

## A MATHEMATICAL MODEL TO STUDY THE XANES SPECTRA OF K-EDGE OF SULPHUR IN SOME SYSTEMS.

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### **Abstract :**

XANES studies make it possible to determine the geometrical parameters (interatomic distances and bond angles) around the X-ray absorbing atom. The environment of the absorbing atom is the primary cause for the XANES features. This is the reason these characteristic features are clearly observed for disordered systems. XANES was used to determine the local structure in compounds. A systematic approach based on mathematical methods of solving inverse correlation and taking into account the specifics of XANES is now being developed.

**Keywords :** XANES, Chemical shift, K-edge.

### **Introduction :**

X-Ray spectroscopists of early days could not derive much information about the local structure around the X-ray absorbing atom from XANES. But recent theoretical advancements and the improved experimental facilities have made the quantitative interpretation easier. The form of XANES depends on many quantities primarily on and the geometrical parameters, the parameters of potentials. It is necessary to determine all these parameters simultaneously for the interpretation of spectrum

With the advent of highly collimated synchrotron radiation sources and improved detection methods, the limitation on sensitivity has also been largely overcome such that specific site information may be obtained for literally any element in any situation.

The kinetic energy of the ejected photoelectron is small near the absorption edge. The core potential of central absorbing atoms plus its neighbor(s) and the valence electron charge distribution in the intermolecular region, Sette et.al.<sup>1</sup> influence the scattering process (or resonance). This resonance can be visualized as arising from a scattering process where the photoelectron is resonantly scattered back and forth along the internuclear axis between the absorbing atoms and its neighbor (s), Orel et.al.<sup>2</sup>. Therefore, the co-ordination geometry and the interatomic distances<sup>1,2,3</sup> should have correlation with these continuum peaks. The intense maxima, generally arising from transitions of photoelectrons from the core states to the one - electron quasistationary state (shape resonance)<sup>4-11</sup>. characterizes the X-Ray absorption near edge structure. By the study of XANES spectra of K-edge of Sulphur in CaS, MnS, Mgs, and FeS, and in the graph for  $(E_r - E_b)$  versus  $1/R^2$  Kasra et. al.<sup>12</sup> have shown that the first peak above the main absorption peak correspond to a higher coordination shell. According to Bianconi et.al<sup>13</sup>. the equation (4) is valid for the main absorption peak C and for the peak ~40eV above the edge with different constants. He correlated them to the nearest neighbor shell distance. But they failed in correlating the other continuum absorption peaks to any single shell.

Therefore, the inverse correlation  $ER^2 = \text{constant}$ , is less meaningful with different constants for different XANES peaks (above c) for the same system. When the ejected photoelectron moves into the continuum level, i.e. beyond peak C, it can be assumed to be free. The scattering from different neighboring atoms can directly be related to their distances from the absorbing atom in the systems. Therefore scattering from different shells must be governed by the same constant and hence for different peaks.

According to inverse relation, the scattering taking place from the atoms situated further from the absorbing atom must cast their signature at lower energies and inverse condition, i.e., the scattering atom situated closer to the absorbing atom must project their signature at higher energies. But till date, nature and value of  $C_r$  and  $C_b$  or  $C$  has not been clearly understood. As the chemical shift in XAS provides information about the charge density on the X-Ray absorbing atom, some correlation between the characteristic energy ( $s$ ) and the nearest neighbor distance ( $R$ ) with the effective charge ( $q$ ) on the X-Ray absorbing atoms is highly expected. When we use the characteristic energy ( $s$ ) (the edge energy calculated by our method) in place of  $\Delta E$  in the inverse correlation of Natoli and Bianconi<sup>14</sup>. we get more positive results for bond distance that describes about the real picture and significance of the constants appearing in the famous equation of Natoli and Bianconi<sup>14</sup>.

### **Natoli's Formula For Bond Distance :**

The shape resonance peak energy has inverse correlation with first coordination shell distance according to Kutzler et.al.<sup>15</sup> Using MS theory Natoli has also deduced such relationship. The first-shell ligands cause the molecular potential. Kutzler et.al.<sup>15</sup>. demonstrated from their multiple scattered wave SCF X-alpha Calculation on transition metal K-edge that the first-shell legends have an overall qualitative effects on the observed spectral features. Using multiple scattering theory in XANES, Natoli has given a correlation between the continuum resonance energy ( $E_r$ ) corresponding to peak C (showing maximum absorption peak) and the first coordination shell distance ( $R$ ) by the following relation.

$$(E_r - V_0)R^2 = C_r \quad (1)$$

Where,  $C_r$  is a constant corresponding to  $E_r$  and  $V_0$  is the average interstitial potential and  $R$ , is the nearest neighbor distance. Also for the peak A (a low energy peak of X-Ray K-absorption edge) Natoli has suggested a similar expression as follow :

$$(E_b - V_0)R^2 = C_b \quad (2)$$

Here,  $E_b$  is the bound state energy corresponding to peak A with a different constant  $C_b$ .

From equations (1) and (2) we have

$$(E_r - E_b)R^2 = C_r - C_b \quad (3)$$

Here, one gets rid of  $V_0$  by this modification but  $C_r$  and  $C_b$  are still unknown. The atomic phase shifts depend on the energy in the bound resonance region so cannot be ignored. Because of this fact Natoli<sup>16</sup> suggested that  $C_b$  depends on  $R$ . This further puts complications in the process of determining bond distance. Bianconi et. al.<sup>17</sup> also suggested the following equation.

$$\Delta E.R^2 = C \quad (4)$$

Where,  $C = C_r - C_b$ , is a constant quantity. This relation applies for the bound states (pre peaks) at the K-edge of the transition elements in insulators with tetrahedral coordination elements with variation of  $R$  about 20%. But neglecting the effect of the variation of the phase shift of different elements greatly reduced the practical utility of equation (3) for determining bond distances. The values of constant  $(C_r - C_b)$  or  $C$  will be nearly same for the same pair of absorber and nearest neighbors. It is because there is a small variation in the number of valence electrons of the surrounding atoms in the first shell around the central absorbing atom. The interatomic distance  $R$  can be calculated by using equation (3).

Here, we have attempted to find a formula for the determination of bond distance that may be applicable to maximum number of systems and conditions.

In the present work, we have attempted to understand the nature/values of  $C_r$ ,  $C_b$  and  $C$ . The same constant is valid for the entire continuum resonance peak above the absorption edge.

### Nature of $C_r$ , $C_b$ and $C$ in Natoli and Bianconi equation :

The chemical shift in XAS provides information about the charge density on the X - ray absorbing atom, the edge energy and the nearest neighbor distance (R). Therefore, the edge energy (i.e. characteristic energy S in our proposition) and the first coordination shell distance R must have some co-relation with the effective charge q on the X- ray absorbing atom (s). Here the basic idea we have taken from the inverse square law of Bianconi, i.e.,  $\Delta ER^2 = c$ , and for knowing the nature of c we have tried to search the best fit correlation between the constant c ( $=SR^2$ ) and the effective charge q of the x-ray absorbing atom as the value S has been calculated by taking zero value of energy at beginning of absorption to the value of energy covering maximum area of the XANES. This gives an average energy of K-edge absorption. Taking this into account we have substituted S for the value of  $\Delta E$  and have tried to find an appropriate function between  $SR^2$  and q (the effective charge of the X-ray absorbing atom) for understanding the nature of the constant C appearing in Natoli and Bianconi formula .

We observe that the correlation of  $SR^2$  of X- ray absorbing atom of **Sulphur** in CaS, MnS, MgS and FeS ,With the effective charge q on corresponding K-edge showing higher correlation coefficients (between 90 to 99%). This strengthens our concepts regarding our proposed method for the analysis of XANES and measurement of physico-chemical parameters.

It clearly shows that the constant term C appearing in Natoli and Bianconi formula is directly related to our characteristic energy(s) and bond distance (R), i.e. to  $SR^2$ , and  $SR^2$  varies according to the effective charge of the K-absorption edge. Thus the constant C is directly related to the effective charge of the K-absorption edge as well as to the characteristic energy of the absorption edge. The high degree of correlation coefficient between  $SR^2$  and q suggests that  $C_r$ ,  $C_b$  or C depends upon the chemical environment around the X- ray absorbing atom defined by effective charge on the atom .When we applied the best fit correlation,  $SR^2 = a + bq + cq^2$ ,for the calculation of first coordination shell distance R as,

$$(S - E_p)R^2 = aq^3 + bq^2 + cq + d \quad (5)$$

$$R = \sqrt{\frac{aq^3 + bq^2 + cq + d}{(S - E_p)}} \quad (6)$$

Here,  $E_p = E_A$  for peak A  
 $= E_B$  for peak B  
 $= E_C$  for peak C

We observe the results of calculated values as very close to the standard crystallographic values irrespective of the systems used. Thus we get here more generalized approach for the measurement of bond distance.

### **Formulation for Calculating Bond Distance :**

We have used the polynomial correlation between  $SR^2$  and  $q$  for Bond Distance determination as follows;

$$SR^2 = aq^3 + bq^2 + cq + d \quad (7)$$

or,

$$R = \sqrt{\frac{aq^3 + bq^2 + cq + d}{(S - E_p)}} \quad (8)$$

Using equation (8), the nearest neighbor distance in the systems under study were measured. The result are show in the table (1) and Fig. (1-3).

### **Conclusions :**

The Calculated values of the nearest neighbor distance (R) show in table (1) and Figures (1-3) are very close to the standard crystallographic values. This show that our approach

to calculate R is quite correct, and R can be measured directly from the experimental spectra and also we can identify the nearest neighbor of the X- ray absorbing atom.

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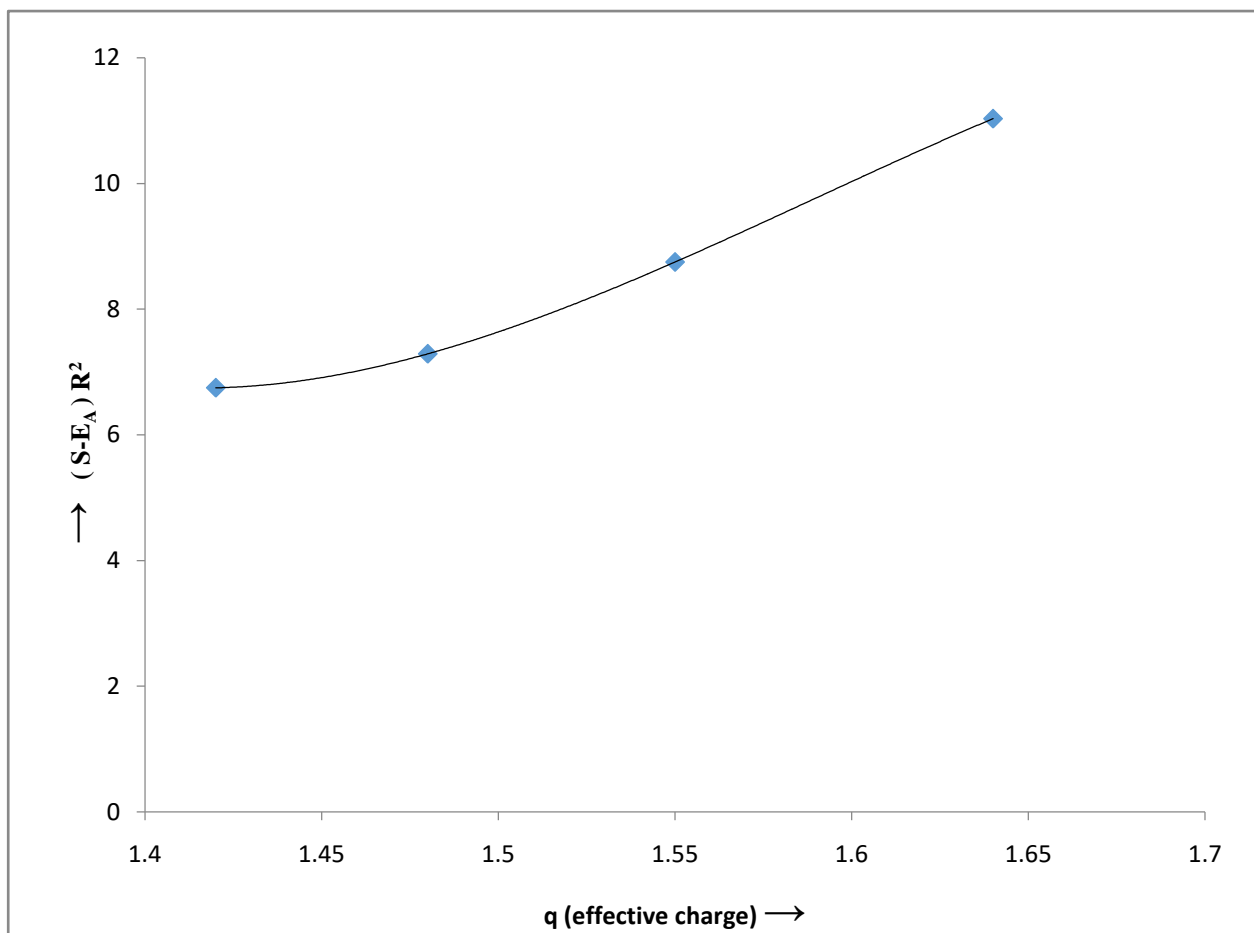
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**Fig.1 : Correlation between  $(S-E_A)R^2$  and the effective charge (q) in Sulphur System.**



**Equation of Graph :  $(S - E_A ) R^2 = a q^3 + b q^2 + c q + d$**

**Coefficient value :**

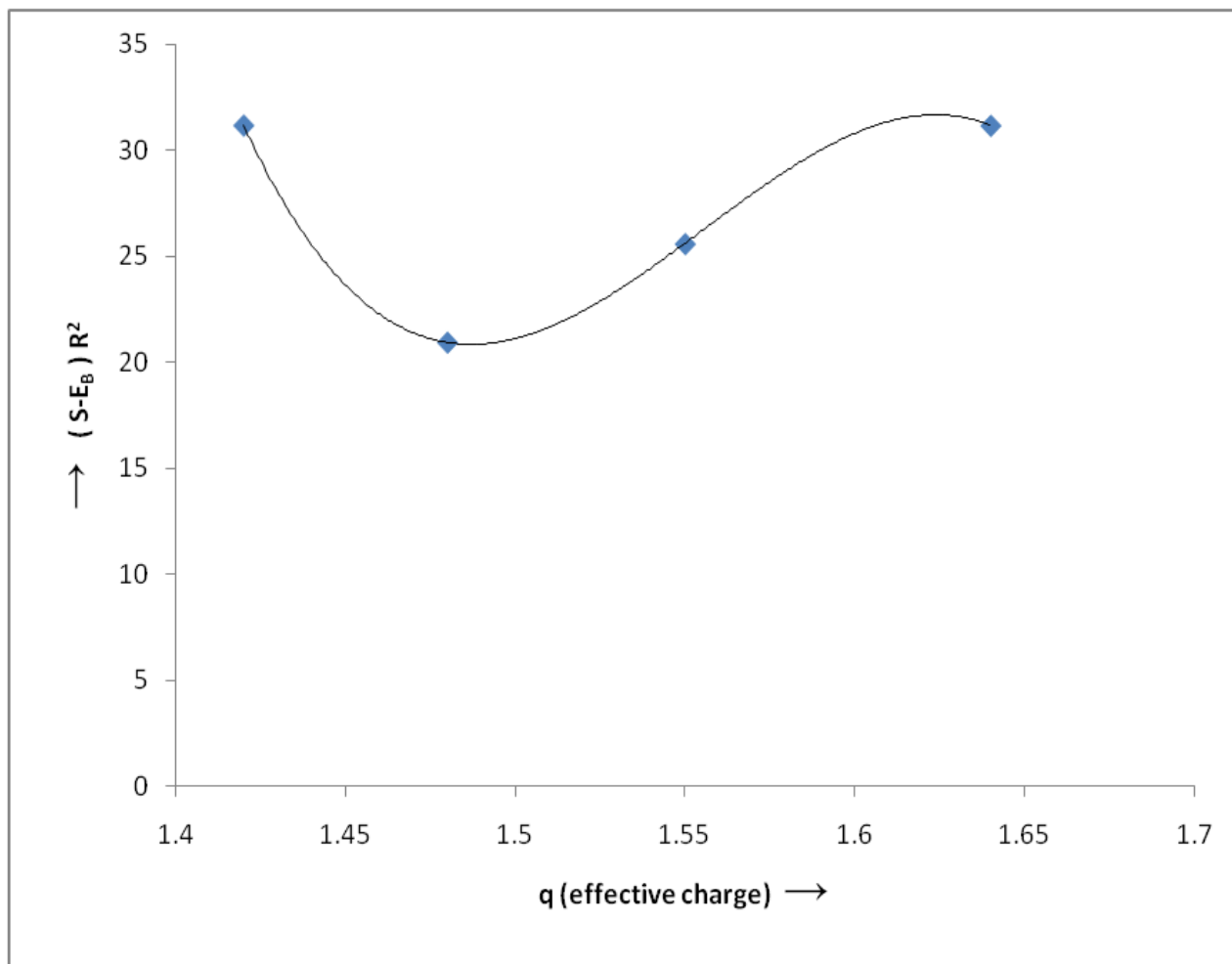
**a = -287.4, b = 1370,**

**c = -2151, d = 1121**

**Correlation Coefficient :**

**$R^2 = 1$**

Fig. 2 : Correlation between  $(S-E_B)R^2$  and the effective charge (q) in Sulphur System.



**Equation of Graph :**  $(S - E_B ) R^2 = a q^3 + b q^2 + c q + d$

**Coefficient value :**

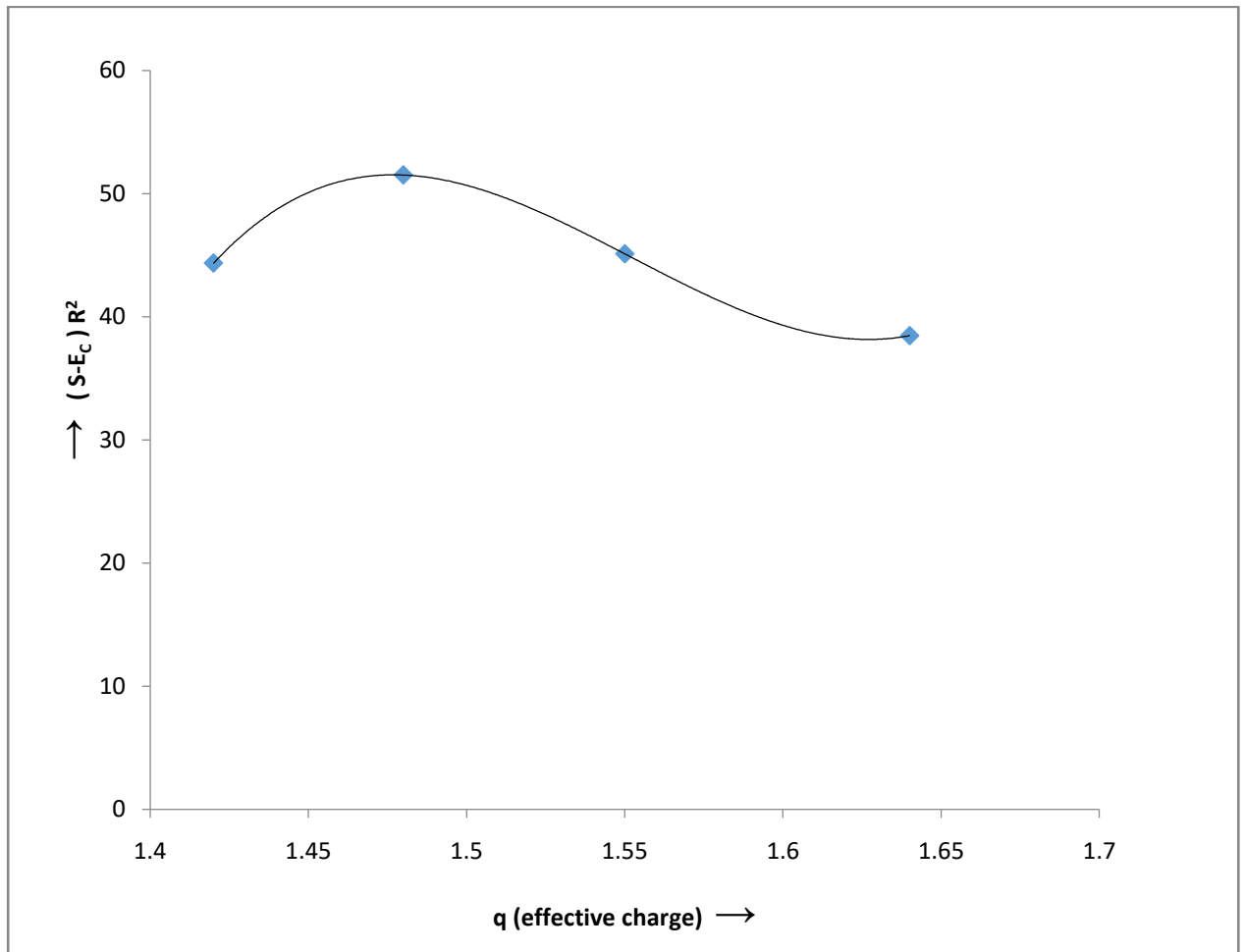
$a = - 8415, b = 39247$

$c = - 60976, d = 31521$

**Correlation Coefficient :**

$R^2 = 1$

**Fig. 3 : Correlation between  $(S-E_c)R^2$  and the effective charge (q) in Sulphur System.**



Equation of Graph :  $(S - E_c ) R^2 = a q^3 + b q^2 + c q + d$

Coefficient value ;

$a = 7864, b = -36619$

$c = 56699, d = -29149$

Corelation Coefficient :

$R^2 = 1$

**Table 1 : Determination of Nearest Neighbour Distance in some systems of Sulphur .**

Absorber	E <sub>A</sub> in eV	E <sub>B</sub> in eV	E <sub>C</sub> in eV	S in eV	q Paulings Method	R (Std.) Å	R <sub>Calculated</sub> – using Å			(S-E <sub>A</sub> )R <sup>2</sup>	(S-E <sub>B</sub> )R <sup>2</sup>	(S-E <sub>C</sub> )R <sup>2</sup>
							E <sub>A</sub>	E <sub>B</sub>	E <sub>C</sub>			
CaS	4.1	9.30	10.2	5.46	1.64	2.848	2.53	2.58	2.85	11.03	31.16	38.47
MnS	5.30	10.1	15.3	6.54	1.48	2.425	2.65	2.68	2.26	7.29	20.93	51.51
MgS	5.2	10.3	13.2	6.05	1.55	2.595	2.594	2.594	2.594	8.75	25.58	45.11
FeS	8.30	13.04	15.6	6.99	1.42	2.27 ±0.05	2.58	2.05	2.28	6.75	31.17	44.36