

# Cumulative coordinates for approximations of atomic multipole moments in cationic forms of aluminosilicates

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Atomic multipole moments (MMs) are calculated for three, LiABW, NaNAT, and BaEDI, aluminosilicates with the periodic Hartree-Fock CRYSTAL95 code. The positions of the cations with/without included water molecules were optimised. Approximate functions for the atomic MMs which can be used for further calculations of the electrostatic potential in any arbitrary zeolite are proposed in terms of charges and geometry of their neighbour atoms.

## 1. INTRODUCTION

The importance of the long-range effects for modelling the structural characteristics and chemical interactions in zeolite frameworks has widely been discussed [1]. However, most modern empirical codes for the simulation of 3D solids and related chemical interactions do not consider neither any charge dependency on the geometry of the framework, nor upper multipole moments (MMs) and their dependences. This drawback can however be corrected by constructing a “cumulative” coordinate sequence based on expansion series including the known geometry and approximations of the low order MMs to consequently describe the high MMs of each crystallographically independent type of atom in the frameworks [2].

But evident questions appear with respect to the application of this scheme to structures which include cations with non-directional bonds between the cation and the framework. Is it possible to find analogous relations for the cations and how to determine the necessary nearest neighbour atoms to consider for them? Testing the relations of the proposed scheme for the cationic forms is thus one of the goals of this paper. Moreover, natural cationic zeolites contain water. How strongly is water coordinated to the cation and does it influence their properties like MMs and mobility as compared to the dehydrated zeolites? The important electric field measured experimentally should distort water molecules and avoids to easily evaluate the water coordination on the basis of its characteristics in the gas state. It is thus important to verify if its distortion in the framework comes from the electric field effects, or if it is the result of different coordinations of both protons to the framework oxygens.

Elucidating the two questions above evidently requires the study of the interactions between water, the cations, and the zeolite framework for a wide set of structures as well as the application of *ab initio* solid state computations because molecular mechanics does not include all interaction energy terms and therefore their answers could not be certain. In this paper, we thus wish to

compare 3D zeolite models and cation/water clusters in order to understand the influence of the water molecules on the electronic distribution of the cation in terms of their MMs.

## 2. THEORETICAL PART

### 2.1. Approximate expressions for the multipole moments (MMs)

Expressions connecting the central and local moments for an atom in a molecule were already developed [3]. Even if the first term only in the series (1) is considered, a useful relation can be obtained for the behaviour of the MM of an atom A with respect to the charges  $Q_0^0(i)$  and geometry of the respective fragment:

$$Q_L^m(A) = \sum_{i=1}^N \sum_{S=0}^L \sum_{P=-S}^S a_{LmSP} Q_S^P(i) R_{L-S}^{m-P}(A, i) = \sum_{i=1}^N a_{Lm00} Q_0^0(i) R_L^m(A, i) + \dots \quad (1)$$

where  $R_L^m(A, i)$  corresponds to the respective Legendre polynomial whose argument is the vector between the considered atom A and neighbour site  $i$ ,  $Q_L^m(i)$  is the  $m$ -component of the  $L$ -order MM, the summation  $i$  running over all the  $N$  neighbour atoms of A,  $a_{LmSP}$  being dependent on the  $R_L^m(A, i)$  functions used. In 3D solids, the definition of the number of neighbours  $N$  requires testing. Replacing the angular Legendre polynomials  $R_L^m(A, i)$  by those expressed through the nucleus cartesian coordinates of A and its neighbours  $i$  ( $X_i - X_A, \dots$ ) as developed in [1], one gets:

$$X_L^m(A, i) = \sum_{(t,u,v)} D_L^m(t,u,v) (X_i - X_A)^t (Y_i - Y_A)^u (Z_i - Z_A)^v \quad (2)$$

the coefficients  $D_L(t,u,v)$  being tabulated [1]. Then, one can deduce the coordinates for the charge and geometry dependences of the MMs from equation (1) as:

$$Q_L^m(A) = a_{Lm00} R_L^m(A) + b_{Lm00} \quad (3)$$

where  $a_{Lm00}$  and  $b_{Lm00}$  will be fitting parameters, and the  $R_L^m(A)$  functions correspond to the unnormalized functions (2) considered in CRYSTAL [4]:

$$R_L^m(A) = \sum_{i=1}^N Q_0^0(i) X_L^m(A, i) \quad (4)$$

instead of  $R_L^m$  (used in equation 1) of Stone's method. In order to emphasise the difference between the central moment described by relation (1) and a local one which should be less dependent on the moments of the remoted atoms *versus* the closest ones, we decided to consider, instead of coordinate form (4), a modified form:

$$R_L^m(A) = \sum_{i=1}^N Q_0^0(i) X_L^m(A, i) d_{iA}^{-K} \quad (5)$$

which includes a term inversely proportional to the distance between the  $i$  neighbour and A atom,  $d_{iA} = ((X_i - X_A)^2 + (Y_i - Y_A)^2 + (Z_i - Z_A)^2)^{1/2}$ ,  $K$  being an empirical value whose choice for all the results presented further has been determined as  $K = 2L + 1$ . Both last functions  $R_L^m(A)$  (equations 4 and 5) should thus be analysed in terms of a quantity dependent on the closest  $N$  atoms. For most of the atoms within the structural models studied here, *i.e.*, zeolites, an evident first choice for the neighbour

atoms to be included in equation (3) can be proposed easily. For Si and Al, it is logical to consider 4 neighbours; for O, one considers 2 or 3 neighbours, including a cation if present. For cations and H atoms, N varied between 4-6.

## 2.2. Computational details

Three "small size" cationic forms of aluminosilicate, LiABW, NaNAT, and BaEDI (Table 1), were optimised at the STO-3G level for the framework atoms and 6-1G, 8-511G, and pseudopotential Hay-Wadt (small core or HWSC) basis sets for Li, Na, and Ba (with d polarization functions), respectively, with the periodic Hartree-Fock (PHF) CRYSTAL95 code [4], in which we adopted the Polak-Ribiere algorithm. PHF optimisations were performed for the cations and water atoms for NaNAT and for the water atoms only for BaEDI. For LiABW, the three cell parameters and coordinates of all atoms were optimised. Series of small  $\text{Me}^{\text{tn}}(\text{H}_2\text{O})_m$  clusters were also considered with GAUSSIAN98 [8] in order to estimate the basis set quality used with the PHF approach.

Table 1

Symbol, number of atoms, of different Al, Si, and O types, of atomic orbitals (AO) per unit cell (UC), and symmetry group of the cationic forms of aluminosilicates

Name	Ref.	Symbol	Atoms/UC <sup>a)</sup>	$n_{\text{Al}}/n_{\text{Si}}/n_{\text{O}}$	AO/UC <sup>b)</sup>	Symmetry
LiABW	5	LiABW	28/40	1/1/4	464	Pna2 <sub>1</sub>
Natrolite	6	NaNAT	34/46	1/2/5	578	Fdd2
Edingtonite	7	BaEDI	32/56	1/2/5	380 <sup>c)</sup>	P2 <sub>1</sub> 2 <sub>1</sub> 2

<sup>a)</sup>for dehydrated/hydrated forms; <sup>b)</sup>hydrated form at the ps-21G\*\* level; <sup>c)</sup>HWSC3-1G/6-21G

Single point calculations were used at higher basis set levels to determine all atomic MMs up to 4<sup>th</sup> order *via* distributed multipole analyses [4]. Pseudopotential (ps) bases of Durant-Barthelat were considered on Si and Al, ps-21G\*\* and ps-21G\* with/without d polarization functions on Li and Na, and 6-21G\* basis on H and O. The used sp/d exponents were 0.9, 0.12339/0.5, 0.17/0.45, and 0.42/0.6 au<sup>-2</sup> on the H, Al, Si, and O atoms. The d exponents on Li and Na were 0.8 au<sup>-2</sup> and Na 0.175 au<sup>-2</sup>, respectively.

All computations with the CRYSTAL95 and GAUSSIAN98 codes were carried out on an IBM 15-node (120 MHz) Scalable POWERparallel platform (1 Gb of memory/CPU) with conventional tolerance criterions. Total geometry optimisation of the hydrated LiABW form (27 variables) within 6-1G/STO-3G took nearly 670 hours on the above cited CPU.

## 3. RESULTS AND DISCUSSION

### 3.1. Dehydrated zeolite forms

The smaller dehydrated LiABW form was studied in detail. The behaviour of Li could be described by a movement in the 6T window to a nearly symmetric position *versus* the three framework O atoms. So, Li initially separated from the O by 1.913, 1.968, and 1.981 Å [5] moves to positions remoted by 1.764, 1.770, and 1.796 Å upon variation of its coordinates and of those of the closest oxygens, with fixed cell parameters. These distances are smaller than the sum of the Li

and O van der Waals radius, *i.e.*, 1.91 Å [9]. The Li<sup>+</sup>...O decrease becomes even more important with 1.714, 1.716, and 1.738 Å distances when considering the variation of the cell sizes. This final Li position corresponds to a plane with the three O atoms, with O...Li...O angles of 119.9, 119.7, and 120.3°. The total energy variation is large, 87.7 kcal/mol, but it corresponds to a reasonable decrease of the cell volume by 1.6 % upon “dehydration”.

### 3.2. Hydrated zeolite forms

The definition of a precise geometry of the water molecules is a common problem for all three structures studied here because of the difficulty to determine the proton coordinates. X-ray data (XRD) correspond to strongly distorted water molecules, while PHF optimisations lead to bond angles closer to the geometry in the gas state (Table 2).

Table 2

Experimental (XRD), CRYSTAL (PHF), and clusters GAUSSIAN98 (G98) coordination of cation to the framework atoms and geometry of the Me<sup>+n</sup>(H<sub>2</sub>O)<sub>w</sub> clusters

Me	Method	R <sub>Me-O</sub> , Å <sup>a)</sup>	R <sub>OH</sub> , Å	H-O-H, °
Li	LiABW, XRD [5]	1.913, 1.968w, 1.981, 1.942	0.955, 1.096	126.4
	PHF/6-1G/STO-3G <sup>b)</sup>	1.814w, 1.878, 2(1.942)	1.012, 0.993	105.4
	G98/MP2/6-311+G <sup>**</sup>	1.866	0.965	105.0
Na	NaNAT, XRD [6]	2.367, 2.370w, 2.391w, 2.395, 2.518	0.974, 0.968	114.0
	PHF/8-511G/STO-3G <sup>c)</sup>	2.345w, 2.368, 2.380, 2.382w, 2.512	1.003, 0.995	109.2
	G98/8-511G/STO-3G <sup>d)</sup>	2.022	0.981	103.7
	G98/MP2/6-311+G <sup>**e)</sup>	2.290	0.963	103.9
Ba	BaEDI, XRD [7]	2(2.792w), 2(2.788w)	2(0.959, 0.928), 2(0.942, 0.956)	2(101.7), 2(111.3)
	PHF/HWSC3-1G* /STO-3G <sup>f)</sup>	2(2.729w), 2(2.746w)	2(0.993, 0.994), 2(0.993, 0.995)	2(100.9), 2(104.1)
	G98/B3LYP/LANL2MB* /6-311+G <sup>**g)</sup>	4(2.720)	4(0.969)	4(104.1)
	Experiment (gas phase)		0.959	103.9

<sup>a)</sup> w denotes water oxygens; <sup>b)</sup> PHF optimisation of cell sizes and all atomic coordinates; <sup>c)</sup> PHF optimisations of Na<sup>+</sup> and H<sub>2</sub>O coordinates only; <sup>d)</sup> RHF SCF cluster optimisation with fixed O...Na<sup>+</sup>...O angle of 141.2°; <sup>e)</sup> MP2 cluster optimisation allowing variation of O...Na<sup>+</sup>...O angle up to 180°; <sup>f)</sup> PHF optimisation of H<sub>2</sub>O coordinates; <sup>g)</sup> total cluster optimisation with pseudopotential LANL2MB basis set including 31 split-valence [8] plus d functions on Ba<sup>+2</sup>; resulting O...Ba<sup>+2</sup>...O angles 2(110.6), 2(110.7), 107.1, 107.2° are close to tetrahedral ones

In all cases, the STO-3G basis on all atoms (with exception of the cation) leads to a longer OH bond length but this difference with respect to XRD does not lead to a serious drawback of the model. The longer OH distance could be interpreted as a result of the anharmonic effects of the OH

bond (around of 0.02 Å). However, this unequivalence of the H atoms could lead to a difference of the respective dependences of the MMs as we shall discuss below.

The PHF optimisation of a relatively crude initial model for LiABW resulted in energy gains of 75.9 kcal/mol with 6-1G/STO-3G and of 54.8 kcal/mol with 6-1G\*/ps-21G\*. For NaNAT, the optimisation with STO-3G, with an energy decrease of 13.8 kcal/mol, is in contrary *ratio* with single point calculations at the 8-511G\*/ps-21G\* level, which led to a slightly more stable zeolite model from XRD [6] by 3.1 kcal/mol. Even if geometries were very close (Table 2), differences were observed between the charges calculated here and *via* multipole X-ray fitting [6] (Table 3). The O charges become closer with higher quality basis set as already mentioned [10]. The experimental estimate of the charge of the H<sub>2</sub>O molecule, +0.01 e [6], becomes negative -0.07 e at the 8-511G/ps-21G\* level and does not change sign with further addition of d functions on Na. The H charges are also closer to each other than experimental ones.

Table 3

Multipole X-ray fitted charges [6] and Mulliken atomic charges of the PHF optimised models of hydrated NaNAT

X	Multipole X-ray treatment	X-ray/8-511G /ps-21G*	X-ray/8-511G* /ps-21G*	PHF/8-511G /STO-3G	PHF/8-511G* /ps-21G*
Si <sub>1</sub>	1.84	1.926	1.933	1.299	1.932
Si <sub>2</sub>	1.65	1.837	1.849	1.260	1.849
Al	1.51	1.675	1.692	1.106	1.692
O <sub>1</sub>	-0.90	-1.030	-1.028	-0.744	-1.028
O <sub>2</sub>	-1.21	-1.080	-1.042	-0.739	-1.041
O <sub>3</sub>	-1.03	-1.068	-1.042	-0.747	-1.042
O <sub>4</sub>	-1.07	-1.065	-1.039	-0.744	-1.039
O <sub>5</sub>	-0.87	-1.013	-1.010	-0.732	-1.010
Na	1.00	0.852	0.666	0.666	0.666
O <sub>w</sub>	-0.59	-0.620	-0.561	-0.425	-0.602
H <sub>1</sub>	0.24	0.277	0.276	0.234	0.303
H <sub>2</sub>	0.36	0.272	0.272	0.217	0.286

For EDI, we did not considered any PHF computation with higher levels of basis set than HWSC3-1G/6-21G. The structure of Ba surrounding the four water O atoms corresponds to a distorted pyramid with O...Ba<sup>+2</sup>...O angles of 66.3, 118.6, 72.7, and 65.2°, the largest angle being between the molecules which are closest to Ba. The PHF optimisation (of the water coordinates) changes only slightly the geometry up to 64.6, 118.3, 72.0, and 66.4°.

Usually, PHF optimisations of the zeolite models can only be done with a moderate quality basis sets and distortions in the interatomic distances of the optimised structure could appear. In order to verify the basis set level and its influence on the relative location of the cation and H<sub>2</sub>O molecules (at the level of the calculated MMs), we compared the PHF optimised structures with several charged Me<sup>+n</sup>(H<sub>2</sub>O)<sub>m</sub> clusters, *i.e.*, without crystalline environment (Table 2). There are 4 H<sub>2</sub>O molecules and 4 Na atoms/UC in NaNAT, the second H<sub>2</sub>O molecule being in contact with a Na of the neighbour UC. In order to compare the location of water, we thus considered the Na<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> cluster. It is

worthwhile to mention that the H-O-H angle was not distorted in  $\text{Na}^+(\text{H}_2\text{O})_2$  at the same level of basis set as used for the PHF optimisation. The O-H elongation in the cluster is only slightly smaller than in the zeolite despite the fact that the  $\text{Na}^+\dots\text{O}$  distance is shorter by 0.32 Å for the same  $\text{O}\dots\text{Na}^+\dots\text{O}$  angle (Table 2). The resulting distances between the cation and oxygens are usually close to the sum of van der Waals radii ( $\text{O} = 1.35$ ,  $\text{Li} = 0.56$ ,  $\text{Na} = 0.98$ ,  $\text{Ba} = 1.35$  Å) [9] in the clusters, while in zeolites, only the  $\text{Li}^+\dots\text{O}$  distance is shorter.

### 3.3. MMs of the cations and framework atoms

The proposed approximation (3) yielded a reasonable precision for the high order MMs of the cations (lines in Fig. 1). Undoubtedly, the use of these relations will improve the electrostatic potential (EP) evaluation owing to a serious contribution of these high order MMs. As a result of the high coordination of the cation within the frameworks, *i.e.*, 3 or 4 oxygen atoms are close to Li and Na, respectively, the low order MMs are smaller than the higher ones. The relations of the largest  $|\text{Q}_L^m(\text{Me})|$  components could be crudely given from hexadecapole ( $L = 4$ ) to dipole ( $L = 1$ ) as 1, 1/50, 1/400, and 1/6000 for Na and as 1, 1/5, 1/700, and 1/7700 for Li. Comparing to the usual distance from the cation to the adsorbed molecule of around 3-4 Å, one can conclude to a dominance of the high order MMs for the EP value. But a precise approximation of the  $\text{Q}_1^m(\text{Na})$  and  $\text{Q}_2^m(\text{Na})$  moments is however required because their absolute values are comparable to those of Si and Al, so that quantitative EP errors could be appreciable. The low order MMs for Li are rather small.

It is instructive that the addition of d functions on the cation is strongly different for Li and Na (Figs. 1a-c). The  $\text{Q}_4^m(\text{Na})$  increase in the order  $8\text{-}511\text{G}/\text{ps}\text{-}21\text{G}^* < 8\text{-}511\text{G}/\text{STO}\text{-}3\text{G} < 8\text{-}511\text{G}^*/\text{ps}\text{-}21\text{G}^*$ . For Li, the variation of all MMs as well as charges is just negligible (gray and black symbols coincide in Figs. 1a, c), which can be related with a high exponent value of the d function and higher localisation of the d orbitals. One should remark that good cation MM dependences cannot be obtained if any of the 3-4 closest zeolite oxygens is neglected.

The addition of d polarization functions also illustrates the closeness of the different O atoms, particularly for NaNAT, which redistributes the atomic O charges (Table 3). The decrease by -0.186 e of the Na charge accompanies the large increase by 0.038 e of the two  $\text{O}_2$  ( $\text{Na}^+\dots\text{O}_2 = 2.518$  and  $2.615$  Å), while one gets the same smaller 0.026 e change on  $\text{O}_3$  and  $\text{O}_4$  despite the smaller distances ( $\text{Na}^+\dots\text{O}_3 = 2.367$ ;  $\text{Na}^+\dots\text{O}_4 = 2.395$  Å). The large decrease of the water O charge by 0.06 e, even it is not the closest atom ( $\text{Na}^+\dots\text{O}_w = 2.370$  Å), shows the particular role of  $\text{H}_2\text{O}$ . The total  $\text{H}_2\text{O}$  charge increases from -0.071 to -0.013 e and remains equivalent for the zeolite partially optimised with 8-511G/STO-3G, where the water O becomes the closest atom ( $\text{Na}^+\dots\text{O}_w = 2.345$ ;  $\text{Na}^+\dots\text{O}_3 = 2.368$  Å).

More precise dependences for the cation MMs could *a priori* be obtained from a separate consideration of the hydrated and dehydrated forms, but the dependences are very close as shown with 8-511G/STO-3G in Fig. 1b (only hydrated forms are applied for other basis set levels here). This slight  $\text{H}_2\text{O}$  influence is in partial contradiction with the appreciable “charge transfer” from O to Na upon addition of the d functions and requires a further study.

The MM approximations for the framework atoms are of the same quality as it was earlier obtained for the H-forms (Figs. 1d, 2b, and 2c); however, the  $\text{Q}_3^m(\text{Si})$  are less well described in

LiABW (Fig. 2c). The influence of the basis set variation on Li does not change the MMs so that they coincide; such influence is however more important for Na (Fig. 1b).

### 3.4. MMs of the water atoms

The most accurate approximations for O and H water atoms were also obtained for the high order MMs. Two examples are presented in Figs. 2a for O (black signs) and Fig. 2d for H. For the gas state model, the dependences for each atom should coincide but there is a difference between the H atoms in the water molecules located in different zeolite media (Fig. 1d). The sharp difference between the approximations for the water and zeolite O atoms is illustrated in Fig. 2a, while the absolute MM values are close.

## 4. CONCLUSIONS

High order MMs of the cations and zeolite framework atoms of LiABW, NaNAT, and BaEDI were approximated using a “cumulative” coordinate approach [2]. The periodic Hartree-Fock (PHF) optimisation of the hydrated/dehydrated frameworks did not lead to particular MM dependences of the framework atoms so that the MMs of all cationic structures can be described by similar type dependences.

The MMs of the cations depend only very slightly on the presence of the water molecules despite of their close positions to the cation. This slight effect can be justified by a “compensation” of the whole neutral molecule on the atomic electronic distribution as compared to the influence of the partially charged framework atoms. A crude MM approximation can be obtained neglecting the influence of water. Despite a “charge transfer” from O to Na upon addition of d polarisation functions on Na was related with a charge variation on the closest O atom of water, the MMs of Na can be approximated together for both the hydrated and dehydrated NaNAT forms.

The optimised geometry of water is less distorted as compared to X-ray data; the H-O-H angle is larger than in the gas state. The bond distortion could not clearly be estimated with the small basis set used for the PHF optimisation. However, the elongation of the O-H distance is slightly overestimated as compared to the water clusters at the same basis set level.

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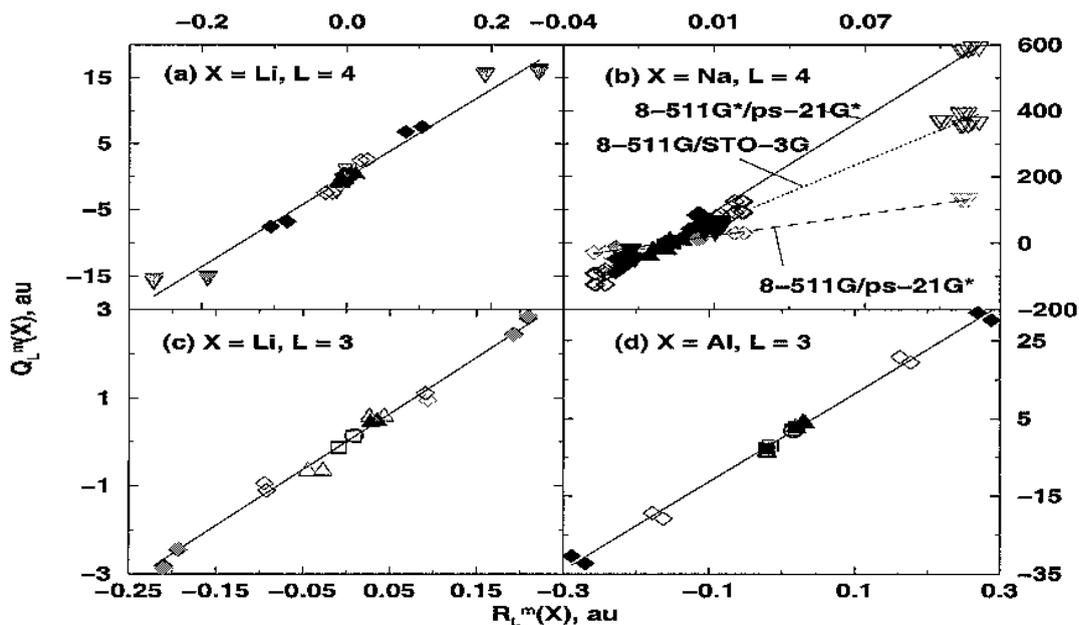


Figure 1. Dependence of the multipole moments  $Q_L^m(X)$  components *versus* the  $R_L^m(X)$  coordinate (equation 3) for the (a, b) hexadecapole and (c, d) octupole for (a,c)  $X = \text{Li}$ , (b)  $X = \text{Na}$ , and (d)  $X = \text{Al}$  (NaNAT) atoms:  $m = 0$  (circles),  $|m| = 1$  (squares),  $|m| = 2$  (triangles up),  $|m| = 3$  (diamonds),  $|m| = 4$  (triangles down), positive  $m$  values (open signs), negative  $m$  values (filled signs). Basis sets in (a, c, d): ps-21G\* (black signs); ps-21G\*\* (gray signs). Approximation (equation 3) is depicted by lines.

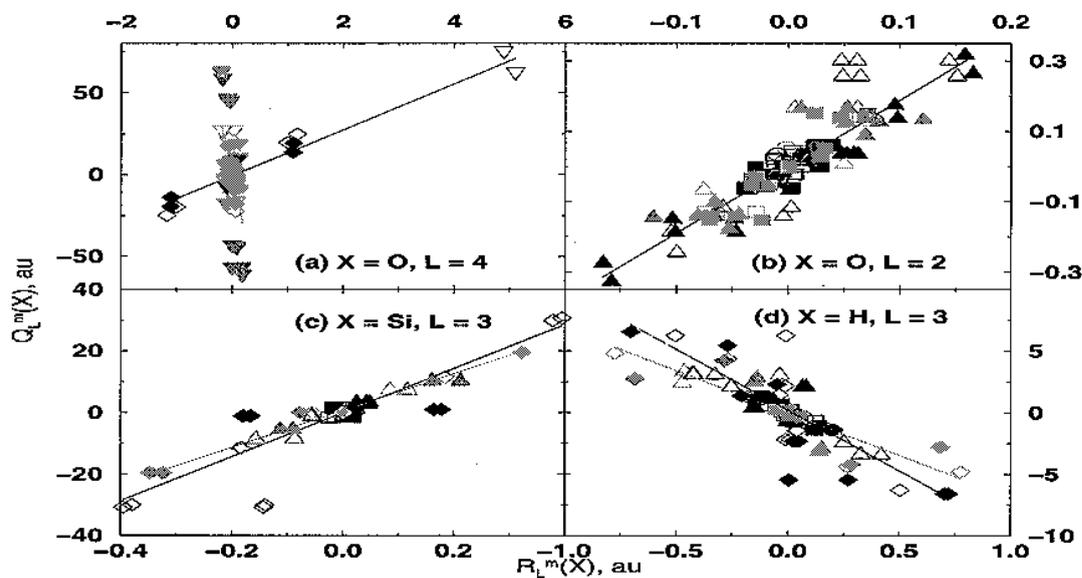


Figure 2. Dependence of the multipole moments  $Q_L^m(X)$  components *versus* the  $R_L^m(X)$  coordinate (equation 3) for the (a) hexadecapole (b) quadrupole and (c, d) octupole for the (a, b)  $X = \text{O}$ , (c)  $X = \text{Si}$ , and (d)  $X = \text{H}$  atoms calculated with ps-21G\* (case a with ps-21G\*\*):  $m = 0$  (circles),  $|m| = 1$  (squares),  $|m| = 2$  (triangles up),  $|m| = 3$  (diamonds),  $|m| = 4$  (triangles down), positive  $m$  values (open signs), negative  $m$  values (filled signs). Case (a): O atoms of water (black signs); O atoms of LiABW zeolite (gray signs). Zeolite forms in (b-d): LiABW (black signs); NaNAT (gray signs). Approximation (equation 3) is depicted by lines.