

## Quantization of Molecules, Inter- and Intramolecular Forces<sup>1</sup>

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In diatomic molecules (e.g.,  $P_2$ ) the distinction is made between the quantization of the electrons of the atomic cores ( $P^{5+}$ ), which is assumed to be the same ( $1^2 8^3$ ) as in the free atom (P), and of the valence electrons  $3^2 2(P^{5+})II^2(P^{5+})3^2 2$ . The latter can be quantized with respect to the field of both cores ("shared"  $II^2$  electrons) and to the field of single cores ("unshared"  $3^2 2$  electrons). The Pauli principle is applied separately to the quantization of the "shared" electrons and to the others. On this basis it is possible to interrelate the great difference in the

strength of the external field (intermolecular forces) of  $N_2$  and  $P_2$  with the size of the atomic cores  $N^{5+}$  and  $P^{5+}$ . The comparison of the intramolecular binding strength in  $(AB)$  with that in  $(AB)^+$  supports the conclusions: in  $N_2$  all ten (not merely six) valence electrons, in  $HCl$  all eight (not two) participate in the binding of the cores  $N^{5+}$  and  $N^{5+}$ ,  $H^+$  and  $Cl^{7+}$ ; the molecules of monohydrides of positively di- and trivalent elements, like those of positively monovalent elements, contain hydrogen as a more or less strongly deformed  $H^-$ .

### 1.

THE method of quantization of molecules proposed in communications II, III, V differs from other methods in that it attempts to picture the actual properties of the molecule without stressing its origin. In the Hund-Mulliken method of molecular orbitals  $N_2$  is, for example, considered as intermediate between the state of two infinitely separated N atoms and their complete coalescence to an atom of Si. The comparison with the N atoms leads<sup>2</sup> to the formula of  $N_2$ :

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2. \quad (1)$$

The formula (2) for the molecule  $P_2$  is analogous<sup>2</sup> to (1), but the whole outer shell is characterized in (1) by the principal quantum number  $n=2$ , in (2) by  $n=3$ , corresponding to the state of the valence electrons in the free atoms.

$$KKLL(\sigma_g 3s)^2(\sigma_u 3s)^2(\sigma_g 3p)^2(\pi_u 3p)^4. \quad (2)$$

Our method should be able to express the great difference in the properties of  $P_2$  and  $N_2$ . The latter behaves like a noble gas (b.p.  $77^\circ K$ ).  $P_2$  has a strong external field shown by its polymerization to  $P_4$  which only partly dis-

sociates at  $2000^\circ K$ . In III the quantum formula  $KK1^2 2^8$  was proposed for  $N_2$ . An alternative way to write it is:

$$(N^{5+})I^2 II^8 (N^{5+}). \quad (3)$$

Formula (3) indicates that the two electrons with the principal quantum number  $n=I$  and the eight with  $n=II$  are common to both atomic cores  $N^{5+}$  or, more exactly, are quantized with respect to the field of both cores. With respect to quantization, the two cores in  $N_2$  play a role similar to the nucleus  $Ne^{10+}$  in the neon atom.

### 2.

The exact quantitative meaning of the values of  $n$  in molecules is less evident than in atoms and for this reason roman numerals are used in formula (3) and later for the principal quantum number of electrons quantized with respect to more than one core. However, in atoms and molecules the main quantum number  $n$  can be considered as closely related to the energy of the electron or to its average distance from the nuclei. This can be explained by Fig. 1. In  $N_2$  (C), the two electrons with  $n=I$  can be considered as moving predominantly between the  $N^{5+}$  cores.<sup>3</sup> The distance between the center of the molecule and the nuclei is  $0.55A$ ; half of

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<sup>1</sup> Communication VI on "Electronic Structure of Molecules." The previous communications in *J. Chem. Phys.* **10** (1942) will be quoted by the corresponding roman numerals. I. K. Fajans and N. Bauer, p. 410; II. T. Berlin and K. Fajans, p. 691; III-V. K. Fajans, pp. 759-761.

<sup>2</sup> G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 368.

<sup>3</sup> The radial electron density in number of electrons per  $A$  in the free atomic cores, pictured in Fig. 1, has been calculated by means of the wave functions of J. Slater, *Phys. Rev.* **34**, 1293 (1929); **36**, 57 (1930). In  $Na^+$  and  $P^{5+}$  only the  $L$  shell at large distances from the nuclei are significant for the above considerations. Concerning  $H^-$ , see H. Bethe, *Zeits. f. Physik* **57**, 815 (1929).

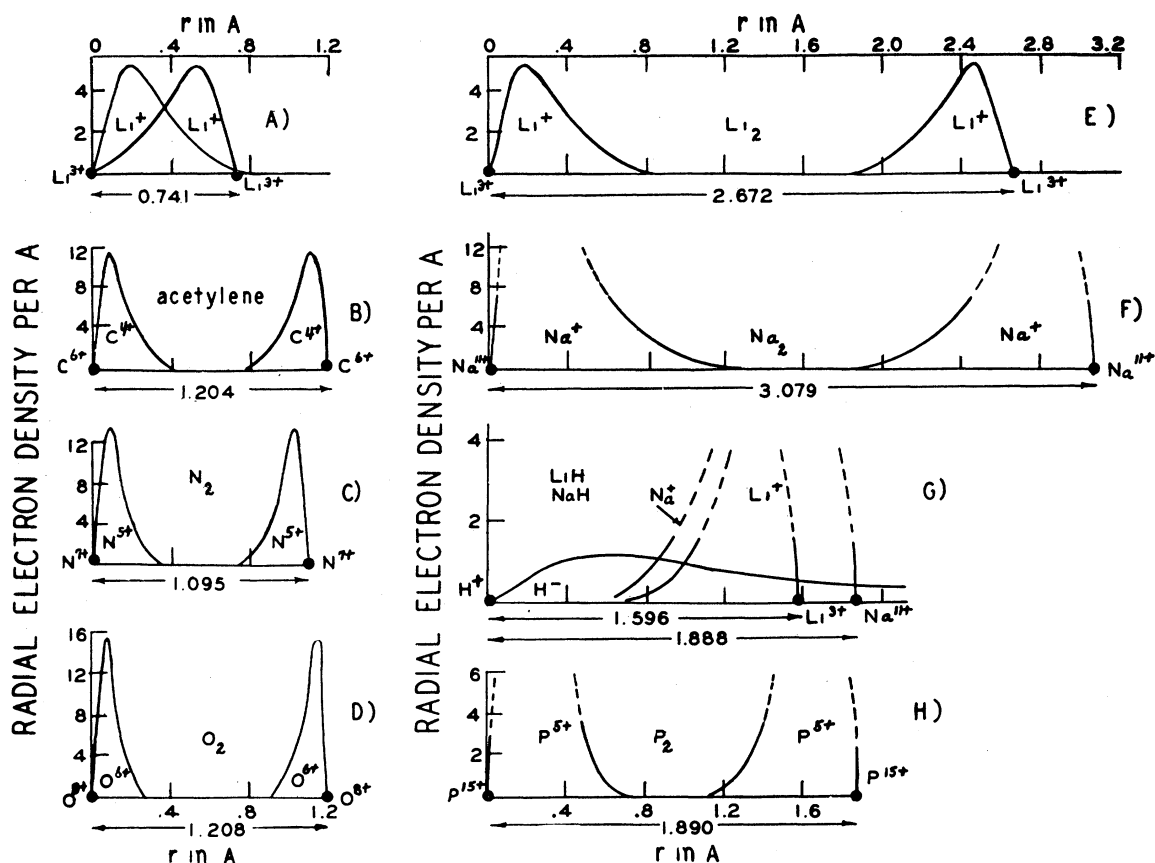


FIG. 1. Radial electron density in number of electrons per angstrom of gaseous atomic cores (in G also of H<sup>-</sup>) placed at the internuclear distance observed in the indicated molecules.

the distance between the centers of neighboring N<sub>2</sub> molecules in the close packed crystal lattice<sup>4</sup> is 2.00Å. The latter value is an estimate of the "radius" of the outer shell II<sup>8</sup>. These eight electrons will participate in the binding only during the time their path lies between the cores.

Another example of the meaning of the principal quantum number in molecules is offered by comparing H<sub>2</sub>, Li<sub>2</sub>, Na<sub>2</sub>. In Fig. 1A, two Li<sup>+</sup> cores overlap extensively and there is little space 0.74Å of H<sub>2</sub> ( $n=1$ ). The electronic shells of the cores overlap extensively and there is little space left for the binding electron pair. The actual, nearly four times larger, distance 2.67Å in Li<sub>2</sub> (E) indicates a quantum effect and the formula (Li<sup>+</sup>)II<sup>2</sup>(Li<sup>+</sup>).<sup>5</sup>

<sup>4</sup> *Strukturbericht*, Vol. II (Akademische Verlagsgesellschaft, Leipzig, 1937), p. 14.

<sup>5</sup> The values calculated for the process  $2X^+ + 2e^- = X_2$  on the basis of the Bohr model of H<sub>2</sub>, with the cores considered as point charges, gave (II) for  $n=2$  an internuclear distance

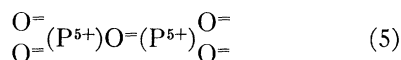
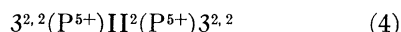
The internuclear distance in Na<sub>2</sub> (Fig. 1F) being only 15 percent larger than in Li<sub>2</sub> suggests that its formula is (Na<sup>+</sup>)II<sup>2</sup>(Na<sup>+</sup>), i.e., that  $n \neq 3$  as could be assumed by a schematic application of the Pauli principle to molecules.<sup>5</sup> This last result and the value  $n=1$  for two of the binding electrons in N<sub>2</sub> (outside the two *K* electron pairs) mean that an electron quantized with respect to the field of *two* cores can have a lower principal quantum number than the lowest it can assume when quantized with respect to only one of these cores. This is understandable since the strength of the field of two cores (N<sup>5+</sup>) is intermediate between that of the single core and a nucleus (Ne<sup>10+</sup>) with the same total charge.

We consider the symbols used in this paper for of 2.33Å and a binding energy of -7.5 ev. The experimental values for Na<sub>2</sub> (3.08Å; -10.9 ev) correspond better, as will be explained in a detailed paper, to these values than to the values (5.35Å; -3.9 ev) for point charges and  $n=3$ .

the quantum states of the molecules as provisional and subject to an extension including the angular momentum of the molecules. Thus, formula (3) does not imply that all eight electrons with  $n=II$  have the same energy, but the notation is sufficient to indicate that in respect to the external field this electronic shell deviates little from that of a noble gas and the field of  $(N^{5+})II^2(N^{5+})$  from that of a nucleus with a charge  $8+$ .

## 3.

From Fig. 1, one can see that the electronic shells of the  $P^{5+}$  cores ( $H$ ) would considerably overlap at the internuclear distance of the  $N^{5+}$  cores ( $C$ ). Thus,  $n=I$  appears to be improbable for  $P_2$ . If the lowest state of the valence electrons is  $n=II$ , the ten electrons of  $P_2$  can not form a closed noble gas shell.<sup>5a</sup> Eight electrons quantized with respect to both cores could have  $n=II$  and the two remaining  $n=III$ . However, the analogy (see V) between an electron pair and the oxygen ion  $O=$  makes formula (4), analogous to (5), which could be expected for a  $P_2O_5$  molecule, more probable.



In (4) the distinction is made between the  $II^2$  electrons quantized with respect to both  $P^{5+}$  cores (analogous to the "shared" electrons in the G. N. Lewis theory) and the four  $3^2$  electron pairs. The latter are analogous to the "unshared" electrons but, from the point of view of charge distribution, they must be considered as moving part of the time between both cores. Attempting to assign to electrons within molecules definite quantum states, it appears logical to consider those four pairs as quantized with respect to single cores and to assign to them the value  $n=III$  which they would have in the free  $P$  atom. In respect to motion, they differ from the  $II^8$  electrons of  $N_2$  in that they are considered as moving predominantly near the single cores.

Formulae (4) and (5) make it understandable that  $P_2$  and  $P_2O_5$  polymerize to  $P_4$  and  $P_4O_{10}$ ,

<sup>5a</sup> Another reason against a closed eight electron shell is the larger deviation of the axial field of the  $P^{5+}$  cores, as compared with the  $N^{5+}$  cores, from central symmetry.

respectively. In the single molecules 4/5 of the electron pairs or  $O=$  are unshared. In the polymers the  $P^{5+}$  cores are tetrahedrally arranged and six of the ten electron pairs or  $O=$  respectively are electrically bound by two cores (see V). On the other hand, in  $N_2$  the field of the cores is practically completely screened by the outer  $II^8$  electrons and cannot interact with electrons of other molecules.

## 4.

The distinction between quantization of electrons of diatomic molecules with respect to both or to single cores proves to be useful in considering the role the electrons play in the binding of the cores. The monohydrides can serve as an example.

According to the method of quantization proposed, hydrogen can be bonded in molecules only in two forms; either as a more or less

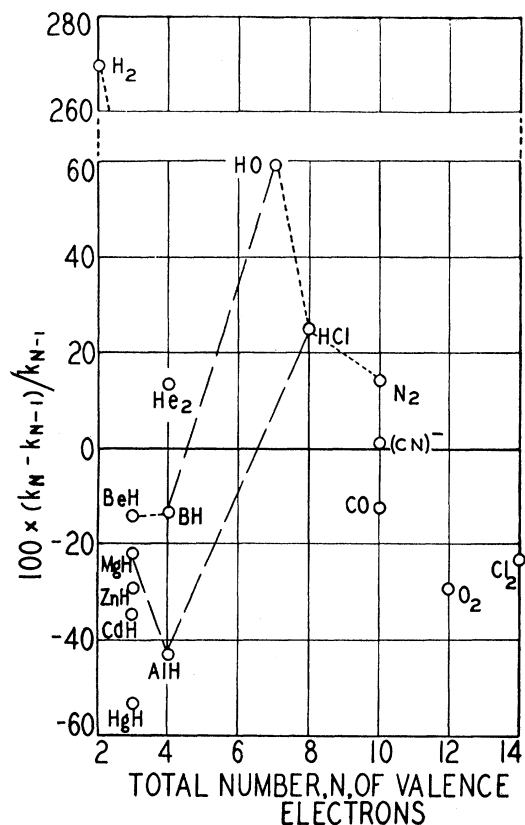


FIG. 2. Percent change in the force constant,  $k_{N-1}$ , on addition of the  $N$ th electron to a particle with  $N-1$  valence electrons.

deformed<sup>6</sup>  $H^-$  (in combination with electro-positive elements) or as a proton having a common shell with some other cores (of negative elements). It has been concluded (III, reference 4) from the discontinuity of the gradation of internuclear distances in monohydrides that the binding character of hydrogen changes, within the periods of the system, between BH and HC, AlH and HSi, TiH and HPb or near these places. Accordingly, one would formulate, e.g., HO as  $(H^+)II^7(O^{6+})$ , HCl as  $(H^+)III^8(Cl^{7+})$  and the hydrides of the first three groups as  $(M^+)(H^-)$ ,  $n^1(M^{3+})(H^-)$ ,  $n^2(M^{3+})(H^-)$ .<sup>7</sup>

## 5.

Figure 2 offers strong support for these formulations. It shows the relative change of the force constant  $k^8$  caused by the addition of an electron to singly charged positive ions.

The binding in the monohydrides containing  $H^-$  is due to its attraction by the positive charge of the core, which in hydrides of divalent and trivalent elements, e.g., in  $3^2(Al^{3+})(H^-)$ , is partially screened by the electrons quantized with respect to these cores. In the ion  $(AlH)^+$ , which can be formulated as  $3^1(Al^{3+})(H^-)$ , one of these screening electrons is eliminated; the binding should become stronger. Figure 2 confirms this expectation, the value  $100(k_N - k_{N-1})/k_{N-1}$  is negative for all listed monohydrides of divalent and trivalent elements, changing from  $-13.8$  for BH to  $-53.5$  for HgH.<sup>9</sup>

On the other side, the positive values of the ordinate for HO and HCl show that the seventh and eighth electrons increase the value of  $k$ ,

<sup>6</sup> A strong tightening of  $H^-$  in the LiH and NaH molecules is indicated in Fig. 1G by the considerable overlapping which undisturbed electronic shells of ions would have at the actual internuclear distances of these molecules.

<sup>7</sup> E.g., BH would be  $2^2(B^{3+})(H^-)$  or  $2^2(B^{3+})(H^+)1^2$ .

<sup>8</sup> The force constants  $k$  were derived from the frequencies at the minimum of the potential curves given by G. Herzberg (reference 2, see p. 105 and Table 36). The comparison of the internuclear distances of the ionized and neutral molecules leads throughout to the same result about the direction of the change in binding strength.

<sup>9</sup> The negative values for CO, O<sub>2</sub>, and Cl<sub>2</sub> have a different reason and will be discussed, as well as the case of  $(CN)^-$ , in a paper to follow.

which proves that they take part in the binding of the cores, and the same is true for H<sub>2</sub>, He<sub>2</sub>, and N<sub>2</sub>. That not only the  $N$ th electron but all electrons common to both cores in H<sub>2</sub>, HO, HCl, and N<sub>2</sub> participate in the binding is supported by the fact that the relative strengthening of the binding caused by addition of the  $N$ th electron is the larger the smaller the value of  $N$ . This is shown in the figure by the line connecting N<sub>2</sub>, HCl, and HO and its extrapolation to H<sub>2</sub>.

Thus, not only in H<sub>2</sub> and N<sub>2</sub> (see III) but also in HCl all valence electrons participate in the binding of the cores ( $H^+$  and  $Cl^{7+}$ , see I). This result cannot be brought into agreement with the usual formula  $H-Cl$  of the valence bond theory or with its electronic interpretation  $H:\ddot{C}l:$ , which assumes that only two electrons take part in the binding.

## 6.

As Fig. 2 shows, He<sub>2</sub> does not fit into the line connecting H<sub>2</sub>, HO, HCl, and N<sub>2</sub>. One would expect that the fourth electron of He<sub>2</sub> increases the  $k$  value of He<sub>2</sub><sup>+</sup> by about 180 percent, but in reality the increase is only 13 percent. This peculiar molecule He<sub>2</sub> has been found in the spectrum in spite of its instability with respect to two normal He atoms and on the basis of the Hund-Mulliken method it appears that its lowest observed state is not the ground state.<sup>10</sup> Our method suggests, for the lowest possible state of He<sub>2</sub> the formula  $1^1(He^{2+})I^2(He^{2+})1^1$ , for He<sub>2</sub><sup>+</sup> the formula  $1^1(He^{2+})I^2(He^{2+})$ . The formulae, in which the electrons quantized with respect to the single cores He<sup>2+</sup> are unpaired, agree with the fact that the number of unpaired electrons is two in He<sub>2</sub> and one in He<sub>2</sub><sup>+</sup> (see reference 2, p. 488). The relatively small contribution of the fourth electron of He<sub>2</sub> to the binding strength indicates that its motion brings it infrequently between the cores, which is not surprising for an "unshared" electron.

<sup>10</sup> See G. Herzberg, reference 2, p. 390 and F. L. Arnot and M. B. M'Ewen, Proc. Roy. Soc. A171, 106 (1939).