# QUANTUM MECHANICAL STUDIES OF ATOMIC, BOND AND MOLECULAR POLARIZABILITIES: MOLECULES OF SIX, SEVEN AND EIGHT RESIDUAL ATOMIC POLARIZABILITY DEGREES OF FREEDOM

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A brief survey is made of the various quantum mechanical models hitherto developed for calculating the atomic and molecular polarizabilities and assessing the extent to which the polarizability could be a useful criterion for testing the utility of the wave functions chosen. The delta-function potential model and its valuable applications in obtaining the necessary derivations by using the variational method and delta-function electronic wave functions are expounded in the case of the necessary calculations of the bond region electron contributions and the nonbond region electron contributions to the bond parallel component of the polarizability, the bond perpendicular component of the polarizability, and the average or mean molecular polarizability of both diatomic and polyatomic molecules. The Lewis-Langmuir octet rule, modified by Linnett as a double-quartet of electrons, has been employed for such investigations. Atomic, bond and molecular polarizabilities have been computed for many polyatomic molecules having six, seven and eight residual atomic polarizability degrees of freedom. The available experimental values of molecular polarizabilities for many of the molecules studied here are in good agreement with those calculated on the basis of the delta-function potential model. The results are discussed in relation to the nature of various characteristic bonds, distribution of the electrons, and the configurations of molecular systems.

## 1. Introduction

One of the fundamental electrical properties of a molecular system is molecular polarizability. It cannot be measured directly, but can be deduced from the measurement of some bulk macroscopic properties, such as dielectric constant, dipole moment and index of refraction, by employing such well-known relations as the Clausius-Mossotti equation, the Langevin-Debye equation or the Lorentz-Lorenz equation. This deduction is necessarily based upon an assumption regarding the nature of the symmetry of the molecular system and the extent of each local molecular field. An average molecular

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polarizability may, however, be obtained by averaging the three directional diagonal components of the polarizability tensor, *i. e.*, if

$$\bar{\alpha} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \quad \text{then } \bar{\alpha}_M = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

where $\bar{\alpha}_M$ is the average or mean molecular polarizability. On the basis of the quantum mechanical models, several investigations were undertaken in many ways to compute the atomic and molecular polarizabilities for many ions, atoms and simple diatomic molecules in order to test the utility of the wave functions adopted. In spite of the progressive developments in adopting various potential models, such investigations were limited to simple atoms, ions and diatomic molecules, and did not involve triatomic or any simple polyatomic molecules. Polarizabilities for the helium atom and lithium ion were calculated by Hasse [1] by the use of a variational method involving several types of ground state as well as perturbed state wave functions in terms of the perturbing potential. Hirschfelder [2] computed the polarizabilities of molecular hydrogen and the diatomic hydrogen ion by applying the variational method of Hasse [1] and Hylleraas [3] upon the eigenfunctions proposed by Rosen [4] and Wang [5]. But the calculated values of Hirschfelder [2] were not in satisfactory agreement with those of Mrowka [6] and Steensholt [7]. It was found that the Kirkwood formula [8] was applicable to the diatomic hydrogen ion and the polarizabilities were calculated for many internuclear separations by using the eigenfunctions developed by Guillemin and Zener [9]. Van Vleck [10] and Atanasoff [11] pointed out from the results of their investigations that the Hylleraas method [3] was not strictly applicable to approximate eigenfunctions and might yield results either too small or too large. The approach of Buckingham [12], based on the variational method of Kirkwood [8] and involving heavier atoms, led to complex self-consistent field wave functions in his calculations of atomic polarizabilities for Ne, $Na^+$, $Cl^-$, A, $K^+$, Kr and $Cs^+$. The polarizabilities for the $H_2^+$ and $H_2$ molecules for six different unperturbed wave functions were calculated by Bell and Long [13], but their results were insensitive to the wave functions chosen. Abbott and Bolton [14] studied the $H_2^+$, $H_2$ and $N_2$ molecules, and used the polarizability as a criterion for determining the molecular wave function of a system by a known self-consistent method. Later, Kolker and Karplus [15] calculated the electric polarizability tensor $\bar{\alpha}$ with *ab initio* wave functions for a series of first row diatomic molecules, such as $H_2$, $Li_2$, $N_2$, LiH, KF and CO. Kolos and Wolniewicz [16] furthered such studies with many modifications. Hence, it is clear from these methods that the potential models developed so far were limited to simple atoms, ions and diatomic molecules, and were rather not extended to the computations of polarizabilities even for simple triatomic molecules.

In studies of the properties of chemical bonds, a delta-function potential model was first used by Rudenberg and his associates [17, 18]. Later, Frost [19] applied a delta-function model of chemical binding in calculations of energies of conjugated hydrocarbons with the introduction of a branching condition, and further investigations on this aspect were made by Lippincott [20] with a semi-empirical delta-function potential model. On

the basis of this semi-empirical delta-function potential model, Lippincott and Dayhoff [21] predicted the bond dissociation energies, vibrational frequencies, anharmonicities and equilibrium internuclear distances for various diatomic molecules and bonds of polyatomic systems, and their calculated values were in good agreement with the available experimental results. Lippincott and Stutman [22] recently applied the same semi-empirical delta-function potential model in calculations of bond and molecular polarizabilities for various diatomic and polyatomic molecules. Such studies were limited to only molecules consisting of elements from and beyond the IV$A$-group of the periodic table, but not from the I$A$, II$A$, III$A$, VIII or any of the $B$-groups of the periodic table. Furthermore, Lippincott and Stutman [22] assumed that in a polyatomic molecule each bond is a pure diatomic molecule and the contributions of all the bonds in the entire molecular system can be summed up to obtain the average or mean molecular polarizability. As an example, the $C = C$ bond in ethylene cannot be considered as a pure diatomic molecule, because the delta-function strength of the carbon atom in ethylene is smaller than in a pure diatomic molecule. The main reason for this is that there is a greater distribution of polarizability along the bonds from the carbon atom of ethylene than from the carbon atom of a pure diatomic molecule. Though the assumption that every bond of a polyatomic molecule is a pure diatomic molecule will not lead to any considerable deviation from the true value of mean or average molecular polarizability of a simple polyatomic molecule, it will certainly do so in the case of heavier and highly complex molecules. Hence, the goal here is to compute the delta-function strengths, atomic polarizabilities, contributions of the nonbond region electrons, and mean or average molecular polarizabilities of a few polyatomic molecules having their elements from both the $A$- and $B$-groups of the periodic table. Moreover, the values of the present study are compared with available experimental ones in order to show the extent to which the polarizability could be a useful criterion of testing the utility of the wave functions chosen. This comparison also demonstrates when the delta-function potential model, among the various quantum mechanical model developed so far, would be the most useful one for calculating the atomic, bond (parallel and perpendicular) polarizabilities, contributions of the nonbond region electrons, and mean or average molecular polarizabilities of both diatomic and polyatomic molecules having their elements from any group of the periodic table.

## 2. Delta-function potential model

The stationary state Schrödinger wave equation may be used to determine all measurable properties of a particle of mass $m$ moving in a potential field $V(x, y, z)$. It reads

$$-\frac{h^2}{2m} \Delta^2 \psi + V(x, y, z)\psi = E\psi \tag{1}$$

in which the different values of the mass and the potential alone distinguish one system from another. A model of a system, even of the most complex nature, is an idealized picture of the behaviour of the potential energy function $V(x, y, z)$. The free electron and the "particle-in-a-box" models would be helpful for molecular electronic systems. The free

electron treatment developed by many investigators [23–26] found considerable application in helping to understand electronic excitation energies in conjugated π-electron systems, but failed to generate an acceptable interatomic potential energy function. The more refined model of the electron in finite square potential wells was used by Bayliss [27, 28] for conjugated polyenes, but it could not allow for any change of internuclear distance. Nor was the structure of his model amenable to the investigation of saturated compounds. The delta-function potential model can be explained by considering an electron in a diatomic molecule moving in a potential field consisting of two finite potential wells, one about each nucleus; the width of each potential well is allowed to shrink and the height is at the same time allowed to increase without limit in such a way that the area remains finite and constant. The potential about each nucleus then becomes a delta-function. The integral of the potential over all space, however, is finite and equal to a parameter, called the "delta-function strength" or "reduced electronegativity", and is analogous to the "effective nuclear charge" of Slater. The major advantage of a delta-function potential model lies in its one-diemensional nature. Each bond is considered to be a separate one-dimensional entity, and since the potential has a non-zero value at only two points along any given bond, the problems of calculation become trivial from the following:

The potential energy for the $n$-electron problem is considered to be the sum of the single delta-function potentials, each having the following form for a diatomic system:

$$V = -[A_1 g \delta(x - \tfrac{1}{2}a) + A_2 g \delta(x + \tfrac{1}{2}a)] \tag{2}$$

where $x$ — is the coordinate of motion along the internuclear axis, $a$ — the delta-function spacing, $A_1$ and $A_2$ — the delta-function strengths or reduced electronegativities for the nuclei 1 and 2, respectively, $g$ — the unit delta-function strength (the value for the hydrogen atom), and $\delta(x)$ a delta-function whose properties are described by the following:

$$\left.\begin{array}{ll} \delta(x) = 0, & \text{when } x \neq 0 \\ \delta(x) = \infty, & \text{when } x = 0 \\ \int\limits_{-\infty}^{\infty} \delta(x)dx = 1. & \end{array}\right\} \tag{3}$$

Thus, the potential is zero everywhere except at the delta-function positions where it is infinite in such a way that

$$A_1 g \int\limits_{-\infty}^{\infty} \delta(x - \tfrac{1}{2}a)dx = A_1 g \tag{4}$$

and

$$A_2 g \int\limits_{-\infty}^{\infty} \delta(x + \tfrac{1}{2}a)dx = A_2 g. \tag{5}$$

The delta-function strength obtainable from separated atom energies $E_i$ is defined as $A = (-2E_i)^{\frac{1}{2}}$. This can be obtained either from the first ionization potential or from the solution of the atomic problem using the delta-function potential model.

The solution of the Schrödinger equation for the molecular problem yields separate wave functions for the bonds; correspondingly, the $i$-th bond wave function has the form

$$\psi_i = N[\exp(-c_i|x_i + \tfrac{1}{2}a|) \pm \exp(-c_i|x_i - \tfrac{1}{2}a|)] \tag{6}$$

where

$$N = [(2/c_i)\{1 \pm \exp(-c_i a) \pm 2a \exp(-c_i a)\}]^{-\frac{1}{2}} \quad \text{and} \quad c_i = (-2E_i)^{\frac{1}{2}}.$$

The delta-function branching conditions outlined by Frost [19] can then be applied to obtain the following expression for the homonuclear case:

$$c_i = Ag[1 \pm \exp(-c_i a)] \tag{7}$$

where the plus and minus signs correspond to the attractive and repulsive states, respectively. By combining the equations $c_i = (-2E_i)^{\frac{1}{2}}$, $A = (-2E_i)^{\frac{1}{2}}$ and $Ag = (-2E_i)^{\frac{1}{2}}$, one may obtain the following relation

$$\lim_{a \to \infty} c_i = Ag = (-2E_i)^{\frac{1}{2}}. \tag{8}$$

The problem of obtaining $c_i$ for each individual electron is simplified by properly generating a "super" one-electron situation. Following this, a resultant $c$ written as $c_R$ may be obtained and assumed to account for all electrons in the system. One may, then, have $c_R = A(nN)^{\frac{1}{2}}$ for the homonuclear case, where $A$ is the one-electron delta-function strength for the atom, $n$ the principal quantum number of the valence shell, and $N$ the number of electrons making the contributions to the binding or two times the column number in the periodic table. One may take

$$c_{R_{12}} = (c_{R_1} c_{R_2})^{\frac{1}{2}} = n_1 n_2 N_1 N_2 (A_1 A_2)^{\frac{1}{2}} \tag{9}$$

for the heteronuclear case by forming a geometric mean molecular delta-function strength $c_{R_{12}}$, and solve the wave equation as if the molecule were homonuclear.

Two kinds of delta-function strengths have been considered in the present study. The delta-function strenght for an atom having a bonding with another is different from that of the same having two or more bondings with other atoms, and this is due to the difference in the electronic distributions. As an example, the delta-function strength for the sulfur atom in an SO molecule is different from that of the same in $SO_2$ and $SO_3$ molecules, whereas the delta-function strength for the oxygen atom is considered to be the same in all these molecules. The delta-function strength of an atom in a bond of a diatomic molecule and that of an atom in a bond of polyatomic molecule have been, in line with earlier studies [21], obtained from the following:

$$A = [x/(2.6n - 1.7p - 0.8D + 3.0F)]^{\frac{1}{2}} \tag{10}$$

$$(A^*)^2 = A^2(n-3)/(n-1) \tag{11}$$

Here $x$ is the electronegativity on Pauling's scale [29], $n$ the principal quantum number, $p$ is 1 for an atom with $p$-electrons in the valence shell and 0 for an atom with no $p$-electrons in the valence shell, $D$ the total number of completed $p$ and $d$ shells in the atom, $F$ the total number of completed $f$ shells in the atom, $A$ the delta-function strength for an atom in the bond of a diatomic molecule, and $A^*$ the delta-function strength for an atom in a bond of a polyatomic molecule.

### 3. Atomic, bond and molecular polarizabilities

On the basis of the variational treatment [30] first introduced by Hylleraas [3] and Hasse [1], one may generate the polarizability component $\alpha_{xx}$ in the following form:

$$\alpha_{xx} = \frac{4nA}{a_0}\left[\langle(x_1-\langle x\rangle)^2\rangle - (n-1)\langle(x_1-\langle x\rangle)(x_2-\langle x\rangle)\rangle\right]^2 \qquad (12)$$

where $x_1$ is the coordinate of any one of $n$ equivalence classes of electrons which falls in the first equivalence class, $\langle x\rangle$ the average coordinate of any one of these electrons, $A$ the reduced electronegativity of the nucleus, and $a_0$ the radius of the first Bohr orbit of the hydrogen atom. The above equation (12) can be further simplified if the following assumptions, which are implicit in the choice of a delta-function potential model, are made:

The first assumption is that $\langle x\rangle = 0$ for a homonuclear diatomic molecule, because of the symmetrical placement of the delta-function potentials.

The second assumption is that $\langle(x_1-\langle x\rangle)(x_2-\langle x\rangle)\rangle = 0$, because the delta-function potential model allows no electron correlation.

The third assumption is that $x = x_1 = x_2 = x_3 = x_4 = \ldots\ldots\ldots$, because all the bonding electrons are considered to be perfectly equivalent.

On the basis of these assumptions the above equation (12) can be reduced to

$$\alpha_{xx} = \frac{4nA}{a_0}(\langle x_1^2\rangle)^2 \qquad (13)$$

or equivalently

$$\alpha_{xx} = \frac{4A}{a_0}\sum(\langle x_i^2\rangle)^2. \qquad (14)$$

In order to obtain the expectation values of $\langle x^2\rangle$ for atoms, every atom is assumed to be perfectly isotropic, and hence, one has the following:

$$\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = \langle r^2\rangle/3. \qquad (15)$$

On the basis of the delta-function potential model located at the nucleus, one has in polar coordinates:

$$\psi = N\exp(-Ar). \qquad (16)$$

On normalization,

$$N = A^{3/2}\,\Pi^{-\frac{1}{2}}. \qquad (17)$$

Thus,

$$\langle r^2\rangle = \int_0^\pi\int_0^{2\pi}\int_0^\infty \psi r^2\psi^*r^2\sin\theta\,d\theta\,d\varphi\,dr = 3/A^2 \qquad (18)$$

and hence,

$$\langle x^2\rangle = 1/A^2. \qquad (19)$$

Solving for a negative value of $E$ yields the following expression:

$$-\tfrac{1}{2}\frac{\delta^2\psi}{\delta r^2} = -\frac{A^2}{2}\psi = E\psi. \tag{20}$$

Hence, $A = (-2E)^{\frac{1}{2}}$ is the same delta-function strength of the atom obtainable either from the first ionization potential or from the reduced electronegativities of the elements. Finally, the polarizability along the $x$ axis of an atom is given as

$$\alpha_{xx} = 4/a_0^3 A^3. \tag{21}$$

This equation gives the polarizability component of an atom in any desired direction.

Considering a diatomic molecule which has an axis of symmetry, the mean molecular polarizability can be written as $\bar{\alpha}_M = (1/3)(\alpha_{\parallel} + 2\alpha_{\perp})$, where $\alpha_{\parallel}$ is the bond parallel component and $\alpha_{\perp}$ the bond perpendicular component of the polarizability. If the axis is considered to be the internuclear axis for a homonuclear diatomic molecule with the zero point at the center of the electronic charge distribution, then $\langle x \rangle$ becomes zero. The bond parallel component can be obtained from the contribution of two sources, namely, the bond region electrons, and nonbond region electrons. The contribution to the parallel component of the polarizability by the bond region electrons is calculated by using a linear combination of atomic delta-function wave functions representing the two nuclei involved in the bond, i. e., the expectation value of the electronic position squared $\langle x^2 \rangle$ along the bond axis is calculated, and this is used to obtain the bond parallel component of the polarizability $\alpha_{\parallel b}$ from the following:

$$\alpha_{\parallel b} = \frac{4nA}{a_0}(\langle x^2 \rangle)^2 \tag{22}$$

where $n$ is the bond order and the other quantities are well known. The evaluation of the expectation value $\langle x^2 \rangle$ for a one-electron homonuclear diatomic molecule using the delta-function wave functions was easily carried out earlier [22] and is given as

$$\langle x^2 \rangle = \frac{R^2}{4} + \frac{1}{2c^2} \tag{23}$$

where $R$ is the internuclear distance at the equilibrium configuration which is here allowed to equal the delta-function spacing, $a$. If one considers a heteronuclear diatomic molecule, the equations (22) and (23) can be written as

$$\alpha_{\parallel b} = \frac{4nA_{12}}{a_0}(\langle x^2 \rangle)^2 \tag{24}$$

$$\langle x^2 \rangle = \frac{R^2}{4} + \frac{1}{2(c_{R_{12}})^2} \tag{25}$$

where $A_{12}$ is the root mean-square delta-function strength of the nuclei 1, and 2, respectively, and $c_{R_{12}} = (c_{R_1}c_{R_2})^{\frac{1}{2}} = n_1 n_2 N_1 N_2 (A_1 A_2)^{\frac{1}{2}}$. In case the bond is of the heteronuclear type, the bond parallel component of the polarizability must be corrected to allow

for a charge density not in the bond region by virtue of the polarity induced by the electronegativity difference of the atoms. Hence, the charge density in the bond region should, then, be related to the percent covalent character believed to exist in the form

$$\sigma = \exp\left[-(1/4)(x_1 - x_2)^2\right] \tag{26}$$

where $x_1$ and $x_2$ are the electronegativities of the atoms 1 and 2, respectively, on Pauling's scale [29]. Thus, the bond parallel component of the polarizability, after introducing the polarity correction, is given as

$$\alpha_{\|p} = \sigma\alpha_{\|b}. \tag{27}$$

The contribution of the nonbond region electrons to the bond parallel component of the polarizability $\alpha_{\|n}$ is calculated from the remaining valence electrons not involved in the bonding. The basis for such calculations is the Lewis-Langmuir octet rule [31,32] modified by Linnett [33] as a double-quartet of electrons. On the basis of the Linnett model [33], the most stable electronic configurations in the ground state for nitrous oxide, hydrogen cyanide, nitric acid, and aluminum trichloride dimer are given in Fig. 1,
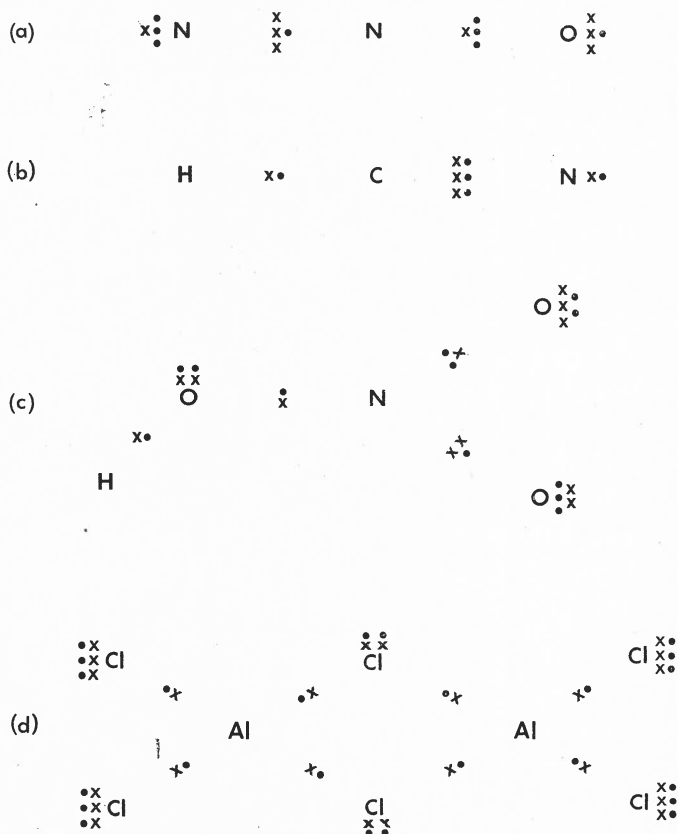
Fig. 1. Electronic configurations in the ground state for (a) nitrous oxide, (b) hydrogen cyanide, and (c) aluminum trichloride dimer

where the "dots" represent the electrons with spin quantum number of $+\frac{1}{2}$ and the "crosses" the electrons with spin quantum number of $-\frac{1}{2}$, or *vice versa*. The contribution of the nonbond region electrons to the bond parallel component of the polarizability $\alpha_{\|n}$ for nitrous oxide can be written as

$$\alpha_{\|n} = (4/5)\alpha_N + (4/6)\alpha_O \tag{28}$$

where $\alpha_N$ and $\alpha_O$ are the atomic polarizabilities of nitrogen and oxygen, respectively. Hence, the general expression for the contribution of the nonbond region electrons to the bond parallel component of the polarizability $\alpha_{\|n}$ is written as

$$\alpha_{\|n} = \sum f_i \alpha_i \tag{29}$$

where $f_i$ is the fraction of the valence electrons in the $i$th atom not involved in the bonding, and $\alpha_i$ the atomic polarizability of the $i$th atom obtainable from the delta-function strength $A_i$.

The bond perpendicular component of a diatomic molecule is, on the basis of a semi-empirical delta-function potential model, simply the sum of the two atomic polarizabilities. If the electronic shape of an atom is assumed to be viewed from a point on a line perpendicular to the internuclear axis, whereas on a line passing through the nucleus the shape approximates that of the nonbonded atom, then the bond perpendicular component of the polarizability can be written as

$$\alpha_\perp = 2\alpha_A \text{ for a nonpolar } A_2 \text{ molecule} \tag{30}$$

and

$$\alpha_\perp = \alpha_A + \alpha_B \text{ for a polar } AB \text{ molecule} \tag{31}$$

where $\alpha_A$ and $\alpha_B$ are the atomic polarizabilities of the atoms $A$ and $B$, respectively. If atom $A$ is less electronegative than atom $B$, the atomic contributions would be considered here according to the square of their respective electronegativities; and the bond perpendicular component of the polarizability can be written as

$$\alpha_\perp = 2(x_A^2 \alpha_A + x_B^2 \alpha_B)/(x_A^2 + x_B^2). \tag{32}$$

If there are three atoms $A$, $B$, and $C$ located at the corners of a triangle, and if all of them are nonbonded, then each atom has three "polarizability degrees of freedom", and the average molecular polarizability is written as

$$\bar{\alpha}_M = (1/3)(3\alpha_A + 3\alpha_B + 3\alpha_C) = \alpha_A + \alpha_B + \alpha_C. \tag{33}$$

If there are bonds between $A$ and $B$ and between $B$ and $C$ for the same system, then one atomic polarizability degrees of freedom is taken up per bond per atom, and the mean molecular polarizability is then

$$\bar{\alpha}_M = (1/3)(\alpha_{\|AB} + \alpha_{\|BC} + \sum 2\alpha_{\perp i}) \tag{34}$$

where the sum of the bond perpendicular components can be written as

$$\sum 2\alpha_{\perp i} = (3N - 2n_b)(\sum x_i^2 \alpha_i / \sum x_i^2). \tag{35}$$

Here, $N$ is the number of atoms in the molecule, $n_b$ the number of bonds in the molecule, $x_i$ the electronegativity of the $i$-th atom on Pauling's scale [29], and $\alpha_i$ the atomic polarizability of the $i$-th atom. The term $(3N-2n_b)$ gives the number of remaining (residual) atomic
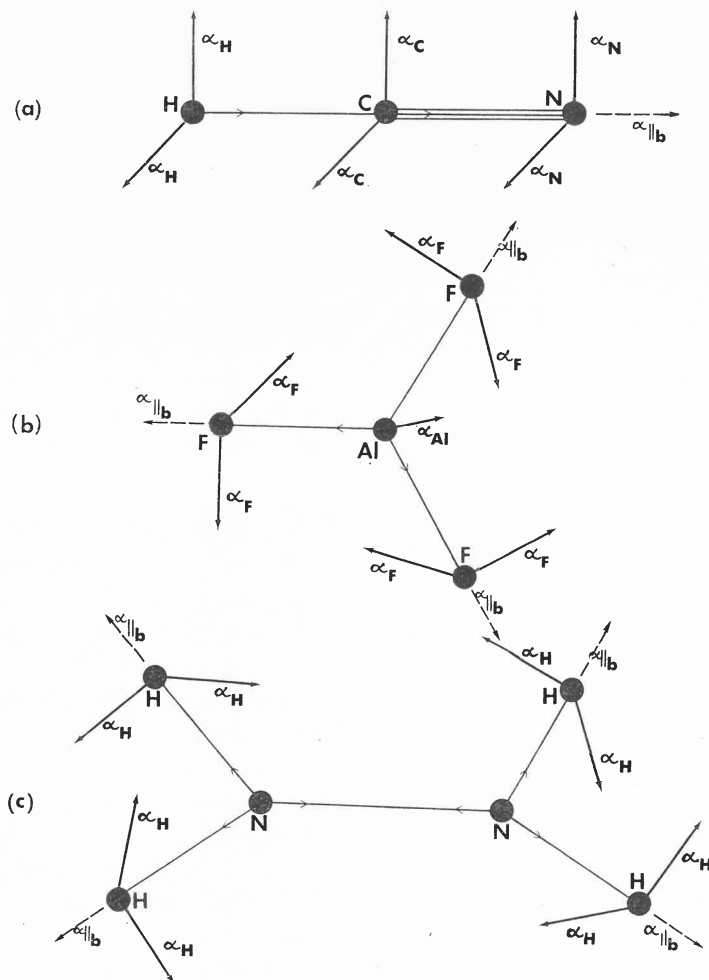


Fig. 2. Residual atomic polarizability degrees of freedom for (a) hydrogen cyanide, (b) aluminum trifluoride, and (c) hydrazine

polarizability degrees of freedom, denoted, $n_{df}$. This is directly obtained by considering the symmetry or geometry of the molecular system. It is assumed then that every isolated atom is allowed to possess three degrees of polarizability freedom and every bond which is formed between two atoms removes two of these polarizability degrees of freedom, with the exception that if two bonds are formed from the same atom (carbon in carbon dioxide) and exist in a linear configuration, then only three atomic polarizability degrees of freedom are lost, and if three bonds are formed from the same atom (sulfur in sulfur

trioxide) and exist in a planar configuration, then only five atomic polarizability degrees of freedom are lost. Thus, the sum of the perpendicular components of the polarizability is given as

$$\sum 2\alpha_{\perp i} = n_{df}(\sum x_i^2 \alpha_i / \sum x_i^2) \tag{36}$$

schematic representations of the residual atomic polarizability degrees of freedom for hydrogen cyanide, aluminum trifluoride and hydrazine are given in Fig. 2. The value of $n_{df}$ is six for hydrogen cyanide, seven for aluminum trifluoride, and eight for hydrazine. Hence, the analytical expression for the average or mean molecular polarizability for a polyatomic molecule is given as follows;

$$\bar{\alpha}_M = (1/3)\left[\sum \sigma\alpha_{||b_i} + \sum f_i\alpha_i + n_{df}\frac{\sum \alpha_i x_i^2}{\sum x_i^2}\right] \tag{37}$$

$$\alpha_M = (1/3)\left[\sum \alpha_{||p_i} + \sum \alpha_{||n} + \sum 2\alpha_{\perp i}\right]. \tag{38}$$

## 4. Results

In order to test how far the polarizability could be a useful criterion for testing the utility of the delta-function potential model adopted, several molecules having six, seven and eight residual atomic polarizability degrees of freedom $(n_{df})$ were considered, and the polarizabilities were computed by using the equations given above. The molecular structural data used for such computations were taken from Sutton [34] and some recent microwave and electron diffraction studies [35, 36]. The Lewis-Langmuir octet rule [31, 32] modified by Linnett [33] as a double-quartet of electrons has been considered here for most of the molecules. The required data for such computations are the molecular structural data, electronegativities of the elements on Pauling's scale [29], delta-function strengths, the parameter "$c$" values, and the atomic polarizabilities. For twenty elements involved in the molecules of the present study, the delta-function strengths in atomic units, the parameter "$c$" values in atomic units, and the atomic polarizabilities in $10^{-25}$ cm³ were calculated, and their values are given in Table I for the bonds of both diatomic and polyatomic systems. The molecules for which the bond parallel components, the contributions of the nonbond region electrons and the bond perpendicular components were calculated from the delta-function potential model have been classified here on the basis of their respective number of residual atomic polarizability degrees of freedom $(n_{df})$, and the calculated values in $10^{-25}$ cm³ are given in Tables II to IV. The available experimental values of the dielectric constants, refractive indices, dipole moments and molar refractions were used to obtain the average molecular polarizabilities through the well-known Clausius-Mossotti, Langevin-Debye and Lorentz-Lorenz equations. The obtained values in $10^{-25}$ cm³ are also given in Tables II to IV.

The perpendicular components were experimentally obtained by Denbigh [37] and Vickery and Denbigh [38], and their perpendicular components are qualitatively equal to the sum of the respective atomic polarizabilities calculated in the present in-

TABLE I

Delta-function strengths in atomic units, $c$ values in atomic units, and atomic polarizabilities in $10^{-25}$ cm$^3$ of some elements for bonds of diatomic and polyatomic systems

| Element | $A$ | $A^1$ | $c$ | $c^1$ | $\alpha_A$ | $\alpha_A{}^1$ |
|---|---|---|---|---|---|---|
| Hydrogen | 1.000 | | 1.414 | | 5.92 | |
| Beryllium | 0.538 | 0.481 | 1.522 | 1.361 | 38.02 | 53.42 |
| Magnesium | 0.414 | 0.393 | 1.434 | 1.361 | 83.70 | 97.94 |
| Calcium | 0.337 | 0.323 | 1.348 | 1.292 | 154.76 | 176.38 |
| Strontium | 0.319 | 0.311 | 1.427 | 1.391 | 182.42 | 197.62 |
| Barium | 0.289 | 0.283 | 1.416 | 1.386 | 245.84 | 262.27 |
| Zinc | 0.393 | 0.380 | 1.361 | 1.316 | 97.94 | 108.33 |
| Boron | 0.785 | 0.687 | 2.626 | 2.349 | 13.58 | 19.07 |
| Aluminum | 0.533 | 0.506 | 2.261 | 2.147 | 39.18 | 44.63 |
| Gallium | 0.472 | 0.456 | 2.312 | 2.234 | 56.35 | 62.69 |
| Carbon | 0.846 | 0.757 | 3.384 | 3.028 | 9.78 | 13.70 |
| Germanium | 0.536 | 0.518 | 3.032 | 2.930 | 38.48 | 42.77 |
| Nitrogen | 0.927 | 0.829 | 4.146 | 3.707 | 7.43 | 10.43 |
| Phosphorus | 0.630 | 0.598 | 3.451 | 3.275 | 23.67 | 27.80 |
| Antimony | 0.564 | 0.484 | 3.507 | 3.422 | 48.64 | 52.43 |
| Oxygen | 1.000 | 0.895 | 4.899 | 4.385 | 5.92 | 8.29 |
| Sulfur | 0.688 | 0.653 | 4.128 | 3.918 | 18.20 | 21.35 |
| Fluorine | 1.065 | 0.953 | 5.635 | 5.043 | 4.90 | 6.87 |
| Chlorine | 0.753 | 0.715 | 4.880 | 4.634 | 13.88 | 16.26 |
| Bromine | 0.633 | 0.612 | 4.737 | 4.580 | 19.41 | 25.93 |

[1] The values for the bonds of polyatomic systems.

TABLE II

Experimental and calculated polarizabilities in $10^{-25}$ cm$^3$ for molecules of six residual atomic polarizability degrees of freedom

| Molecule | $\Sigma\alpha_{\parallel\,p_i}$ | $\Sigma\alpha_{\parallel\,n}$ | $\Sigma 2\alpha_{\perp\,i}$ | $\bar{\alpha}_M$(calc.) | $\bar{\alpha}_M$(exper.) |
|---|---|---|---|---|---|
| $N_2O$ | 30.140 | 9.891 | 46.266 | 28.766 | 29.164[a, b] |
| HCN | 28.456 | 2.972 | 53.099 | 28.176 | 25.913[c] |
| $BeF_2$ | 5.833 | 8.400 | 42.455 | 18.896 | 16.167[d] |
| $BeCl_2$ | 31.907 | 23.794 | 99.373 | 51.691 | |
| $MgF_2$ | 8.834 | 8.400 | 49.218 | 22.151 | 18.426[d] |
| $MgCl_2$ | 43.246 | 23.794 | 113.278 | 60.106 | 53.851[d] |
| $CaF_2$ | 11.746 | 8.400 | 56.647 | 25.598 | 24.964[d] |
| $SrF_2$ | 14.019 | 8.400 | 61.676 | 28.032 | 30.195[d] |
| $BaF_2$ | 23.896 | 8.400 | 69.125 | 33.807 | 38.516[d] |
| $BaCl_2$ | 87.145 | 23.794 | 143.212 | 84.717 | 79.806[d] |
| $ZnCl_2$ | 28.942 | 23.794 | 153.859 | 68.859 | 67.363[d] |

[a] H. E. Watson, G. G. Rao, K. L. Ramaswamy, *Proc. Roy. Soc.*, **A143**, 558 (1934).

[b] H. E. Watson, G. P. Kane, K. L. Ramaswamy, *Proc. Roy. Soc.*, **A156**, 144 (1936).

[c] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, New York 1954.

[d] S. S. Batsonov, *Refractometry and Chemical Structure*, translated by P. P. Sutton, Constants Bureau, New York 1961.

TABLE III

Experimental and calculated polarizabilities in $10^{-25}$ cm³ for molecules of seven residual atomic polarizability degrees of freedom

| Molecule | $\Sigma\alpha_{\parallel p_i}$ | $\Sigma\alpha_{\parallel n}$ | $\Sigma 2\alpha_{\perp i}$ | $\bar{\alpha}_M$(calc.) | $\bar{\alpha}_M$(exper.) |
|---|---|---|---|---|---|
| GeH$_3$Cl | 101.128 | 11.897 | 93.942 | 68.989 | 66.967[a] |
| SO$_2$F$_2$ | 49.005 | 20.240 | 48.557 | 39.267 | |
| SO$_2$Cl$_2$ | 126.652 | 35.633 | 75.861 | 79.382 | 82.025[b] |
| AlF$_3$ | 24.115 | 12.600 | 46.753 | 27.823 | |
| AlCl$_3$ | 121.421 | 35.691 | 113.718 | 90.277 | 89.435[c] |
| AlBr$_3$ | 160.947 | 49.911 | 151.284 | 120.714 | 124.464[c] |
| AlI$_3$ | 276.226 | 76.423 | 219.223 | 190.624 | 199.079[c] |
| COH$_2$ | 30.216 | 3.947 | 53.899 | 29.354 | 27.738[d] |
| COCl$_2$ | 79.463 | 27.739 | 78.244 | 61.815 | 65.778[e] |
| COBr$_2$ | 128.997 | 37.221 | 92.669 | 86.296 | |

[a] C. P. Smyth, A. J. Grossman, S. R. Ginsburg, *J. Amer. Chem. Soc.*, **62**, 192 (1940).
[b] I. E. Coop, L. E. Sutton, *Trans. Faraday Soc.*, **35**, 505 (1939).
[c] See footnote d of Table 2.
[d] E. C. Hurdis, C. P. Smyth, *J. Amer. Chem. Soc.*, **65**, 89 (1943).
[e] C. P. Smyth, K. B. McAlpine, *J. Amer. Chem. Soc.*, **56**, 1697 (1934).

TABLE IV

Experimental and calculated polarizabilities in $10^{-25}$ cm³ for molecules of eight residual atomic polarizability degrees of freedom

| Molecule | $\Sigma\alpha_{\parallel p_i}$ | $\Sigma\alpha_{\parallel n}$ | $\Sigma 2\alpha_{\perp i}$ | $\bar{\alpha}_M$(calc.) | $\bar{\alpha}_M$(exper.) |
|---|---|---|---|---|---|
| BrF$_5$ | 115.400 | 26.546 | 49.561 | 63.836 | |
| IF$_5$ | 99.661 | 27.278 | 53.588 | 60.176 | |
| PF$_5$ | 47.603 | 20.999 | 47.045 | 38.549 | 36.455[a] |
| PCl$_5$ | 257.667 | 59.483 | 118.030 | 145 060 | |
| SbCl$_5$ | 291.544 | 59.486 | 131.692 | 160.907 | 156.758[a] |
| Al$_2$Cl$_6$ | 284.490 | 63.451 | 126.609 | 158.183 | |
| Ga$_2$Cl$_6$ | 342.156 | 63.451 | 140.464 | 182.024 | |
| HNO$_3$ | 48.515 | 13.813 | 54.238 | 38.855 | 38.397[a] |
| NFO$_3$ | 69.607 | 18.013 | 51.847 | 46.489 | |
| N$_2$H$_4$ | 35.993 | 5.944 | 65.582 | 35.839 | 34.553[a] |
| B$_2$O$_2$ | 69.976 | 7.893 | 36.943 | 38.271 | |
| Al$_2$O$_2$ | 290.266 | 7.893 | 43.857 | 114.005 | |

[a] See footnote d of Table II.

vestigation. As an example, the values of atomic polarizabilities in $10^{-25}$ cm³ derived from the experimental values of perpendicular components [37, 38] for hydrogen, oxygen, nitrogen, and carbon atoms are 4.48, 5.94, 7.24 and 10.22, respectively, and the computed values from the delta-function potential model for the same atoms are 5.92, 5.92, 7.43 and 9.78, respectively. Thus, the computed values of atomic polarizabilities are in good agreement with the experimental ones.

The electronic configuration of nitrous oxide in the ground state given in Fig. 1 is in accordance with the results of electron diffraction, microwave and spectroscopic studies [39–42], and yields good agreement between the experimental and computed values of molecular polarizabilities (see Table II). Hydrogen cyanide has a double-quartet of electrons around carbon and nitrogen atoms, and the agreement between experimental and computed values of molecular polarizabilities is good. The dihalides of group II$A$ have only single bonds with a double-quartet of electrons around the halogen atoms, and their calculated values of molecular polarizabilities are in reasonable agreement with experimental data (see Table II).

The molecule chlorogermane has only single bonds; every atom except hydrogen is surrounded by a double-quartet of electrons satisfying the Lewis-Langmuir octet rule [31, 32] and the Linnett model [33]; and there is good agreement between the experimental and computed values of molecular polarizabilities (see Table III). A single bond for the sulfur-oxygen distance has been considered here for sulfuryl fluoride and sulfuryl chloride, and the computed values of polarizabilities are given in Table III. If a double bond is considered for the sulfur-oxygen distance for these two molecules, one obtains the following values in $10^{-25}$ cm$^3$: $\Sigma\alpha_{\|p_i} = 86.324$, $\Sigma\alpha_{\|n} = 16.293$, $\Sigma 2\alpha_{\perp i} = 48.557$, and $\bar{\alpha}_M = 50.391$ for sulfuryl fluoride; $\Sigma\alpha_{\|p_i} = 164.634$, $\Sigma\alpha_{\|n} = 31.687$, $\Sigma 2\alpha_{\|i} = 75.861$ and $\bar{\alpha}_M = 90.727$ for sulfuryl chloride. The observed values for the sulfur-oxygen distance in both of these molecules in 1.43 Å, and this value actually represents nearly a double bond for the sulfur-oxygen distance of many molecules [34]. If a double bond is considered for the sulfur-oxygen distance, both these molecules fail to obey the Lewis-Langmuir octet rule [31, 32] and Linnett model [33] due to the presence of ten valence electrons around the sulfur atom. The experimental value of the molecular polarizability for sulfuryl chloride is thus not in reasonable agreement with the value calculated from the delta-function potential model. If a single bond is considered for the sulfur-oxygen distance, both these molecules obey the Linnett model [33] and Lewis-Langmuir octet rule [31, 32], and the experimental value of molecular polarizability for sulfuryl chloride is in good agreement with the value calculated from the delta-function potential model. The trihalides of aluminum have single bonds, whereas formaldehyde and its halogen-substituted compounds have double bonds for the carbon-oxygen distance, and all experimental values of molecular polarizabilities are in good agreement with those computed (see Table III). More results would be presented later for similar molecules.

The experimental investigations [34] favour a trigonal bipyramidal configuration for the pentahalides of bromine, iodine, phosphorus and antimony. On the basis of this configuration, there is a double-quartet of electrons around the peripheral halogen atoms, while ten electrons surround the central phosphorus and antimony atoms and twelve electrons surround the central bromine and iodine atoms. Though these molecules partly obey the Lewis-Langmuir octet rule [31, 32] and Linnett model [33], the agreement between the experimental and computed values of the molecular polarizabilities is good for phosphorus pentafluoride and antimony pentachloride. The electronic configuration in the ground state given in Fig. 1 for aluminum trichloride dimer satisfies the Linnett model [33] and Lewis-Langmuir octet rule [31, 32] and is in accordance with earlier investigations by

Fajans [43]. The same configuration has been adopted here for the $Ga_2Cl_2$ molecule. The electronic configuration of nitric acid in the ground state is given in Fig. 1, where $ONO_2$ group is planar and NOH plane is perpendicular to the $ONO_2$ plane. The observed value of 1.22 Å has been accepted for the shorter nitrogen-oxygen distance with $1\frac{1}{2}$ as the bond order, and the observed value of 1.41 Å has been taken for the longer nitrogen--oxygen distance with 1 as the bond order. The proposed configuration here for nitric acid obeys the Lewis-Langmuir octet rule [31, 32] and Linnett model [33], satisfies the experimental values of bond distances [34], and yields good agreement between the experimental and computed values of molecular polarizabilities. The boron oxide dimer and aluminum oxide dimer molecules have single and double bonds with a double-quarter of electrons around the oxygen atom. The nonplanar hydrazine molecule has single bonds with a double--quartet of electrons around the nitrogen atom, and the experimental and computed values of molecular polarizabilities tally (see Table IV).

Thus, the delta-function potential model clearly gives explicit expressions for the bond parallel component, bond perpendicular component, contribution by the nonbond region electrons and mean molecular polarizability for the complex as well as simple molecules. All these are in accordance with the investigations of Denbigh [37] in which the molar refraction of a molecule is assumed to be the sum of refractions of all bonds in the molecule, and similarly, the molecular polarizability is assumed here to be the sum of the bond polarizabilities. The contributions by the bond region electrons and the non-bond region electrons are clearly distinguished. The bond parallel component is a linear combination of atomic polarizabilities and independent of the internuclear distance. The bond parallel components can easily be transferred from one molecular system to another, irrespective of the configurations of the two different molecular systems, provided the internuclear distances in the two different molecular systems are nearly identical. The small changes in the values of the parallel components from one molecular system to another may be due to the slightly different values of bond distances, as the parallel component is roughly proportional to the fourth power of the internuclear distance. In addition to these special features of the delta-function potential model, one finds that there is good agreement between the experimental and computed values of the atomic and molecular polarizabilities. Thus, the present investigation clearly shows that the delta-function potential model is very useful in evaluating the atomic, bond and molecular polarizabilities for any molecular system.

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