Approximations of the Mulliken Charges for the Oxygen and Silicon Atoms of Zeolite Frameworks Calculated with a Periodic Hartree–Fock Scheme

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ABSTRACT: Distributed multipole analysis (DMA) on the basis of periodic Hartree–Fock (PHF) calculations, using the CRYSTAL code, is applied to five different all-siliceous zeolite models: chabazite, gmelinite, merlinoite, montesommaite, and RHO. Mulliken charges of the framework atoms were calculated with a pseudopotential ps-21G* basis set for silicon and a 6-21G* basis for oxygen. The charge values of the silicon atoms were approximated by a simple one-dimensional function with respect to the average Si—O distance within the respective SiO_4 tetrahedra, whereas a two-dimensional function with respect to the average Si—O distance and the Si—O—Si angle was used for the oxygen atoms. Both dependences were then utilized to evaluate the Mulliken atomic charges of 10 other frameworks with a larger number of atoms per unit cell. The validity of such application is confirmed by comparison with results obtained through direct PHF calculation for all-siliceous mordenite.
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Key words: Mulliken charges; zeolite; periodic Hartree–Fock

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Introduction

Aluminosilicate zeolite frameworks with a high Si/Al ratio, such as MCM-22 (Si/Al = 10–14), ZSM-5 (Si/Al = 20–50), Beta (Si/Al = 5–15), etc. constitute an important class of adsorbent and catalyst materials. The necessity to consider accurate electrostatic interactions to locate the preferential positions of an adsorbed species is now confirmed by direct ab initio Hartree–Fock calculations on systems such as the all-siliceous form of ZSM-5, i.e., silicalite [1]. All-siliceous forms are the simplest models which can be considered by three-dimensional (3D) periodic ab initio Hartree–Fock (PHF) computations and whose study could provide a deeper knowledge to simulate electrostatic interaction effects. The modeling of the behavior of an adsorbed molecule then requires the most accurate estimation of the field which is created only by the silicon and oxygen atoms of the all-siliceous frameworks (or mainly by these atoms within zeolites with high Si/Al ratio). Therefore, the largely used cluster embedded models require to consider the long-range interactions between the adsorbed molecule and the inert rest of the zeolite structure. In the case of embedded cluster models, which include a molecule near a cation or near a bridged hydroxyl group linked to the closest aluminum atom [2], the electrostatic long-range interactions have often been estimated as created by these last two types of framework atoms only.

A conventional way to evaluate the electrostatic field is through the derivation of the atomic multipole moments for the total host–guest system for which we can calculate the wave function. The distributed multipole analysis (DMA) scheme related to the atomic positions developed by Saunders et al. [3] allows to express these moments in terms of internal geometric coordinates. For the case of zeolite frameworks, the application of the DMA scheme was proposed first through ab initio computations of some zeolite models with a relatively small number of atomic orbitals (AO) per elementary unit cell (UC) considering basis sets of a relatively advanced level [4, 5]. More particularly, it allowed to derive simple analytical approximations of the calculated multipole moments with respect to some internal geometric characteristics of each atom, which interestingly can be applied to other zeolites with a higher number of AOs per UC, those latter constituting most of the materials effectively used in various types of chemical catalytic processes.

In our previous works, the Mulliken charges (moments of zeroth order) were calculated with the ab initio Hartree–Fock linear combination of atomic orbital (LCAO) code CRYSTAL92 [6] for two types of periodic systems [4, 5]. One-dimensional expressions with respect to the average T—O distance (T = Al, P, Si) were then fitted to represent the Mulliken charges of the silicon atoms within all-siliceous structures [4] and of both the aluminum and phosphorus atoms within aluminophosphates (Al/P = 1) [5]. It has also been shown that various distortions of the TO_4 tetrahedra do not influence strongly the charge value of the T atoms. A two-dimensional type dependence was obtained for the Mulliken oxygen charges within all-siliceous analogs and a three-dimensional one for the Mulliken charges and dipolar atomic moments of oxygens within the aluminophosphate (ALPO) frameworks [5].

In order to verify our method of estimating the multipole moment dependences for any arbitrary siliceous zeolite or ALPO based on the approximate results obtained for structures with a relatively small number of AOs per UC, the behavior of both types of dependence of each multipole moment and their convergence need to be confirmed with different basis sets. To our knowledge, this has so far been discussed only for the Mulliken charges [7–9], but not for their dependences with the internal geometric characteristics of the respective atom.

In our previous study treating a series of all-siliceous zeolites [4], we confirmed the use of a same type of two-dimensional analytical dependence for the Mulliken oxygen charges and of a one-dimensional expression for the silicon charges with two basis sets, i.e., the STO-3G and a 6-21G type quality basis. In this study, we analyze the evaluation of their dependences with higher quality basis sets, including a split valence pseudopotential ps-21G* (Durant–Barthelat) on Si and 6-21G* on O, for 5 all-siliceous zeolites, i.e., chabazite (CHA), gmelinite (GME), merlinoite (MER), montesommaite (MON), and RHO. In total, this amounts of 6 different types of silicon atoms and 19 types of oxygens.

In the next section, we briefly discuss the basis sets together with the characteristics of the frameworks. In the third section, we present the fitting

of the atomic Si and O charges with respect to the internal geometric parameters using the dependences obtained previously [4, 5]. In the last section, the approximations using the herein computed parameters are applied to predict the Mulliken charges of 10 siliceous zeolites with a larger number of AOs per UC, for which the direct solution can hardly be achieved with the most modern available computing platforms and electronic structure codes. The validity of such an application is confirmed by comparison with available results obtained by direct PHF calculation for all-siliceous mordenite with a basis set of 6-21G* quality [10].

Theoretical Aspects

The theoretical bases for the solution of the Schrödinger electronic problem in three dimensions considering periodic boundary conditions have already largely been described in the literature [3, 6, 11, 12]. The choice of the siliceous structures was done on the basis of a relatively small number of atoms per UC, hence a reasonable number of two-electronic Coulomb and exchange integrals to evaluate. The characteristics of the 5 all-siliceous frameworks, which were treated with the CRYSTAL92 code, have been taken from the MSI database [13] (Table I). The characteristics of the other 10 all-siliceous forms whose charge values were predicted on the basis of the herein derived approximations are presented in Table II.

The pseudopotential Durant–Barthelat ps-21G* basis set on silicon atoms [26] and 6-21G* on oxygens [27] with conventional exponents for the *d*-polarization functions, i.e., 0.5 and 0.92 a.u.$^{-2}$ for Si and O, respectively, was applied to all zeolites considered in Table I. An exponent value of 0.35 a.u.$^{-2}$ for the oxygen *d*-polarization function was optimized in the case of the MON zeolite, but we held the value of 0.92 a.u.$^{-2}$ providing acceptable computation limits for all 5 frameworks. No convergence could be reached for DAC and MON, whereas the other zeolites could not be treated with the ps-21G*(Si)/6-21G*(O) basis set because the number of atomic orbitals in their UC was too large.

Computations with the CRYSTAL92 code were carried out partly on an IBM RISC 6000 model 560 workstation (with 256 Mb of memory) and partly on an IBM 15-node (120 MHz) Scalable POWER-parallel platform (with 1 Gb of memory/CPU). For all cases, the thresholds for the calculations were fixed to 10^{-5} for the overlap Coulomb, the penetration Coulomb, and overlap exchange, to 10^{-6} and 10^{-11} for the pseudo-overlap exchange, and to 10^{-5} for the pseudopotential series.

Approximation of the Mulliken Charges of the Si and O Atoms in Small Size Type Zeolites

Omitting *d*-polarization functions on the oxygen atom, we first wished to compare the quality of the basis sets chosen with available results of Apra et al. for the ''Opt3'' model of silico-chabazite [8]. The Mulliken total silicon charge 12.230 $|e|$ calculated with the CRYSTAL92 code and ps-21G*

TABLE I
Symbol, number of different silicon and oxygen types, of total atoms, and of atomic orbitals (AO) per unit cell (UC) using the ps-21G*(Si) / 6-21G*(O) basis set, and symmetry group of the considered zeolite frameworks.[a]

Name	Symbol[b]	n_{Si}/n_O	Atoms / UC	AO / UC	Symmetry group
Montesommaite	MON	1 / 3	24	328[d]	$I4_1$ / amd
Chabazite[c]	CHA	1 / 4	36	492	R3c
Merlinoite	MER	2 / 6	48	656	Immm
Gmelinite	GME	1 / 4	72	984	$P6_3$ / mmc
RHO	RHO	1 / 2	72	984	Im3m

[a]All coordinates are from Ref. [13] if no other reference is given.
[b]Ref. [14].
[c]Ref. [6, 8].
[d]368 for basis set 6-21G* on both atoms.

TABLE II
Symbol, number of different silicon and oxygen types, of total atoms, and of atomic orbitals (AO) per unit cell (UC) using the STO-3G basis set, and symmetry group of the zeolite frameworks whose charge distributions were predicted on the basis of the estimations with functions (1) and (2).

Name	Symbol[a]	n_{Si}/n_O	Ref.	Atoms / UC	AO / UC (STO-3G)	Symmetry group
Ferrierite	FER	4 / 8	15	54	342	Immm
ZSM-57	MFS	8 / 14	16	54	342	Imm2
Mordenite	MOR	4 / 9	17	72	456	$Cmc2_1$
ZSM-12	MTW	7 / 14	18	84	532	C2 / c
Mazzite	MAZ	2 / 6	19	108	684	$P6_3$ / mcm
VPI-5	VFI	2 / 6	20	108	684	$P6_3$ / mcm
ZSM-11	MEL	7 / 15	21	144	912	I4m2
Beta	BEA	9 / 17	22	192	1216	$P4_122$
NU-87	NES	17 / 34	23	204	1292	$P2_1$ / c
MCM-22	MCT[b]	8 / 12	24	216	1368	$P6_3$ / mmm
Silicalite	MFI	12 / 26	25	288	1824	Pnma

[a]Ref. [14].
[b]Symbol from Ref. [13].

basis coincides exactly with the value given in [8] (below for simplicity, we consider the difference between the number of electrons of the neutral atom, i.e., 14 $|e|$ for Si and 8 $|e|$ for O, and the Mulliken charge).

The PHF computation of the 5 all-siliceous frameworks allowed us to obtain the Mulliken charges with the ps-21G* basis set for 6 different types of silicon atoms and 19 types of oxygens (Table I). Then, a fitting of the Si charges ($|e|$) was made using a simple 1D expression with respect to the average Si—O distance $R = (\Sigma_{k=1}^{4} R_{SiOk})/4$ (Å) of each Si atom within its respective SiO_4 tetrahedron [4]:

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

with $a_1 = 2.019$, $a_2 = -0.771$, and $a_3 = 1.517$ being obtained by fitting. For the oxygen charges ($|e|$), we fitted the calculated values with a 2D function depending on the average Si—O distance of each O atom $R' = (R_{OSi2} + R_{OSi1})/2$ (Å) and Si—O—Si angle (ϑ, radian) [5]:

$$Q_0^0(R', \vartheta) = b_1 e^{nR'} + b_2 e^{m(R'-R_0)} \cos(\vartheta - \vartheta_0) \quad (2)$$

with $b_1 = -1.373$, $n = -0.277$, $b_2 = 0.198$, $m = -0.595$, $R_0 = -0.139$, and $\vartheta_0 = 0.091$ being obtained by fitting. The root mean square deviation (RMSD) values for the approximate Mulliken charges obtained with the ps-21G* basis for the Si and O atoms are 0.40 and 1.23%, respectively. Function (2) leads to a better RMSD for the two STO-3G and 8-31G(Si)/6-21G(O) basis sets, i.e., 1.57 and 0.77%, respectively, as compared to 2.0 and 1.2% presented earlier [4]. The positions of the calculated Si charge values (open circles) relative to the approximate function (1) is presented in Figure 1 together with the other results obtained with STO-3G (diamonds) and with a basis of 6-21G quality (triangles) [4]. One can remark a very slight variation of the slope of the new dependence (1) obtained for the different basis sets. But the principal conclusion is that the conservation of the same type of approximate functions with all three basis sets for both the Si and O atomic charges is clearly verified.

The quality of function (1) obtained here with only 6 silicon charge values needed to be tested. For this, we compared our results with those calculated with the 6-21G* basis [10] for siliceous mordenite. The closeness between the 6-21G* and ps-21G* basis sets suggests that dependence (1) corresponding to 6-21G* could be estimated using a simple shift by a constant value (vertical arrow in Fig. 1) from the charge values obtained with ps-21G* (Table III). Namely, a value of 0.223 $|e|$ obtained as the difference between the Si charge values 2.102 (triangles in Fig. 1) and 1.879 $|e|$ obtained for MON with the 6-21G* and ps-21G* basis, respectively. The average Si charge value 1.872 $|e|$ evaluated with dependence (1) for the MOR framework was corrected accordingly to 2.095 $|e|$ (corresponding to the average value over the 4 charges depicted by $*$) which nearly coin-

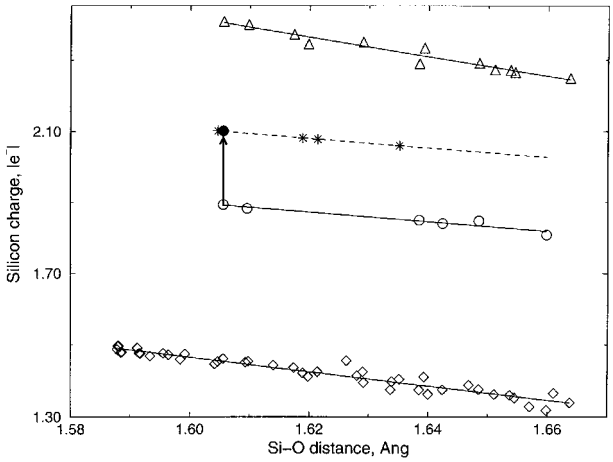

FIGURE 1. Mulliken Si charge values (in $|e|$) of various zeolite models calculated with: STO-3G (diamonds, Ref. [4]), 8-31G (Si) / 6-21G (O) (triangles, Ref. [4]), ps-21G* (empty circles), and 6-21G* (filled circles, MON zeolite) compared to the approximate dependence [eq. (1)] (solid lines) *versus* the average Si—O distance $R = (\Sigma_{k=1}^{4} R_{SiOk}) / 4$ (in Å). The dashed line corresponds to function (1) corrected for the 6-21G* level charges (stars) in the case of MOR. The vertical arrow depicts the difference between the charges of MON estimated with ps-21G* and 6-21G* basis sets.

cides with 2.09 $|e|$ [10]. An analogous correction of the average O charge -0.935 $|e|$ for the same framework in the opposite direction by half of the upper estimated correction (-0.112 $|e|$) led to -1.047 $|e|$ also in agreement with the direct PHF calculated value -1.04 $|e|$ [10] (Table IV).

TABLE III

Mulliken silicon charges ($|e|$) for the MOR zeolite approximated via function (1) including the average Si—O distance $R = (\Sigma_{k=1}^{4} R_{SiOk}) / 4$ using the parameters fitted over the Mulliken charges calculated with ps-21G* for five smaller size type zeolites.

Type	R, Å	Q_0^0
2	1.6047	1.893
1	1.6189	1.874
4	1.6214	1.870
3	1.6352	1.851
Average		1.872
Correction[a]		0.223
Corrected		2.095
Calculated with 6-21G* basis set [10]		2.09

[a]From the calculation with the MON zeolite (see text).

TABLE IV

Mulliken oxygen charges ($|e|$) for the MOR zeolite approximated via function (2) including the average Si–O distance $R' = (R_{OSi1} + R_{OSi2}) / 2$ and Si—O—Si angle (ϑ) using the parameters fitted over the Mulliken charges calculated with ps-21G* basis sets for five smaller size type zeolites.

Type[a]	R', Å	ϑ, degree	$-Q_0^0$
7	1.5872	180.00	0.955
2	1.6060	158.00	0.942
3	1.6115	168.45	0.945
4	1.6116	144.37	0.931
5	1.6243	150.52	0.932
6	1.6295	137.26	0.920
1	1.6313	145.81	0.927
9	1.6373	146.80	0.926
8	1.6408	147.17	0.925
	Average		0.935
	Correction[b]		0.112
	Corrected		1.047
	Calculated with 6-21G* basis set [10]		1.04

[a]Numbering from Ref. [10].
[b]From the calculation with the MON zeolite (see text).

These results suggest that function (1) is precise enough despite the small number of charge values. It also proves the validity of a similar behavior of dependence (1) obtained with the ps-21G* and 6-21G* basis sets here applied. We hence conclude that functions [(1) and (2)] for the Si and O charges conserve their types with all three basis sets. However, on the other hand, this coincidence could be due to the relative short differences between the Si—O distances within the mordenite framework (stars in Fig. 1). Further studies would thus be useful to clearly ascertain the extrapolation of one dependence *versus* another corresponding to a different basis set.

Evaluation of the Mulliken Charges of the Si and O Atoms in Larger Size Zeolites

The good agreement obtained above between the calculated and approximate [functions (1) and (2)] charge values for the mordenite framework permits us to evaluate the charge distributions of some other all-siliceous zeolites. Moreover, this work is very useful considering the absence, to our

knowledge, of any data about the electrostatic field for most of the herein studied zeolite forms. Thus, we chose some zeolite forms whose UC sizes make the direct calculation with a periodic Hartree–Fock approach and an advanced basis set (like ps-21G*) either rather "expensive" or even nonrealistic. The simple charge evaluations with formulas (1) and (2) for the chosen zeolites can indeed be easily performed knowing the geometric parameters of all types of silicon (i.e., R) and oxygen (i.e., R' and ϑ) within the frameworks (Table V and VI).

TABLE V
Mulliken oxygen charges $Q_0^0(|e|)$ approximated with function (2) including the average Si—O distance $R' = (R_{OSi1} + R_{OSi2})/2$ (in Å) and Si—O—Si angle ϑ (in degree).

Type	Atom numb.[a]	R'	ϑ	$-Q_0^0$
BEA	16	1.6155	154.80	0.938
	4	1.6158	153.27	0.937
	2	1.6158	148.29	0.933
	9	1.6159	137.46	0.924
	8	1.6159	162.35	0.942
	15	1.6160	149.23	0.934
	12	1.6160	144.86	0.930
	5	1.6160	148.28	0.933
	17	1.6160	150.62	0.935
	6	1.6161	157.91	0.939
	13	1.6161	154.81	0.937
	1	1.6161	163.02	0.942
	10	1.6161	143.84	0.930
	3	1.6161	156.45	0.938
	14	1.6162	165.58	0.943
	7	1.6162	154.53	0.937
	11	1.6163	137.45	0.924
FER	6	1.5910	153.26	0.944
	5	1.5916	180.00	0.954
	4	1.5974	157.95	0.945
	8	1.6029	147.35	0.936
	7	1.6108	152.85	0.938
	2	1.6148	152.67	0.936
	1	1.6179	169.27	0.944
	3	1.6251	153.52	0.934
MAZ	6	1.6403	136.64	0.917
	2	1.6407	171.19	0.938
	3	1.6414	146.54	0.925
	4	1.6429	144.74	0.923
	5	1.6488	137.34	0.915
	1	1.6558	149.24	0.923
MCT	1	1.4457	180.00	0.997
	11	1.5194	157.04	0.966
	6	1.5632	164.50	0.958
	9	1.5874	159.45	0.948
	10	1.5952	143.22	0.935
	3	1.6093	136.21	0.925
	5	1.6225	180.00	0.945
	4	1.6323	145.83	0.927
	2	1.6409	142.13	0.921
	12	1.6458	145.82	0.923
	8	1.6482	151.18	0.926
	7	1.6502	159.31	0.931
MEL	14	1.5578	165.13	0.959
	9	1.5619	158.57	0.955
	3	1.5800	150.96	0.945
	7	1.5855	151.92	0.944
	13	1.5871	165.27	0.951
	2	1.5895	146.59	0.939
	12	1.5983	145.64	0.936
	15	1.6006	160.43	0.945
	6	1.6049	147.55	0.936
	1	1.6148	149.77	0.934
	8	1.6155	144.07	0.930
	4	1.6171	161.00	0.941
	11	1.6291	145.37	0.927
	10	1.6326	159.10	0.935
	5	1.7452	120.59	0.874
MFS	8	1.5814	162.19	0.951
	3	1.5818	162.32	0.951
	2	1.5842	158.00	0.948
	6	1.5851	157.17	0.948
	4	1.5854	158.00	0.948
	13	1.5855	158.95	0.948
	10	1.5898	154.93	0.945
	11	1.5916	149.55	0.941
	7	1.5938	148.56	0.939
	12	1.5944	147.58	0.939
	9	1.5955	147.69	0.938
	14	1.5961	146.67	0.937
	1	1.5981	145.40	0.936
	5	1.6043	145.13	0.934
MTW	6	1.5641	144.77	0.945
	8	1.5673	155.57	0.952
	2	1.5685	156.21	0.952
	13	1.5777	146.09	0.942
	3	1.5877	146.37	0.940
	14	1.5891	145.86	0.939
	10	1.5926	152.09	0.943
	12	1.5936	144.86	0.937
	5	1.6014	148.05	0.937
	7	1.6042	156.91	0.942
	4	1.6228	157.94	0.938
	1	1.6236	158.59	0.938
	11	1.6292	152.79	0.933
	9	1.6340	134.39	0.917

TABLE V (Continued)

Type	Atom numb.[a]	R'	ϑ	$-Q_0^0$
VFI	4	1.4339	164.41	0.995
	1	1.5766	180.00	0.958
	3	1.6074	131.02	0.920
	6	1.6250	156.52	0.936
	2	1.6551	174.48	0.935
	5	1.7025	167.59	0.920
NES	3	1.5713	136.21	0.935
	17	1.5714	156.91	0.951
	18	1.5749	151.91	0.947
	19	1.5764	153.04	0.947
	16	1.5787	166.49	0.954
	2	1.5847	168.10	0.953
	20	1.5875	145.64	0.939
	7	1.5876	170.98	0.953
	22	1.5880	145.19	0.938
	27	1.5883	150.87	0.943
	10	1.5890	141.46	0.935
	8	1.5898	164.28	0.950
	5	1.5905	143.54	0.936
	23	1.5906	148.84	0.941
	14	1.5910	157.54	0.946
	9	1.5922	148.73	0.940
	29	1.5925	145.98	0.938
	33	1.5939	143.91	0.936
	34	1.5942	156.27	0.944
	28	1.5948	143.37	0.935
	4	1.5949	154.64	0.943
	6	1.5953	160.26	0.946
	31	1.5956	137.72	0.930
	21	1.5963	140.07	0.932
	12	1.5982	149.76	0.939
	30	1.5995	140.75	0.932
	26	1.6016	146.65	0.936
	32	1.6020	164.84	0.947
	15	1.6101	145.91	0.933
	13	1.6107	158.69	0.941
	11	1.6191	146.81	0.931
	1	1.6287	167.36	0.940
	24	1.6301	157.03	0.935
	25	1.6358	150.57	0.929
MFI	17	1.5378	149.61	0.956
	19	1.5538	171.81	0.963
	13	1.5608	175.00	0.962
	15	1.5620	157.40	0.954
	10	1.5704	159.94	0.953
	3	1.5724	174.01	0.958
	6	1.5736	162.62	0.954
	22	1.5788	149.49	0.944
	4	1.5808	162.14	0.951
	7	1.5811	156.40	0.948
	12	1.5819	155.59	0.948
	2	1.5839	145.18	0.940
	11	1.5839	158.93	0.949
	14	1.5852	166.54	0.952
	21	1.5859	150.86	0.943
	24	1.5910	142.85	0.936
	25	1.5930	152.73	0.943
	9	1.5947	153.39	0.943
	5	1.5982	146.12	0.936
	26	1.6049	145.84	0.934
	18	1.6148	139.89	0.927
	8	1.6156	155.37	0.938
	20	1.6165	148.21	0.933
	1	1.6223	142.61	0.927
	23	1.6375	156.04	0.932
	16	1.6554	151.94	0.925

[a]Numbering of the atoms from references given in Table II.

TABLE VI
Mulliken silicon charges $Q_0^0(|e|)$ approximated with function (1) including the average Si—O distance $R = (\Sigma_{k=1}^{4} R_{SiOk})/4$ (in Å).

Type	Atom numb.[a]	R	Q_0^0
BEA	8	1.6159	1.878
	5	1.6159	1.878
	1	1.6159	1.878
	9	1.6159	1.878
	4	1.6160	1.878
	3	1.6160	1.878
	6	1.6161	1.877
	2	1.6161	1.877
	7	1.6163	1.877
FER	4	1.5964	1.905
	3	1.5984	1.902
	1	1.6140	1.880
	2	1.6263	1.864
MAZ	2	1.6405	1.844
	1	1.6513	1.830
MCT	7	1.5485	1.972
	6	1.5801	1.927
	5	1.5861	1.919
	2	1.5914	1.912
	4	1.5932	1.909
	3	1.6071	1.890
	8	1.6268	1.863
	1	1.6604	1.818

TABLE VI (Continued)

Type	Atom numb.[a]	R	Q_0^0
MEL	2	1.5617	1.954
	6	1.5783	1.930
	3	1.6048	1.893
	7	1.6050	1.893
	5	1.6170	1.876
	1	1.6290	1.860
	4	1.6596	1.819
VFI	2	1.5948	1.907
	1	1.6064	1.891
MFS	4	1.5878	1.917
	2	1.5879	1.917
	7	1.5881	1.916
	1	1.5886	1.916
	3	1.5912	1.912
	6	1.5915	1.911
	5	1.5917	1.911
	8	1.5933	1.909
MTW	1	1.5677	1.945
	3	1.5901	1.913
	2	1.5971	1.904
	7	1.5984	1.902
	5	1.6007	1.859
	6	1.6094	1.887
	4	1.6146	1.880
NES	8	1.5814	1.926
	2	1.5841	1.922
	14	1.5849	1.921
	15	1.5852	1.920
	1	1.5867	1.918
	3	1.5868	1.918
	16	1.5877	1.917
	7	1.5904	1.913
	6	1.5910	1.912
	17	1.5940	1.908
	9	1.5958	1.905
	11	1.6023	1.896
	12	1.6057	1.892
	10	1.6079	1.889
	13	1.6082	1.888
	4	1.6095	1.887
	5	1.6211	1.871
MFI	8	1.5610	1.955
	6	1.5734	1.937
	10	1.5756	1.934
	11	1.5768	1.932
	4	1.5769	1.932
	5	1.5831	1.923
	3	1.5874	1.917
	9	1.5935	1.909
	7	1.5941	1.908
	1	1.6007	1.899
	2	1.6137	1.881
	12	1.6257	1.864

[a]Numbering of atoms from references given in Table II.

Two evident features of the charge estimations can be emphasized. First, all the charge values are strictly related to the spatial models referenced in Table II. Any optimization of these initial coordinate sets would alter the internal geometry and hence the charge distribution. But evidently, a spatial optimization using empirical type potentials could lead to reasonable results if the dependences [(1) and (2)] are also taken into account. Second, the charge distribution obtained herein with the ps-21G* basis set can be corrected to the level corresponding to 6-21G* considering the simple shift by a constant value of 0.223 $|e|$ for the Si charges and by -0.112 $|e|$ for the O charges. Caution should, however, be taken if the zeolite system under study has very large Si—O bond lengths. The boundaries for the hopeful estimates applying the charge distribution shift may be evaluated from the extremal values of the Si—O distances for the 4 types of Si charges of mordenite, i.e., 1.605 to 1.635 Å.

Conclusions

The Mulliken charges for 5 all-siliceous zeolites, i.e., chabazite, gmelinite, merlinoite, montesommaite, and RHO, were calculated using the CRYSTAL92 code with a pseudopotential ps-21G* (Durant–Barthelat) basis set on the silicon and 6-21G* on the oxygen atoms. The Si charge values were approximated by a simple one-dimensional function with respect to the average Si—O distance within the respective SiO_4 tetrahedra. A two-dimensional function with respect to the average Si—O distance and Si—O—Si angle was con-

sidered for the O atomic charges. Both types of approximate functions were found to be appropriate to fit the charge values computed with this presently proposed basis set in the same way as it was shown previously for charges obtained with STO-3G and 6-21G sets [4, 5]. The comparison between the atomic charges computed directly with the CRYSTAL92 code for mordenite showed a good agreement with our estimations based on the two simple proposed analytical functions. This also allowed to evaluate the charge distribution for some zeolites with a larger number of atoms per elementary unit cell without the necessity to pass thru the direct solution of the electronic problem.

The knowledge of the Mulliken charges only provides a rather qualitative level for the evaluation of the electrostatic field [3, 9]; however, it is useful to estimate an order of magnitude for the electrostatic field of the considered host system and hence to propose preferential positions of any adsorbed molecule. We hope that the approximate charge (multipole moments of zeroth order) dependences for both the silicon and oxygen atoms could be completed later by similar types of approximate dependences for the hydrogen and aluminum atoms obtained on the basis of analogous fitting of the charges and higher order multipole moments for a series of H-form zeolite models with a small number of atomic orbitals per UC. The direct calculations of these moments with the CRYSTAL code are presently in progress.

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