

Note on the Nature of Valence Forces

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Although several empirical rules connecting bond lengths and force constants exist¹ only few attempts have been made to derive such relations on a theoretical basis. However, a simple approximate formula can be obtained from classical-mechanical considerations as follows: Let us picture the valence force between two atoms "i" and "j" as a bundle of parallel arranged springs each of which has the same strength and modulus. A "single bond" may then be represented by a certain number of "unit" springs, a "double bond" by twice this number and so on. Assuming Hooke's law to be valid we must apply a force ΔK given by

$$\Delta K = C \cdot \frac{\Delta X}{d_{ij}}$$

in order to obtain the relative change in length, $\Delta X/d_{ij}$, where d_{ij} is the distance between the atoms and ΔX the displacement of say atom "i". If we have P_{ij} such springs side by side between the two atoms the force required will be

$$\Delta K = C \cdot \frac{\Delta X}{d_{ij}} \cdot P_{ij}$$

Dividing by ΔX we get the force constant, K_{ij} , and we may write:

$$\frac{K_{ij} \cdot d_{ij}}{P_{ij}} = C \quad (1)$$

Interpreting P_{ij} as the total bond order this relation may be expected to hold as long as we consider bonds between the same kind of atoms. Table 1 shows that — within the uncertainty inherent in the force constants as well as in the

Table 1.

Atom pair	Compound	Bond length	Bond order	Force constant	$\frac{K_{ij} \cdot d_{ij}}{P_{ij}}$	Mean value
C≡C	C ₂ H ₂	1.20 Å	3.0	15.7·10 ⁵	6.3·10 ⁻³	
C=C	C ₂ H ₄	1.33 »	2.11	9.6 »	6.0 »	
C...C	C ₆ H ₆	1.39 »	1.67	7.60 »	6.3 »	
C...C	C ₂ N ₂	1.38 »	1.46	6.24 »	5.9 »	
C—C	C ₂ H ₆	1.54 »	1.11	4.5 »	6.2 »	6.14 · 10 ⁻³
C≡N	C ₂ N ₂	1.15 »	2.5	16.6 »	7.6 »	
(C=N		1.30 »	2.0	12.1 »	7.85 » ¹	
C—N	CH ₃ NH ₂	1.47 »	1.0	5.0 »	7.35 »	
C—N	CH ₃ NC	1.47 »	1.0	5.5 »	8.1 »	
C...N	C ₂ N ₂	2.53 »	0.34	1.02 »	7.5 »	7.65 »
C≡O	CO	1.13 »	3.0	18.9 »	7.1 »	
C...O	CO ₂	1.16 »	2.2	14.12 »	7.4 »	
C=O	CH ₂ O	1.21 »	2.0	12.3 »	7.4 »	
C—O	CH ₃ OH	1.42 »	1.0	5.0 »	7.1 »	7.25 »
N≡N	N ₂	1.09 »	3.0	22.4 »	8.1 »	
N=N	N ₃ ⁻	1.24 »	2.0	11.7 »	7.3 »	
N...N	C ₂ N ₂	3.68 »	- 0.46	- 0.96 »	7.7 »	7.7 »

bond orders — this is a rather good approximation. It is an interesting point that (1) also seems to be valid for bonds between non adjacent atoms. Such forces are expected from the molecular orbital theory and may be computed for some simple molecules. In several cases of linear molecules it has been possible to obtain both bond order, interatomic distances, and force constants between "separated" atoms within the same molecule so that the validity of (1) could be tested. Some examples have been included in Table 1.

For carbon-carbon links Coulson² has derived a formula connecting the π -bond order, p , and the length, r_a , of an actual bond with those of the single and double carbon bonds and involving also the force constants K_s and K_d for the latter ones. Calling the lengths of a single and double bond s and d respectively his formula may be written

$$\frac{d \cdot K_d - r_a \cdot K_d}{r_a \cdot K_s - s \cdot K_s} = \frac{1-p}{p} \quad (2)$$

Table 2.

Atom pair	Compound	Bond length	Force constant	$K_{ij} \cdot d_{ij}$	Ionic refraction ³
HF	HF	0.92 Å	$9.7 \cdot 10^5$	$8.9 \cdot 10^{-3}$	2.20 cc
HO	H ₂ O	1.02 »	7.6 »	7.7 »	4.06 »
HCl	HCl	1.28 »	5.15 »	6.6 »	8.45 »
HBr	HBr	1.41 »	4.11 »	5.8 »	11.84 »
HS	H ₂ S	1.33 »	4.25 »	5.65 »	15.0 »
HSe	H ₂ Se	1.53 »	3.37 »	5.16 »	17.3 »
HJ	HJ	1.60 »	3.14 »	5.0 »	18.47 »
HN	(NH ₃)	1.01 »	6.86 »	6.9 »	(7) »
HC	(CH ₄)	1.09 »	5.45 »	6.0 »	(12) »

Let us apply our relation (1) to an actual (resonating) bond with π -bond order p and force constant K and let us first calculate the constant C from a single bond and next from a double bond. Then we get

$$\frac{K \cdot r_a}{1+p} = K_s \cdot s \quad \text{and} \quad \frac{K \cdot r_a}{1+p} = \frac{K_d \cdot d}{2}$$

From these two equations we obtain:

$$\frac{dK_d - r_a K}{r_a K - sK_s} = \frac{1-p}{p} \quad (3)$$

The similarity with Coulson's formula is striking and in fact (3) seems to give at least as good results as (2).

One might ask whether the constant C in (1) is the same for all atoms. That this is not the case is seen from the hydrogen halides in Table 2.

It is tempting to relate C to the polarizability of the halide ions in these cases. Imagine a proton approaching a big halide ion, then it induces an electric moment αE where E is the electrical field strength due to the proton at the centre of the halide ion and α is the polarizability. The increase in electrostatic energy can be shown to be $\frac{1}{2} \alpha E^2$. Hence a force

$$K = -\frac{\partial}{\partial x} (\frac{1}{2} \alpha E^2)$$

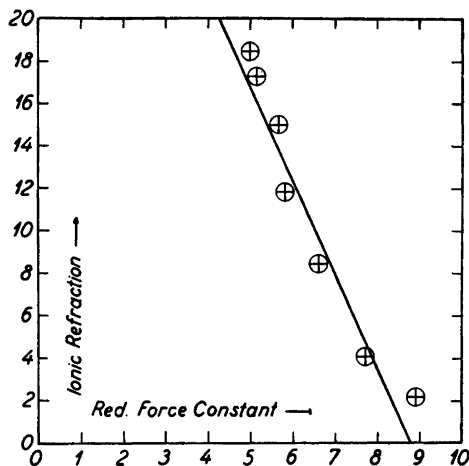


Fig. 1. Relation between "reduced force constant" (see text) and ionic refraction of the X-atom for some H-X-bonds (cp. Table 2).

will act on the proton and for a small displacement ΔX there will be an additional force

$$\Delta K = -\frac{\partial^2}{\partial x^2} \left(\frac{1}{2} \alpha E^2 \right) \Delta X$$

so that we get a contribution to the force constant K_{ij} of

$$\Delta K_{ij} = -\frac{1}{2} \alpha \frac{\partial^2}{\partial x^2} E^2$$

If we assume $\frac{\partial^2 E^2}{\partial x^2}$ to be approximately the same for the different atoms or ions we should expect the C 's to be roughly proportional to the ionic refractions $A = \frac{4\pi N}{3} \alpha$. The graph (Fig. 1) shows that this really is the case for a series of bonds involving hydrogen, and in fact we can put

$$\frac{K_{ij} \cdot d_{ij}}{P_{ij}} = 8.8 - 0.23 A_i \quad (4)$$

for compounds of this type. Unfortunately the ionic refractions are not known for carbon or nitrogen but if we postulate the validity of (4) also for CH and NH we obtain $A_C \approx 12$ and $A_N \approx 7$.

Relation (1) has already proved to be useful in problems where one wants the bond order for a special bond and the pure theoretical calculation cannot be carried through.

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