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The Bond Number Relationship for the O—H...O Systems

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The bond number idea may be derived from the Morse function. The same may be done for different potential functions, for example Buckingham or Rydberg potentials. The agreement between the values of the bond number obtained from different definitions is excellent. The relation $R_{o\ldots o}$ *vs.* r_{OH} may be obtained from the definition of the bond number.

INTRODUCTION

The distance criterion between bonds and nonbonded contacts may not be so sharp.[1] Following Pauling,[2,3] the length of the bond r_i is related to the bond number n_i by

$$r_i - r_o = \Delta r_i = -c \log n_i \tag{1}$$

where c is an empirical constant and r_o is the reference bond length of a single bond.

The idea based on eq. (1) is useful for considerations concerning crystal chemistry and stereochemistry.[4-7] Bürgi has pointed out that apart from relation (1) there are various other relationships between structural parameters and the value of the bond number[4]. For example, he has found for tetrahedral fragments of molecules showing approximate C_{3v}-symmetry that the relations of the bond numbers may be expressed in terms of bond angles.[4]

Appart from the relation (1), Pauling postulated that the sum of all bonds around the central atom is constant.[2] Pauling's postulate has been supported by latter investigations.[1,4,8] For example, the relation for triatomic systems has been used[4]

$$n_i + n_j = 1 \tag{2}$$

where n_i, n_j = the bond numbers.

The idea mentioned above and based on the bond order conservation was first introduced by Johnston[9] and has been used by Dunitz[1] for I—I...I, S—S...S and O—H...O systems.

From eqs. (1) and (2) one obtains

$$10^{-\Delta r_i/c} + 10^{-\Delta r_j/c} = 1. \tag{3}$$

Constant c may be obtained for the appropriate triatomic system from relation (1) for $r_i = r_{1/2}$

$$r_{1/2} - r_o = - c \log 1/2 \tag{4}$$

where $r_{1/2}$ is the length of the bond in the triatomic system with equal bond lengths.

Very recently, a modification of the Morse equation has been shown to yield several relationships among energies, bond lengths and force constants.[10] The authors have shown that the other types of interatomic potential functions may be modified in connection with the bond number (the general inverse power potential has been considered).

THE MODEL

It has been pointed out that the logarithmic relation (1) is a consequences of the exponential character of interatomic forces.[2] Dunitz[1] has derived eq. (1) from the Morse function:

$$V(r_i - r_o) = D\{1 - \exp[- b(r_i - r_c)]\}^2. \tag{5}$$

He has introduced the modified function of (5):

$$V(\Delta r_i) = D[1 - 2 n_i \exp(- b \Delta r_i) + \exp(-2 b \Delta r_i)], \tag{6}$$

where $\Delta r_i = r_i - r_o$, and the attractive term has been multiplied by n_i.

The first derivative of $V(\Delta r_i)$ is equal to zero when:

$$\Delta r_i = - (1/b) \ln n_i. \tag{7}$$

One can replace $2.3/b$ by c to obtain the known Pauling's relation.

The bond number can be derived from the Morse function, but it is well known that the other types of the function may describe the bond, *i. e.*, Rydberg's function[11] or Varshni's potential,[12] the other functions describe the atom-atom contacts, *i. e.* the Buckingham potential function or the Lennard-Jones potential.

The aim of this section is to show how the bond number can be derived from other types of the function than Morse, *i. e.* Buckingham and Varshni potentials.

For example, the Varshni potential is as follows:

$$V = D\{1 - (r_o/r_i) \exp[- \beta (r_i^2 - r_o^2)]\}^2 \tag{8}$$

where: D = dissociation energy, r_i = bond length, r_o = bond length for the minimal value of V, and β = constant.

Following Dunitz' treatment of the Morse function[1] one can introduce n_i (the bond number) into the attracive term of the energy given by eq. (8):

$$V = D\{1 - 2n_i (r_o/r_i) \exp[- \beta (r_i^2 - r_o^2)] + (r_o^2/r_i^2) \exp[- 2 \beta (r_i^2 - r_o^2)]\}. \tag{9}$$

Using the condition $dV/dr = 0$, one obtains:

$$n_i = (a/r_i) \exp(- \beta r_i^2) \tag{10}$$

where a and β are constants.

So we have the new relationship for the bond number. Constants a and β may be obtained from the relations:

$$(a/r_o)\exp(-\beta r_o^2) = 1 \quad \text{and} \quad (a/r_{1/2})\exp(-\beta r_{1/2}^2) = 0.5. \tag{11}$$

The values of r_o and $r_{1/2}$ are usually known from the experiment. The appropriate relation for the bond number may be obtained also from the Buckingham type of the function.

$$V = A\exp(-\alpha r_i) - B/r_i^6 \tag{12}$$

where: A, α, B are the constants and r_i is the bond length.

B as a coefficient of the attractive term of eq. (12) may be treated as the bond number, so it is possible to obtain:

$$n_i = C r_i^7 \exp(-\alpha r_i), \tag{13}$$

where C and α are constants (C is expressed in terms of α and A). C and α may be obtained from the relation similar to eq. (11). The last case considered here is the Rydberg potential.[11] In the way described for the above presented functions one can obtain the definition of the bond number from the Rydberg potential's modification (n_i in exponential term):

$$V = D[1 + a(r_i - r_o)]\exp(-n_i a(r_i - r_o)) \tag{14}$$

And the expression for the bond number:

$$n_i = 1/(b + g r_i) \tag{15}$$

where: b and g are constants which may be obtained from the relation similar to eq. (11).

DISCUSSION

We have four definitions of the bond number:

$n_M = A\,10^{-r/c}$ which can be derived from the Morse function[1] (A, c — constants),

$n_V = a/r\exp(-\beta r^2)$ the relation derived from the Varshni function,[12]

$n_B = C r^7 \exp(-\alpha r)$ the bond number derived from the Buckingham potential and

$n_R = 1/(b + gr)$ from the Rydberg potential,[11]

where we have r instead of r_i and n_M, n_V, n_B, n_R instead of n_i to indicate the function from which definitions of the bond numbers have been derived. For all cases the constant values can be obtained from the knowledge of r_o and $r_{1/2}$.

In order to compare these four treatments of the bond number it will be useful to consider the O—H...O hydrogen bond systems. For the O—H...O systems $r_o = 0.957$ Å, $r_{1/2} = 1.22$ Å (averaged value from data listed by Speakman[13]).

Table I presents the values of n_i for different lengths of bond O—H; these values for different treatments of n_i (from Morse, Buckingham, Varshni, Rydberg potentials) agree to a surprising extent. Only the values obtained from the Rydberg function differ a little from the others.

TABLE I

*Values of the Bond Number for Different r_{OH} Bond Lengths**

r_{OH} length (in Å)	Morse	Varshni	Buckingham	Rydberg
0.957	1	1	1	1
1	0.8929	0.8957	0.9198	0.8595
1.05	0.7826	0.7869	0.8212	0.7388
1.1	0.6860	0.6903	0.7217	0.6478
1.15	0.6013	0.6043	0.6250	0.5768
1.2	0.5271	0.5280	0.5342	0.5198
1.22	0.5	0.5	0.5	0.5
1.25	0.4620	0.4603	0.4510	0.4730
1.3	0.4050	0.4004	0.3767	0.4340
1.35	0.3550	0.3474	0.3112	0.4009
1.4	0.3111	0.3007	0.2549	0.3725
1.45	0.2727	0.2595	0.2066	0.3479
1.5	0.2391	0.2234	0.1662	0.3263
1.55	0.2095	0.1917	0.1326	0.3072
1.6	0.1837	0.1641	0.1052	0.2903
1.65	0.1610	0.1400	0.0827	0.2751
1.7	0.1411	0.1191	0.0647	0.2614

* The definition of the bond number has been derived from four cases of atom-atom potentials (Morse, Varshni, Buckingham and Rydberg potentials).

TABLE II

The $R_{O\ldots O}$ vs, r_{OH} *Relations Obtained from Various Definitions of the Bond Number (All Values in Å)*

$R_{o\ldots o}$	n_M	n_V	n_B	n_R	H-bond model*
2.45	1.156	1.160	1.172	1.174	1.151
2.50	1.082	1.091	1.083	1.121	1.115
2.55	1.047	1.058	1.046	1.096	1.079
2.60	1.025	1.036	1.023	1.080	1.051
2.65	1.009	1.020	1.007	1.068	1.033
2.70	0.997	1.008	0.995	1.058	1.019
2.75	0.988	0.998	0.987	1.050	1.007
2.80	0.981	0.991	0.980	1.044	0.998

* The values obtained by Lippincott and Schroeder.[14]

Using relation (3) for n_M, n_V, n_B, and n_R one can obtain four equations of the form:

$$A\,10^{-r/c} + A\,10^{-(R-r)/c} = 1,$$

$$(a/r)\exp(-\beta r^2) + [a/(R-r)]\exp[-\beta(R-r)^2] = 1,$$

$$C r^7 \exp(-\alpha r) + C(R-r)^7 \exp[-\alpha(R-r)] = 1,$$

$$1/(b + g r) + 1/(b + g(R-r)) = 1. \qquad (16)$$

After applying the method of successive aproximations, one can obtain the values of r for different values of the length of O..O distance (R) (the last equation may be solved exactly). The four treatments for the bond number agree well (Table I). The values of n_i derived from Morse or Varshni potentials are practically equivalent.

The four curves $r = f(R)$ — Table II agree well with the values obtained by Lippincott and Schroeder[14] from their hydrogen bond model and agree with the experimental data.[15] The curve of Ichikawa[15] is in agreement with our models and data obtained from the traditional definition of the bond number.[2] The results show that eqs. (16) may be useful for the finding of the position of hydrogen atom in the O—H...O system. It is useful for the data obtained from X-ray diffraction measurements where the position of H-atom obtained may not be accurate.

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SAŽETAK

Relacija za težinu veze sustava O—H...O

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Ideja težine veze može se izvesti iz Morseove funkcije. Isto se može provesti za različite funkcije potencijala, na primjer, za Buckinghamove ili Rydbergove potencijale. Slaganje između vrijednosti za težinu veza dobivenih s pomoću različitih modela jest dobro. Odnos $R_{O...O}$ prema r_{OH} može se dobiti iz definicije težine veze.