

Extending and simplifying the electronegativity equalization method¹

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Abstract

The Electronegativity Equalization Method (EEM), developed by Mortier et al. [J.W. Mortier, S.K. Ghosh, S. Shankar, J. Am. Chem. Soc., 108 (1986) 4315; G.O.A. Janssens, B.G. Baekelandt, H. Toufar, W.J. Mortier, R.A. Schoonheydt, J. Phys. Chem., 99 (1995) 3251], is extended with a shielded external potential to improve its accuracy. EEM is also simplified in the sense that one type of hydrogen atom is used to describe positively as well as negatively charged hydrogen atoms instead of two as in the original formula. The parameters are calibrated to sets of Mulliken charges obtained from STO-3G and STO-3G* calculations, containing Al, C, H, N, O and Si atoms, and also Ge and Ti atoms for which no parameters were found in literature yet. Furthermore, the parameters (Ge and Ti excluded) are also calibrated to a set of potential derived charges (Merz–Kollman–Singh scheme). It seems that the EEM formalism, after appropriate parameterization, can reproduce the results of different charge partitioning schemes applied to calculations with different basis sets. Extending the EEM formula leads to a better reproduction of the charges. However, the parameters are highly correlated and, therefore, depend strongly on the calibration set used. All charges are well reproduced, except on titanium. A sensitivity analysis of the charges with the original and extended EEM formalism shows that their results differ, but are strongly correlated. The applicability of the EEM approach and the parameters derived is shown in a molecular dynamics calculation on ethene absorbed in H-ZSM-5. It appears that the EEM approach in such calculations can help to understand chemical reactivity in zeolites. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Electronegativity Equalization Method (EEM), developed by Mortier et al. [1,2], is a semi-empirical approach to density functional

theory. It allows the direct calculation of the average electronegativity and the charge distribution in a molecule or solid. The following equation is used:

$$\chi = \chi_i^* + 2\eta_i^* q_i + 14.4 \sum_{i \neq j}^n \frac{q_j}{R_{ij}} \quad (1)$$

with χ the electronegativity of the system, χ_i^* and η_i^* the electronegativity and the hardness

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¹ Dedicated to Professor Herman van Bekkum on the occasion of his 65th birthday.

of atom i and q_i the charge on atom i . The last term in Eq. (1) is called the external potential, in which 14.4 is a conversion factor. A set of n of these equations, with n the number of atoms in the system, is solved along with the equation that constrains the net charge in the system. For each element values for the electronegativity χ_i^* and the hardness η_i^* have to be known. In literature [3], values for Al, C, H, N, O, P and Si can be found (Table 1). They have been determined by calibration to a set of Mulliken charges for some small molecules, obtained from STO-3G calculations. The value χ_O^* is fixed to 8.5 eV. The H atom is a special case [4] and is treated differently: parameters have been determined for H($\delta+$) as well as H($\delta-$).

Rappé and Goddard III [5] have developed a related scheme, the charge equilibration (QEq) approach, to predict charge distributions in molecules. They use the following equation:

$$\chi = \chi_i^0 + J_{ii}^0 q_i + \sum_{i \neq j}^n q_j J_{ij} \quad (2)$$

with χ the electronegativity of the system, χ_i^0 and J_{ii}^0 the electronegativity and the Coulomb repulsion between two electrons in the valence orbital on atom i , and J_{ij} the Coulomb repulsion between two electrons in the valence orbitals on atoms i and j . Values for χ_i^0 and J_{ii}^0 are obtained from ionization energies and electron affinities corrected for exchange interactions. J_{ij} 's are geometry dependent and are calculated from normalized ns Slater orbitals in

which the orbital exponents ξ are related to the covalent radii. The ξ 's are geometry independent except for ξ_H , because its value is charge dependent. This makes QEq an iterative scheme.

Motivated by a comparison between exact and approximated curves of J_{ij} as a function of R , Louwen and Vogt [6] have simplified the calculation of J_{ij} in the QEq scheme as follows:

$$J_{ij} = 14.4 J_{ij}^* \quad (3)$$

$$J_{ij}^* = \frac{1}{\left(R_{ij}^3 + \left(\frac{1}{J_{ij}^0} \right)^3 \right)^{\frac{1}{3}}}$$

in which they only calculate J_y^0 at $R_y = 0$. However, the QEq scheme is still iterative because of ξ_H being charge dependent.

Except in their treatment of the external potential EEM and QEq are quite similar. QEq takes shielding between overlapping charge clouds explicitly into account, whereas EEM is computationally simpler. The EEM scheme is not iterative and can, therefore, be implemented in classical force fields in a way that allows the calculating of the first derivatives of the potential energy with respect to the atomic coordinates without calculating the first derivatives of the charge distribution with respect to the atomic coordinates [7]. This is a considerable advantage in molecular mechanics and molecular dynamics calculations.

In our laboratory EEM has been used successfully in empirical force fields for aluminum phosphates [8], alkanes and non-conjugated alkenes [9], and tertiary carbocations [10]. The purpose of the study reported in this paper is two-fold: (i) determination of EEM parameters for Ti and Ge to study isomorphous substitution in zeolites, and (ii) incorporation of a shielded external potential in EEM to improve its accuracy. Following the approach of Louwen and Vogt [6], which seems more accurate than earlier attempts by Ohno [11,12] and Mataga and

Table 1
EEM parameters³ [eV]

Atom type	χ^*	η^*
H($\delta+$)	4.40877	13.77324
H($\delta-$)	3.17392	9.91710
C	5.68045	9.05058
N	10.59916	13.18623
O	8.50000	11.08287
Al	-2.23950	7.67245
Si	1.33182	6.49259
P	2.90541	6.29415

Nishimoto [13], the following extended EEM equation is obtained:

$$\chi = \chi_i^* + 2\eta_i^* q_i + 14.4 \sum_{i \neq j}^n \frac{q_j}{\left(R_{ij}^3 + \frac{1}{(J_{ij}^0)^3} \right)^{1/3}}$$

$$J_{ij}^0 = (J_{ii}^0 J_{jj}^0)^{1/2} \quad (4)$$

in which a further approximation is made: the geometrical mean of J_{ii}^0 and J_{jj}^0 replaces J_{ij}^0 . In consequence of this the number of parameters only increases with m , the number of elements present, instead of with $1/2m(m-1) + m$, the number of all possible element pairs. In order to avoid an iterative scheme J_{ii}^0 and J_{jj}^0 are calibrated to a set of Mulliken STO-3G charges and J_{HH}^0 is chosen to be charge independent. However, different atom types for positively and negatively charged H are considered.

The choice of the STO-3G basis set is justified by the presence of Ti in our parameter set and our intention to extend EEM and to compare the results with Mortier's original work. Leaving Ge and Ti out of the calibration set, we

also determine parameters for STO-3G potential derived Merz–Kollman–Singh charges [14,15], which are, compared to Mulliken charges, known to be much less basis set dependent.

One of the parameter sets presented has already been used in a molecular dynamics study on the absorption of methane in the all-silica zeolites MFI and MEL [16]. The results of this study show that the extended EEM equation and the parameters are quite useful in understanding catalysis in microporous materials. This is further exemplified in this paper with results from a molecular dynamics study on ethene absorbed in H-ZSM-5.

2. Calculations

In this work, all calculations were carried out on a SG Indigo XZ 4400 workstation. EEM as well as 'EEM extended' parameters for Ti and Ge, and Al, C, H, N, O and Si, were determined using two sets of charges, i.e., 968 Mulliken STO-3G, 734 Mulliken STO-3G* charges. EEM extended parameters were also calibrated for Al, C, H, O and Si on a set of 350 Merz–

Table 2
Calibration set

Organic molecules	X = Ti, Si, Ge	Al clusters	Double clusters
Acetaldehyde	X(OH) ₄	Al(OH) ₃	(CH ₃) ₃ TiOTi(CH ₃) ₃ ^b
Acetone	X(OH) ₃ (CH ₃) ^{a(Si),b(Si,Ge)}	Al(OH) ₂ (CH ₃) ^b	(CH ₃) ₃ TiOSi(CH ₃) ₃ ^b
Dimethylamine	X(OH) ₂ (CH ₃) ₂	Al(OH)(CH ₃) ₂	(CH ₃) ₃ TiOGe(CH ₃) ₃ ^b
Dimethylether	X(OH)(CH ₃) ₃	Al(CH ₃) ₃	(CH ₃) ₃ SiOSi(CH ₃) ₃ ^b
Ethene	X(CH ₃) ₄	Al(NH ₂) ₃	(CH ₃) ₃ SiOGe(CH ₃) ₃ ^b
Formaldehyde	X(CH ₃) ₃ (NH ₂)	Al(NH ₂) ₂ (OH)	(CH ₃) ₃ GeOGe(CH ₃) ₃ ^b
Formamide	X(CH ₃) ₂ (NH ₂) ₂	Al(NH ₂)(OH) ₂	(CH ₃) ₂ AlOAl(CH ₃) ₂ ^b
Formic acid	X(CH ₃)(NH ₂) ₃	AlH ₃	(CH ₃) ₃ GeOAl(CH ₃) ₂ ^b
Methanol	X(NH ₂) ₄	AlH ₂ (OH)	H ₃ TiOTiH ₃
Methylamine	X(NH ₂) ₃ (OH)	AlH(OH) ₂	H ₃ TiOSiH ₃
Propane	X(NH ₂) ₂ (OH) ₂		H ₃ TiOGeH ₃
Propene	X(NH ₂)(OH) ₃ ^{b(Si)}		H ₃ SiOSiH ₃
Water	XH ₄		H ₃ SiOGeH ₃
	XH ₃ (OH)		H ₃ GeOGeH ₃
	XH ₂ (OH) ₂		
	XH(OH) ₃		

^{a(X)} Not in STO-3G set.

^{b(X)} Not in STO-3G* set.

Table 3
Number of atoms per atom type

Atom type	STO-3 G	STO-3G *	STO-3G
	Mulliken	Mulliken	MKS
Al	13	9	9
C	120	73	43
Ge	25	19	–
H–	72	59	30
H+	536	398	186
N	57	56	25
O	98	82	40
Si	23	18	17
Ti	24	20	–

Kollman–Singh STO-3G charges. All charges were calculated with the Gaussian 92 program [14] after full geometry optimization. Energy minima were checked by a calculation of the vibrational frequencies. Table 2 gives an overview of the molecules used in the calibrations and Table 3 gives the number of atoms of each type in the calibration sets. A non-linear least squares fit was conducted to determine the parameters in the EEM and EEM extended equations using Marquardt's compromise [17] to ensure convergence.

Molecular dynamics (MD) calculations were carried out at 300 K in the NVE ensemble on 16 molecules of ethene absorbed in 2 unit cells H[Al]ZSM-5, 2 Al atoms per unit cell, with

Table 4
Mulliken charges (a.u.) on Ge, Si and Ti in some clusters^a

Cluster ^b	STO-3G			STO-3G *		
	Si	Ti	Ge	Si	Ti	Ge
XA4	1.320	0.921	1.310	0.802	0.974	0.634
XA3B	–	0.885	1.190	–	0.928	–
XA2B2	1.121	0.875	1.080	0.785	0.908	0.466
XAB3	1.026	0.882	0.968	0.767	0.902	0.375
XB4	0.936	0.897	0.862	0.741	0.900	0.278
XB3C	1.031	0.929	0.990	0.805	0.941	0.374
XB2C2	1.135	0.961	1.126	0.863	0.981	0.469
XBC3	1.250	0.996	1.268	0.922	1.022	0.566
XC4	1.358	1.038	1.403	0.972	1.069	0.660
XC3A	1.353	1.001	1.387	0.933	1.038	0.655
XC2A2	1.344	0.973	1.373	0.888	1.015	0.652
XCA3	1.328	0.947	1.339	–	0.994	0.643

^aFor a few clusters no energy minimum was reached.

^bX = Si, Ti, Ge; A = (OH); B = (CH₃); C = (NH₂).

Table 5
Standard deviation of the Mulliken charges (a.u.) and $\cos \alpha$

	STO-3G		STO-3G *	
	σ	$\cos \alpha$	σ	$\cos \alpha$
EEM	0.02640	0.9978	0.02948	0.9960
EEM ext.	0.02160	0.9986	0.02262	0.9977
EEM ext. sim.	0.02157	0.9986	0.02483	0.9972

periodic boundary conditions using the force field described earlier [16]. The frame work atoms were kept at their position of minimum energy, the molecules were treated completely flexible. The time step in the MD simulation was 0.5 fs. After equilibrium (100 000 steps), the coordinates, the velocities and the atomic charges were collected every 5th step for 654 650 steps (327.28 ps).

3. Results and discussion

The ab initio calculations gave two remarkable results. Firstly, we notice that the geometry of the optimized Ti-clusters is quite different from the geometry of the optimized Si- and Ge-clusters. The Ti–O–H angles have values between $\sim 170^\circ$ and $\sim 180^\circ$, while the Si–O–H and Ge–O–H angles are approximately 108° . This may be caused by the fact that only Ti has partly filled *d*-orbitals. Secondly, it can be ob-

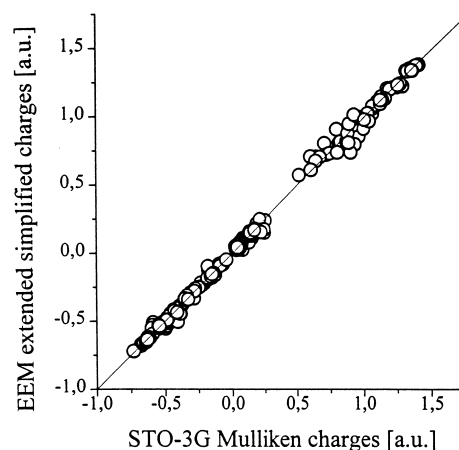


Fig. 1. *q* EEM extended simplified vs. *q* STO-3G.

Table 6

Correlation coefficient, average and maximum deviations in the Mulliken charges (a.u.) per atom type (STO-3G)

Atom type	EEM			EEM ext.			EEM ext. sim.		
	<i>R</i>	Average	Maximum	<i>R</i>	Average	Maximum	<i>R</i>	Average	Maximum
Ti	0.790	0.072	0.136	0.814	0.067	0.158	0.814	0.067	0.157
Al	0.960	0.023	0.059	0.972	0.020	0.059	0.972	0.020	0.057
H	0.981	0.012	0.132	0.986	0.011	0.096	0.986	0.011	0.098
Si	0.992	0.022	0.045	0.996	0.013	0.046	0.996	0.012	0.045
C	0.985	0.020	0.078	0.995	0.011	0.049	0.995	0.011	0.049
N	0.995	0.006	0.023	0.993	0.007	0.033	0.993	0.007	0.032
Ge	0.992	0.024	0.062	0.995	0.018	0.065	0.995	0.017	0.060
O	0.920	0.024	0.152	0.958	0.017	0.093	0.957	0.017	0.095
All	0.998	0.016	0.132	0.999	0.013	0.103	0.999	0.013	0.103

served in Table 4 that the STO-3G as well as the STO-3G* charges on Ge, Si and Ti are not arranged according to a simple periodicity. For instance, the order of increasing charge in the STO-3G set is Ti, Ge, Si for XA4, whereas for XCA3 it is Ti, Si, Ge. However, the effect of the substituent on Ge, Si and Ti is regular, i.e., in every column a certain periodicity can be observed except in the column for Ti in the STO-3G set.

Using the STO-3G and STO-3G* Mulliken charges parameter sets were determined for (i) the original EEM formula, (ii) the extended EEM formula, and (iii) the extended simplified EEM formula in which positively and negatively charged hydrogen atoms do not have

separate parameters. Table 5 gives the standard deviation of the charges and the cosine of the angle between the vector of the ab initio charges and the vector of the calculated charges for each calibration. Fig. 1 gives the charges calculated with the extended simplified EEM formula as a function of the ab initio charges. The standard deviations of the STO-3G charges are smaller than the STO-3G* ones and the cosines are closer to one, but the differences are small. It seems that the EEM formalism can reproduce charges from different basis sets. Table 6 gives the correlation coefficients and the average and maximum values of the absolute deviations between the calculated and STO-3G charges per element. Fig. 2 gives the charges for C calculated with the extended simplified EEM formula

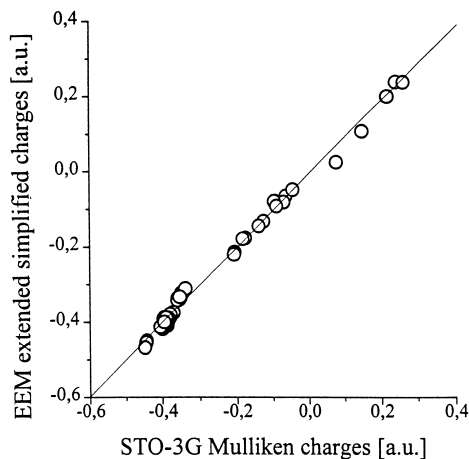
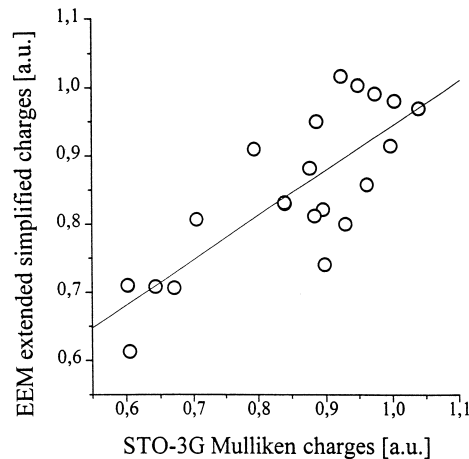
Fig. 2. q EEM extended simplified vs. q STO-3G for carbon.Fig. 3. q EEM extended simplified vs. q STO-3G for titanium.

Table 7
EEM parameters (eV) calibrated to STO-3G Mulliken charges

Atom type	χ^*	σ_χ	η^*	σ_η
Ti	-8.00933	0.74731	10.81661	0.38945
Al	-8.98883	1.27637	9.26028	0.54389
H(δ^+)	3.12248	0.28024	11.99058	0.30567
H(δ^-)	1.60055	0.44105	14.28377	1.07238
Si	-1.73485	0.40397	6.74707	0.11437
C	4.29652	0.25268	9.69495	0.06749
N	7.55898	0.36675	11.68861	0.22745
Ge	-0.47248	0.35629	6.06359	0.08487
O	8.50000	0.00000	13.65673	0.27514

as a function of the ab initio charges, Fig. 3 for Ti. It can be noticed that the estimation of the charges is less accurate on Ti than on the other elements, while the charges on N are in remarkably good agreement with the ab initio calculations.

Tables 7–9 give the parameter sets for the different calibrations. It can be observed that in all cases N is less electronegative than O, which is in agreement with the periodic table of elements, but not with the original parameters of Mortier et al. The parameter sets in Tables 1 and 7 are totally different. Keeping the original parameter values of Baekelandt et al. [3] constant for continuity reasons has the disadvantage that all variance between the STO-3G and the EEM charges is expressed in Ge and Ti. Therefore, the only option available was to optimize all parameters simultaneously.

The data in Table 7 show that the standard deviations estimated for the parameters are quite large, especially those for Ti and Al. Inspection

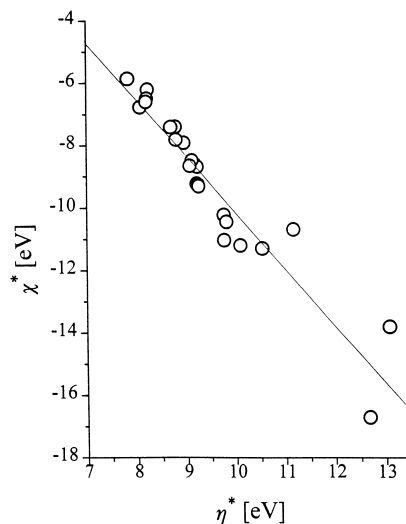


Fig. 4. Correlation between the EEM parameters for aluminum.

of the variance-covariance matrix reveals that the parameters for Al and Ti are strongly correlated. Fig. 4 gives the results for Al of a separate correlation test in which 25 sets consisting of 60 randomly chosen clusters each (690 charges on average) were used to determine 25 parameter sets. The figure clearly shows that χ^* and η^* for Al are strongly correlated. This correlation can be expected, because for χ and η , the electronegativity and hardness for free atoms, we can write in a finite difference approximation:

$$\chi = 1/2(\text{IE} + \text{EA})$$

$$\eta = 1/2(\text{IE} - \text{EA})$$

with IE the ionization energy and EA the electron affinity. As $\text{IE} \gg \text{EA}$, χ and η are highly

Table 8
EEM ext. parameters (eV) calibrated to STO-3G Mulliken charges

Atom type	χ^*	σ_χ	η^*	σ_η	$J_{ii}^0/14.4$	$\sigma_j/14.4$
Ti	2.71283	0.54534	5.55615	0.28093	0.19966	0.00655
Al	0.69456	0.78797	5.73595	0.33185	0.20799	0.00779
H(δ^+)	6.42403	0.19138	6.10042	0.34888	0.29986	0.01582
H(δ^-)	6.55435	0.24373	6.15063	0.52457	0.28700	0.01917
Si	3.76047	0.43088	4.64844	0.17644	0.21231	0.00643
C	7.04733	0.14185	5.34004	0.21234	0.34069	0.01457
N	8.05609	0.11361	6.31869	0.31904	0.41755	0.02335
Ge	4.60792	0.34387	4.27747	0.14084	0.21267	0.00650
O	8.50000	0.00000	7.35386	0.36661	0.44578	0.02573

Table 9
EEM ext. sim. parameters (eV) calibrated to STO-3G Mulliken charges

Atom type	χ^*	σ_χ	η^*	σ_η	$J_{ii}^0/14.4$	$\sigma_J/14.4$
Ti	2.69282	0.53400	5.56939	0.27426	0.20081	0.00621
Al	0.89502	0.71140	5.65494	0.30019	0.20940	0.00727
H	6.41660	0.18732	6.05239	0.30270	0.29884	0.01159
Si	3.79552	0.41318	4.63407	0.16705	0.21292	0.00510
C	7.03524	0.14183	5.35780	0.21043	0.34225	0.01449
N	8.04404	0.11336	6.32621	0.31406	0.41765	0.02292
Ge	4.61487	0.33214	4.27621	0.13409	0.21354	0.00547
O	8.50000	0.00000	7.39796	0.36709	0.44798	0.02563

correlated. We can conclude that the parameters reproduce the charges well, although some parameters have a rather large standard deviation. These large standard deviations are caused by correlation and therefore are not disturbing. But in consequence of this correlation, we should realize that the parameters obtained depend strongly on the data used in the calibration.

Introducing a shielded external potential in EEM leads to a better fit to the ab initio data. The standard deviation of the charges decreases noticeably (Table 5). For all atom types the correlation coefficient and the average deviation between the calculated and STO-3G charges (Table 6) improve with implementation of the

shielded potential, except for N, for which the fit is already very good in the original EEM formalism. Not unexpectedly, considering the equations discussed in the introduction, the variance-covariance matrix shows that J_{ii}^0 is stronger correlated to η^* than to χ^* in all cases. The values of J_{ii}^0 are in the same range as the values calculated from Slater orbitals. In Table 8 the J_{ii}^0 values for H($\delta+$) and H($\delta-$) are almost similar, therefore we also have conducted calibrations in which one type of H is used. This leads to still better results (Table 6).

In Table 10, parameters for Al, C, H, N, O and Si are given based on both Mulliken and potential derived charges determined using the

Table 10
EEM ext. sim. parameters (eV) calibrated to STO-3G Mulliken and Merz-Kollman-Singh charges

Atom type	χ^*	σ_χ	η^*	σ_η	$J_{ii}^0/14.4$	$\sigma_J/14.4$
<i>Mulliken</i>						
Al	-1.4260	0.8948	6.5768	0.3478	0.2250	0.0080
H	5.7876	0.2544	7.7331	0.4316	0.3569	0.0150
Si	2.7660	0.5207	5.1150	0.1936	0.2364	0.0065
C	6.5716	0.1933	6.0945	0.2487	0.3919	0.0194
N	7.8167	0.1023	6.9907	0.3675	0.4683	0.0315
O	8.5000	0.0000	8.4214	0.4857	0.5191	0.0402
<i>Merz-Kollman-Singh</i>						
Al	-8.2033	1.8971	8.5968	0.6452	0.3751	0.0349
H	4.1775	0.2906	8.7226	0.3199	0.4783	0.0262
Si	2.0413	0.3256	5.2213	0.0833	0.2953	0.0148
C	4.9783	0.2708	6.3095	0.1367	0.4633	0.0200
N	8.1458	0.3233	8.3024	0.2514	0.6574	0.0402
O	8.5000	0.0000	9.8705	0.2150	0.8000	0.0000

$$\sigma_{\text{Mulliken}} = 0.01139, \sigma_{\text{Merz-Kollman-Singh}} = 0.03845.$$

$$\cos \alpha_{\text{Mulliken}} = 0.9996, \cos \alpha_{\text{Merz-Kollman-Singh}} = 0.9980.$$

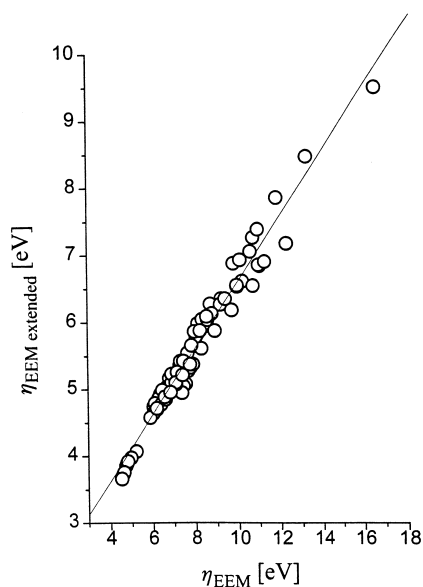


Fig. 5. Correlation between the global hardness, η , calculated with the original EEM formula and the extended EEM formula.

same calibration set (Table 3). The Mulliken as well as the Merz–Kollman–Singh charges are well reproduced by the extended and simplified EEM formula. Apparently, the EEM formalism is able to reproduce different charge partitioning schemes. The Mulliken charges are better reproduced than the Merz–Kollman–Singh charges. However, it is well known that the latter are much less basis set dependent and reproduce dipole moments better.

To compare the extended EEM with the original EEM formula, the parameter sets shown in Tables 7 and 8 were used to determine the average electronegativity of the molecules in the calibration set. In accordance with the differences between the atomic electronegativities in

both parameter sets, the average electronegativity of the molecules is larger for the extended EEM. Furthermore, the global hardness η , which is the second derivative of the energy with respect to the number of electrons [18], was computed. A strong correlation is found between the results obtained with the original and extended formula (Fig. 5).

Application of the extended EEM formula to the solid state is straightforward. The long-range interactions might be calculated using either a Taper function [19] or a shifted force modification [16,20,21] of the potential. The Ewald summation [22], however, cannot be used to determine the long-range interactions due the presence of J_{ij}^0 in the denominator of the extended formula.

We can conclude that extending the EEM formula leads to a better reproduction of the ab initio charges. Charges on Al, C, Ge, H, N, O and Si are well reproduced. The charges on Ti are less well reproduced, it has to be seen if the correlation between EEM and ab initio charges is sufficient to use the Ti parameters in force field calculations. This will be subject to further investigations.

The applicability of the present approach follows from the molecular dynamics calculations on methane absorbed in all silica MFI [16] and on ethene absorbed in H[Al]ZSM-5. Calculated heats of absorption and diffusion coefficients agree reasonably well with experimental data (Table 11). Not unexpectedly, the calculated distribution of the ethene molecules reaches a maxima at the center of the channel intersections in H[Al]ZSM-5 (Fig. 6a). The adsorption of ethene is considerably enhanced at the loca-

Table 11
Results of molecular dynamics calculations compared to experimental data

System	Heat of absorption (kJ mol^{-1})		Diffusion coefficient ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	
	Calculated value	Experimental value	Calculated value	Experimental value
Methane/MFI	25.3 ^a	18.1 ^b –28.0 ^c	6.2 ^a	1.2 ^b ; 11.0 ^c
Ethene/H-ZSM-5	31.2	26.5 ^d ; 32.7 ^b	1.6	0.48 ^b

^aRef. [16]; ^bRef. [23]; ^cSee references in Table 2 of Ref. [16]; ^dRef. [24].

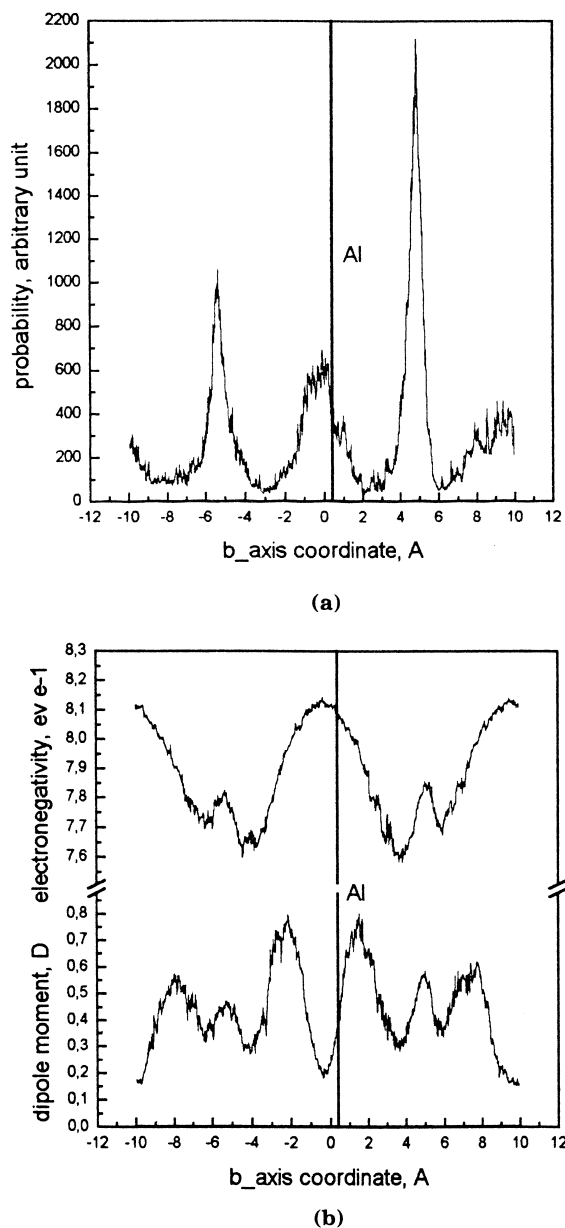


Fig. 6. Dependence of the molecular distribution (a), the molecular dipole moment and electronegativity (b) in one of the straight channels of two unit cells of H[Al]ZSM-5. Channel intersections are found at -5 and 5 Å. The Al atom is at position T2.

tion of the bridging hydroxyl site. Surprisingly, the effect of the Al substitution on the molecular dipole moment and electronegativity (Fig. 6b) is much less. As in the CH_4/MFI study [16] it appears that the edges of the intersections of the channels are the most active places for

chemical reactions. A more detailed discussion of the $\text{C}_2\text{H}_4/\text{H}[\text{Al}]\text{ZSM-5}$ results will be given in a forthcoming paper.

4. Conclusions

The extension of EEM with a shielded potential improves its accuracy. This improved accuracy can be attained without compromising its computational advantage over QEq. MD studies, as presented in this paper, would be much more expensive with QEq. It appears that EEM can reproduce different charge partitioning schemes. Mulliken charges are slightly better reproduced than the potential derived MKS charges. However, parameters based on MKS charges should be preferred because they are much less basis set dependent.

The calibration of parameters on ab initio charges raises some questions. In the first place, it is clear that calibration of parameters for transition metals would require much larger basis sets than those used in this study. In the second place, each additional element would, because the EEM parameters are highly correlated, require a new parametrization. It would be of interest to investigate if QEq-like parameters [6] can be combined with the computational simplicity of EEM. In particular, can a high quality CIEEM force field [7] with good predictive power be developed along these lines?

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