

dimensional structure of G_{AI} will be carried out and this study will lead to a better understanding of molecular basis of its structure.

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An Empirical Net Atomic Charge Calculation Method of Ligand-Metal Ion Complex

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An accurate description of electrostatic potentials is crucial importance in connection with the study of intermolecular interactions, especially, between polar molecules. For calculating the reliable electrostatic potentials, both quantum mechanical¹⁻⁸ and empirical point charge models⁹⁻¹⁴ were proposed by several workers. For large molecules, empirical models are adequate for the point charge calculation because of the limitations in the computing power which is necessary for large scale quantum mechanical calculations. Therefore, several empirical point charge calculation methods have been proposed for the point charge calculation of large molecules, *i.e.* proteins, nucleic acids, and zeolites, etc. Most of the methods were developed based on the *Electronegativity Equalization* (EE) concept.¹⁵⁻¹⁸

In the EE based methods, the *equalization* occurs by transferring electron partially through covalent bonds. As a consequence of the physical basis of the EE concept, these methods can be applied for the molecules which have covalent bonds only. Whereas, the bonds formed between ligands and metal ions are neither covalent bond nor pure non-bond. In the ligand-metal ion bonds, there are some partial electron transfer between contacting atoms and the degree of the electron transfer depends on there distance. Therefore, one can neither apply the EE method to the ligand-metal ion bond nor put fixed integer net atomic charge on the ion. In the computer simulation of metal ion bound system, since the distance between the ion and the ligand atom changes at every evolution step, it is physically unrealistic to use fixed charges for the ion and ligand atoms. Since the electrostatic interaction energy contributes dominantly to the total interaction energy between polar molecules, even if the change in the net atomic charge is small, the total binding energy changes considerably. Therefore, it is indispensable to describe the net atomic charges of the ion and the ligand atoms as a function of the ligand atoms-ion distances.

In this work, an empirical point charge calculation method for the ligand-ion complex was developed based on the *Partial Equalization of Orbital Electronegativity* (PEOE) method proposed by Gasteiger *et al.*¹⁹ The degree of the partial electron transfer between the ion and the ligand atom was expressed as a function of the ligand atom-ion distance. As a model compound, Na-A zeolite was introduced. In the PEOE method,¹⁹⁻²⁴ the magnitude of the fractional charge transfer $dq^{(n)}$ between covalent bonding atomic pair *A-B* was described as

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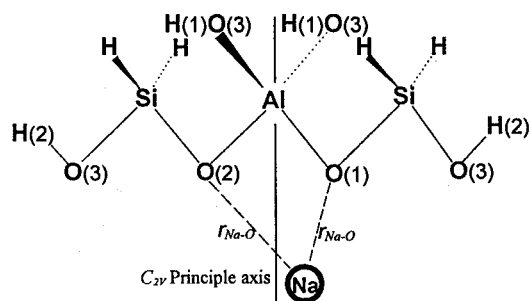


Figure 1. The model compound $(\text{Si}_2\text{AlO}_6\text{H}_8)\text{Na}$ corresponds to a fragment of the A zeolite.

$$dq^{(n)} = \frac{\chi_A^{(n-1)} - \chi_B^{(n-1)}}{\chi_A + \chi_B} (f_{A-B})^n \text{ for } \chi_B^{(n-1)} > \chi_A^{(n-1)}. \quad (1)$$

The symbols have their usual meaning used in Gasterger *et al.*'s works.¹⁹ The electronegativity of an atom i at n th iteration step, $\chi_i^{(n)}$, was approximated as a linear function of the net atomic charge of the atom i , $Q_i^{(n)}$.

$$\chi_i^{(n)} = a_i + b_i Q_i^{(n)} \quad (2)$$

The net atomic charge on atom A at the n th iteration, $Q_A^{(n)}$, is calculated as

$$Q_A^{(n)} = Q_A^{(0)} + \sum_B \sum_{n'} dq_{AB}^{(n')}. \quad (3)$$

In the modified PEOE method,²⁴ the initial charges, $Q_i^{(0)}$, were introduced as a parameter and the damping factors, f_{A-B} , were classified according to the bond type of the bond $A-B$ and were optimized, whereas, in the original PEOE method,¹⁹ 0.5 was used for every bond type. In the present proposed model, the damping factor for the ion and the ligand atom pair was described as a function of the distance between them, r .

$$f_{\text{Na-O}}(r) = \frac{c_2}{1 + c_1 e^{ar}} \quad (4)$$

The parameters of the proposed model, a , b , f , and (α, c_1, c_2) , were obtained by using two constraints; the *ab initio* electrostatic potentials, $V_{ab,i}$, around the model compound and the *ab initio* binding energy, $E_{ab,j}$, between the ion and the zeolite framework. The parameter set, $(\{a\}, \{b\}, \{f\}, \alpha, c_1, c_2)$, which gives a minimum value of the following function F was obtained.

$$F = \sum_j \sum_i (V_{cal,i} - V_{ab,j,i})^2 + W \sum_j (E_{cal,j}^b - E_{ab,j}^b)^2 \quad (5)$$

where $V_{cal} = V(\{a\}, \{b\}, \{f\}, \alpha, c_1, c_2)$ and $E_{cal}^b = E(\{a\}, \{b\}, \{f\}, \alpha, c_1, c_2)$.

The model compound $(\text{Si}_2\text{AlO}_6\text{H}_8)\text{Na}$, Figure 1, corresponds to the fragment of the A-type zeolite and the broken bonds were terminated with hydrogen atoms. The geometry of the model cluster was optimized with 6-31G** *ab initio* HF calculation. It belongs to C_{2v} point group. At fixed geometry of the $(\text{Si}_2\text{AlO}_6\text{H}_8)$, the Na ion was put to several different positions. For each conformation j , the binding energy, $E_{ab,j}$, was obtained and the electrostatic potential, $V_{ab,j,i}$, was calculated at about one thousand points with the 6-31G** basis set. The points, designated by i , were sampled between van der

Table 1. The optimized electronegativity parameters for Na-A zeolite

Atomic Species	Initial Charge $Q^{(0)}$ (in e)	Electronegativity Parameter	
		a	b
H(O) ^a	0.	8.3760	7.7448
H(Si) ^b	0.	6.9341	4.0188
O	-0.45 ^c , 0.	12.804	11.799
Si	0.45	4.3280	12.556
Al	0.	5.1463	9.2221
Na	0.9	7.0701	8.0952

Bond Type	Damping Factor		
	α	c_1	c_2
$f_{\text{Na-O}}$	12.076	24.069	0.4501
$f_{\text{O-H}}$		0.	0.3901
$f_{\text{T-O}^d}$		0.	0.4261
$f_{\text{T-H}^d}$		0.	0.7282

^aHydrogen atom bonded to oxygen. ^bHydrogen atom bonded to silicon. ^cIf the oxygen is bonded to Al then $-0.45e$ was used as initial charge otherwise zero was used. ^dT represents Si or Al.

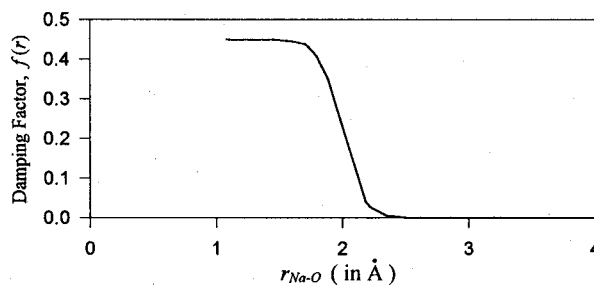


Figure 2. The damping factor, $f_{\text{Na-O}}$, plotted against the distance between ion and ligand oxygen atom, $r_{\text{Na-O}}$.

Waals surface and the van der Waals surface +3 Å region.

The optimized parameters are listed in Table 1. For the oxygen atoms which are bonded to Al, the initial charges, $Q^{(0)}$, were set to $-0.45e$ and for the Si atoms, $+0.45e$ was put as the initial charge. $+0.9e$ was put as the initial charge of the Na. The damping factor $f_{\text{Na-O}}(r)$ is plotted in Figure 2. $f_{\text{Na-O}}$ becomes 0.45 and 0.21 at $r_{\text{Na-O}}$ is 1.5 Å and 2 Å, respectively, and it starts to converge to zero when $r_{\text{Na-O}}$ is larger than 2.5 Å. There is sharp decline from 1.5 Å to 2.5 Å and no more charge transfers between Na and the ligand oxygen atom when $r_{\text{Na-O}}$ is beyond 2.5 Å. In Figure 3, the net atomic charges of the atoms in the model are plotted as the Na ion moves out from the $\text{Si}_2\text{AlO}_6\text{H}_8$ along the C_{2v} principal axis. The change in the Q_{Na} is about $+0.4e$ and the transferred counter electronic charge, $-0.4e$, is distributed among the $\text{Si}_2\text{AlO}_6\text{H}_8$. This electronic charge is distributed more to the Al and the oxygen atoms, (O(2)), which are closely contacted to the Na compared with the other atoms in the model.

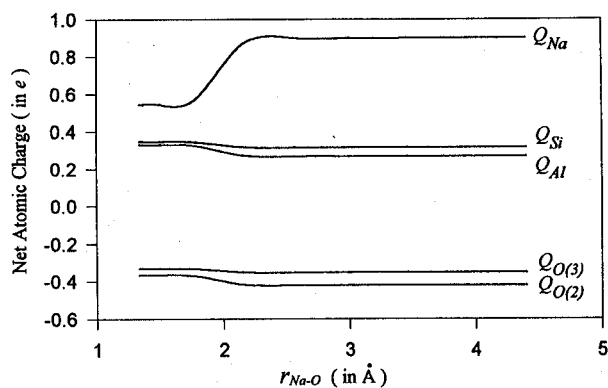


Figure 3. The net atomic charges of the atoms in the model are plotted as the Na moves out along the C_{2v} principal axis.

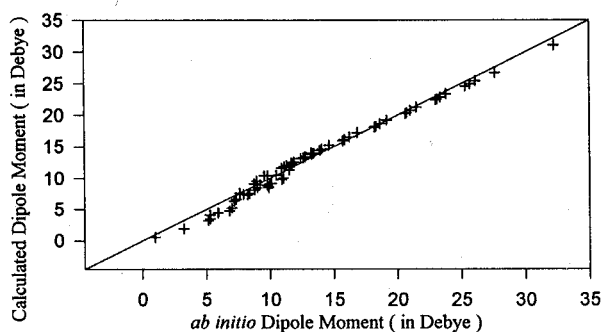


Figure 4. The dipole moments of the model compound at several Na ion configurations are calculated both with our point charges and the *ab initio* method.

Table 2. The net atomic charge sets used for the electrostatic binding energy calculation

Atom	MullI	MullII	PDI	PDII
Al	1.150	1.265	1.246	1.062
O(1)	-0.868	-0.958	-0.849	-0.994
O(2)	-0.776	-0.751	-0.849	-0.746
H(1)	0.286	0.286	0.294	0.365
Si	1.185	1.198	1.589	1.312
O(3)	-0.776	-0.708	-0.849	-0.746
H(2)	0.286	0.335	0.294	0.365
H(Si)	-0.222	-0.185	-0.397	-0.270
Na	1.0	0.684	1.0	0.906

The dipole moments of the model compound at several Na configurations calculated with the point charges obtained by the proposed method. The dipole moments are plotted against those obtained with 6-31G** *ab initio* MO calculations, Figure 4. The point charges could reproduce the *ab initio* dipole moments of the ligand-ion complexes very well.

To test the validity of the proposed model in the electrostatic energy calculation, the electrostatic potential energies were calculated from the Potential Derived (PD) charges, Mulliken population (Mull), and the charges obtained with the proposed method. In Table 2, the tested point charge

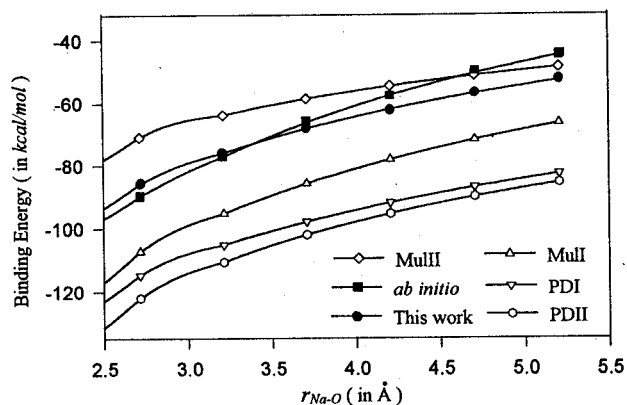


Figure 5. The electrostatic energies calculated with several point charge sets are plotted along r_{Na-O} on the C_{2v} axis and are compared with *ab initio* binding energies.

sets are summarized. The point charges of the atoms in Mull and PDI are determined with the Q_{Na} fixed to $+1e$. Whereas, in the calculation of MullII and PDII point charge sets, all the point charges are determined at the minimum energy conformation of the model compound. The point charges of MullI, MullII, PDI, and PDII are fixed during the electrostatic interaction energy calculation between the Na ion and $Si_2-AlO_6H_8$. The calculated electrostatic energies are plotted against r_{Na-O} along the C_{2v} axis and they are compared with the *ab initio* binding energy curve, Figure 5. Since the contribution of the sum of the other energy components to the binding energy is relatively small, less than 1 kcal/mol, when r_{Na-O} is larger than 2.5 Å, the calculated electrostatic interaction energies, E_{el}^b , can be directly compared with the *ab initio* binding energy. When the Q_{Na} is fixed to $+1e$, the E_{el}^b is overestimated about 20 kcal/mol with MullI and about 35 kcal/mol with PDI. MullII charge set is used, then the E_{el}^b underestimated about 20 kcal/mol compared with the *ab initio* binding energy. Both PD charge sets overestimate the E_{el}^b . The Q_{Na} obtained from the PD method at its equilibrium position is $+0.906e$. The E_{el}^b calculated with PDII deviates much from the *ab initio* binding energy, about 45 kcal/mol, even at the minimum energy conformation at which the PDII charge set was determined. The proposed method could reproduce the binding energy curve well.

In conclusion, we have shown that, for the physically realistic description of the electrostatic interaction energy of the ligand atom-ion interaction with empirical potential energy function, the net atomic charges must be described as a function of the ligand atom-ions distances.

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Redistribution of Bis- and Tris(silyl)methanes Catalyzed by Red-Al

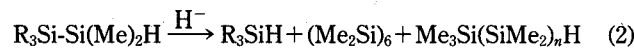
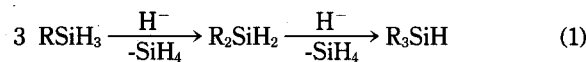
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Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride) is known to catalyze the polymerization of lactams and olefins and the trimerization of isocyanates.¹ Corriu and coworkers reported the exchange reactions of di- and trihydrosilanes^{2a} (eq. 1) and the oligomerization of disilanes^{2b} (eq. 2), catalyzed by inorganic hydrides (e.g., NaH, KH, etc.). They suggested a mechanism *via* the intermediacy of a pentacoordinated hydrosilyl anion,^{2c} which is formed by addition of hydride (H⁻) on the silanes.



Riviere *et al.* described the preparation of oligogermane (PhHGe)_n by redistribution of PhH₂GeGeH₂Ph with PhH₂GeLi.³ The Lewis acid AlCl₃ is well known to catalyze redistribution reaction of hydroarylsilane to afford quaternary arylsilane and SiH₄.⁴ We recently reported the dehydropolymerization of bis(silyl)alkylbenzenes catalyzed by group 4 metallocene complexes, generated *in situ* from Cp₂MCl₂/Red-Al, to produce highly cross-linked polysilanes.⁵ During the study we found an intriguing redistribution of bis- and tris(silyl)methanes, catalyzed by Red-Al.

2-Phenyl-1,3-disilapropane **1**,⁵ 1-phenyl-3,5-disilapentane **2**,⁶ and 1-phenyl-4-silyl-3,5-disilapentane **3**⁶ were prepared by reaction of corresponding chlorosilane with LiAlH₄. In a typical experiment, **1** (0.18 g, 1.18 mmol) was slowly added to a Schlenk flask charged with Red-Al (17 μL, 0.058 mmol; 3.4 M solution in toluene) and toluene (5 mL). (*Warning! In the absence of toluene solvent, rapid addition of 1 to Red-Al resulted in a violent explosion with fire due to the drastic production of SiH₄, which is an explosive gas upon contact with air. Therefore, the reaction should be performed in the dilute condition with suitable precaution. We recommend you not to exceed the reaction scale employed here.*) The reaction started immediately, as monitored by the immediate release of SiH₄ gas. After being stirred for 1 h, GC/MS analysis and ¹H NMR spectroscopy showed that **1** was quantitatively converted to benzylsilane as major and as yet uncharacterized high-boiling oligomers as minor. The starting silane **1** was completely disappeared. However, it was difficult to assign the exact composition and yields of the products because the minor product could be a mixture of high-boiling oligomers, and the amount of evolved gases is difficult to measure. Similarly, the bis(silyl)methane **2** was quantitati-