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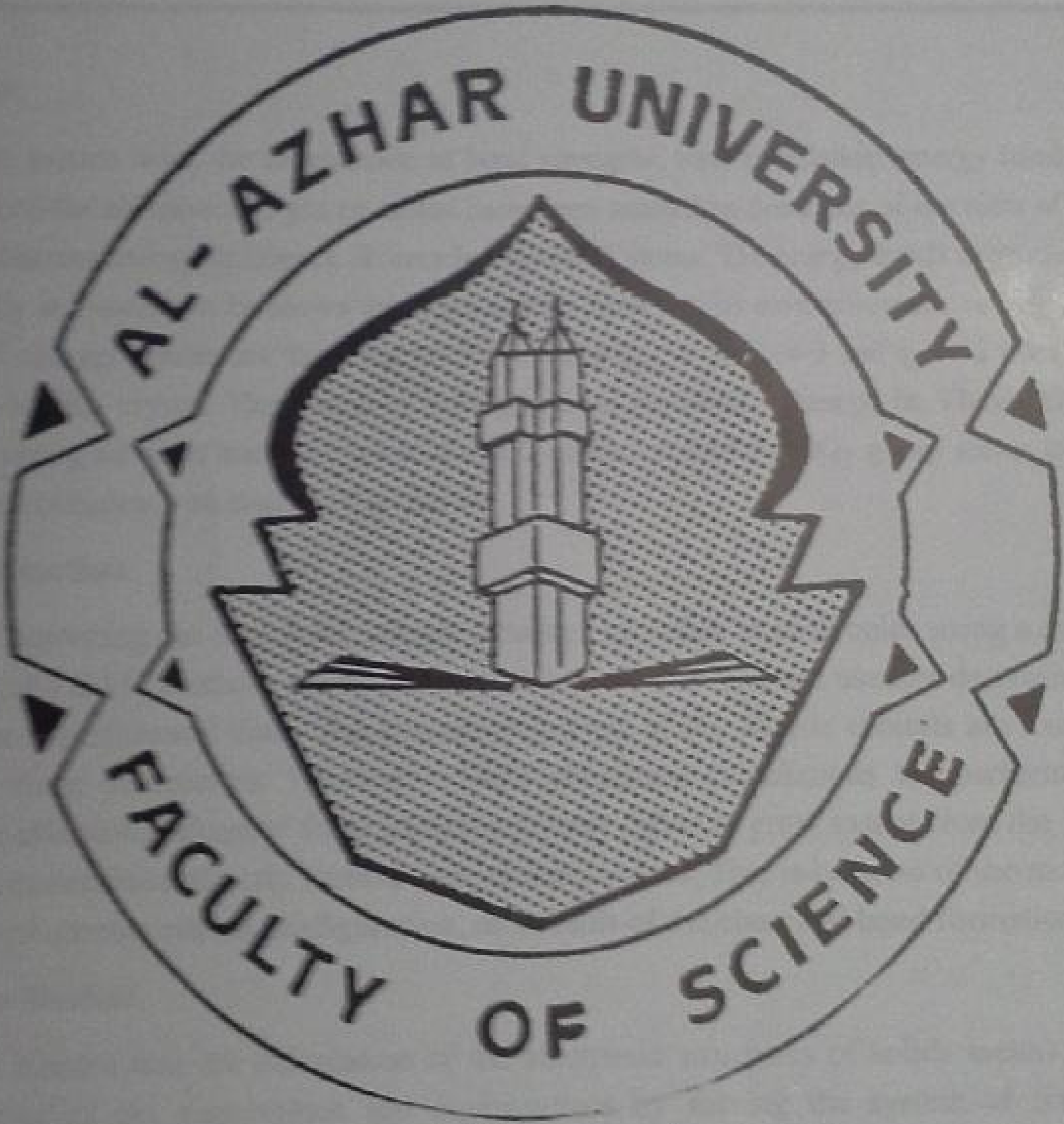

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THE EFFECT OF THE RATIO OF IONIZATION ENERGY ON THE PHYSICAL PROPERTIES OF NANO$_2$

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Abstract

In the present work the dependence of bond strengths, total population, energy bands at Γ-point and the effective charges on atoms have been studied as functions of the ratio of the valence electron energy difference δε between N and O atoms. The energy bands dependence of NaNO$_2$ at Γ-point on δε shows [illegible] energy band has its own minimum value. The values of charges denote that the [illegible] which $q_{Na} = 1$, $q_N = 3$ and $q_o = -2$ does not occur in NaNO$_2$ crystal. The system [illegible] for the small values of δε. These values indicate strong covalent bonds between N and O atoms, so that the NO$_2$ group seems to be compacted complex with high covalent nature.

1- Introduction

In Calculating the electronic energy structure of solids or molecules using a semiempirical LCAO method, many parameters are used, which are usually determined from the experimental data. The ionization energy of the atomic orbitals are examples of these parameters. However, if self consistent calculations are performed, then the effective values of these parameters may differ to great extent from the initial values obtained directly from the experimental data. This is because of the modification of atomic orbital configuration, as a result of the chemical bond formation.

2- *The Method*

It is Known that the calculation of the electronic structures of solids means the foundation of the eigenvalues and eigenvectors by solving the system of linear equations

$$\sum_j \left[H_{ij}(\vec{K}) - E_a(\vec{K}) S_{ij}(\vec{K}) \right] C_{a,j}(\vec{K}) = O \qquad (1)$$

Refreed by: A. El-Sharkawy & A. El-Dieb

Where α denotes different eigenvalues, $\vec{K}$ is the wave vector, i, j denote different atomic orbitals, $H_{ij}(\vec{K})$ and $S_{ij}(\vec{K})$ are the Hamiltonian and overlap matrix elements, and $E_\alpha(\vec{K})$ are the energies (eigenvalues) of the eigenvectors $C_{\alpha j}(\vec{K})$.

The overlap matrix elements are given by

$$S_{ij}(\vec{K}) = \sum_{\vec{R}_n} S_{ij}(\vec{R}_n)\exp.(i\vec{K}.\vec{R}_n) \tag{2}$$

$$S_{ij}(\vec{R}_n) = \int \phi_i^*(\vec{r})\phi_j(\vec{r}-\vec{R}_n-\vec{R}_{\nu\nu'})d\tau \tag{3}$$

Where $\phi_i(\vec{r})$ is the atomic wavefunction, $\vec{R}_\nu$ and $\vec{R}_{\nu'}$ are the coordinate vectors of atoms ν and ν' in the first primitive cell at which ϕ_i and ϕ_j exist, $\vec{R}_{\nu\nu'} = \vec{R}_\nu - \vec{R}_{\nu'}$, and $\vec{R}_n$ is the translation vector.

The Hamiltonian matrix elements are given by:

$$H_{ij}(\vec{K}) = \sum_{\vec{R}_n} \tilde{H}_{ij}(\vec{R}_n)\exp.(i\vec{K}.\vec{R}_n) \tag{4}$$

Where

$$\tilde{H}_{ij}(\vec{R}_n) = \int \phi_i^*(\vec{r})\overset{H}{\underset{\wedge}{\,}}\phi_j(\vec{r}-\vec{R}_n-\vec{R}_{\nu\nu'})d\tau \tag{5}$$

Neglecting the three center type integrals, it can be seen that

$$\tilde{H}_{ij}(\vec{R}_n) = \int \phi_i^*(\vec{r})\left[-\frac{1}{2}\nabla^2 + V^{\nu}(\vec{r}) + V^{\nu'}(\vec{r}-\vec{R}_n-\vec{R}_{\nu\nu'})\right]\phi_j(\vec{r}-\vec{R}_n-\vec{R}_{\nu\nu'})d\tau \tag{6}$$

Where $V^{\nu}(\vec{r})$ and $V^{\nu'}(\vec{r}-\vec{R}_n-\vec{R}_{\nu\nu'})$ are the potentials due to atoms ν, ν' at which $\phi_i(\vec{r})$ and $\phi_j(\vec{r}-\vec{R}_n-\vec{R}_{\nu\nu'})$ exist. Within the mentioned above approximation given by eq. (6) and by the analogy with the semiempirical theory in molecules, it is clear that.

$$\tilde{H}_{ij}(\vec{R}_n) = \text{function of } \{S_{ij}(\vec{R}_n)\} = F(S_{ij}(\vec{R}_n)) \tag{7}$$

It is reasonable, therefore, to consider a semiemprical formula for the Hamiltonian matrix elements $H_{ij}(\vec{K})$ for crystals. According to Eldib [1].

$$\tilde{H}_{ij}(\vec{K}) = \sum_{\vec{Rn}} \{(2 - |S_{ij}(\vec{R}_n)|)\, S_{ij}(\vec{R}_n)\, (H_{ii}(\vec{q}) + H_{jj}(\vec{q})/2\} \exp.(i\vec{K}.\vec{R}_n) \quad (8)$$

Using the overlap values as given by eqs. (2), (3), the values of the coefficients $C_{a,j}(\vec{K})$ from eq. (1) and Mulliken population analysis [7], then the effective charges can be obtained as

$$q_v = Z_v - \sum_{a=1}^{n} \eta_a \left\{ \sum_j \left| C_{a,j} \right|^2 + \sum_i \sum_{j \neq i} C^*_{a,i} C_{a,j} S_{ij} \right\} \quad (9)$$

Where Z_v is the number of valence electrons considered from atom υ, n is the number of filled eigenfunctions, η_a is the number of electrons in orbit a.

Using a self-consistent iteration procedure, the diagonal matrix elements H_{ii} (q) in eq. (8) can be corrected using the [illegible] obtained from eq. (9). The dependence of H_{ii} on q is assumed to be in the form of a power series

$$H_{ii}(q_v) = \sum_m Am\, q^m = A_o + A_1 q_1 + A_2 q_2^2 + \quad (10)$$

Where A_m are the atomic orbital constants to be determined using the spectroscopic parameters for ionization energy of neutral and non-neutral atoms, as explained by[2].

In this work the diagonal matrix elements H_{ii} (q) are taken to be equal. to the ionization energy of the atomic orbital (ε). However, according to[1,2,3] in the semiemprical LCAO method the Hamiltonian (and in turn the corresponding eigenvalues and eigenfunctions) depends on the ionization energy of the atomic orbitals (ε). To study the dependence of the energy bands and some other physical properties of the $NaNO_2$ crystal on the ionization energy (ε) in the present work, we use the ratio of the valence electron energy difference δε in the form.

$$\delta\varepsilon = [(|\varepsilon_N(q)| - |\varepsilon_o(q)|) / |\varepsilon_N(q)|] * 100$$

Where ε_N and ε_o are the ionization energies of N and 0 atoms and q is the atomic effective charge. If q = 0, then $\varepsilon_{(o)}$ equals the atomic energy of isolated atom.

In the present work the bond strengths (S), the total population (TP), the energy bands, and the effective charges on atoms are calculated as functions of δε.

3- Results and Discussions:

The bond strengths as a function of the ratio of the valence electron energy difference ($\delta\varepsilon$), are shown in Fig. (1). It is shown from the results that the N -O bond changes approximately linearly when Sa is far from zero. The largest values of N -O bond as shown from the figure occur in the range of $\delta\varepsilon$ confined as

$$- \ 13 \leq \delta\varepsilon \leq 13$$

The N -O bond attains its maximum value when $\delta\varepsilon \rightarrow -8.5$ approximately. In other words, when the difference between the first ionization potentials of N and O atoms is given as:

$$|\, \varepsilon_n (q) \,| - |\, \varepsilon_o (q) \,| \approx 1.24 \ \text{eV}$$

It should be mentioned that, the consideration of the electrostatic potential due to the effective charges on atoms reduces $\delta\varepsilon$ to zero. This can be explained using the results of Madelung Potential given by [4], from which we can find

$$\varepsilon_o + \mu_o \approx \varepsilon_N$$

The Na - O, Na - N and O - O bonds as shown from the figure are antibonds for all positive values of $\delta\varepsilon$. On the other hand for negative values of $\delta\varepsilon$, the Na - O bond changes to be bonding for $\delta\varepsilon < -23$.

However, the significant here is the sudden change of the slope of these antibonds at the value of $\delta\varepsilon$, at which N - O bond attains its maximum value. This may indicate a type of equilibrium between the interacting forces at this value of $\delta\varepsilon$.

Fig. (2) gives the dependence of the total population (TP) on the ratio of the ionization energy difference $\delta\varepsilon$. It is shown that the population of Na is affected little by $\delta\varepsilon$. On the other hand the populations of N and O are directly affected. Increasing $\delta\varepsilon$ the oxygen population increases, while the nitrogen population decreases and in turn less interaction between the two atoms. This observed divergence between the TP of N and O atoms is accompanied with some artificial ionic character which leads to less equilibrium state for the system. However for $\delta\varepsilon < O$, the dependence of TP on $\delta\varepsilon$ becomes non linear, and the system becomes covalent.

Fig. (3) shows the dependence of the energy bands of $NaNO_2$ at Γ-point on the ionization energy difference ratio $\delta\varepsilon$. It is shown from this figure that each energy band has its own minimum value. For, the lower bands, the minimum occurs at $\delta\varepsilon$ equal about-15. However the point at which the minimum energy occurs shifts towards $\delta\varepsilon$ equal to zero for higher bands. According to these results one can expect that the system as a whole has its ninimum energy when the values of $\delta\varepsilon$ tends to zero. At these values, the system becomes more stable.

As shown from Fig. (3) the relation between the energy bands and $\delta\varepsilon$ in general is non linear for all bands as expected. The lowest bands from 1 to 9 are filled with electrons. The bands from 10 to 13 are empty bands. The bands from 1 to 10 decrease with increasing $\delta\varepsilon$. Each of these bands has its own minimum. When increasing $\delta\varepsilon$ more these energy bands begin to increase. Another increase of $\delta\varepsilon$ causes another decrease for these bands to another minimum. However the first minimum which occurs in the range of $-10 \leq \delta\varepsilon \leq 10$, represents a real minimum of the system. This mentioned range corresponds to the bond strengths which indicate the highest covalent state at which the system becomes stable. On the other hand the second minimum occurs when the system is made artificially to be ionic, so that this second minimum is not actual minimum for the system and does not represent its stationary state.

The effect of the ratio of the ionization energy difference on the charges of Na, N and O atoms is shown in Fig. (4). At $\delta\varepsilon \approx -23$ the sodium charge (q_{Na}) is ~ 0.86. On increasing $\delta\varepsilon$, q_{Na} increases nonlinearly in the covalent region. At values of $\delta\varepsilon > -10$ in the ionic region q_{Na} begins to increase linearly on increasing $\delta\varepsilon$. The Na charge acquires its maximum value ~ 0.98 when $\delta\varepsilon > 70$. The charges on nitrogen (q_N) and on Oxygen (q_o) are affected more strongly than that of q_{Na}. The nitrogen charge (q_N) acquires negative values in the region $-23 \leq \delta\varepsilon \leq -13$.

For values of $\delta\varepsilon > -13$ in the ionic region, q_N becomes positive, while $\frac{dq_N}{d\varepsilon}$ decreases as $\delta\varepsilon$ increases. The maximum value of $q_N \approx 1.64$ reached at $\delta\varepsilon \approx 70$, at which $\frac{dq_N}{d\varepsilon} \approx$ zero.

On the other hand q_o is always negative. At $\delta\varepsilon \approx -23$, $q_o \approx -0.31$. However $\frac{dqo}{d\varepsilon}$ tends to zero as $\delta\varepsilon$ increases. At $\delta\varepsilon \approx 70$, $\frac{dqo}{d\varepsilon} \approx$ zero and $q_o \approx -1.31$. It should be mentioned that the values of charges obey the relation.

$$q_{Na} + q_N + 2q_o = o$$

From these results it can be seen that the extreme values of charges are $q_{Na} \approx 0.86$, $q_N = -0.24$ and $q_o \approx -0.31$ in the valence region, and $q_{Na} \approx 0.98$, q_N 1.64 and $q_o \approx -1.31$ in the ionic region. These values of charges denote that the ionic model in which $q_{Na} = 1$, $q_N = 3$ and $q_o = -2$ does not occur in $NaNO_2$ crystal.

These results assert the following facts:

1- The system is more stable for the small values of $\delta\varepsilon$. These values indicate covalent character.

2- The system in this region tends to form strong covalent bonds between N and O atoms, so that NO_2 group is compacted complex with high covalent nature.

3- Sodium atom does not interact strongly with NO_2 group by means of covalent bonds but ionic bonds. That the electrostatic potentials due to charges on atom are balanced with the bonds and antibonds in "$NaNO_2$" formula unit.

4- Using the obtained nitrogen charges the calculated spontaneous polarization agrees with[4] to be in the range.

$$8.61 < P_s < 12.43\ \mu c/cm^2$$

The experimental values of P_s exists between these limits 8 $\mu c/cm^2$[5] and 12.8 $\mu c/cm^2$[6]. Calculating P_s using $q_N = 1.62$ gives $P_s = 47.43\ \mu c/cm^2$.

These indicate the fact that only small negative charges are allowed for nitrogen in $Na\,NO_2$.

5- The last fact with those mentioned above leads to the conclusion that the ionic model in $Na\,NO_2$ is not valid.

6- Since in semiempirical methods ε are usually determined by means of the experimental spectroscopic data for certain configuration according to suitable guess for the configuration interaction, there fore, the effect of the configuration interaction on the Hamiltonian can be examined at certain basis set by the method explained above. The effect of the configuration interaction leads finally to an adjustment of the diagonal Hamiltonian matrix - elements H_{ii}. This way enables- one to determine not only the optimum values of the atomic orbital energies and in turn the diagonal elements of the Haniltonian, when calculating the physical properties of a system, but also to obtain some valuable information about the properties themselves.

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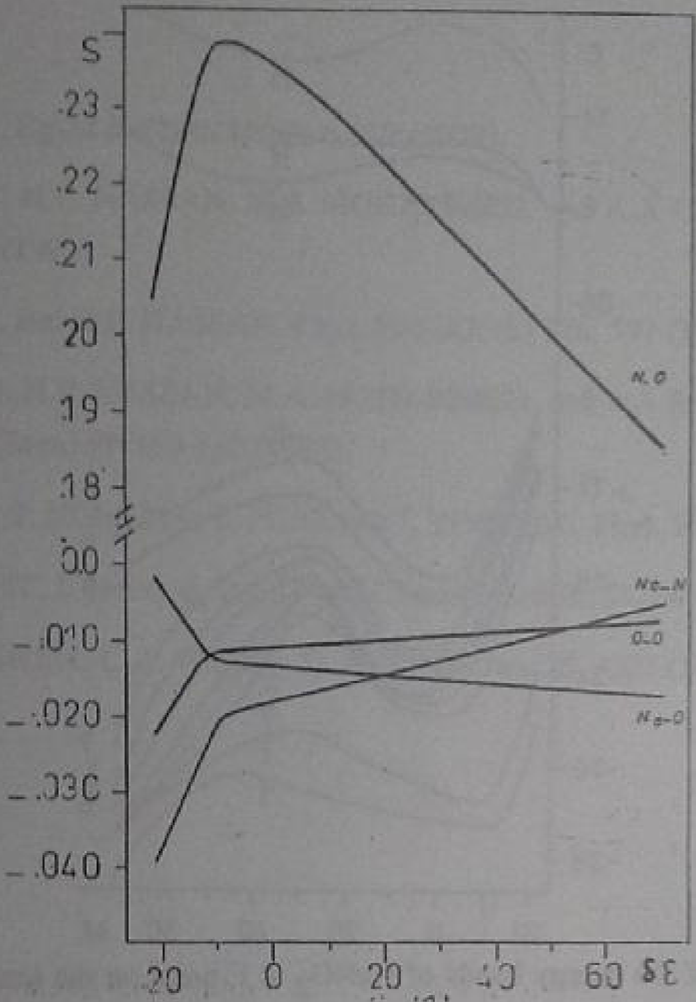

Fig. (1): The bond strengths (S) as a function of the ratio of the valence electron energy difference (δε).

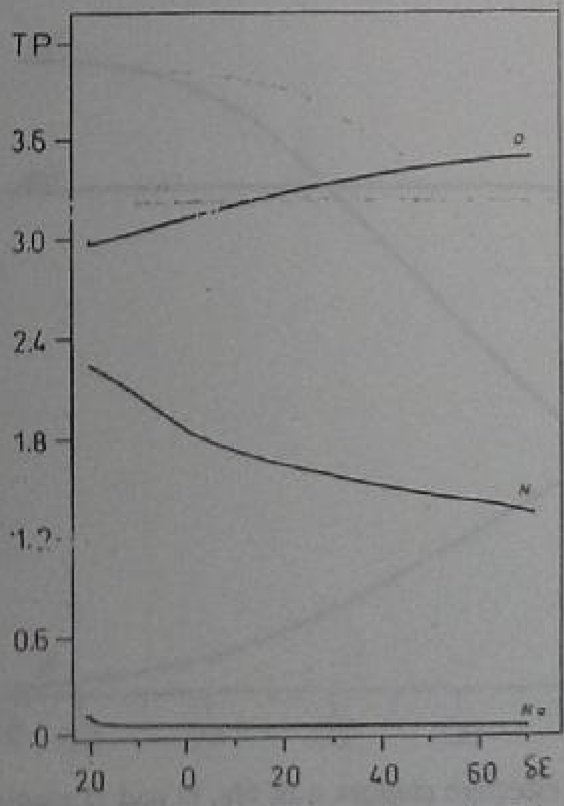

Fig. (2): Dependence of the total population (TP) on the ratio of ionization energy difference (δε).

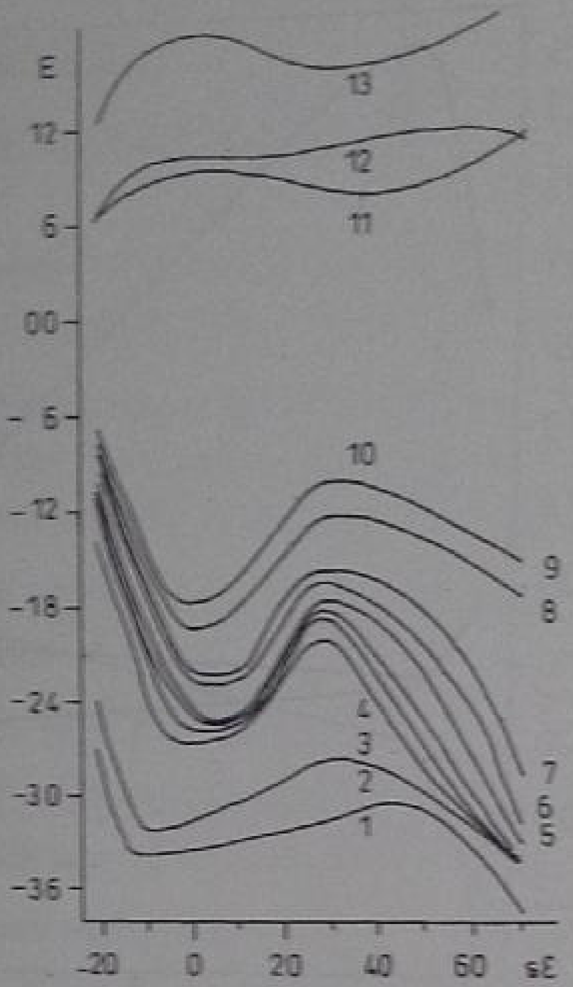

Fig. (3): Dependence of the energy bands of $NaNO_2$ at Γ-point on the ionization energy difference (δε).

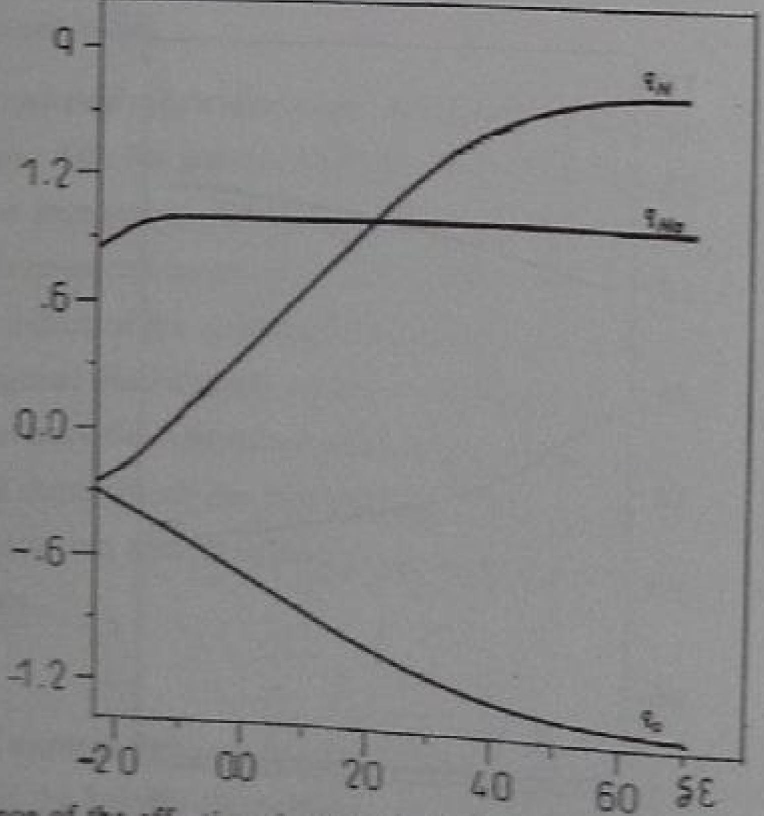

Fig. (4): Dependence of the effective charges q of Na, N and O atoms on the ratio of ionization energy difference (δε).

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