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# Approximation of Mulliken charges for the silicon atoms of all-siliceous zeolites<sup>☆</sup>

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## Abstract

Distributed multipole analysis on the basis of periodic Hartree–Fock (PHF) calculations, using the CRYSTAL code, is applied to 13 all-siliceous zeolite with a reasonable number of atoms per unit cell (UC). Mulliken charges of the silicons were calculated with three basis sets: STO-3G for all frameworks, a 6-21G quality basis for five of them, and a 6-21G\* quality basis set for chabazite. A simple one-dimensional function of the dependence of the charges obtained with the two first bases is found with respect to the average Si–O distance within the respective SiO<sub>4</sub> tetrahedra. Its application for the evaluation of the charges in frameworks with a larger number of atoms per UC is confirmed by comparison with results of direct PHF calculations for silicalite. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* A. microporons materials; D. electronic structure

## 1. Introduction

The understanding of the molecular behaviour of a guest molecule in the adsorbed state requires the evaluation of its interaction energy with the adsorbent. Therefore, a correct representation of the electrostatic field created by the adsorbent is often important [1]. Moreover when considering adsorbed states with particularly short ‘host–guest’ distances, it has been shown that good convergence of the electrostatic interactions could be provided via distributed electrostatic multipole moments of both the adsorbent and the guest molecule. In this context, one of the most commonly used implementations for the calculation of distributed multipole moments is the algorithm developed by Stone et al. [2,3].

Although distributed electrostatic multipole moments of several di- and triatomic guest molecules have already been considered [3], a systematic study of zeolite frameworks, which constitute an important class of ad-

sorbents, has not been performed to our knowledge. An approximate scheme for the analysis of the multipole moments proposed by Saunders et al. [4] based on Stone’s algorithm has been implemented in the CRYSTAL92 [5] and CRYSTAL95 [6] ab initio periodic Hartree–Fock LCAO codes. As has been shown previously [4], this scheme enables electrostatic field values to be obtained to an accuracy below 1% using multipole moments up to the fourth order related to the atomic positions only. Within the same work [4], Saunders et al. also showed that Mulliken charges (i.e., multipole moments of zeroth order) are sufficient to provide a quite realistic representation of the electrostatic field as compared to a totally ionic zeolite model. Hence, the most precise calculation of the atomic charges within this type of scheme would provide a correct description of the main part of the field (created by the charges only) within the frameworks.

In a previous study [7], we analyzed the behaviour of Mulliken charges for the oxygen atoms of 12 all-siliceous zeolites using the CRYSTAL92 code [5]. More particularly, it was shown that two-dimensional charge surfaces with respect to the Si–O–Si angle and average Si–O distance approximate quite satisfactorily the Mulliken charges of the oxygens calculated with two Gaussian basis sets, the minimal STO-3G basis and a 6-21G split-valence quality basis set. For both of them, a very simple two-dimensional analytical representation was obtained by

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fitting all charges of the various oxygens present in the different frameworks.

In this paper, we will discuss several approximations of the Mulliken charges for the zeolite silicon atoms calculated with the same basis sets as already used previously for oxygen [7]. The distributed multipole analysis scheme [4] will be applied to 13 all-siliceous zeolites with a reasonable number of atoms per unit cell (UC) to study the dependence of the atomic multipole moments of the silicons with respect to one internal parameter, i.e., the average Si–O distance. In Section 2, we briefly describe the calculation procedure together with the characteristics of the zeolite frameworks considered. In Section 3, after discussing three types of approximate dependences of the atomic silicon charges with respect to the average Si–O distance, the approximate charge values are compared with those already available in the literature for silicalite.

## 2. Theoretical aspects

The computational aspects have already been discussed in our first paper devoted to the approximation of the multipole moments for the oxygen atoms [7]; so we will not repeat the theoretical background referring to the respective periodic Hartree–Fock literature sources [4,8].

We have chosen all-siliceous zeolite frameworks with a relatively small number of atoms per elementary unit cell (UC). The characteristics of the zeolite frameworks taken from the MSI database [9,10] are given in Table 1. We did not optimize the framework geometries of the structures hoping that the X-ray experimental errors are negligible considering the wide range of the Si–O distances within the zeolites chosen. Practically, we tried to propose several simple functional ‘geometric’ dependences valid for a wide

Table 1  
Symbol, number of atoms, of different silicon and oxygen types ( $n_{\text{Si}}/n_{\text{O}}$ ), of atomic orbitals (AO) per unit cell (UC) (all coordinates are from [9,10], if no other reference is given), and symmetry group of the zeolite frameworks considered

Name	Symbol <sup>a</sup>	Atoms/UC	$n_{\text{Si}}/n_{\text{O}}$	AO/UG (STO-3G)	Symmetry group
Montesommaite	MON	24	1/3	152	I4 <sub>1</sub> /amd
Tetha-1	TON	36	4/7	228	Cmc2 <sub>1</sub>
Dachiardite	DAC	36	4/9	228	C2/m
Chabazite <sup>b</sup>	CHA	36	1/4	228	R3c
Brewsterite	BRE	48	4/8	304	P2 <sub>1</sub> /m
Phillipsite	PHI	48	4/9	304	P2 <sub>1</sub> /m
Merlinoite	MER	48	2/6	304	Immm
ZSM-57	MFS	54	8/14	342	Imm2
Ferrierite	FER	54	4/8	342	Immm
Heulandite	HEU	54	5/10	342	C2/m
Gmelinite	GME	72	1/4	456	P6 <sub>3</sub> /mmc
Rho	RHO	72	1/2	456	Im3m
Mordenite	MOR	72	4/9	456	Cmc2 <sub>1</sub>

<sup>a</sup> Ref. [11].

<sup>b</sup> Refs. [6,12].

range of Si–O distances (in the same manner as in Ref. [7]), from which all the charges within other non-considered structures could be deduced. As compared to the first work [7], we added two frameworks — tetha-1 and brewsterite — but we no longer considered the losod zeolite, in which the average Si–O distance of the two silicon atom types (1.73 Å) is too large as compared to the usual Si–O range (1.58–1.66 Å). A test with the approximate functions given below indeed led to an appreciable deviation of the Si charges for this zeolite.

Three different Gaussian basis sets were considered. The minimal STO-3G (named hereafter basis A) [13] could be applied for all systems studied. A mixed split-valence basis set, standard 6-21G for oxygen [13] and 8-31G for silicon [14] (named hereafter basis B), could also be applied with successful SCF convergence for the CHA, DAC, MER, MON, and PHI zeolites. For this last basis set we, however, needed to optimize the exponent of the 2sp' orbital on the oxygen as 0.34 and of 3sp' on the silicon as 0.10 (instead of 0.37 and 0.14, respectively, as given in Refs. [13,14]) in the case of MON. We finally considered a third basis set (named hereafter basis C) by adding, to the previous basis, d-polarisation functions with exponents 0.85 for O, and 0.34 for Si, respectively, which converged properly for the CHA zeolite. No convergence could be reached for DAC and MON, whereas the other zeolites again could not be treated with the last basis set because the number of atomic orbitals in their UC was too large.

All computations with the CRYSTAL92 code [5] were carried out on an IBM RISC 6000 model 560 workstation (with 256 Mb of memory). For all cases, the thresholds for the calculations were fixed to 10<sup>-5</sup> for the overlap Coulomb, the penetration Coulomb, and the overlap exchange, and to 10<sup>-6</sup> and 10<sup>-11</sup> for the pseudo-overlap exchange series for both levels of basis sets. ‘Softening’ the criterions up to 10<sup>-4</sup>, 10<sup>-5</sup> and 10<sup>-6</sup>, respectively, changes the values of the resulting atomic charges by less than 1%. For information, full SCF convergence for silico-chabazite with STO-3G and 6-21G\* basis sets took circa 10 min and 7 h, respectively, on the above cited workstation.

## 3. Approximation of the Mulliken charges of the framework silicons

All multipole moments up to the fourth order were determined via the distributed multipole analysis scheme [4] available in the CRYSTAL92 code [5].

For comparison with a previous study [12] and to test basis sets B and C, we took the same optimized structure ‘Opt3’ of the silico-chabazite given therein. The small differences, well below 1%, between the Mulliken silicon charges (core+valence) show that both basis sets herein applied are very close to the respective ones used in Ref. [12] (Table 2).

Table 2

Comparison of the Mulliken charges ( $|e^-|$ ) of the Si atoms in silicochabazite (coordinates of Opt3<sup>12</sup>, average Si–O distance is 1.609 Å)

	Basis set STO-3G	Basis set of 6-21G quality <sup>a</sup>	Basis set of 6-21G* quality <sup>b</sup>
Ref. [12]	12.543	11.655	12.230
This work	12.546	11.619	12.218

<sup>a</sup> Basis set ps-21 in Ref. [12] ('ps' denoting a pseudopotential to describe the core electrons of Si); basis set B in this work.

<sup>b</sup> Basis set ps-21\* in Ref. [12]; basis set C in this work, this value being obtained here for a slightly different geometrical model [6] (with thresholds of  $10^{-4}$ ,  $10^{-5}$ ,  $10^{-6}$ , instead of  $10^{-6}$ ,  $10^{-6}$ ,  $10^{-12}$  used in all other cases considered here for CHA); hence, a strict comparison cannot be made.

Forty-three charge values (for all different Si atom types within all the all-siliceous zeolites given in Table 1) were estimated with STO-3G, whereas only 12 charge values (for all different Si atom types in CHA, DAC, MER, MON, and PHI) were evaluated with basis B. In each case, several simple analytical formulas were fitted to the data points. Interestingly, we found a satisfactory approximation of the Si atomic charges (expressed below as the difference between the number of electrons of the neutral Si atom, i.e.,  $14e^-$ , and the Mulliken charges) calculated with both bases A and B with respect to only one internal geometric parameter characterizing the Si atom. Indeed, three simple one-dimensional functions (1–3) of the average distance  $R = (\sum_{k=1}^4 R_{SiO_k})/4$  (Å) of each Si atom within its respective  $SiO_4$  tetrahedron:

$$Q_0^0(R) = a_1(R - a_2)^{a_3} \quad 1$$

$$Q_0^0(R) = a_1 \exp(a_2(R - a_3)) \quad 2$$

$$Q_0^0(R) = a_1 \exp(a_2 R) + a_3 \quad 3$$

succeed in providing root mean square deviation of 0.95–0.98% for basis A and of 0.51% for basis B (Fig. 1a,b). The parameters  $a_i$  ( $i = 1-3$ ) of the three functions are given in Table 3 for both basis sets applied. The differences between the Si charges calculated with bases A and B and the approximate Si ones are given in Tables 4 and 5, respectively.

We first compared the parameters of dependence (1) for an equivalent set of silicon atoms evaluated with both basis sets A and B. Therefore, we considered the approximation with the same 12 points using basis A (Table 3). We found that the relative changes in the parameter values of the approximate function (1) while decreasing the number of Si charges considered are less pronounced as compared to the respective variation for the oxygens shown in our previous work [7]. Increasing the number of charges (i.e., taking into account more zeolites) would, however, be necessary to definitively ascertain the parameter variations with the higher level basis B.

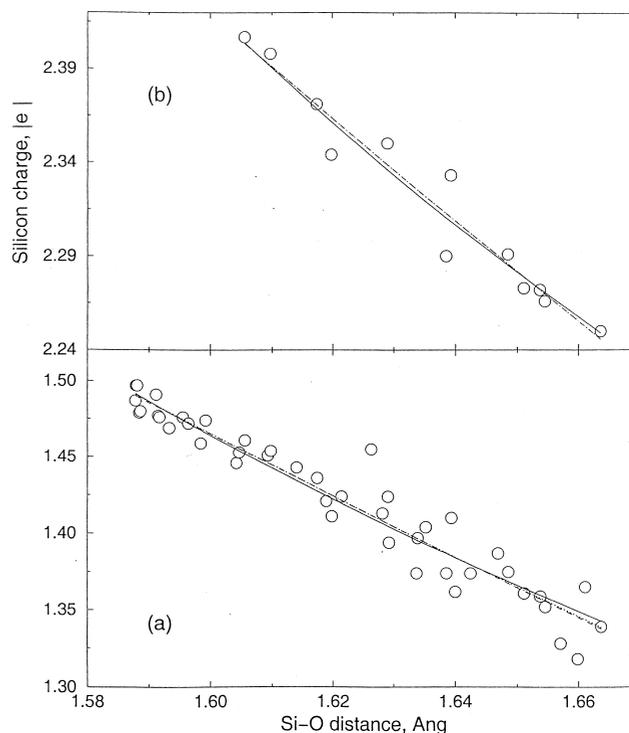


Fig. 1. Approximate charge values relative to the Mulliken charges of the Si atoms (in  $|e^-|$ , given by circles) versus the average Si–O distance  $R = (\sum_{k=1}^4 R_{SiO_k})/4$  (Å) for all considered zeolite frameworks calculated with basis sets: (a) STO-3G; (b) 8-31G (Si) and 6-21G (O). Solid line, function (1); dotted line, function (2); dashed line, function (3).

One may also suggest that a more accurate approximation of the Mulliken Si charges of the zeolites could be achieved by taking into account eventual distortions of the  $SiO_4$  tetrahedra, for example, through the tetrahedral symmetry coordinates. The latter could be expressed via some distortion of both the equilibrium Si–O distances and O–Si–O angles. However, considering the wide series of Si atoms present within the differently distorted  $SiO_4$  tetrahedra, it appears that the influence of such distortions on the calculated Mulliken charges is very minor.

The differences between the precision of functions (1–3) being negligible, a definite choice of one of the forms

Table 3

Parameters and root mean square deviation (RMSD) of the three  $Q_0^0(R)$  functions (1–3) approximating the  $N$  silicon charge values ( $|e^-|$ ) of the considered zeolite frameworks calculated with basis sets A and B

Basis	$N$	Function type	RMSD (%)	$a_1$	$a_2$	$a_3$
A	43	(1)	0.98	0.853	1.303	−0.445
		(2)	0.95	2.020	−1.419	1.373
		(3)	0.95	9.305	−0.823	1.029
A	12 <sup>a</sup>	(1)	0.91	0.852	1.302	−0.452
		B	12 <sup>a</sup>	(1)	0.51	1.572
(2)	0.51	2.096		−1.170	1.773	
(3)	0.51	14.802		−1.089	0.172	

<sup>a</sup> For the CHA, DAC, MER, MON, and PHI zeolites only.

Table 4

Comparison between the Mulliken charges ( $e^-$ ) of the Si atoms calculated with basis set A and approximated by function (1) including the average Si–O distance  $R = (\sum_{k=1}^4 R_{SiO_k})/4$  (Å), with error values  $\delta = (1 - Q_{app}/Q_{cal})$

Type	<i>N</i>	<i>R</i>	$Q_{cal}$	$Q_{app}$	$\delta$
BRE	2	1.6400	1.362	1.383	−0.156E-01
	1	1.6402	1.446	1.454	−0.539E-02
	4	1.6468	1.387	1.372	−0.110E-01
	3	1.6570	1.328	1.354	−0.196E-01
CHA	1	1.6098	1.454	1.442	0.851E-02
DAC	1	1.6174	1.436	1.426	0.667E-02
	2	1.6198	1.411	1.422	−0.753E-02
	3	1.6290	1.424	1.404	0.143E-01
	4	1.6393	1.410	1.385	0.181E-01
FER	4	1.5964	1.472	1.471	0.823E-03
	3	1.5984	1.459	1.466	−0.505E-02
	1	1.6140	1.443	1.433	0.672E-02
	2	1.6263	1.455	1.409	0.317E-01
GME	1	1.6424	1.374	1.378	−0.309E-02
HEU	4	1.6281	1.413	1.405	0.537E-02
	3	1.6292	1.394	1.403	−0.668E-02
	1	1.6337	1.374	1.395	−0.152E-01
	5	1.6339	1.397	1.394	0.183E-02
MER	2	1.6610	1.365	1.347	0.135E-01
	1	1.6385	1.374	1.386	−0.869E-02
	2	1.6485	1.375	1.368	0.508E-02
	MFS	4	1.5878	1.487	1.490
2		1.5879	1.497	1.490	0.463E-02
7		1.5881	1.497	1.490	0.494E-02
1		1.5886	1.480	1.488	−0.571E-02
MON	3	1.5912	1.491	1.483	0.571E-02
	6	1.5915	1.477	1.482	−0.325E-02
	5	1.5917	1.476	1.481	−0.362E-02
	8	1.5933	1.469	1.478	−0.594E-02
MOR	1	1.6056	1.461	1.451	0.698E-02
MOR	2	1.6047	1.453	1.453	0.191E-03
	1	1.6189	1.421	1.423	−0.170E-02
	4	1.6214	1.424	1.419	0.390E-02
	3	1.6352	1.404	1.392	0.853E-02
PHI	1	1.6511	1.361	1.364	−0.182E-02
	4	1.6537	1.359	1.359	0.133E-04
	2	1.6545	1.352	1.358	−0.415E-02
	3	1.6637	1.339	1.342	−0.235E-02
RHO	1	1.6598	1.318	1.349	−0.232E-01
TON	2	1.5884	1.479	1.489	−0.670E-02
	1	1.5955	1.476	1.473	0.217E-02
	4	1.5992	1.474	1.465	0.637E-02
	3	1.6093	1.451	1.443	0.550E-02

versus the others could be done from an analogous analysis performed for other frameworks including atoms as aluminium and phosphorous. Such work is presently under progress.

In general, the zeolite materials effectively used in most crucial catalytic processes contain a relatively large number of atoms per elementary unit cell (UC). Due to the large number of electrons per UC in these zeolites, the electronic problem via codes such as CRYSTAL is still not soluble on most of today's computer platforms even with a minimal basis set. The direct application of the periodic Hartree–Fock scheme to compute the Mulliken silicon

Table 5

Comparison between the Mulliken charges ( $e^-$ ) of the Si atoms calculated with basis set B and approximated by function (1) including the average Si–O distance  $R = (\sum_{k=1}^4 R_{SiO_k})/4$  (Å), with error values  $\delta = (1 - Q_{app}/Q_{cal})$

Type	<i>N</i>	<i>R</i>	$Q_{cal}$	$Q_{app}$	$\delta$
CHA	1	1.6098	2.398	2.391	−0.283E-02
DAC	1	1.6174	2.371	2.370	0.618E-03
	2	1.6198	2.344	2.363	−0.793E-02
	3	1.6290	2.350	2.337	0.564E-02
	4	1.6393	2.333	2.309	0.101E-01
MER	1	1.6385	2.290	2.311	−0.936E-02
	2	1.6485	2.291	2.286	0.213E-02
MON	1	1.6056	2.407	2.405	0.742E-03
PHI	1	1.6511	2.273	2.280	−0.296E-02
	4	1.6537	2.272	2.273	−0.635E-03
	2	1.6545	2.266	2.272	−0.244E-02
	3	1.6637	2.250	2.250	−0.911E-05

charges within these particular zeolite structures could be avoided if functions (1–3) are valid. If these forms (1–3) with other parameter values are valid also for the same approximation of the charge values obtained with a high quality basis set, then the problem of the evaluation of charges could be solved for any zeolite structure. Here we show that a more accurate approximation with a 6-21G type basis as compared to STO-3G (Table 3) allows us to hope that the main features of the geometry dependence of the Si charges is correctly represented by the three proposed functions (1–3) fitting the charge values obtained with a better quality basis set. By comparing the fitting of the Si charges in the same five zeolites (footnote (a) in Table 3) with the A and B bases, we should also remark that the more accurate approximation of the charge values with basis set B is not determined by a smaller number of respective charge values (12 points instead of 43).

The charge values for both Si and O atoms (in absolute value) calculated with basis C (Table 2 herein and Table 2 in Ref. [7]) are intermediate as compared to the respective charges obtained with the A and B bases. One may hypothesize that the Si charges obtained with basis sets of a better quality level will remain within or near these limits. The parameters of the functions (1–3) fitting the atomic charges found with this new basis set could be sought from the approximation of charge values corresponding to atoms in zeolites with smaller UCs only. Hence, charges of the Si atoms of a zeolite with a larger UC could be evaluated on the basis of the proposed approximate dependences (1–3).

To demonstrate the usefulness of our way of evaluation, we estimated the Si charges of some 'large' zeolites, presented in Table 6, for which we could not perform the direct calculation due to hardware limits of our computer facilities (remark: we succeeded to perform the direct solution at the STO-3G level only for the MOR zeolite). The estimation was done on the basis of function (2) whose parameters were obtained by fitting the Mulliken Si

Table 6

Approximate Mulliken charges ( $|e^-|$ ) of the Si atoms of zeolites with a large number of atoms per unit cell evaluated by function (2) including the average Si–O distance  $R = (\sum_{k=1}^4 R_{SiO_k})/4$  (Å) using the parameters fitted over Mulliken charges calculated with basis sets A and B for the smaller size type zeolites (all coordinates from Ref. [9], if no other reference is given)

Type	$R$	Charges		Other results	
		A	B		
FAU <sup>a</sup>	1.6203	1.423	2.363	1.47973 <sup>a</sup>	
	1.6207	1.423	2.362	1.45987	
	1.6235	1.417	2.354	1.41763	
LTA	1.6085	1.447	2.395	1.905 <sup>d</sup>	
MFI <sup>b</sup>	1.5800	1.507	2.477		
	1.5832	1.500	2.467		
	1.5832	1.500	2.467		
	1.5833	1.500	2.467		
	1.5843	1.498	2.464		
	1.5855	1.495	2.461		
	1.5879	1.490	2.454		
	1.5881	1.490	2.453		
	1.5891	1.488	2.450		
	1.5902	1.486	2.447		
	1.5903	1.485	2.447		
	1.5911	1.484	2.445		
	MFI <sup>c</sup>	1.5610	1.548	2.532	
		1.5734	1.521	2.496	
		1.5756	1.517	2.489	
1.5768		1.514	2.486		
1.5769		1.514	2.486		
1.5831		1.501	2.468		
1.5874		1.491	2.455		
1.5935		1.479	2.438		
1.5941		1.477	2.436		
1.6007		1.464	2.417		
MOR	1.6137	1.437	2.381		
	1.6257	1.413	2.348		
	Average	1.490		1.48 Basis A <sup>e</sup>	
	1.6047	1.455	2.406	2.09 Basis 6-21G* <sup>f</sup>	
	1.6189	1.426	2.366		
	1.6214	1.421	2.340		
	1.6352	1.394	2.322		

<sup>a</sup> Coordinates from Ref. [15].

<sup>b</sup> Coordinates from Ref. [16].

<sup>c</sup> Coordinates from Ref. [17].

<sup>d</sup> Ref. [18].

<sup>e</sup> Ref. [19].

<sup>f</sup> Ref. [20].

charges calculated with bases A and B for smaller size zeolites (respective charge sets are named below and in Table 6 as charge sets A and B).

Firstly, we may note a very close average Si charge estimate  $1.490 |e^-|$  as compared to the published average charge  $1.48 |e^-|$  [19] obtained by computations using the CRYSTAL code (STO-3G level) for silicalite (MFI) with the coordinates given by Olson et al. [17]. Additionally, two different sets of atomic coordinates [16,17] were used to demonstrate the importance of the choice of the framework geometry on the resulting charge values and charge ratio (between the different crystallographic types of Si atoms). In all ways, the coordinates corresponding to

an optimized structure are preferable to estimate precisely the electrostatic field.

The charges calculated for MOR also using CRYSTAL with the 6-21G\* basis set [20] are intermediate between those calculated with the STO-3G and the 6-21G (ps-21G [12]) basis sets in accordance with the results of [12] and with our previous work [7]. It confirms again that the approximate charge surfaces for the atomic oxygens fitted to the charges corresponding to the two bases A and B are close to the upper and lower bounds of analogous surfaces calculated with any basis of a better quality than 6-21G, as we already formulated above.

Another feature which can be deduced from the comparison of the Si charges of the FAU framework shown in Table 6 is the close coincidence between the charge ratio obtained here and the value based on the EEM principle by Uytterhoeven et al. [15]. However, if the atomic O charges obtained using the EEM principle [15] are intermediate, in absolute value, between the charge sets A and B [7], here the EEM estimations for Si are closer to the charges obtained with basis A. For information, we just noted a very recent article [21], wherein the structure of the all-siliceous fajaussite framework has been optimized with the same periodic HF scheme at the 6-21G\* level for Si and 6-21G for O. The authors present electrostatic potential maps but no Mulliken charges are given; hence, a verification of the values estimated herein cannot thus be made.

The Mulliken Si charge of NaA (LTA), estimated by fitting of the band shift and band splitting values of adsorbed hydrogen [18], is intermediate between the charges calculated with bases A and B.

An analogous type of expression, based on the influence of the internuclear distances (not the angles), to evaluate the effective point charge values  $q(X_i)$  was proposed recently for all zeolite atom types  $X_i$  by Hill and Sauer [22]:

$$q(X_i) = \sum_{j=1} \delta_{ij} (R_{ij} - R_{ij}^0) + \delta_{ij}^0 \quad 4$$

the summation running over all  $X_j$  neighbours of  $X_i$ , separated by the distance  $R_{ij}$  and  $\delta_{ij}$ ,  $R_{ij}^0$ ,  $\delta_{ij}^0$  being fitted parameters. In our previous work [7], we clearly showed the importance of the Si–O–Si angle on the resulting O charge, while here for the Si atoms any dependence (1–3) is accurate enough in accordance with expression (4) without any angular variable [22]. The appreciable difference (factor of two or larger) between the charge values estimated with (4) or derived herein with expressions (1–3) comes from the different charge values used to fit the parameters. Our charge values have been obtained with the PHF approach of CRYSTAL (Tables 4–5), whereas the charges considered by Hill and Sauer [22] were computed using the isolated cluster approach. In some cases, the latter (for example,  $1.35$ – $1.43 |e^-|$  with STO-3G [23]) are close to the charge values obtained by PHF (Table 4) with the same basis set. Modelling zeolite

structures with any molecular mechanics potential simulating Coulomb interactions [22] was found to provide good agreement between theoretical and experimental results, if part of the *ab initio* charge values is considered as effective point charge. This practice led to a scaling of the *ab initio* charges. For example, the charge value  $0.5244 |e^-|$  was obtained via expression (4) for an Si atom surrounded by four O neighbours with standard Si–O lengths  $R_{\text{SiO}}^0 = 1.6104 \text{ \AA}$  [22].

Functions (1–3) could also be applied to the modelling of zeolite structures with any molecular mechanics potential simulating Coulomb interactions [22]. Such dependence could be induced directly to calculate the Si charges, even if such application was considered as rather artificial by Hill and Sauer [22] as the notion of Mulliken charge does not correspond to a point charge model. The application of expressions (1–4) fitting the Mulliken charges without scaling (multiplication by 1/2 or any other factor) is feasible if one takes into account a very wide interval of charge values involved in the derivation of the molecular mechanics potentials. Larger effective charges ranging from  $q(\text{Si}) = 2.7226$  to  $3.0906 |e^-|$  as compared to the charge values proposed by Schröder et al. [24] are also in good agreement with the fitted data obtained with other types of model potentials [25–27]. Usually Mulliken charge values estimated with the 3D PHF approach [12,19,20] led to intermediate values (Tables 4–5) between the two groups of effective charges, proposed either in [27], or in [24]. Anyway, the consideration of dependences (1–3) could be reasonable within any fitting procedure with a model potential including Coulomb interactions whose effective charge values depend on the geometrical characteristics of the zeolite studied. Selecting one of the forms (1–3), their parameters could be chosen in order to provide the best coincidence between the theoretical and available experimental results, such as spatial zeolite parameters, elastic moduli, enthalpy of the silica transformation between different forms, etc.

Ideally, the estimation of the electrostatic field for any siliceous zeolite with a large UC should be possible, with any required precision, if an analytical representation in terms of the basic geometrical characteristics as discussed above could be obtained for all required multipole moments. For this at first step, one should unify the respective two-dimensional surfaces for the representation of the oxygen charges as done in our previous work [7] and function (1) of this paper for the silicon charges obtained with a basis set of advanced level for the zeolites studied. Using these approximations for both the Si and O atoms and the respective known internal geometric parameters of the atoms in zeolites with a larger UC, one could obtain a first evaluation of the electrostatic field within their framework. In a second step, similar approximations in terms of geometrical coordinates should be developed for all other multipole moments (up to fourth order) of the framework atoms of the larger UC type zeolites in the

same manner as for the Mulliken charges. Later, one could repeat the same procedure for Al-substituted frameworks to estimate the multipole moments of the Al and H atoms. Finally, atomic multipole moments of the cations (i.e., alkaline and rare earth metals) often present in most zeolite frameworks should also be calculated and approximated.

#### 4. Conclusions

Distributed multipole analyses on the basis of periodic Hartree–Fock (PHF) type calculations, using the CRYSTAL92 program, were applied to 13 different all-siliceous zeolite models. An analysis of the Mulliken charges  $Q_0^0$  of the framework silicon atoms has been performed in terms of the average Si–O distance  $R = (\sum_{k=1}^4 R_{\text{SiO}_k})/4$ . More particularly, we were able to propose a simple power and two exponential expressions  $Q_0^0(R)$  which adequately approximate the atomic Si charges obtained with two basis sets, the minimal STO-3G and a split-valence 6-21G type quality basis. The estimations of the Si charges within MFI, i.e., a zeolite with a large number of atoms per elementary unit cell (UC), using these dependences are in good agreement with results obtained using PHF calculations. Further studies on the variation of the dependence with a higher level basis set would be useful to evaluate all the atomic multipole moments of zeolites with a large number of atoms per elementary UC on the basis of calculations of the charge dependence for zeolites having a smaller number of atoms per elementary UC.

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