The three-center electrostatic model of diatomic bonds

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Abstract

In this paper, a three-center electrostatic model of diatomic bonds was put forward, as well as four physical parameter expressions of effective bonding charges, which support this model. Thus, a semi-empirical method, used to quantitatively study some physical chemistry phenomena, was raised. With the upper method in the article, many theoretical formulas were deduced for such important physical parameters as bond moment, force constant, field gradient and nonlinear optical coefficient of crystals. The available calculated values of every physical parameter basically conformed to its measured magnitude on the condition that parameters were nonadjustable.

Keywords: Diatomic bond; Effective bonding charge; Bond moment; Force constant; Field gradient

1. Introduction

By discovering the relation between wave mechanics and classical electrostatic mechanics in the system consisting of nucleus and electrons, Hellmann–Feynman theorem made it possible for Coulomb’s Law to be used to analyze this molecular system on a new basis, that was to say, extra-nuclear electrons distributed themselves with cloud shapes according to Shletingel formula. Many persons devoted themselves to construct molecular models with the help of this theory. For example, Berlin built a electrostatic model of diatomic molecules [1]; Bader and his cooperators drew a contour graph about constant of single electronic difference density of diatomic molecule [2]. It was testified that, during the formation of chemical bonds, electron cloud would aggregate among nucleus and deviate in one direction in molecules of different kernels. However, as Berlin said, this achievement was qualitative in essence with the main purpose of describing the states of chemically bonding [1]. It could never be used to extensively and quantitatively solve some physical and chemical questions, especially to those molecules containing heavy elements.

In his electrostatic force theory, Nakatsuji proposed a three-center model [3], which was successful in explaining molecular shapes. But, as a concise and qualitative treating method was not obtained, its application was largely limited.

In this paper, a three-center electrostatic model of diatomic bonds was put forward and Hellmann–Feynman theory was also employed to gain several expressions of physical parameters. Moreover, some theoretical formulas of important physical constants were acquired; efforts were paid to provide theoretical evidence for illuminating some physical and chemical phenomena and exploring new materials.

2. The three-center electrostatic model of diatomic bonds and several basic expressions of physical parameters

‘Every chemical process could be defined as a chemical absorbing and repelling’. If external condition (such as heat, light, electricity, magnetism and sound) permitted, a strong chemical absorbing and repelling would always generate a chemical combination of two atoms A, B. The bonding process could be divided into three steps. First, when the inter-nuclear distance of atom A and B reduced from infinity to radius of action, the bonding electron clouds began to overlap and contract as absorption exceeded exclusion,
which was caused by the diatomic sucking; and when the distance was equal to the sum value of covalent radii of A and B, the homo-polar overlapping and contracting ended. The charge gravity center of this overlapping domain was located at C point (Fig. 1), the jointing edge of covalent radii of A and B. Secondly, if the electrostatic forces at C point, caused by effective nuclear charges of A and B, were unequal, the core point of negative charges would migrate towards B, which had a higher attractive power. So B was partially negatively charged. On the other hand, because the shielding parameters increased, the effective nuclear charges of B were decreased and the attractive force of B shielding parameters increased, the effective nuclear charges of A and B, were partially negatively charged. On the other hand, because the shielding parameters increased, the effective nuclear charges of B were decreased and the attractive force of B also reduced; at the same time, however, A was taking opposite changes. When the gravity site of negative charges moved to point C', A had the same electrostatic force with B and electrons 1 and 2, could be written as follows:

$$\begin{align*}
H_{AB} &= -\frac{1}{2}(P_1^2 + P_2^2) - \frac{Z_A^*}{r_{A1}} - \frac{Z_B^*}{r_{B1}} - \frac{Z_A^*}{r_{A2}} - \frac{Z_B^*}{r_{B2}} \\
&\quad + \frac{1}{r_{12}} + \frac{Z_A^* Z_B^*}{R_{AB}} \tag{1}
\end{align*}$$

$Z_A^*$ and $Z_B^*$ were the effective nuclear charges of A and B, respectively. As H–F theorem was applied, the two nuclei of A and B met the following equations:

$$\begin{align*}
F_A &= -\nabla_A E = -\nabla_A (\psi | H_{AB} | \psi) = -\langle \psi | \nabla_A H_{AB} | \psi \rangle = 0, \\
F_B &= -\nabla_B E = -\nabla_B (\psi | H_{AB} | \psi) = -\langle \psi | \nabla_B H_{AB} | \psi \rangle = 0
\end{align*} \tag{2}$$

$E = \langle \psi | H_{AB} | \psi \rangle$ represented the whole energy of system, $H_{AB}$ the Hamilton amount shown in Eq. (1), $| \psi \rangle$ the normalizing electron wave function of the system, $\nabla$ wedge-shaped operational symbol, $F_A$ the force enforced on core A.

To sustain this model, there existed several expressions of physical parameters. With these formulas, this model could be used to study lots of physical and chemical subjects.

2.1. The effective bonding charge $q$ and its migration distance $r_m$

**Deduction 1.** Supposing Hellmann–Feynman theorem [4] was suitable to every bond of molecule and the Hamilton amount (atomic unit) of AB bond (Fig. 1), made up by atoms A and B and electrons 1 and 2, could be written as follows:

$$\begin{align*}
F_{(\psi)} &= \left( \frac{\partial}{\partial x} \psi \right) = 0, \\
F_{(\nabla)} &= \left( \frac{\partial}{\partial \theta} \psi \right) = 0
\end{align*} \tag{3}$$

Eq. (1) was substituted into (3), then what was got as follows:

$$\begin{align*}
-\left( \frac{2Z_A^*}{r_A^2} \cos \theta_A \right)_{AV} + \frac{Z_A^* Z_B^*}{R_{AB}^2} &= 0, \\
-\left( \frac{2Z_B^*}{r_B^2} \cos \theta_B \right)_{AV} + \frac{Z_A^* Z_B^*}{R_{AB}^2} &= 0 \tag{4}
\end{align*}$$

Here, $\cos \theta_A$ (or $\cos \theta_B$) was the $x$ directional cosine of $r_A$ (or $r_B$). The first part represented the electrostatic absorbing force between atomic core and the bonding electron clouds; the second represented the electrostatic repelling force between A and B.

**Deduction 2.** According to the three-center electrostatic model of diatomic bonds, the first part of Eq. (4) could be
approximately rewritten as:

\[- \left( \frac{2Z^*_A \cos \theta_A}{r_A} \right)_{AV} = - \frac{qZ^*_A}{(R_A + r_m)^2}, \]

\[- \left( \frac{2Z^*_B \cos \theta_B}{r_B} \right)_{AV} = - \frac{qZ^*_B}{(R_B - r_m)^2}. \]  \hspace{1cm} (5)

Here, \( R_A \) and \( R_B \) were covalent radii of atoms A and B; \( q \), called as effective bonding charge, was the inter-nuclear gathering charge as a result of orbits overlapping; \( r_m \) was the distance that \( q \) moved from the jointing point C of covalent bond radii to \( C' \) (Fig. 1) because of the effects of ion potential. By deducting (2), Eq. (4) could be as follows:

\[- \frac{qZ^*_A}{(R_A + r_m)^2} + Z^*_A Z^*_B \frac{1}{R^2_{AB}} = 0, \]  \hspace{1cm} (6)

\[- \frac{qZ^*_B}{(R_B - r_m)^2} + Z^*_A Z^*_B \frac{1}{R^2_{AB}} = 0 \]

\( r_m \) and \( q \) could be obtained by solving Eq. (6):

\[ r_m = \frac{R_B \sqrt{Z^*_A} - R_A \sqrt{Z^*_B}}{\sqrt{Z^*_A} + \sqrt{Z^*_B}} \]  \hspace{1cm} (7)

\[ q = \frac{Z^*_A Z^*_B}{(\sqrt{Z^*_A} + \sqrt{Z^*_B})^2} \frac{(R_A + R_B)^2}{R^2_{AB}} \]  \hspace{1cm} (8)

For homo-nuclear diatomic bonds, the upper two equations could be written as:

\[ r_m = 0 \]  \hspace{1cm} (9)

\[ q = Z^*_A/4 \]  \hspace{1cm} (10)

In the above several equations, \( R_A, R_B, Z^*_A \) and \( Z^*_B \) were the corresponding covalent radii and effective nuclear charge of atom A and B. \( R_{AB} \) was the length of AB bond.

2.2. The primary polarization energy \( \Delta E \)

As the amount of system energy reduction \( \Delta E \), caused by the migration of bonding charges, displayed the effect magnitude of Primary Polarization, the above three-center model of diatomic bonds could be applied to calculate the value of \( \Delta E \) with the following method, in response to the principles used in computing the energy difference of isoelectronic process with Hellmann–Feynman theory [5].

Let \( \psi_{I1} \) represent the normalized wave function of post-migration of bonding charges with \( H_{I1} \) referring to Hamilton amount and \( E_{I1} \) to self-energy. Suppose that, before the migration of bonding charges, the orbit of un-polarized bonding molecules was expressed with \( \psi_1 \) and it had corresponding \( H_1 \) and \( E_1 \). According to the integral H–F theory [5], the energy differences before and after the migration of bonding charges could be shown as:

\[ \Delta E = E_{I1} - E_1 = \left< \psi_1 \left| H_{I1} - H_1 \right| \psi_{I1} \right> - \left< \psi_1 \left| \psi_{I1} \right> \]  \hspace{1cm} (11)

For isoelectronic process I–II, it was concluded that:

\[ H_{I1} - H_1 = \Delta V_{\text{nn}} + \sum_i H'_i(i) \]  \hspace{1cm} (12)

Here, \( \Delta V_{\text{nn}} \) was the variation of inter-nuclear repelling energy resulted from transition; \( H'_i(i) = V^I_{ne}(i) - V^I_{ne}(i) \) was the variation of electron-nuclear absorption energy during the transition of the \( i \)th electron. Substituting Eq. (11) with Eq. (12) to get a single electronic form:

\[ \Delta E = \Delta W_{\text{nn}} + \int \rho_{I1}(1) H'_1(1) \, d\tau_1 \]  \hspace{1cm} (13)

\( \Delta W_{\text{nn}} \) was the variation of inter-nuclear repelling energy between I and II, \( H'_1(1) \) the variation of electron-nuclear absorbing operator for electron 1, \( \rho_{I1}(1) \) the normalized single-electron transiting density between \( \psi_1 \) and \( \psi_{I1} \), namely:

\[ \rho_{I1}(1) = \frac{N \int \psi_1 \psi_{I1} \, d\tau_2 \ldots d\tau_N}{\int \psi_1 \psi_{I1} \, d\tau_1 \ldots d\tau_N} \]  \hspace{1cm} (14)

Deduction 3. Supposed that the migration of bonding charges was stiff movement**, its electron cloud had a invariant space distribution and thus \( \psi_1 \) equals \( \psi_{I1} \). According to Deductions 1 and 2, and Fig. 1, \( H_1, H_{I1} \) could be obtained. Solving Eq. (13), we obtained:

\[ \Delta E = q \frac{(R_B \sqrt{Z^*_A} - R_A \sqrt{Z^*_B})^2}{R_A R_B (R_A + R_B)} - \frac{Z^*_A Z^*_B (R_A + R_B - R_{AB})}{R_{AB} (R_A + R_B)} \]  \hspace{1cm} (15)

If the reduction of bond length was omitted, Eq. (15) could be changed to:

\[ \Delta E = q \frac{(R_B \sqrt{Z^*_A} - R_A \sqrt{Z^*_B})^2}{R_A R_B (R_A + R_B)} \]  \hspace{1cm} (16)

\( q \) was the effective bonding charge shown in Eq. (8); \( R_A, R_B, Z^*_A, Z^*_B \) in Eq. (16) were covalent radii and effective nuclear charge of corresponding atoms.

2.3. The reduction of bond length caused by primary polarization

The original equilibrium would always be broke in that the migration of bonding charge brought a reduction to system energy. At the meantime, the absorption force exceeded that of repelling so much that a non-zero static load was applied to core A and B. Thus, the positive A and B would migrate towards negative \( q \), which would lead to a higher shielding resistance, a reduction of effective charges of A and B, a lower absorption force of bonding charges attracting A and B. As soon as absorbing and repelling forces were equal to each other, when A migrated \( r_1 \) and B
The static electronic force loaded on A:

$$F_A(x_1) = -\frac{qZ_A^*}{x_1^2} + Z_A^*Z_B^* \frac{Z_A^*Z_B^*}{(x_1 + R_B)^2}$$

The static electronic force loaded on B:

$$F_B(x_2) = -\frac{qZ_B^*}{x_2^2} + Z_A^*Z_B^* \frac{Z_A^*Z_B^*}{(x_2 + R_A - r_1)^2}$$

Then the total work done by static force was:

$$W = \int_{R_A}^{R_A-r_1} F_A(x_1)dx_1 + \int_{R_B}^{R_B-r_2} F_B(x_2)dx_2$$

Substituting Eq. (18) with Eq. (17) and calculating the integration in the conditions as follows: first, $Z_A^*$ and $Z_B^*$, varying with $r$, were continuous variable in the space interval and $1/r^2$ kept homogeneous; $q$ was constant; took first approximation and indicated $r_1 = r_2 = r$, then it was concluded:

$$W = \left[ q \frac{R_A^2Z_A^* + R_B^2Z_B^*}{R_A^2R_B^2} - \frac{2Z_A^*Z_B^*}{(R_A + R_B)^2} \right] \tilde{r}$$

It was easily found that Eq. (16) was identically equal to (19), so:

$$\tilde{r} = \frac{R_AR_B(R_A + R_B)\sqrt{Z_A^*} - R_A\sqrt{Z_B^*} }{(R_A + R_B)^2(R_A^2Z_A^* + R_B^2Z_B^*) - \frac{2Z_A^*Z_B^*}{q R_A^2R_B^2}Z_A^*Z_B^*}$$

$q$ was the effective bonding charge represented in Eq. (8); $R_A$, $R_B$, $Z_A^*$, $Z_B^*$ in the Eq. (20) were covalent radii and effective nuclear charge of corresponding atoms.

Up to this point, expressions of physical parameters, such as $r_m$, $q$, $\Delta E$ and $\tilde{r}$, had been obtained. $\Delta E$, whose calculated and measured values were shown in Table 1, was approximately equal to the heat of bonding formation. $\tilde{r}$ was nearly equivalent to $\delta = R_A + R_B - R_{AB}$. For HF, HCl, HBr and HI, their calculated molecular $\tilde{r}$ were 0.115, 0.072, 0.042 and 0.006 Å, respectively; $\delta$ values were 0.162, 0.090, 0.098 and 0.096 Å. For $r_m$ and $q$, there were no substantive measured counterparts, but some indirect determinations could be made, for example, the following computation of physical parameters.

### 3. The theoretical representations of some physical constants

#### 3.1. Dipole moment

For a bond AB, if its gravity center of the nuclear charge was not coincident with that of its electronic charge, a bond moment would existed. The common gravity center of molecular nuclear charge was:

$$D_n = \sum_k R_kQ_k$$

$R_k$ and $Q_k$, respectively represented the position vector and charge of core $k$. The electron cloud gravity center of a ground state molecule was:

$$D_e = \frac{\left\langle \psi_G \left| \sum_{i=1}^{N} er_i |\psi_G \right\rangle \right\rangle}{eN}$$

$N$ was the total number of electrons in the molecule; $r_i$ was position vector of $i$th electron. A neutral molecule should obey the following:

$$\sum_k Q_k = -eN$$

Then its dipole moment could be written as:

$$\mu = eN(D_n - D_e)$$

The dipole moment of a hetero-polar AB bond was composed of four parts as:

$$\mu_{AB} = \mu_p + \mu_s + \mu_n + \mu_i$$
\[ \mu_p = q r_m \]

If the post-migrating \( q \) was not at the mid-point of bond, the homo-polar moment \( \mu_s \) would appeared. Its representation could be drawn from Fig. 3:

\[ \mu_s = q \left( r_m - \frac{R_B - R_A}{2} \right) \]

Eqs. (27) and (28) were amalgamated without taking the reduction of bond length into account, then it was concluded:

\[ \mu_{AB} = q r_m + q \left( r_m - \frac{R_B - R_A}{2} \right) \]

Table 2 shows a comparison of calculated and measured \( \mu_{AB} \) obtained according to Eq. (29) without using adjustable parameters.

### Table 2

A comparison of the calculated and measured bond matrix according to formula (29)

<table>
<thead>
<tr>
<th>Bond A-B</th>
<th>( r_m (\text{Å}) )</th>
<th>( q (e) )</th>
<th>( \mu^c_{AB} ) (D)</th>
<th>( \mu^m_{AB} ) (D)</th>
<th>Bond A-B</th>
<th>( r_m (\text{Å}) )</th>
<th>( q (e) )</th>
<th>( \mu^c_{AB} ) (D)</th>
<th>( \mu^m_{AB} ) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li–F</td>
<td>0.553</td>
<td>0.82</td>
<td>5.35</td>
<td>6.6</td>
<td>C–F</td>
<td>0.110</td>
<td>1.10</td>
<td>1.30</td>
<td>1.41</td>
</tr>
<tr>
<td>K–Cl</td>
<td>0.930</td>
<td>0.83</td>
<td>9.45</td>
<td>10.5</td>
<td>C–I</td>
<td>0.014</td>
<td>0.93</td>
<td>1.10</td>
<td>1.19</td>
</tr>
<tr>
<td>Rb–Br</td>
<td>0.975</td>
<td>0.82</td>
<td>9.70</td>
<td>10.5</td>
<td>Ge–Br</td>
<td>0.163</td>
<td>1.04</td>
<td>1.83</td>
<td>2.10</td>
</tr>
<tr>
<td>Cs–Cl</td>
<td>1.13</td>
<td>0.85</td>
<td>11.9</td>
<td>10.4</td>
<td>Sn–Br</td>
<td>0.267</td>
<td>1.10</td>
<td>3.26</td>
<td>3.0</td>
</tr>
<tr>
<td>Cs–Br</td>
<td>1.10</td>
<td>0.84</td>
<td>11.2</td>
<td>10.7</td>
<td>Sn–I</td>
<td>0.180</td>
<td>1.10</td>
<td>1.96</td>
<td>1.55</td>
</tr>
<tr>
<td>TI–F</td>
<td>0.575</td>
<td>1.04</td>
<td>7.8</td>
<td>7.6</td>
<td>Pb–Cl</td>
<td>0.394</td>
<td>1.09</td>
<td>5.55</td>
<td>4</td>
</tr>
<tr>
<td>TI–Cl</td>
<td>0.472</td>
<td>0.89</td>
<td>5.2</td>
<td>5.1</td>
<td>Pb–Br</td>
<td>0.340</td>
<td>1.08</td>
<td>4.57</td>
<td>3.9</td>
</tr>
<tr>
<td>TI–Br</td>
<td>0.422</td>
<td>0.90</td>
<td>4.5</td>
<td>4.5</td>
<td>Pb–I</td>
<td>0.252</td>
<td>1.08</td>
<td>3.18</td>
<td>3.3</td>
</tr>
<tr>
<td>I–Br</td>
<td>0.095</td>
<td>1.32</td>
<td>1.81</td>
<td>1.2</td>
<td>P–Pr</td>
<td>0.061</td>
<td>1.10</td>
<td>0.53</td>
<td>0.36</td>
</tr>
<tr>
<td>H–F</td>
<td>0.220</td>
<td>1.04</td>
<td>2.06</td>
<td>1.91</td>
<td>As–Br</td>
<td>0.105</td>
<td>1.13</td>
<td>1.30</td>
<td>1.27</td>
</tr>
<tr>
<td>C–S</td>
<td>0.055</td>
<td>1.10</td>
<td>1.30</td>
<td>0.90</td>
<td>As–I</td>
<td>0.015</td>
<td>1.08</td>
<td>0.50</td>
<td>0.78</td>
</tr>
</tbody>
</table>

\( \Delta H_{AB} \) was cited from McClellan, Aubrey Lester, ‘Table of Experimental Dipole Moments’, San Francisco, Freeman, 1963.
$Z_A^*$ and $Z_B^*$ were the effective nuclear charges of A, B; $q$ was the effective bonding charge of AB bond. $r_A$, $r_B$ of the last section referred to the distance between core A, B and the gravity center $C_0$ of the effective bonding charges at equilibrium state (shown in Fig. 1). Substituting (35) for (34), then:

$$\frac{dE}{dR} = -Z_A^*Z_B^* - \frac{1}{2} \frac{q}{R} \left( \frac{Z_A^*}{r_A} + \frac{Z_B^*}{r_B} \right)$$

(36)

Then the force constant could be achieved by Eq. (36):

$$k = \frac{d^2E}{dR^2} = 2 \frac{Z_A^*Z_B^*}{R^2} - \frac{q}{R^2} \left( \frac{Z_A^*}{r_A} + \frac{Z_B^*}{r_B} \right)$$

(37)

$r_A = R_{m_A}, r_B = R_{m_B}, r_m$ and $q$ were individually expressed in Eqs. (7) and (8). For a covalent dominant bond, Eq. (37) could be changed into:

$$k = \frac{2Z_A^*Z_B^*}{R^2} - \frac{q}{R^2} \left( \frac{Z_A^*}{r_A} + \frac{Z_B^*}{r_B} \right)$$

(38)

$r_A$ and $r_B$ referred to the covalent radii of atom A and B. As homo-nuclear bond was considered, $r_m = 0$ and $R_A = R_B = R/2$. Therefore, Eq. (37) could be changed into:

$$k = (2Z_A^*^2 - 4qZ^*)/R^3 = Z^*^2/R^3$$

(39)

Here, $Z_A^* = Z_B^* = Z^*$ and formula (10) was cited.

In the above various representations, the force constant expressed with dyne/centimeter unit was obtained only if $R$ was shown with Å; $Z^*$ denoted electron charge; the calculated number multiplied conversion factor of unit as $2.315 \times 10^5$. For some homo-nuclear and hetero-nuclear diatomic molecules, a comparison of the calculated and measured value of force constant was shown in Tables 3 and 4 in response to Eqs. (39) and (38).

It should be noticed that, in Eq. (39), a simple method of getting effective nuclear charges of corresponding elements was offered through measured force constant and inter-nuclear distance. $Z^*_m$, obtained through Eq. (39), was named measured effective nuclear charge (shown in Table 5). Table 6 displayed a comparison between measured force constant values of inter-halogen

### Table 3

A comparison of the calculated and measured value of force constant of A–A molecule according to Eq. (39)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$R_{A-A}$ (Å)</th>
<th>$Z_A^*$ (e)</th>
<th>$k_c \times 10^5$ dyne/cm</th>
<th>$k_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–H</td>
<td>0.742</td>
<td>1</td>
<td>5.7</td>
<td>5.75</td>
</tr>
<tr>
<td>Li–Li</td>
<td>2.673</td>
<td>1.3</td>
<td>0.205</td>
<td>0.255</td>
</tr>
<tr>
<td>Na–Na</td>
<td>3.079</td>
<td>1.6</td>
<td>0.203</td>
<td>0.172</td>
</tr>
<tr>
<td>K–K</td>
<td>3.923</td>
<td>1.6</td>
<td>0.0975</td>
<td>0.0985</td>
</tr>
<tr>
<td>Rb–Rb</td>
<td>4.190</td>
<td>1.6</td>
<td>0.0805</td>
<td>0.0820</td>
</tr>
<tr>
<td>Cs–Cs</td>
<td>4.570</td>
<td>1.6</td>
<td>0.0622</td>
<td>0.0690</td>
</tr>
</tbody>
</table>


### Table 4

A comparison of the calculated and measured value of force constant of M–H molecule according to Eq. (38)

<table>
<thead>
<tr>
<th>Molecules A–C</th>
<th>$R_{A-H}$ (Å)</th>
<th>$Z_A^*$ (e)</th>
<th>$Z_B^*$ (e)</th>
<th>$q$ (e)</th>
<th>$k_c \times 10^5$ dyne/cm</th>
<th>$k_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li–H</td>
<td>1.5954</td>
<td>1.3</td>
<td>1</td>
<td>0.284</td>
<td>0.810</td>
<td>1.026</td>
</tr>
<tr>
<td>Na–H</td>
<td>1.8873</td>
<td>1.6</td>
<td>1</td>
<td>0.31</td>
<td>0.587</td>
<td>0.789</td>
</tr>
<tr>
<td>K–H</td>
<td>2.244</td>
<td>1.6</td>
<td>1</td>
<td>0.31</td>
<td>0.327</td>
<td>0.561</td>
</tr>
<tr>
<td>Rb–H</td>
<td>2.367</td>
<td>1.6</td>
<td>1</td>
<td>0.31</td>
<td>0.265</td>
<td>0.515</td>
</tr>
<tr>
<td>Cs–H</td>
<td>2.494</td>
<td>1.6</td>
<td>1</td>
<td>0.31</td>
<td>0.220</td>
<td>0.467</td>
</tr>
<tr>
<td>Be–H</td>
<td>1.3431</td>
<td>2.0</td>
<td>1</td>
<td>0.242</td>
<td>2.150</td>
<td>2.263</td>
</tr>
<tr>
<td>Mg–H</td>
<td>1.7306</td>
<td>2.3</td>
<td>1</td>
<td>0.239</td>
<td>1.165</td>
<td>1.274</td>
</tr>
<tr>
<td>Ca–H</td>
<td>2.002</td>
<td>2.3</td>
<td>1</td>
<td>0.239</td>
<td>0.734</td>
<td>0.977</td>
</tr>
<tr>
<td>Sr–H</td>
<td>2.1455</td>
<td>2.3</td>
<td>1</td>
<td>0.239</td>
<td>0.580</td>
<td>0.854</td>
</tr>
<tr>
<td>Ba–H</td>
<td>2.2318</td>
<td>2.3</td>
<td>1</td>
<td>0.239</td>
<td>0.500</td>
<td>0.809</td>
</tr>
<tr>
<td>H–F</td>
<td>0.9171</td>
<td>1</td>
<td>4.76</td>
<td>1.04</td>
<td>5.25</td>
<td>9.655</td>
</tr>
<tr>
<td>H–Cl</td>
<td>1.2746</td>
<td>1</td>
<td>4.94</td>
<td>0.78</td>
<td>3.80</td>
<td>5.157</td>
</tr>
<tr>
<td>H–Br</td>
<td>1.414</td>
<td>1</td>
<td>5.14</td>
<td>0.76</td>
<td>3.10</td>
<td>4.116</td>
</tr>
<tr>
<td>H–I</td>
<td>1.604</td>
<td>1</td>
<td>5.14</td>
<td>0.73</td>
<td>2.30</td>
<td>3.141</td>
</tr>
</tbody>
</table>

Taking $k_m$ from Table 3, the following are the same.
Table 5
A comparison between measured effective nuclear charges of some elements and their estimated ones (according to Eq. (39))

<table>
<thead>
<tr>
<th>Elements</th>
<th>$Z_m^*$ (e)</th>
<th>$Z^*_0$ (e)</th>
<th>Elements</th>
<th>$Z_m^*$ (e)</th>
<th>$Z^*_0$ (e)</th>
<th>Elements</th>
<th>$Z_m^*$ (e)</th>
<th>$Z^*_0$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>1</td>
<td>Se</td>
<td>3.96</td>
<td>4.45</td>
<td>C</td>
<td>3.05</td>
<td>2.99</td>
</tr>
<tr>
<td>F</td>
<td>3.02</td>
<td>4.76</td>
<td>Te</td>
<td>4.22</td>
<td>4.45</td>
<td>Si</td>
<td>4.44</td>
<td>3.17</td>
</tr>
<tr>
<td>Cl</td>
<td>3.35</td>
<td>4.94</td>
<td>N</td>
<td>3.61</td>
<td>3.68</td>
<td>Li</td>
<td>1.45</td>
<td>1.30</td>
</tr>
<tr>
<td>Br</td>
<td>3.56</td>
<td>5.14</td>
<td>P</td>
<td>4.04</td>
<td>3.86</td>
<td>Na</td>
<td>1.47</td>
<td>1.60</td>
</tr>
<tr>
<td>I</td>
<td>3.77</td>
<td>5.14</td>
<td>As</td>
<td>3.98</td>
<td>4.06</td>
<td>K</td>
<td>1.61</td>
<td>1.60</td>
</tr>
<tr>
<td>O</td>
<td>2.99</td>
<td>4.08</td>
<td>Sb</td>
<td>4.15</td>
<td>4.06</td>
<td>Rb</td>
<td>1.62</td>
<td>1.60</td>
</tr>
<tr>
<td>S</td>
<td>3.80</td>
<td>4.26</td>
<td>Bi</td>
<td>3.91</td>
<td>4.06</td>
<td>Cs</td>
<td>1.69</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Compounds and their calculated ones, gained with $Z_m^*$ through Eq. (38).

3.3. Field gradient in the coupling constants of nuclear quadrupole moment

While $Q$ looked as the quadrupole moment of nuclear charges, $Q_{N}$ represented the coupling constant of nuclear quadrupole moment. For a definitive element, $Q_{N}$ was invariable. So the most important of a series of compounds was to study the variation of $q_{N}$, which was the core $N$ site electrical gradient produced by extra-nuclear charge along axis $x$:

$$q_{N} = \frac{\partial \rho_{ext}}{\partial x_N^2} \quad (40)$$

$\rho_{ext}$ referred to the core $N$ electrostatic potential loaded by its extra-nuclear charge. $q_{N}$ could be measured by the superfine structure of rotation spectrum or by $\rho_{ext}$ of Eq. (40).

According to three-center model of diatomic bonds and its correlative Deductions 1, 2, and 4, the core $N=A$ electrostatic potential of A–B bond, loaded by extra-nuclear electrical fields, was approximately:

$$\rho_{ext}^N = -\frac{q}{r_A} + \frac{Z_B^*}{R_{AB}} \quad (41)$$

The field on core A was:

$$\frac{\partial \rho_{ext}}{\partial x_A} = \frac{q}{r_A R_{AB}} - \frac{Z_B^*}{R_{AB}^2} \quad (42)$$

and its field gradient was:

$$q_A = \frac{\partial \rho_{ext}}{\partial x_A^2} = \frac{2 Z_B^*}{R_{AB}^3} - 2 \frac{q}{r_A R_{AB}^2} \quad (43)$$

Similarly,

$$q_B = \frac{2 Z_A^*}{R_{AB}^3} - 2 \frac{q}{r_B R_{AB}^2} \quad (44)$$

In the above equations, $q_A$ and $q_B$ expressed electrical field gradient, while $q$ was the effective bonding charge of AB and $r_A=R_A+r_m$, $r_B=R_B-r_m$. Similar to Eq. (38), Eqs. (43) and (44) could be written as follows:

$$q_A = \frac{2 Z_B^*}{R_{AB}^3} - 2 \frac{q}{r_A R_{AB}^2} \quad (45)$$

$$q_B = \frac{2 Z_A^*}{R_{AB}^3} - 2 \frac{q}{r_B R_{AB}^2} \quad (46)$$

For homo-nuclear diatomic molecules, $r_A = r_B = \frac{1}{2} R_{AB}$ and $q = (Z^*/4)$. Thus, (43) and (44) were simplified as:

$$q_{N} = Z_{N}^*/R_{N-N} \quad (47)$$

There was a relation, inferred from (47) and (39), between $q_{N}$ and $k_{N-N}$:

$$k_{N-N} = Z_{N}^*/q_{N} \quad (48)$$

This formula conformed to the strict treating conclusion in Ref. [6]. There were similar relations for $k_{AB}$, $q_A$ and $q_B$ of hetero-nuclear bonds.

According to Eq. (47), the H$_2$ calculated $q_{H}$ was 5.7 and its corresponding measured value was 5.44. According to (43) and (44), the calculated $q_{H}$ of HF, HBr and HI was, respectively, 13, 5.3, 0.70 and 3.75 while measured numbers [6] were 8.2, 3.1, 0.8 [6] and 2.7. All the former values were expressed by a unit of $\times 10^5$ dyne/cm.

3.4. The crystal nonlinear optical coefficients

Propelled by laser technique, the research of the crystal nonlinear optics coefficients was widely noticed [7,8]. For those electromagnetic waves whose frequencies were lower than that of transiting electrons but far higher than that of crystal lattice vibration, local valence electrons of every crystal bond contributed most to

Table 6
A comparison between measured force constants of inter-halogen compounds and calculated ones according to Eq. (38) with the help of $Z_m^*$

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$R_{AB}$ (Å)</th>
<th>$q$ (e)</th>
<th>$\times 10^5$ dyne/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{c}$</td>
<td>$k_{m}$</td>
<td></td>
</tr>
<tr>
<td>I–F</td>
<td>1.906</td>
<td>0.970</td>
<td>3.28</td>
</tr>
<tr>
<td>Br–F</td>
<td>1.7556</td>
<td>0.917</td>
<td>4.12</td>
</tr>
<tr>
<td>Cl–F</td>
<td>1.6281</td>
<td>0.875</td>
<td>5.05</td>
</tr>
<tr>
<td>I–Cl</td>
<td>2.3207</td>
<td>0.886</td>
<td>2.31</td>
</tr>
<tr>
<td>I–Br</td>
<td>2.434</td>
<td>0.943</td>
<td>2.34</td>
</tr>
<tr>
<td>Br–Cl</td>
<td>2.138</td>
<td>0.863</td>
<td>2.80</td>
</tr>
</tbody>
</table>
optical crystal rate. Therefore, tetrahedral crystals could be seen as a macromolecule composed by the accumulation of every sectional bond and macro-optical polarization rate could be achieved by the summation of micro-optical polarization rate of every bond. This accumulation could be carried out by geometrical factors of special-lattice mono-cell and bonds’ numbers of unit volume. When the measured macro-linear polarization rate was cited in the calculation, the majority of local-field corrections were included naturally [9].

When bonding, the bonding charge \( q \) of AB migrated from the joining points C of covalent bonds to the equilibrium site \( C' \). If an outside electrical field appeared, \( q \) would receive a slight perturbation and moved from \( C' \) to \( C'' \), as shown in Fig. 5. Under the action of outside electrical field \( e \), the migration of \( q \) provided a accompanying bond moment of the field.

\[
\Delta \mu_{\|} = q \Delta r = \alpha_{\|} e_{\|} \tag{49}
\]

If the coherent strong light was generated by laser device, its high-order term of the polarization field could be observed; the representation of bond polarization could be:

\[
\Delta \mu_{\|} = \alpha_{\|} e_{\|} + \beta_{\|} e_{\|}^2 + \gamma_{\|} e_{\|}^3 + \ldots. \tag{50}
\]

\( \alpha, \beta \) and \( \gamma \), respectively, characterized the optical micro-coefficients of linear, quadric and cubic relations. The expressions between them and macro-coefficients were as following:

\[
\chi_{o\omega} = \frac{N}{3} \left( \alpha_{11} + 2 \alpha_{1} \right) = \frac{N}{3} \alpha_{11} (1 + 2 \kappa) \tag{51}
\]

\[
\chi_{2\omega} = \frac{N}{3\sqrt{3}} \left( \beta_{11} - 3 \beta_{1} \right) \tag{52}
\]

\[
\chi_{3\omega} = Nr \tag{53}
\]

\( \chi_{o\omega}, \chi_{2\omega} \) and \( \chi_{3\omega} \) individually represented the optical macro-coefficients of linear, quadric and cubic relations. \( N = 3\sqrt{3}/4d^3 \) was the bond number of per unit volume, \( d \) the length of AB bond. \( \alpha_{1} \) and \( \alpha_{1} \) were the two constitutes, parallel and vertical to bonding axis, of linear coefficient. \( \chi = (\alpha_{1}/\alpha_{1}) \) indicated the anisotropism of the bonding polarization rate, \( \beta_{\|} \) and \( \beta_{\perp} \) were the correlative components of binomial coefficient and \( \beta_{\|} \gg \beta_{\perp} \).

The relation between the bonding polarization rate and energy band could also be rewritten as [10]:

\[
\chi_{\|} (1 + 2 \kappa) = \frac{3(h\Omega_p)^2}{16\pi NE_g^2} \tag{54}
\]

\( h\Omega_p \) was the plasma energy in the free gas of crystal bonding electrons. \( E_g \) the width of crystal forbidden bands, approximately to the energy gap between the bonding molecule orbit and the anti-bonding molecule orbit. In the presence of this, the relation between molecular energy levels and crystal polarization rate could be discovered. \( E_g \) contained two sections: homo-polar and hetero-polar [9].

\[
E_g^2 = E_h^2 + c^2 \tag{55}
\]

Under the action of ion potential, the hetero-polar part \( C \) was provoked through bonding charge \( q \) migrating from the joining site of covalent radii of A, B. Learned from Ref. [11], the migrating distance \( r_m \) was:

\[
r_m = \frac{\lambda^2 R_B - R_A}{1 + \lambda^2} \tag{56}
\]

\( R_A \) and \( R_B \) referred to the covalent radii of atom A, B, \( \lambda \) the polarity coefficient of molecule orbit function. In response to our model, the ratio, between migrating distance \( r_m \) and half of the bonding length \( (d/2) \), showed the ionicity of bonds. In accordance with Ref. [9], the latter equation should be tenable.

\[
\frac{C}{E_g} = \frac{r_m + \Delta r}{d/2} = \frac{2(\lambda^2 R_B - R_A)}{(1 + \lambda^2 d)} \tag{57}
\]

The above equation indicated that, if any foreign factors could change the position of bonding charges, the crystal ionicity would alter with it and so did \( C \) and \( E_g \). Then the polarizability represented in (54) would shift.

When a electrical field \( e \), who was parallel with bonding axis, happened, \( q \) would move \( \Delta r \) in the opposite direction of electrical field. Then, \( C \) would transformed into \( C(e) = C + \Delta C(e) \) with Eq. (57) rewritten as:

\[
\frac{C + \Delta C}{E_g(e)} = \frac{r_m + \Delta r}{d/2} \tag{58}
\]

If \( E_g(e) \approx E_g \), then

\[
\frac{\Delta C}{E_g} = \frac{2\Delta r}{d} \tag{59}
\]

Substitute (59) with (49), then approximately:

\[
\Delta C = \frac{2}{qd} \frac{\alpha_{\|} E_g}{\varepsilon_\|} \tag{60}
\]

\( \Delta C \) was the change of bonding ionicity caused by outside electrical field.

In fact, the bonding polarity was determined not only by ionicity, but also by homo-polarity, quite similar to Eq. (57).

\[
E_h = \frac{(r_m - (R_B - R_A)/2)}{E_g} \tag{61}
\]
Table 7
A comparison between the calculated values and experimental ones of nonlinear optical coefficient $\chi_{2\omega}$ according to Eq. (70)

<table>
<thead>
<tr>
<th>Crystals (type)</th>
<th>$\chi_{2\omega}$ [12] (esu)</th>
<th>$E_g$ [12] (eV)</th>
<th>$C$ [12] (eV)</th>
<th>$\chi_{2\omega}^2$ (10^{-7} esu)</th>
<th>Experimental values (10^{-7} esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs(Z)</td>
<td>0.79</td>
<td>5.2</td>
<td>2.9</td>
<td>17.8</td>
<td>9–18 16±3</td>
</tr>
<tr>
<td>GaSb(Z)</td>
<td>1.07</td>
<td>4.13</td>
<td>2.1</td>
<td>27.6</td>
<td>30 25–31</td>
</tr>
<tr>
<td>InAs(Z)</td>
<td>0.90</td>
<td>4.58</td>
<td>2.74</td>
<td>28.9</td>
<td>20 24</td>
</tr>
<tr>
<td>InSb(Z)</td>
<td>1.17</td>
<td>3.74</td>
<td>2.11</td>
<td>44.9</td>
<td>33 33±7</td>
</tr>
<tr>
<td>GaP(Z)</td>
<td>0.65</td>
<td>5.75</td>
<td>3.23</td>
<td>12.8</td>
<td>5.2 6±1</td>
</tr>
<tr>
<td>ZnS(Z)</td>
<td>0.33</td>
<td>7.85</td>
<td>6.2</td>
<td>3.8</td>
<td>1.7 1.78±0.6</td>
</tr>
<tr>
<td>ZnSe(Z)</td>
<td>0.39</td>
<td>7.02</td>
<td>5.57</td>
<td>5.3</td>
<td>2.2 3.7±1.4</td>
</tr>
<tr>
<td>ZnTe(Z)</td>
<td>0.50</td>
<td>5.34</td>
<td>4.48</td>
<td>8.9</td>
<td>7.3 6.6±3</td>
</tr>
<tr>
<td>CdTe(Z)</td>
<td>0.49</td>
<td>5.40</td>
<td>4.40</td>
<td>8.1</td>
<td>8.0 8.0±3</td>
</tr>
</tbody>
</table>

$\chi_{2\omega} = d_{123}(Z) = d_{131}(W)(10^{-7} \text{ esu})$.

When outside electrical field appeared, analogy to (58):

$$
\frac{E_h + \Delta E_h}{E_g} = \frac{(r_m - (R_B - R_A)/2) + \Delta r}{d/2} \tag{62}
$$

Substituting (61) for (62):

$$
\frac{\Delta E_h}{E_g} = \frac{\Delta r}{d/2} = \frac{2\alpha_{\parallel}}{qd} \tag{63}
$$

Under the acting of outside field, Eq. (54) could be written as:

$$
\alpha_3(e_{\parallel}) + 2\alpha_\perp = \frac{3(h\Omega_p)^2}{16\pi NE_g^2(e_{\parallel})} \tag{64}
$$

As $\beta_3 > \beta_\perp$, the accompanying polarization rate of $\alpha_\perp$ could be omitted. And

$$
\alpha_3(e_{\parallel}) = \alpha_\parallel + \beta_\parallel e_{\parallel} + \gamma_\parallel e_{\parallel}^2 \tag{65}
$$

$E_g^2(e_{\parallel})$ of Eq. (64) could be noted as:

$$
E_g^2(e_{\parallel}) = E_g^2 + (2C\Delta C + 2E_0\Delta E_h) + (\Delta C^2 + \Delta E_h^2) \tag{66}
$$

Substituting (66) for (64):

$$
\alpha(e) = \frac{2C\Delta C + 2E_0\Delta E_h}{E_g^2} \alpha - \frac{\Delta C^2 + \Delta E_h^2}{E_g^2} \alpha \tag{67}
$$

Eqs. (60), (61) and (63) were taken into (67), then compared with Eq. (65):

$$
\beta_{\parallel} = -\frac{4(2\kappa + 1)}{qd} \frac{C}{E_g} \alpha_{\parallel}^2 = \frac{8(2\kappa + 1)}{qd^2} \left(\frac{r_m - R_B - R_A}{2}\right) \alpha_{\parallel}^2 \tag{68}
$$

$$
\gamma_{\parallel} = \frac{8(2\kappa + 1)}{q^2d^2} \alpha_{\parallel}^3 \tag{69}
$$

(51)–(53) were considered, the above two formulas could be expressed by macro-polarizability:

$$
\chi_{2\omega} = -\frac{16d^2}{3(2\kappa + 1)qE_g} \chi_{\omega}^2 - \frac{32d}{3(2\kappa + 1)q} \left(\frac{r_m - R_B - R_A}{2}\right) \chi_{\omega}^2 \tag{70}
$$

$$
\chi_{3\omega} = \frac{128}{(2\kappa + 1)^2q^3} \chi_{\omega}^3 \tag{71}
$$

In Eqs. (68)–(71), $\alpha$, $\beta$ and $r$, respectively, represented optical micro-coefficients of linear, quadric and cubic relations, while $\chi_{\omega}$, $\chi_{2\omega}$ and $\chi_{3\omega}$ referred to the opposite macro counterparts. $d$ was the bond length, bonding charge $q$ and its migrating distance $r_m$ were noted in Eqs. (8) and (7). $E_g$ was the width of crystal forbidden band with $C$ taken as the ionic part. Those two factors used test value, as well as $\chi_{\omega}$. For bond sp^3, $\kappa$, which denoted the aeolotropism of bonding polarization rate, nearly stayed at 1/2 [11].

Table 8
A comparison between the calculated and experimental $\chi_{3\omega}$ values for some crystals according to Eq. (71)

<table>
<thead>
<tr>
<th>Crystals (type)</th>
<th>$\chi_{\omega}$ (esu)</th>
<th>$\chi_{3\omega} = C_{1111} (10^{-11} \text{ esu})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(d)</td>
<td>0.86</td>
<td>– 2.5</td>
</tr>
<tr>
<td>Ge(d)</td>
<td>1.19</td>
<td>– 35</td>
</tr>
<tr>
<td>GaAs(Z)</td>
<td>0.79</td>
<td>– 5</td>
</tr>
<tr>
<td>GaSb(Z)</td>
<td>1.07</td>
<td>– 800</td>
</tr>
<tr>
<td>InAs(Z)</td>
<td>0.90</td>
<td>– 60</td>
</tr>
<tr>
<td>InSb(Z)</td>
<td>1.17</td>
<td>– 500</td>
</tr>
<tr>
<td>CdS(W)</td>
<td>0.33</td>
<td>–</td>
</tr>
</tbody>
</table>

$\chi_{3\omega} = C_{1111} = d_{1111}(W)(10^{-11} \text{ esu})$. $\text{MO}$ method, $\text{Bounding}$ [14] $\text{electrons}$, $\text{Non-parabolic}$ types [14], $\text{Textural}$ values [8], $\text{Levine}$ values [8].
In this paper, $k$ was treated as $(2k + 1) = 2$. In the upper four equations, the theoretical formulas of nonlinear optical coefficient between ionicity and homo-polarity, were taken into account. Table 7 showed that the calculated $\chi_{2\omega}$ agreed well with experimental value without using adjustable parameters. Table 8 displayed that the obtained $\chi_{3\omega}$ was approximate to experimental number and was located among other theoretical values.

4. Conclusions

Based on the Hellmann–Feynman theory, the three-center electrostatic model of diatomic bonds and its corresponding simplified assumptions discovered the charges redistributions (the basic character) of chemical bonding process by several expressions of physical parameters. The distinguishing feature of this model was to calculate many physicochemical properties of vast scale of compounds containing all the elements only by using two atomic parameters: covalent radii and effective nuclear charges. The difficulties existed in the calculation and solving procedures of wave functions with H–F theory could be avoided. When adjustable parameters were not involved, the calculated values of the obtained theoretical expressions, such as dipole matrix, force constant, field gradient and nonlinear optical coefficient, had a satisfied conformity to their measured ones. These theoretical expressions could be applied in such a vast studying field where the strict calculation of quantum mechanics was currently impossibly employed.

However, the calculating accuracy of this model and its correlative parametric expressions were affected by the approximation of effective nuclear charges and the hardness involved in the precise computation of effective nuclear charges of the bonding atoms [15,16]. In addition, the completely overlooking of orbital space features was also a large defect of this model. How to improve these two problems would be explained in other articles.

References