understood if one derives the molecule

from P^{6+} and O^- . The one-sided polarization leads to shorter distances than a many-sided polarization.² The structure of P_4O_6 is similar to that of P_4O_{10} suggesting that the $4O^-$ have been replaced by 4 unshared electron pairs. Finally, in P_4 , which also has a tetrahedral structure, the $6O^-$ of P_4O_6 can be considered to be replaced by electron pairs, each pair shared by two P^{6+} .

Coordination compounds are characterized by the binding of stable molecules or of radicals stabilized by the binding process.[†] The remarkable group of isoelectronic substances $Ni(CO)_4$, $Co(CO)_3(NO)$, and $Fe(CO)_2(NO)_2$ is diamagnetic. The C-O distance ($1.15 \pm 0.03A$)³ in these compounds differs slightly from that in free CO ($1.128A$), the N-O distance ($1.11 \pm 0.04A$) is near that in NO^+ ($1.073A$). We suggest that the compounds contain deformed CO and NO^+ , both of which have great stability as particles with ten electrons (III). Accordingly, the metals are present in these compounds in the isoelectronic form Ni , Co^- , and Fe^- , having the electron configuration $K^2L^8(M+N)^{18}$. In the normal stable paramagnetic state of the Ni atom, the electrons beyond the L shell are subdivided into $3s^23p^63d^8$ and $4s^2$. The transfer of the two N electrons into the M shell would complete it and make it diamagnetic. We therefore conclude that this state of higher energy is stabilized by the energy of binding between particles with 10 and 18 electrons.

The boron hydrides can be fitted into the above scheme, e.g., B_4H_{10} can be formulated as $BH_3 \cdot B_2H_4 \cdot BH_3$. The radical B_2H_4 is a member of the isoelectronic series N_2 , HCN , $HCCH$, H_2BBH_2 in which the successive splitting of the nucleus (III) leads to the loosening of the system. Similarly, B_3H_9 is $B_3H_6 \cdot BH_3$, the former of the two radicals having an 18 electron shell.⁴

The above offers examples of stabilization of radicals with various numbers of electrons, $2(2e^-)$, $6(BH_3)$, $8(O^-)$, $10(B_2H_4)$, $18(Ni)$ within ionic, covalent, and coordination compounds. In papers to follow this binding principle will be extended to many other cases.

I appreciate the valuable discussions with Professor Norman Bauer, University of New Hampshire, and Mr. Theodore Berlin.

* This is communication V on "Electronic Structure of Molecules." See communication IV, preceding letter.

¹ L. R. Maxwell, *J. Opt. Soc. Am.* **30**, 374 (1940). As will be shown in a detailed paper, the gradation of the distances in P_4 , P_4O_6 , P_4O_{10} can be understood from the above point of view.

² K. Fajans, *J. Chem. Phys.* **9**, 378 (1941).

[†] The binding is due to dipoles and polarizability.

³ L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.* **33**, 1233 (1937).

⁴ The proposed structures are in agreement with the electron diffraction results of S. H. Bauer and L. Pauling, *J. Am. Chem. Soc.* **58**, 2403 (1936).