

A new atomic deformation constraint rule and its application

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Abstract

This paper presents a new rule to constrain the change of atomic states in heteronuclear diatomic molecules. The relationship between atomic hardness and charge of atom can be derived by this rule. This model has one free parameter which was fitted by the graphical method. A new equation is obtained for the calculation of the potential energy of diatomic molecules using the hardness and configuration parameters of atoms. The calculation results show that the constraint rule can be applied to heteronuclear diatomic molecular systems and the calculated dissociation energy is in good agreement with the known experimental values.

1. INTRODUCTION

The method of deformed atoms in the homonuclear diatom molecules has been proposed in the preceding paper[1]. Using the theory of atomic deformation model potential, study of behavior of the energy near the local maximum point shows that critical phenomena can take place when some parameter in the deformation model of the system is varied. An interesting result is that the paper presents a new equation of state of the atom. Each atom in a homonuclear diatomic molecule is described by three parameters a , b and ζ_0 and the atoms are the most stable when the value $a\zeta_0/b$ is constant(2.601824). The energy of a system of two atoms depends on the exchange charge between them and the limits of exchange charge are determined by position of critical point of the potential energy curve. Estimating the critical parameter is very important in determining if a homonuclear diatomic molecule is stable or not.

The aim of this paper is to develop the theory of atomic deformation model potential for calculating critical parameters of heteronuclear diatomic molecules. A method to determine the critical point of potential curve with choosing atomic charge under the control of the constraint rule is presented. In particular, calculating the atomic charges by this method gives results which are in accordance with the intuitive graphic way.

2. EXCHANGE CHARGE MODEL

2.1 Mathematical Model

The ability of an atom in homonuclear diatomic molecules(A_2) to attract bonding electron to itself is different in a heteronuclear diatomic molecule(AB). If it is energetically favorable for the valence electron to be closer to the B atomic nucleus than the A atom, the B atom assumes a slightly negative character and the A atom a slightly positive character: $A^{+\delta}B^{-\delta}$, where δ is the charge of the atomic particles. Like the homonuclear diatom molecules also, the heteronuclear diatom molecule may be represented by two structures and the actual diatomic molecule is a sort of hybrid.

$$A + B = \frac{1}{2}[A^{+\delta+x}B^{-\delta-x} + A^{+\delta-x}B^{-\delta+x}] \quad (1)$$

Formal charge x is a mathematical construct that is useful to understand the behavior of atomic particle. The process of particle $A^{+\delta}$ losing electrons is accompanied by some alteration in hardness

and configuration of the particle and $A^{+\delta+x}$ hardness is defined as

$$\begin{aligned}\eta_A^+ &= \eta_A^+(x) \\ &= a_A + b_A(\delta + x)\end{aligned}\quad (2)$$

where a_A and b_A are parameters for the A atom isoelectronic series, the parameters a and b are different for different atoms. The deformation function, $\varepsilon_A(x)$, is given by [1]

$$\begin{aligned}\varepsilon_A^+(x) &= \frac{(a_A + b_A\delta)v_{A_0^+}}{b_A} \left\{ K_0\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta\right) I_0\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta + \zeta_A x\right) \right. \\ &\quad \left. - I_0\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta\right) K_0\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta + \zeta_A x\right) \right\}\end{aligned}\quad (3)$$

where $v_{A_0^+}$ is the initial velocity of the particle $A^{+\delta}$, and ζ_A is an undetermined parameter. The Bessel functions $I_n(x)$ and $K_n(x)$ are defined in Ref[2,3,4]

therefore

$$\begin{aligned}\frac{d^2\varepsilon_A^+(x)}{dx^2} &= \frac{(a_A + b_A\delta)\zeta_A^2 v_{A_0^+}}{b_A} \left\{ K_0\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta\right) \left[I_2\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta + \zeta_A x\right) + \frac{1}{x} I_1\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta + \zeta_A x\right) \right] \right. \\ &\quad \left. + I_0\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta\right) \left[\frac{1}{x} K_1\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta + \zeta_A x\right) - K_2\left(\frac{a_A\zeta_A}{b_A} + \zeta_A\delta + \zeta_A x\right) \right] \right\}\end{aligned}\quad (4)$$

taking into account the above functions, the potential energy $E_{A^{+\delta+x}}(x)$ is defined as

$$E_{A^{+\delta+x}}(x) = \eta_A^+(x) \frac{d^2\varepsilon_A^+(x)}{dx^2} \varepsilon_A^+(x) \quad (5)$$

the derivation of $E_{B^{-\delta-x}}(x)$ is analogous to $E_{A^{+\delta+x}}(x)$.

$$\begin{aligned}\eta_B^- &= \eta_B^-(-x) \\ &= a_B + b_B(-\delta - x)\end{aligned}\quad (6)$$

$$\begin{aligned}\varepsilon_B^-(-x) &= \frac{(a_B - b_B\delta)v_{B_0^-}}{b_B} \left\{ K_0\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta\right) I_0\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta - \zeta_B x\right) \right. \\ &\quad \left. - I_0\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta\right) K_0\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta - \zeta_B x\right) \right\}\end{aligned}\quad (7)$$

where $v_{B_0^-}$ is the initial velocity of the particle $B^{-\delta}$, and ζ_B is an undetermined parameter.

$$\begin{aligned}\frac{d^2\varepsilon_B^-(-x)}{dx^2} &= \frac{(a_B - b_B\delta)\zeta_B^2 v_{B_0^-}}{b_B} \left\{ K_0\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta\right) \left[I_2\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta - \zeta_B x\right) + \frac{1}{x} I_1\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta - \zeta_B x\right) \right] \right. \\ &\quad \left. + I_0\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta\right) \left[\frac{1}{x} K_1\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta - \zeta_B x\right) - K_2\left(\frac{a_B\zeta_B}{b_B} - \zeta_B\delta - \zeta_B x\right) \right] \right\}\end{aligned}\quad (8)$$

the potential energy $E_{B^{-\delta-x}}(x)$ is defined as

$$E_{B^{-\delta-x}}(x) = -\eta_B^-(x) \frac{d^2 \varepsilon_B^-(-x)}{dx^2} \varepsilon_B^-(-x) \quad (9)$$

Furthermore, $E_{A^{+\delta-x}}(x)$ and $E_{B^{-\delta+x}}(x)$ can be written as

$$E_{A^{+\delta-x}}(x) = -\eta_A^-(x) \frac{d^2 \varepsilon_A^-(-x)}{dx^2} \varepsilon_A^-(-x) \quad (10)$$

$$E_{B^{-\delta+x}}(x) = \eta_B^+(x) \frac{d^2 \varepsilon_B^+(x)}{dx^2} \varepsilon_B^+(x) \quad (11)$$

An energy formula for the reaction equation(1) is given

$$E(x) = \frac{1}{2} [E_{A^{+\delta+x}}(x) + E_{B^{-\delta-x}}(x) + E_{A^{+\delta-x}}(x) + E_{B^{-\delta+x}}(x)] \quad (12)$$

In most cases atoms will be unstable on their own and they have to bond with others and exchange charge for stability. The energy of a system of homonuclear diatomic molecules depend on the exchange charge between them and the potential energy minimum occur at $\zeta = \zeta_0$. The stable atoms is found to obey the equation of state given by[1]

$$\frac{a\zeta_0}{b} = 2.601824 \quad (13)$$

When the atom is in a different environment, the deformation parameters and the hardness coefficient should be changed. Using Eq.(13), it is easy to obtain the state equation of unlike atoms

$$\zeta\left(\frac{a}{b} \pm \delta\right) = 2.601824 \quad (14)$$

The atom B is relatively negatively charged and the atom A is given a partial positive charge, so that the parameters ζ_A and ζ_B can be given by

$$\zeta_A = \frac{2.601824b_A}{a_A + b_A\delta} \quad (15)$$

$$\zeta_B = \frac{2.601824b_B}{a_B - b_B\delta} \quad (16)$$

the Eqs.(15)and(16) may be inserted in Eq.(12). In this case, the problem is to find the solution of an equation with a variable(x) and a free parameter(δ).

$$E = E(x, \delta) \quad (17)$$

2.2 Methods of Calculation

The parameters a and b were obtained in Ref. [1] for a few atoms, their exact value depends on the total number of points in the fit and they are most reliable for the first three rows in the periodic table[5,6]. In homonuclear diatomic molecules, the initial reaction velocity depends on the ground state electron configuration of the atom and an empirical formula is proposed to estimate the v_0

$$v_0 = 2^{\ell/2} \cdot (N - \ell) \cdot \frac{J^{1/2}}{P^{1/2}} \quad (18)$$

where

$$J = \left(\frac{d+V}{2}\right)^{1/2} + (dV)^{3-N} + (d-1) \left\{ \frac{2d}{d+V} + \frac{(-1)^V d}{NV} \cot\left(\frac{(2V-3)\pi}{2N}\right) \right\} + \left(\frac{d-V}{4}\right) \tan\left(\frac{5\pi}{2N}\right) \quad (19)$$

and

$$P = 2^{(\ell-1)\Gamma(N)} N^{(1-\ell)(N+1)/2} (N + 2^{N-1}) \quad (20)$$

$\Gamma()$ is the Gamma function, N is the principal quantum numbers, ℓ is the azimuthal quantum numbers, d are unpaired electrons of the ground state electron outside the nucleus and V are empty slots in its valence electron orbits.

In heteronuclear diatomic molecules, the initial velocity of an atomic particle related not only to the structure of electrons that an atom possesses but also to the particle charge. The initial velocity of the atomic particle can be expressed as

$$v_{A_0^+} = v_{A_0} \left(\frac{d_B}{d_A}\right)^{\frac{d_A-1}{2}} + \lambda_A \delta^{1/6} \quad (21)$$

$$v_{B_0^-} = v_{B_0} \left(\frac{d_A}{d_B}\right)^{\frac{d_B-1}{2}} - \lambda_B \delta^{1/6} \quad (22)$$

where v_{A_0} and v_{B_0} are the initial velocity of the atom A and B, respectively. λ_A and λ_B are given by

$$\lambda_A = \left(\frac{V_A + d_A}{2d_A}\right) \left\{ \left(\frac{1}{N_A}\right)^{1-\ell_A} \theta(i) + \left(\frac{\Gamma(N_A - \ell_A)}{V_B^{1-\ell_A}}\right) 4^{\theta(m) \cos(\ell_B+1)\pi} \right\} \quad (23)$$

$$\theta(i) = \begin{cases} 1, & i = \frac{d_A}{N_A} \neq 1 \\ 0, & i = \frac{d_A}{N_A} = 1 \end{cases} \quad (24)$$

$$\theta(m) = \begin{cases} 1, & m = \frac{V_A N_A N_B}{d_A(N_A + N_B)} \neq 1 \\ 0, & m = \frac{V_A N_A N_B}{d_A(N_A + N_B)} = 1 \end{cases} \quad (25)$$

$$\lambda_B = \left(\frac{V_A + d_A}{2d_B} \right)^{\frac{d_A \Gamma(V_A)}{2V_A} - \frac{1}{2}} \left\{ \frac{(N_B - 1)^{\ell_B}}{\Gamma(2 + d_B - d_A)} \cdot 4^{\theta(t) + \sin(\frac{N_B + \ell_B}{N_A - \ell_A})\pi} \right. \\ \left. + \frac{\Gamma(N_B) - 1}{N_B - \ell_B} \cdot \left(\frac{3}{4} \right)^{\theta(s)} \cdot \left[\frac{2d_A}{V_A} + (N_A - 1)(V_A - V_B)^2 + \sin\left(\frac{d_A}{d_B}\right)\pi \right]^{\ell_A} \right\} \quad (26)$$

$$\theta(t) = \begin{cases} 1, & t = \frac{N_B + \ell_B}{N_A - \ell_A} \text{ if } t \text{ is even} \\ 0, & t = \frac{N_B + \ell_B}{N_A - \ell_A} \text{ if } t \text{ is odd} \end{cases} \quad (27)$$

$$\theta(s) = \begin{cases} 1, & s = \frac{N_B}{N_A} = \frac{3}{2} \\ 0, & s = \frac{N_B}{N_A} \neq \frac{3}{2} \end{cases} \quad (28)$$

The values of v_{A_0} , v_{B_0} , λ_A and λ_B (dimensionless) of some molecules are given in Table I.

TABLE I. The values of v_{A_0} , v_{B_0} , λ_A and λ_B (dimensionless) of some molecules

$A^{+\delta}B^{-\delta}$	v_{A_0}	v_{B_0}	λ_A	λ_B
HLi	1.4142	1.1892	0.2500	4.0000
HF	1.4142	1.0000	4.0000	1.0000
HO	1.4142	1.8593	2.0000	0.5000
HS	1.4142	2.1358	2.0000	4.5000
HCl	1.4142	1.5119	4.0000	8.5000
FCl	1.0000	1.5119	5.0000	8.7500
OS	1.8593	2.1358	4.0000	8.7500
OF	1.8593	1.0000	1.0000	1.0000
OCl	1.8593	1.5119	4.0000	9.1250
SCl	2.1358	1.5119	5.0000	9.5000
NO	2.6203	1.8593	2.0000	1.2247
CO	2.2526	1.8593	6.0000	1.5000
CS	2.2526	2.1358	7.5000	14.8125
FS	1.0000	2.1358	5.0000	5.5000
NaF	1.1892	1.0000	8.3333	0.2500
LiNa	1.1892	1.0690	0.7500	0.5000

Energy calculation is carried out according to the following steps: (1) $I_n(x)$ and $K_n(x)$ are given in the form of series, one obtain an approximation $I_n(x)$ and $K_n(x)$ by truncating the series at $2k+n=8$, thus $I_n(x)$ and $K_n(x)$ can be determined at x . (2) The potential $E(x, \delta)$ is plotted as

a function of x by choosing $\delta = \delta_0$, where δ_0 is constants one can manipulate. Now one can investigate functions of the form $E(x)$ by changing the parameter δ and observing the numbers and position of critical points of the graph. Substituting $\delta = \delta_0$ into Eq.(17), the potential energy curves of heteronuclear diatomic molecular were determined by keeping the local maximum point of the graph on the x axis. (3) The potential energy function $E(x)$ with $x > 0$ has a local minimum at $x = x_0$ and a local maximum at $x = x_e$, x_e is the limit of two atomic charge exchanges. At this point, the curve has a slope of zero with $E(x_e) = 0$ and the molecular dissociation.

3. RESULTS

Now the potential energy can be calculated using Eq.(17). The correlations of the particle charge and the position of critical points of the graph can be clearly exhibited. Figure.1 shown a potential energy curve for HF, with $\delta = \delta_0 = 0.00009585$ and the graph of $E(x)$ vs. x has a local maximum point on x axis. The energy of the bond can be calculated from the dimensionless well depth($D=116.810$). The potential energy curve is plummeting on the right side of the local maximum point($x_e = 0.75$) and to fall into a bottomless bit. This means that the limit of the charge exchange can be determined by the position of the critical point.

By similar reasoning, the energy of a system of two heteronuclear atoms depends on the exchange charge between them, the potential energy minimum occurs at exchange charge $x = x_0$, well depth $D = -E(x_0)$, the coordinates of the local maximum point is $(x_e, 0)$. Table II shows the exchange charge x_0 and x_e , the parameters of the potential energy Eq.(17) and calculated the depth of the well for the various heteronuclear diatomic molecules.

TABLE II. Parameters δ_0 , exchange charge (x_0, x_e) and well depth D

$A^{+\delta}B^{-\delta}$	δ_0	x_0	x_e	D
HLi	0.00006485	0.54	0.75	48.423
HF	0.00009585	0.54	0.75	116.810
HO	0.00030840	0.54	0.75	88.028
HS	0.00004842	0.54	0.75	72.511
HCl	0.00000907	0.54	0.75	88.510
FCl	0.00001670	1.56	2.15	53.397
OS	0.00007304	1.39	1.92	105.910
OF	0.00077760	1.40	1.93	45.302
OCl	0.00001325	1.39	1.92	54.761
SCl	0.00001147	1.91	2.64	49.565
NO	0.00045000	1.37	1.89	129.280
CO	0.00078465	1.17	1.63	220.560
CS	0.00002278	1.17	1.62	146.130
FS	0.00009688	1.56	2.15	71.422
NaF	0.00069848	1.37	1.89	97.796
LiNa	0.00100851	0.75	1.04	17.719

Precise experimental dissociation energy data have been obtained for these molecules in the above table II[7]. The well depth (D) is linearly related to the experimental dissociation energy (E_{exp}), the regression equation with the corresponding standard deviation (SD) and correlation coefficient (R) values are given in Eq. (29).

$$E_{exp} = -0.26634 + 4.8816D (R = 0.999982, SD = 1.516) \quad (29)$$

Calculated and experimental data of dissociation energy are given in Table III. The calculated bond energy is in good agreement with the available experimental data.

TABLE III. Calculated and experimental data of dissociation energy for various heteronuclear diatomic molecules (kJ/mol)

Molecule	$E_{calc.}$	$E_{exp.}^a$
HLi	236.115	238.039±0.006
HF	569.953	569.68±0.011
HO	429.451	429.91±0.29
HS	353.703	353.57±0.30
HCl	431.804	431.361±0.013
FCI	260.396	260.83±0
OS	516.744	517.90±0.05
OF	220.880	220±0
OCI	267.055	267.47±0.08
SCI	241.690	241.8±0
NO	630.827	631.62±0.18
CO	1076.419	1076.38±0.67
CS	713.082	713.3±1.2
FS	348.387	343.5±6.7
NaF	477.135	477.3±0
LiNa	86.231	87.181±0.001

^a Come from Reference[7].

Note that F and Cl are form $F^{\delta+}Cl^{\delta-}$. If it is only observation of atomic charge that the result is different from Pauling's method. On the Pauling scale, fluorine is the most electronegative (=3.98)[8]. But the bonding mechanisms between atoms are closely related to the structure of the atoms themselves. According to the constraint rule, the process of atom losing or gaining electrons is accompanied by some alteration in configuration of atom, heteronuclear atoms form charged particles so that value a/b close to each other and the atom attempts to attain a more stable configuration. The ratio between λ_{Cl} to λ_F is 1.75 and Cl atomic configuration has a greater change, the deformation of the H atom in the HF is significantly larger than in the HCl. The H atom possess a positive charge in the HLi, but the Li atom has a larger shape change($\lambda_{Li}/\lambda_H = 16$).

It is probably not enough to understand the electronegativity only from the atomic charge and the calculation results suggest that the atomic configuration has an effect on the bond strength.

4. CONCLUSION

The atom is considered as a whole, the state of an atom in heteronuclear diatomic molecules can be described by four different parameters: a , b , ζ_0 and δ and the relationship between them can then be written as: $\zeta(\frac{a}{b} \pm \delta) = 2.601824$. The atom state equation is used to obtain the critical properties of the system of two atoms. By investigating the behaviour of exchange charge as δ varies, one can see clearly from Figure 1 that there is a vertical jump of potential energy at δ_0 and the dissociation of the diatomic molecule. The partial charges of atoms in molecules are calculated with the help of derived equations. The calculation results show that the new constraint relation can be applied to heteronuclear diatomic molecular systems and the atomic deformation potential model provides a powerful tool to study molecular stability as a function of the exchange charge.

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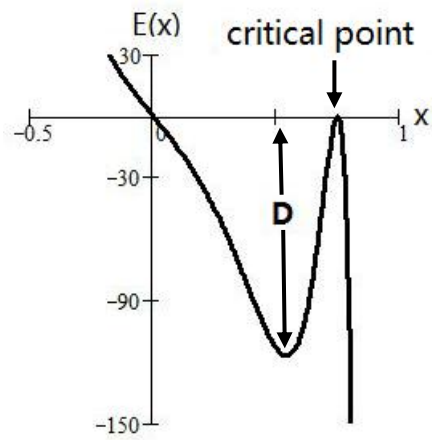


FIG. 1. Potential energy curves for HF , the curves represent the results of potential energy as a function of exchange charge x , the well depth D indicating the bond energy.