

Approximation of the Mulliken-type charges for the oxygen atoms of all-siliceous zeolites

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Abstract

Distributed multipole analysis on the basis of periodic Hartree–Fock (PHF) calculations, using the CRYSTAL code, is applied to 12 all-siliceous zeolite models, plus one H-form type. A simple approximation of the dependence of the Mulliken-type charge of the framework oxygens, calculated with two Gaussian basis sets, is found with respect to the average Si–O distance and Si–O–Si angle. These results allow the estimation of the oxygen charges within zeolites with larger elementary unit cells which are still hardly tractable with the presently available computing facilities. The validity of such an estimation for the oxygens of silicalite is shown by comparison with results of direct PHF calculations. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

A correct representation of the electrostatic field effects is often of prime importance for the determination of the conformational geometry of chain molecules [1], as well as for the calculation of the interaction energy of a guest molecule in the adsorbed state [2], or in clusters [3,4]. Numerous procedures were proposed for the local presentation (related to the atomic centers, interatomic bonds and eventually some intermediate points) of the electrostatic moments. Compared to a conventional representation via the central moments, the local moments provide a convergence of the electrostatic interac-

tions at short interatomic distances between the interacting particles. Most of the applications supplied for such calculations of the local moments with modern programs such as GAMESS [5], CADPAC [6], or CRYSTAL [7,8] are based on the Stone algorithm [9,10]. The different schemes differ in the order of the moments required or in the number of considered expansion points to reach the highest precision for the representation of the electrostatic field. One of the problems of the application of these distributions, however, resides in the angular dependence of the moments [11,12], which creates a serious difficulty particularly when treating relatively flexible organic molecules.

Zeolite structures composed of TO_4 tetrahedra ($T = Si, Al$) present an advantage for the calculation of the local moments due to a rather limited range of the O–T–O angles ($T = Si, Al$) between all possible types of frameworks. In contrast, the variation of the

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T–O–T angle is one of the parameters, among other characteristics (such as chemical composition), which confers the different properties (such as confinement effects, shape selectivity, etc.) of the different frameworks. A precise analysis of the angular T–O–T dependence of the multipole moments could hence be useful. Logically, this could be done first for the oxygen atoms whose multipole moments depend directly on the T–O–T angle.

An approximated scheme [13] of the distributed multipole analysis (DMA) proposed by Saunders et al. has been implemented in the CRYSTAL92 [7] and CRYSTAL95 [8] *ab initio* Hartree–Fock LCAO codes for periodic systems. As it was shown, this scheme permits one to obtain a precision of the electrostatic field values below 1% using moments up to the 4th order related to the atomic positions only [13]. Such precision is for example sufficient for the calculation of the characteristics of the vibrational transitions in IR spectra of guest molecules adsorbed within zeolites [14,15]. Unfortunately, most of the experimentally studied frameworks [14], such as A or Y zeolites, have large elementary unit cells (UC), which make them hardly tractable via, for example, the CRYSTAL code on most of today's existing computing platforms. Hence, an alternative scheme avoiding the direct solution of the periodic Hartree–Fock (PHF) equation for zeolites with a large elementary UC should be developed.

Here we applied the above proposed DMA scheme [7,13] for 12 different all-siliceous zeolites, plus the H-form of natrolite, with small enough elementary UC to study the dependence of the atomic multipole moments with respect to the geometric parameters, i.e. Si–O distance and Si–O–Si angle, obtained by X-ray crystallography. More particularly, we wished to suggest such a representation for the Mulliken oxygen charges, i.e. the multipole moments of zeroth-order within the DMA scheme [13], in order to provide a qualitative estimation of the electrostatic field [13]. We hope to complete this treatment of the Mulliken-type oxygen charges later by analogous approximations of the higher-order multipole moments (including the moments of silicon atoms) to reach a quantitative level in the representation of electrostatic field.

In Section 2 of this Letter, we briefly discuss the basis sets used, together with the characteristics of

the chosen zeolite frameworks. In Section 3, we develop an approximation of the dependence of the Mulliken-type charges for the framework oxygens found with both a minimal and split-valence basis sets, with respect to the above-mentioned geometric parameters. The approximation obtained is then used to estimate the multipole moments for zeolites with a large elementary unit cell: zeolite Y and silicalite. We note that a recent article [16], wherein the structure of all-siliceous fajaussite has been optimized with the same PHF scheme at the 6-21G* level for silicon and 6-21G for oxygen, presents electrostatic potential maps but no Mulliken charge values; hence, a verification of the charges estimated herein for the Y analogue cannot be made.

2. Theoretical aspects

The theoretical backgrounds of the solution of the Schrödinger electronic problem in three dimensions with periodic boundary conditions have already largely been described [7,8,17,18]. The subsequent transformation of the Fock matrix and respective overlap matrix between direct \rightarrow reciprocal \rightarrow direct lattice spaces permits a solution to be reached for a relatively large number of atomic orbitals (AO) as compared to the conventional methods of solution of the Hartree–Fock equation.

The choice of the zeolite structures was done on the basis of all-siliceous zeolite frameworks with a small number of atoms per unit cell (UC) and for which we could compare our results with others published previously [19–23]. The characteristics of the zeolite frameworks, taken from the MSI database [24,25] are given in Table 1. The framework geometries were not optimized, assuming that the experimental errors are negligible considering the wide range of the previously mentioned geometrical parameters of the chosen zeolites.

The minimal STO-3G basis set [29] (named hereafter basis A) was applied for all considered systems, except for the Y-type (FAU) and silicalite (MFI) zeolite, which possess elementary UCs which too are large (Table 1). With the split-valence 6-21G basis set (on both Si, O atoms) [29], the SCF scheme converged properly for the case of chabazite (CHA) only. No convergence could be reached for DAC,

Table 1

Symbol, number of atoms and of atomic orbitals (AO) per unit cell (UC) (all coordinates from Ref. [24,25], if no other reference is given), and symmetry group of the considered zeolite frameworks

Name	Symbol ^a	Atoms/UC	AO/UC (STO-3G)	Symmetry group
montesommaite	MON	24	152	I4 ₁ /amd
natrolite ^b	NAT	34	194	Fdd2
dachiardite	DAC	36	228	C2/m
chabazite ^c	CHA	36	228	R3c
phillipsite	PHI	48	304	P2 ₁ /m
merlinoite	MER	48	304	Immm
ZSM-57	MFS	54	342	Imm2
ferrierite	FER	54	342	Immm
heulandite	HEU	54	342	C2/m
gmelinite	GME	72	456	P6 ₃ /mmc
rho	RHO	72	456	Im3m
losod	LOS	72	456	P6 ₃ /mmc
mordenite	MOR	72	456	Cmc2 ₁
faujasite ^{d,e}	FAU	156	1020	F23
silicalite ^{e,f}	MFI	288	1824	Pnma

^aRef. [26].

^bFramework with Si/Al ratio equals 2.

^cRef. [8].

^dFramework with Si/Al ratio equals 3 [27].

^eNot treated via CRYSTAL92.

^fRef. [28].

MER, MON, NAT and PHI, whereas the other zeolites could not be treated with the split-valence base due to too many atomic orbitals in their UC. As a result, we also considered other possible basis sets for the studied zeolites. The 8-31G basis for silicon ² (Table 2) and standard 6-21G for oxygen [29] (named hereafter basis B) was applied for CHA, DAC, MER, MON and PHI. For this basis set, we optimized the exponent of the 2sp' orbital on the oxygen as 0.34 and of the 3sp' orbital on the silicon as 0.10 (instead of 0.37 and 0.14, respectively, as given in Refs. [29]; see footnote 1) in the case of MON. We finally considered a third basis set (named hereafter basis C) by adding, to the previous basis set, d-polarisation functions with exponents 0.85 for O and 0.34 for Si, respectively, which again 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 due to too many atomic orbitals in their UC.

² N.M. Harrison, supplied materials for CRYSTAL95, available through <http://www.dl.ac.uk/TCS/Software/CRYSTAL>.

Table 2

The 8-31G basis set for the Si atom (see footnote 1)

AO type	Exponent	Coefficient (s)	Coefficient (p)	
1s	149866.	0.0001215	–	
	22080.6	0.0009770	–	
	4817.5	0.0055181	–	
	1273.5	0.0252	–	
	385.11	0.0926563	–	
	128.429	0.2608729	–	
	45.4475	0.4637538	–	
	16.2589	0.2952	–	
	2sp	881.111	–0.0003	0.0006809
		205.840	–0.005	0.0059446
64.8552		–0.0368	0.0312	
23.9		–0.1079	0.1084	
10.001		0.0134	0.2387	
4.4722		0.3675	0.3560066	
2.034		0.5685	0.341	
0.9079		0.2065	0.1326	
3sp	2.6668	–0.0491	0.0465	
	1.078	–0.1167	–0.1005	
	0.3682	0.23	–1.0329	
3sp'	0.14	1.0	1.0	

For comparison, we also performed a STO-3G calculation for the H–natrolite framework which includes Al atoms. In this case, all different types of

the oxygen atoms corresponding to the Si–O–Si, Si–O–Al and Si–O(H)–Al moieties needed to be considered and compared with the results obtained for the all-siliceous frameworks. The position of the compensating hydrogen atom was chosen to satisfy the requirement of the respective geometry: OH length equals 0.96 Å [23,30], Si–O–H angle equals 114°, Al–O–H angle equals 105° [30].

All computations with the CRYSTAL92 code [7] were realized 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^{-5} for the overlap Coulomb and the penetration Coulomb, the overlap exchange and to 10^{-6} and 10^{-11} for the pseudo-overlap exchange series for both levels of basis sets. We found that ‘softening’ the criteria up to 10^{-4} , 10^{-5} and 10^{-6} , respectively, with the second basis set leads to a variation of the atomic charges of nearly 0.6–0.7% in the case of the MON-type zeolite. Usually, the total energy convergence was achieved with less than 15 SCF cycles, except for CHA with basis C where 30 iterations were needed. For information, full SCF convergence for silico-chabazite with STO-3G and 6-21G* basis sets took ca. 10 min and 7 h, respectively, on the above-cited workstation.

The approximation of the oxygen charges Q_0^O in the coordinate system ‘average Si–O distance – Si–O–Si angle’ was done via the FUMILI program [31].

3. Approximation of the Mulliken-type charges of the framework oxygens

All multipole moments up to the 4th order were determined via the approximated scheme [13] available in the CRYSTAL92 code [7]. As it has been shown previously [13], a precise calculation of the Mulliken charges (multipole moments of zeroth order [13]) is sufficient to provide a qualitatively correct electrostatic field as compared to a totally ionic zeolite model. As far as the angular dependence of the oxygen charges depends strictly on the Si–O–Si angle, we considered in this first part only the oxygen atoms.

For comparison with a previous study [19], we took the same optimized structure ‘Opt3’ of the silico-chabazite given therein. The analysis of the Mulliken charges obtained with the three basis sets (A, B, C) shows that the quality of the B and C bases are close to the bases constructed with a pseudopotential part in Ref. [19]. The difference between the Mulliken oxygen charges calculated here and in Ref. [19] is essentially less than 1% (Table 3), which may be considered as negligible.

79 charge values (for all different types of O atoms within all the all-siliceous zeolites given in Table 1, with the exception of faujasite) were estimated with the STO-3G basis set, whereas only 27 charge values (for the different types of O atoms within CHA, DAC, MER, MON and PHI) were

Table 3

Comparison of the Mulliken-type charges (e^-) calculated for the four different types of oxygen atoms in the silico-chabazite (coordinates of Opt3 [19])

Oxygen type	R^a (Å)	R^b (Å)	Basis set A ^a / basis set A ^b	Basis set ps-21 ^{a,c} / basis set B ^b	Basis set ps-21* ^{a,c} / basis set C ^{b,d}
O ₁	1.610	1.6094	8.739/8.714	9.183/9.177	8.894/8.908
O ₂	1.605	1.6048	8.716/8.738	9.160/9.204	8.871/8.865
O ₃	1.607	1.6090	8.720/8.718	9.161/9.178	8.873/8.889
O ₄	1.614	1.6158	8.740/8.738	9.185/9.203	8.901/8.904

^aRef. [19].

^bThis work.

^c‘ps’ denotes a pseudopotential to describe the core electrons of Si.

^dThese values were obtained herein for a slightly different geometrical model [8] (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.

evaluated with basis set B. In each case, a surface was fitted to the data points. A satisfactory approximation of the surfaces of the oxygen atomic charges with respect to the internal geometric parameters characterizing the environment was obtained at both levels of theory, minimal (A) and split-valence (B). Interestingly, a representation of the O charges (expressed below as the difference between the number of electrons of the neutral oxygen atom, i.e. $8e^-$ and the Mulliken charges) as a function of the two coordinates R and ϑ :

$$Q_0^0(R, \vartheta) = a_1 R^n + a_2 (R - R_0)^m \cos(\vartheta - \vartheta_0) \quad (1)$$

ϑ being the $\text{Si}_1\text{-O-Si}_2$ angle (in radian) and $R = (R_{\text{OSi}_1} + R_{\text{OSi}_2})/2$ (in Å) the average Si–O distance, is sufficient to obtain an average error of 1.95% (basis set A) with respect to the values of the Mulliken charges (Table 3). The fitted parameters of function (1) are given in Table 4 for both basis sets applied. The positions of the Mulliken charge values (depicted by squares), relative to the approximated charge surfaces calculated with formula (1) are shown in Fig. 1. Only one charge value corresponding to a rather exaggerated value $R = 1.84$ Å for the LOS framework was omitted. Most probably, the inclusion of a third variable, i.e. the anisotropy of the Si–O distance or simply both Si–O distances, describing the oxygen geometry within the framework may decrease the error, but the simple function (1), providing a reasonable precision, surely deserves some attention.

We first compared the parameters of the dependence (1) for an equivalent set of oxygen atoms evaluated with both basis sets A and B. Therefore, we considered the approximation with the same 27 points using the basis set A (Table 4). The relative

variations in the parameter values are more pronounced as compared to the approximation with all 79 points. This assumes that a change of the coupling between the two coordinates could be stronger when expanding the basis set. Hence, further steps including a larger number of points would be necessary to approximate the surface and verify the validity of the obtained parameters.

It is also instructive to compare the results of the calculations made for all-siliceous zeolites with those obtained for H–natrolite with a ratio $\text{Si}/\text{Al} = 2$ (Table 5). While the charges of the oxygen atoms corresponding to the H-bonded positions differ sharply (30%) from the approximation with the parameters obtained for Si–O–Si bridged oxygens, the charges related to the Si–O–Si case nearly coincide (0.3%) with the approximate surface formula (1) calculated with its respective R and ϑ variable values (Table 5). The charges of the oxygens corresponding to the Si–O–Al chain have an intermediate value, with still a rather serious error. It underlines the fact that a determination of the charges corresponding to the Si–O–Al situation should be done on the basis of the analysis of respective Al-containing zeolites.

An important question is related with the possibility of estimating the variation of the approximate dependence formula (1) while replacing a minimal Gaussian basis set by a more advanced one. The higher precision of the approximation of the results obtained with the B set confirms the validity of formula (1) for a better quality basis set. The relatively slight variation of the parameters of function (1) while shifting from the minimal STO-3G to a split valence 6-21G-type level (Table 4) allows the suggestion that the main feature of the ‘coupling’ between the coordinates R and ϑ may be correctly

Table 4

Parameters of the approximated charge surface $Q_0^0(R, \vartheta) = a_1 R^n + a_2 (R - R_0)^m \cos(\vartheta - \vartheta_0)$ and mean square deviation (MSD) for the N oxygen charge values (e^-) calculated with the different basis sets

Basis set	N	MSD (%)	a_1	$n \cdot 10^2$	$a_2 \cdot 10^3$	R_0 (Å)	m	ϑ_0 (rad)
STO-3G	79	2.0	−0.650	−0.0283	1.500	1.310	−3.360	0.1889
STO-3G	27 ^a	1.9	−0.650	−0.372	1.503	1.310	−3.275	0.1889
8-31(Si) + 6-21(O)	27 ^a	1.2	−1.157	−15.05	4.485	1.222	−3.570	0.1684

^aFor the CHA, DAC, MER, MON and PHI zeolites only.

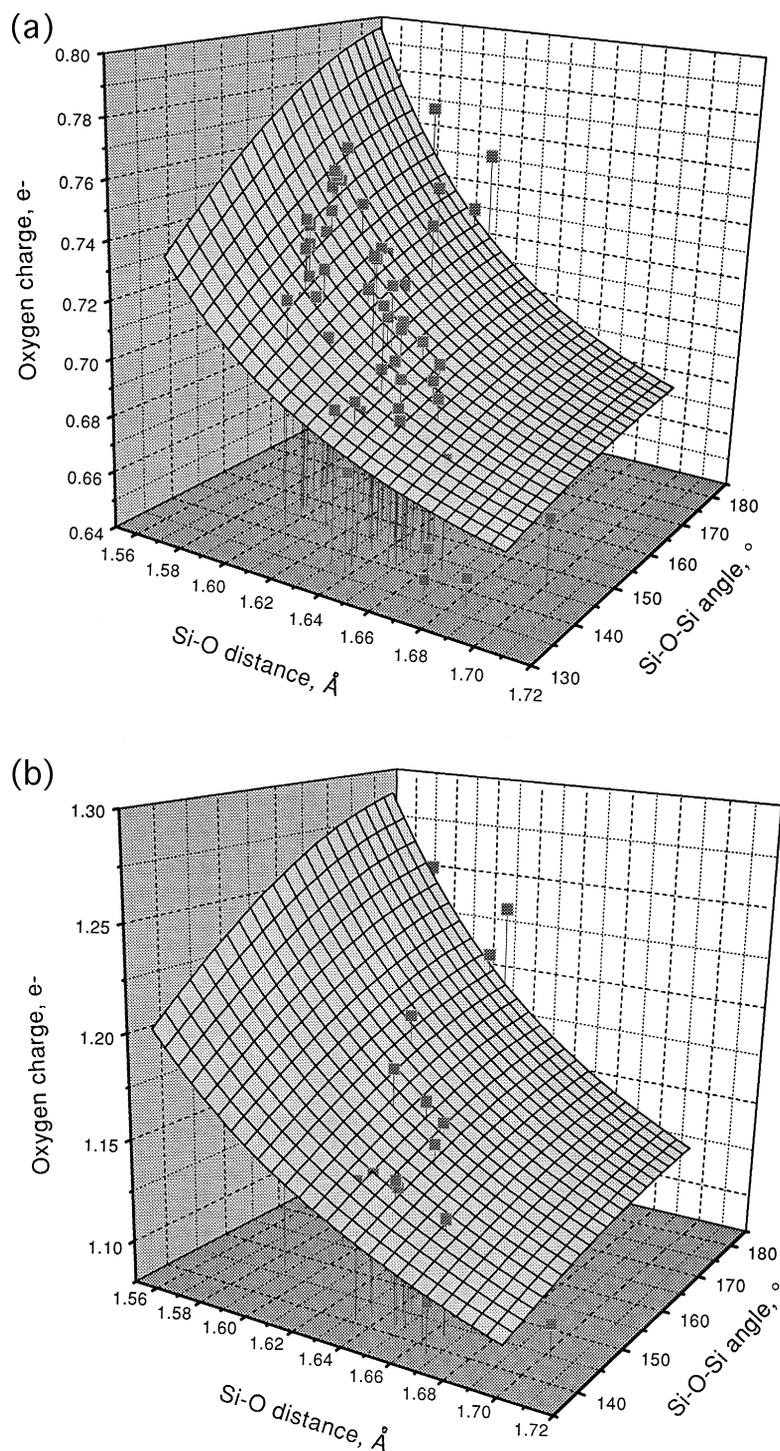


Fig. 1. Position of the approximated charge surface relative to the Mulliken oxygen atomic charge values (in $|e^-|$, given by squares) versus the average Si–O distance R (Å) and Si–O–Si angle ($^\circ$) for all considered zeolite frameworks calculated with the basis sets: (a) STO-3G; (b) 8-31G (Si) and 6-21G (O).

presented by the second term in the right-hand side of Eq. (1). A decrease (in absolute value) of the atomic oxygen charges between the 2nd and 3rd step in the sequence of the three basis A to B to C studied here, or STO-3G to ps-21 to ps-21* in Ref. [19], ('ps' denoting the use of a pseudopotential to describe the Si core electrons in silico-chabazite, Table 3) is observed in both cases, here and in Ref. [19]. On this basis, we hypothesize that a higher quality basis set will lead to a decrease of the atomic charges (in absolute value) relative to the charge values calculated with basis set B (or ps-21G in Ref. [19]). Hence, the atomic charge surface obtained with a basis set defined at a better quality level will be situated within the two surfaces calculated here with the first and second types of AO basis sets. If the variation of the parameters of the second term in (1) remains minor, we may estimate the parameters of the surface calculated using a new basis set from only some points which may be obtained for zeolites with a smaller UC. Then the ionic charges of a zeolite with a larger UC could be evaluated on the basis of the recalculated approximate dependence (1).

Another advantage of the simple estimation expressed by (1) is related to the possibility of a more precise interpretation of some spectroscopic results. The latter are often discussed via the comparison of electrostatic field values assigned to the oxygen atoms as to the main source of it, which seems to be justified for the H-type zeolites, the oxygen charges often being determined through an empirical rule, such as the Sanderson electronegativity principle [32]. The approach derived here allows the evaluation (or

Table 5

Comparison between the Mulliken oxygen charges (e^-) approximated using the function $Q_0^0(R, \vartheta) = a_1 R^n + a_2 (R - R_0)^m \cos(\vartheta - \vartheta_0)$ and calculated with the STO-3G basis set for the five different oxygen atomic types in H-natrolite [24,25]

Oxygen type	R (Å)	ϑ (°)	$-Q_0^0$		Error (%)
			approximated	calculated	
Si–O–Si	1.6381	144.8	0.6870	0.6891	0.3
Si–O–Al	1.6728	139.3	0.6224	0.7310	14.9
	1.6785	135.8	0.6872	0.7261	5.4
	1.6835	129.4	0.5870	0.6917	15.1
Si–O(H)–Al	1.6740	141.2	0.6917	0.5323	30.0

Table 6

Mulliken oxygen charges Q_0^0 (e^-) of silicalite [28] approximated using the expansion $Q_0^0(R, \vartheta) = a_1 R^n + a_2 (R - R_0)^m \cos(\vartheta - \vartheta_0)$ whose parameters were obtained by fitting the Mulliken charges calculated with the basis set A for the other smaller size type zeolites

Atom type ^a	R (Å)	ϑ (°)	$-Q_0^0$
17	1.5378	149.613	0.8107
19	1.5538	171.815	0.8107
13	1.5608	174.997	0.7985
15	1.5620	157.401	0.7765
10	1.5704	159.942	0.7663
3	1.5724	174.015	0.7766
6	1.5736	162.617	0.7646
22	1.5788	149.495	0.7410
4	1.5808	162.138	0.7540
7	1.5811	156.396	0.7473
12	1.5819	155.590	0.7453
2	1.5839	145.182	0.7293
11	1.5839	158.927	0.7467
14	1.5852	166.542	0.7523
21	1.5859	150.862	0.7350
24	1.5910	142.848	0.7194
25	1.5930	152.732	0.7300
9	1.5947	153.387	0.7290
5	1.5982	146.117	0.7176
26	1.6049	145.843	0.7121
18	1.6148	139.888	0.6990
8	1.6156	155.366	0.7134
20	1.6165	148.207	0.7065
1	1.6223	142.612	0.6977
23	1.6375	156.044	0.7002
16	1.6554	151.944	0.6893
average			0.7447
PHF calculation [21]			0.74

^aAtomic numbering from Ref. [28].

even the precise calculation, with a further application using a better quality basis set) of oxygen charges from the sole knowledge of the geometrical parameters (R, ϑ) of the framework oxygen atoms considered.

In the case of the silicalite framework, which possesses a relatively large UC [28], we estimated the charges for all 26 oxygen crystallographic positions (Table 6) with function (1) whose parameters were obtained by fitting the charges calculated with the basis set A for the other smaller size type zeolites. Averaging the charges, we obtained a value of $-0.745 |e^-|$ in accordance with $-0.74 |e^-|$ found

using direct PHF-type calculations with the CRYSTAL code with the same basis set A [21].

As another example of a zeolite with a large UC, we finally tried to estimate the oxygen atomic charges of zeolite Y with both basis sets A and B considered (Tables 1 and 7). We calculated, using the approximation (1), the oxygen charge only for the Si–O–Si moiety, considering the appreciable distinctions between the oxygen charges corresponding to Si–O–Al and Si–O(H)–Al chains discussed for the H–natrolite case (Table 5). The estimations in Table 7 are close to the lower and upper bounds of the charge values which may be obtained from the solution with a basis set of higher level. To confirm this, one should take into account the variations of the charges already discussed when passing from STO-3G to ps-21 to ps-21* [19], as well as our trends observed in the series A to B to C. A common feature of both charge surfaces is the nearly similar charge relations found for the different oxygen types. This is also a consequence of a relatively slight variation of the coupling term in expression (1) with the basis set variation.

It is also interesting that the ratios between our oxygen charge estimations (Table 7) correlate well with those found by the electronegativity equalization method (EEM) [33], while the absolute values are different. The values determined by the EEM approach are intermediate between the upper and lower estimate provided by the basis sets A and B.

Evidently, the respective oxygen charges for the Si–O–Al alternation within the Y zeolite have to be estimated from similar approximation procedures; only this has to be achieved for a series of zeolites with a small UC containing Al atoms. Such calcula-

tions considering multipole moments of higher-order are in progress.

4. Conclusions

Distributed multipole analyses with the CRYSTAL92 program were done on the basis of the Saunders scheme [13] for 12 different all-siliceous zeolite models plus the H-form of natrolite. An analysis of the Mulliken atomic oxygen charges (multipole moments of zeroth order within the scheme [13]) has been performed in terms of two geometrical parameters, i.e. the angle $\vartheta = \text{Si-O-Si}$ and average Si–O distance $R = \sum_{k=1}^2 R_{\text{OSik}}/2$ and a simple approximation, i.e. $Q_0^0(\vartheta, R) = a_1 R^n + a_2 (R - R_0)^m \cos(\vartheta - \vartheta_0)$ has been obtained. A variation of the ‘shape’ of the approximated atomic charge surface was obtained when shifting from a minimal STO-3G to a split-valence 6-21G quality basis set, but the proposed expression is adequate for both cases. The necessity of an estimation of the respective parameters ($a_1, n, a_2, m, R_0, \vartheta_0$) for the Si–O–Al moiety to approximate the oxygen atomic charge values from analogous calculations within H-form type zeolites has also been shown. Using the derived approximation of the charges, we obtained an average atomic oxygen charge value of $-0.745 |e^-|$ in agreement with $-0.74 |e^-|$ for silicalite found previously via PHF-type calculations with the CRYSTAL code. Further studies of the variation of the approximated function with higher quality basis sets would be useful to evaluate the atomic charges of zeolites with a larger number of atoms per unit cell (UC) on the basis of the calculation of the

Table 7

Charges Q_0^0 ($|e^-|$) of oxygen atoms and ratio of the charges for zeolite FAU (Si/Al ratio equals 3 [27]), estimated using the function $Q_0^0(R, \vartheta) = a_1 R^n + a_2 (R - R_0)^m \cos(\vartheta - \vartheta_0)$ with the basis sets STO-3G (A) and 8-31G (Si)/6-21G (O) (B)

Type ^a	R (Å)	ϑ (°)	$-Q_0^0$			$Q_0^0(\text{O}_{22})/Q_0^0(\text{O}_i)$		
			Basis set A	Basis set B	EEM ^a	Basis set A	Basis set B	EEM ^a
O ₂₂	1.6160	147.6	0.7286	1.1881	0.9282	1.000	1.000	1.000
O ₄₁	1.6201	145.1	0.5756	1.0215	0.8225	1.266	1.163	1.128
O ₃₁	1.6202	145.2	0.5773	1.0233	0.8870	1.262	1.161	1.046
O ₁₂	1.6205	144.4	0.5721	1.0171	0.8039	1.273	1.168	1.154

^aRef. [27].

‘geometrical’ dependence of the atomic charges for zeolites with a smaller number of atoms per UC.

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