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THESIS

DETERMINING POINT CHARGES THAT PRODUCE ACCURATE ELECTROSTATIC POTENTIAL FROM THE INFINITE CRYSTAL LATTICE FOR EMBEDDED CLUSTER CALCULATIONS

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Calculations on cluster models of zeolites are popular since they require less computational effort than that of periodic calculations but they neglect, amongst other contributions, the effect of long range electrostatic interaction from the infinite crystal lattice which is important for adsorption processes and surface reactions. We propose a simple method for including this effect into the calculation by generating a finite number of point charges placed upon the lattice sites. These point charges reproduce the infinite electrostatic potential at the chemically important region of the zeolite. We apply this method to the adsorption of pyridine on H-Faujasite zeolite and compare it with calculations without including the field effect. The embedding method gives an adsorption energy of 42.8 kcal/mol, which agrees well with the experimental value of 43.1±1 kcal/mol. Without the electrostatic effect of the crystal field, the value is about 9 kcal/mol higher.

Student's signature

Thesis Advisor's signature

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Narong Pannorad

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LIST OF ABBREVIATIONS

B3LYP	=	Becke's three parameter hybrid functional using the LYP correlation functional
BSSE	=	Basis Set Superposition Error
DFT	=	Density Functional Theory
EEM	=	Electronegativity Equalization Method
FAU	=	Faujasite zeolite
GTO	=	Gaussian Type Orbital
HF	=	Hartree-Fock
H-BEA	=	Proton-Beta zeolite
H-FAU	=	Proton-Faujasite zeolite
H-MOR	=	Proton-Mordenite
H-ZSM-5	=	Proton-Zeolite Socony Mobil 5
INS	=	Inelastic Neutron Scattering
IR	=	Infrared spectroscopy
kcal/mol	=	kilocalorie per mol
MD	=	Molecular Dynamics
MFI	=	Mobile Five framework type code
MM	=	Molecular Mechanics
MO	=	Molecular Orbital
MOR	=	Mordenite zeolite
NMR	=	Nuclear Magnetic Resonance
ONIOM	=	Our own N-layered Integrated molecular Orbital and molecular Mechanics
PA	=	Proton Affinity
QM	=	Quantum Mechanics
QM/MM	=	Quantum Mechanics/Molecular Mechanics
QM/Pot	=	Combined Quantum Mechanics - Interatomic Potential Functions
Py	=	Pyridine

RDF	=	Radial Distribution Function
SCREEP	=	surface charge representing electrostatic embedded potential
UFF	=	Universal Force Field
ZSM-5	=	Zeolite Socony Mobil 5

DETERMINING POINT CHARGES THAT PRODUCE ACCURATE ELECTROSTATIC POTENTIAL FROM THE INFINITE CRYSTAL LATTICE FOR EMBEDDED CLUSTER CALCULATIONS

INTRODUCTION

The cluster calculations are widely applied in quantum chemical calculations on various molecules to obtain detailed information such as geometries, energies, frequencies and etc. of molecules. In a system of small molecules, this method gives satisfactorily accurate results as it includes all the effects of every atom in the system and treats them quantum chemically.

A set of atoms, a cluster, or more specifically a central cluster, is cut from a bulk crystal framework possessing a large or infinite crystal lattice. This central cluster, also known as the quantum mechanical region (QM region), is terminated at the dangling bonds by hydrogen boundary atoms. This method, however, neglects the effects of atoms beyond those in the cluster and, therefore, does not represent the total effect of the large framework. Since hydrogen boundary atoms are not present in the large lattice, considerable errors arise due to their effect on the geometrical and chemical environment.

There are a number of methods to overcome this problem, one of which is the periodic quantum chemical calculation which is able to model the entire infinite periodic molecules such as ionic molecules or zeolites and can calculate all properties quantum chemically. In practice, this method is effective for molecules possessing a small number of atoms per single unit cell. However, a sizable molecule with low symmetry, such as ZSM5 or Faujasite zeolite having hundreds of atoms per single unit cell, the method is not practical with the present limitation of computers.

In addition to the periodic approach, several other techniques have been developed with the consideration being given to accuracy and computational effort in

calculations. The aim of such techniques is to model the rest of the crystal lattice, called the environment, of a lattice which is inhabited by the central cluster based on its long range interaction, the electrostatic effect. In addition, the boundary effects derived from hydrogen boundary atoms which do not exist in the real crystal are counterbalanced to reduce the error of short range force. One of these attempts is the method of embedding a cluster in an infinite crystal lattice by imposing an electrostatic potential on it via the modification of Fox matrix (Teunissen *et al*., 1994). Many techniques have been developed for calculating the accurate matrix elements of the Madelung potential, but there is not one readily available yet which gives satisfactory accuracy.

There are basically two ways to deal with this Coulomb problem in ab initio calculations. The first approach involves a direct summation of the matrix elements of the Ewald potential given by analytical formulas derived by Saunders and his coauthors. Due to the fast convergence of the Ewald type series, in this approach, the accuracy of such calculations can be systematically improved by increasing the ranges of summation over both direct and reciprocal lattices. Although this approach, in principle, provides an ultimate and accurate solution for the electrostatic embedding potential, its implementation in existing molecular quantum chemistry programs requires significant efforts. To our knowledge, the total energy derivatives have not yet been implemented with this embedding method, hence, in most practical calculations in the bulk and on the surface of crystals, another embedded cluster approach has been used thus far.

In this other common methodology approach, the infinite lattice potential is modeled by a finite number of point charges placed outside the cluster. Such an approach is attractive because analytical matrix elements of the point-charge potential, and often their first and second derivatives, are readily available in most quantum chemistry programs (nuclear attraction integrals). However, the accuracy of such a method critically depends on the selection of the total number of point charges, their positions Ri, and values Qi. In most previous embedded cluser studies, these point charges were simply placed at ideal lattice sites and were assigned values

corresponding to ionic charges in the crystal. In slightly more sophisticated methods, positions and/or value of peripheral point charges can be adjusted for better accuracy. A well-known difficulty of such models is that the results converge very slowly, if at all, when the size of the explicitly considered lattice is increased. Thus, there is no simple way for the systematic improvement of results. Moreover, construction of such finite lattice models becomes more difficult for complex low-symmetry systems, such as proteins, zeolites, and crystal surfaces.

Another previous technique was using the Surface Charge Representative of Electrostatic Embedding Potential (SCREEP) method where point charges are placed upon a spherical surface and the potentials at those points are used to optimize the magnitudes of the point charges (Stefanovich and Troung, 1998). Such the method is effective in many systems of cluster calculations (Treesukol *et al.* 2001) as shown in Figure 1 and also the molecular dynamic simulations (Vollmer *et al.* 1999). However, we found that in several systems it is technically difficult to obtain accurate Madelung potentials throughout the quantum region in which the cluster is embedded by means of these surface charges. This technical problem occurs from the way to obtain these solutions; each position of a surface charge is used as a test point where the site potential reproduced by a complete set of surface charges q_j satisfy the matrix equation V = Aq. The vector V contains values of infinite electrostatic potential at a test point R_i on a surface S_i and A is the n x n nonsingular matrix as shown below.

$$\begin{bmatrix} V_1 \\ V_2 \\ \vdots \\ V_n \end{bmatrix} = \begin{bmatrix} A_{11} & \frac{1}{R_1 - R_2} & \cdots & \frac{1}{R_1 - R_n} \\ \frac{1}{R_2 - R_1} & A_{22} & \cdots & \frac{1}{R_2 - R_n} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{1}{R_n - R_1} & \frac{1}{R_n - R_2} & \cdots & A_{nn} \end{bmatrix} \cdot \begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ q_n \end{bmatrix}$$

$A_{ii} = 1.07\sqrt{4\pi / S_i}$ and S_i is the area of each surface element.

Diagonal terms of matrix A indicate the electrostatic potentials from any surface charge q_i at its position Ri where the formula is based on approximations and

experiments. Because of these terms, which are not calculated from analytical formula, errors in optimizing the magnitudes of charges are possibly inevitable, resulting in the mistaken Madelung potential scattering on some part of the quantum cluster region. Furthermore, the radius size of the spherical surface embedding the cluster determines the accuracy of reproduced potentials. If the radius of the sphere containing the point charges is rather small, the accuracy of the potential in the region close to the sphere is good but difficult to maintain. Conversely, if a rather large spherical radius is taken, one must still keep explicit point charges of zeolite atoms inside the sphere that are not parts of the quantum chemically treated region. These charges can cause problems when performing geometry optimizations and other quantum chemical calculations. For example, the interaction of adsorbed pyridine with such close charges is unrealistically attractive, but removing them entirely would lead to a considerable error for the Madelung potential throughout the regions inside the surface. However, such problems can be overcome by a non-spherical closed surface, but with such modifications the simplicity of this method is partially lost.

In view of these problems, we investigated the performance of another simple method which just uses atomic positions of the lattice and is, therefore, easy to use while requiring only a small computational effort compared to that of periodic calculations. In this method as well, a set of point charges is also generated to represent the long-range electrostatic effect of the infinite crystal lattice, but the charges are, however, placed upon the lattice sites of the zeolite crystal. These charges are composed of two zones, the inner zone having a set of point charges that are not optimized and the outer zone possessing varied charges which are fitted so that the electrostatic potential inside the quantum cluster region is well reproduced and are positioned farther from cluster than those in the inner zone. Furthermore, to avoid the problems occurring in the previous method that probe molecules are attracted to the explicit charges near the cluster which perform a stronger effect than that of surface charges located farther away, we created the zone which is closer to the quantum cluster region than to the inner zone, in which no single charge is positioned. Having this zone, any probe molecule is not eccentrically forced by artificial nearest naked charges that we prefer their influence on probe molecules only in the field of

Coulomb potential. Also, we determine the array of grid points throughout the quantum cluster region at which the electrostatic potentials from the infinite crystal lattice are calculated using the Ewald summation method. These grids, as test points, are employed to fit the charges in the outer zone. The point charges generated from this method allow any probe molecules to move freely throughout the quantum cluster region without partially attractive forces towards the naked charges near the cluster region. From this idea, any probe molecules can be investigated without the bottleneck which occurred in previous works.

As the two-layered ONIOM method has shown satisfactory results clearly seen in previous works, the adsorption of molecules in commercially-used zeolites, in which the core part is treated at the high level quantum chemical calculation and the extended framework is represented by the UFF force field, it is fascinating to combine point charges as the third layer to compensate for the abandoned long-range force field. In detail, the high level first layer indicates local interaction between cluster atoms quantum chemically, the low level second layer shows the short range interactions from a series of neighboring atoms around the cluster, and the third layer is a complete set of point charges representing the long range electrostatic field dominating upon the quantum cluster region.

The complete set of point charges is then applied for the system which was not applicable in the previous embedding method, the adsorption of pyridine on H-Faujasite zeolite. Because pyridine is used as a denaturant for ethanol, as a solvent in laboratories as well as for organic salts and chemicals in industry, it is interesting to study its interaction with commercially-used zeolite like Faujasite. Moreover, there are numerous previous experimental and theoretical studies of pyridine adsorbed in various kinds of zeolites which could be the benchmark for us to investigate its properties.

LITERATURE REVIEW

Zeolite is one of the crucial heterogeneous catalysts widely used in various industries today. It has conspicuously particular advantages for enhancing the capability of boosting large-scaled industrial chemical productions. Of importance also is the fact that a variety of zeolites have specifically interesting properties that promote the advancement of research and development. The distinguished attribute of zeolite is its fundamental groups that act as Brønsted acid sites inside the channel system in which molecules can be adsorbed (Hunger *et al.*, 1992; Kenaston *et al.*, 1994). In addition, the complex crystal frameworks with different pore sizes are the major part which contributes to considerable advantages such as the shape selectivity of the reactant and product molecules (Santen and Kramer, 1995).

Synthesises of new zeolites have been performed continuously. As a result, studies of their properties in relation to their ability to adsorb particular molecules and to accelerate industrial chemical reactions both in experimental and theoretical fashions are indispensable. Theoretical studies have been carried out to provide detailed information of adsorptions and reactions of molecules in different kinds of zeolite.

Studies of zeolites with a theoretical approach based on quantum chemistry performed by high efficiency computers are increasingly attractive and ubiquitous. Disregarding the difficulty of experiments which need apparently longer time and in several cases are impractical, this relatively new method is beneficial in anticipating the pathways of reactions, transition states, activation energies, etc. among a series of chemical reactions.

Ab initio calculations are the commencement to the study of the properties of zeolites. Commonly applied for numerous theoretical studies, the cluster calculations are simple and practical for investigating chemical processes occurring in particular region of a zeolite. A set of atoms, referred to as a cluster, is cut from the bulk molecule and terminated at the boundary by hydrogen atoms and then these atoms

represent the whole structure of such a zeolite. Yet, the lack of the long range effect due to Coulomb interactions and other short range forces are incontrovertibly the reasons for unacceptable results. Accordingly, the use of periodic calculations, which include quantum chemically an effect and influence on entire atoms in the cluster, have, therefore become a fascinating aspect in theoretical studies. Periodic calculations are able to treat the periodic molecules in which the unit cell is duplicated three-dimensionally towards infinity. This manner includes the effects of the whole atoms of the zeolite's framework. This has been done, for example, in the ab initio structural study of the Brønsted acid site in Chabazite. Carried out with the gradient-corrected density functional and ultrasoft pseudo potentials, the geometries and stretching frequencies of acidic protons are in agreement with those from experiments (Jeanvoine *et al.*, 1998).

In the study of the local phenomena, such as the active sites or selective adsorptions of zeolites, a larger super cell may be required to avoid unphysical interactions arising from the periodic boundary condition. In addition, geometrical structures as the starting parameters are usually derived from experimental data which in many cases are not satisfactorily accurate. Furthermore, a full geometric optimization is often necessary because of the long-range structure relaxation leading to the need of a soaring computational effort. These are the obstacles for periodic calculation itself due to the limitation of computers today.

The theoretical study of zeolites and interest in them tended to wane with the barrier posed by most commercially used zeolites having very large unit-cells. For example, the single unit-cell of ZSM-5 is composed of 288 atoms and that of Faujasite has a huge number of 576 atoms. Consequently, accurate periodic calculation methods are rather impractical. Alghough the previous study of large and medium unit-cell zeolites, *i.e.*, Faujazite, ZSM-5 or Mordenite, with periodic boundary conditions could be made possible by periodic Hartree-Fock (HF) (Demuth *et al.*, 2000; Kessi and Delley, 1998; Shah *et al.*, 1996), the accuracy of the results was not satisfactory. Instead, attempts to get more accurate results have been fruitful with the use of periodic density functional theory studies of interactions in zeolites

having relatively small atoms per single unit cell (Brändle and Sauer, 1998; Campana *et al.*, 1994; Hill *et al.*, 1999; Jeanvoine *et al.*, 1998; Larin and Vercauteren, 2001; Schwarz *et al.*, 1997; Shah *et al.*, 1997; Sierka and Sauer, 2000; Teunissen *et al.*, 1994). Nevertheless, periodic DFT calculations can treat only the periodic molecules in which the unit cell is rather small. For zeolites having hundreds atomd per single unit cell, it is not practical due to the limited capabilities of computers. For this reason, the periodic DFT is still not feasible for large unit-cell zeolites.

To overcome this obstacle, many methods based on cluster calculations have been initiated. One of these is the hybrid approache guided by the idea that the large system may be partitioned into two regions, the electronically important core part treated quantum chemically, and the auxiliary part, as an environment included in the system as the perturbative fashions. The perturbation may be mainly mechanical, for example, if the outer region forces the quantum region into a particular geometry, but it may also include electronic effects such as electrostatics and polarization. Regarding this concept, a chemical reaction is treated as a transformation involving only the reactive core part which is influenced by its environment.

According to Dirk Bakowies and Walter Thiel's review in 1996, hybrid methods can be categorized into three classes. "Model A" is the simplest one and represents a mechanical embedding of the quantum region. "Model B" includes electrostatic interactions between the quantum mechanics and molecular mechanic regions using suitably defined classical point charges in the MM region which enter the core Hamiltonian. "Model C" includes the polarization of the MM region in the presence of the electric field generated by the QM region. Conceptually, the coupling models focus on the theoretical description of the interaction between two levels of calculation without introducing any changes in each underlying method (Bakowies and Thiel, 1996).

The new ONIOM multi-layered approach has been proposed and shown to be successful in improving the accuracy of the cluster calculation for the very large system (Svensson *et al.*, 1996; Dapprich *et al.* 1999). Similar to the idea that we

described of the hybrid method, a system is divided into an active core part treated at a very high level of ab initio MO theory, a semi-active part that includes important electronic contributions and is treated at the relatively low quntum-chemical level, and a non-active part that is handled using force field approaches. This three-layered scheme has been applied to the activation barriers for the Diels-Alder reaction of acrolein + isoprene, acrolein + 2-tert-butyl-1,3-butadiene, and ethylene + 1,4-di-tert-butyl-1,3-butadiene. In general, the results for both geometry optimizations and single point energy calculations agree well with benchmark predictions and experimental results. The scheme has also been applied to the transition state for the oxidative addition of H2 to Pt(P(t-Bu)3)2.

Due to its computational efficiency and accuracy, the ONIOM approach has been adjusted and applied for investigating the adsorptions of molecules in commercially-used zeolites like ZSM-5 and Faujasite, such as the adsorption of ethylene, benzene, and ethylbenzene over Faujasite zeolite (Kasuriya *et al*., 2003), Adsorption of aromatic hydrocarbon onto H-ZSM-5 (Raksakoon and Limtrakul, 2003), and the effects of the zeolite framework on the adsorption of ethylene and benzene on alkali-exchanged zeolites (Bobuatong and Limtrakul, 2003). These studies have employed the two-layered ONIOM in which the active sites are treated at the B3LYP/6-31G(d,p) level of theory and the extended frameworks influencing directly on atoms in active sites are included using UFF force field (Rappe *et al.* 1992). Also, the three-layered ONIOM has been undertaken in the adsorption of benzene on industrially important nanostructured catalysts (H-BEA, H-ZSM-5, and H-FAU): confinement effects (Rungsirisakun *et al*., 2003). These studies have included the short-range interactions between the active region and the environment that is suitable to the systems of which the long range interactions have small effect and, therefore, can be neglected.

In systems susceptible to long-range interactions, the lattice effect must be included giving direct influence over atoms in the active region. The major part of the lattice effects is the Madelung potential which can be done by means of electronic embedding calculation. This embedding approach accounts for the static electrostatic

Madelung potential from the crystal framework and includes such effects directly in the Fock matrix elements of the quantum cluster resulting in the polarization on its wavefunction. The crystal polarization and long-range structure relaxation in this method are usually considered to be insignificant and are, therefore, typically abandoned. This class of embedding method has been proved to be sufficient for a dominant fraction of zeolite studies, namely the adsorption of adsorbates on the active site (Allouche, 1990; Bredow *et al.*, 1996; Greatbanks *et al.*, 1994; Pisani and Birkenheuer, 1995; Stefanovich and Truong, 1998). Conversely, the mechanical embedding approach (Brändle and Sauer, 1998; Hillier, 1999; Ricchiardi *et al.*, 2000; Sauer and Sierka, 2000) models the crystal framework by a molecular mechanics force field but corrects the interactions in the active site region by isolated quantum mechanical cluster calculations. In this case, the lattice effects do not polarize the quantum cluster wave function but affects it indirectly via the force field. The accuracy of this approach depends significantly on the quality of the potential force field, whose parameters largely depend on the set of systems and properties used in the fitting procedure. Sauer and his groups proposed a method called QM/Pot that provides good results for zeolite and related systems (Brändle and Sauer, 1997; Brändle *et al.*, 1998).

Although the embedding procedures mentioned above have shown good results for many studies on adsorption and reactions at the active sites of zeolites, they have inherent fundamental approximations. Different embedding approaches in which all the lattice effects are accounted the quantum chemically have been proposed (Govind *et al.*, 1998; Sierka and Sauer, 2001) to overcome the limitations of conventional embedding calculations. For example, Carter and coworkers introduced a method to include a periodic-DFT-based potential in the Hamiltonian of a more accurate finite cluster calculation and applied this method to study the systems of Li_2Mg_2 and adsorption of CO on Copper surface (Govind *et al.*, 1998). The EMBED program solves the HF equations for local defects in crystals using the perturbed-cluster method, which explicitly includes the whole crystal with the defect. Sauer's group corrected the interaction in the active site region calculated by periodic DFT calculation with CISD method. Sauer and co-workers also used the same energy

correction expression both within the QM/MM methodology as in the QM-Pot method (Sierka and Sauer, 1997) and within the full quantum embedded cluster methodology in their more recent study (Sierka and Sauer, 2001).

Another simple but effective method created to compensate the long range interaction on the cluster region is the Surface Charge Representative of Electrostatic Embedding Potential know as SCREEP (Stefanovich and Troung, 1998). The finite numbers of surface and explicit charges are generated giving an acceptable Madelung potential calculated from the Ewald formula to the region inside the closed surface. There are a lot of works using this method to investigate the adsorption and reaction of molecules in zeolites (Limtrakul *et al.* 2000; Treesukol *et al.* 2001). Although satisfactory for several systems, this method is not applicable for many other cases. As this method uses a matrix to solve the system of linear equations, in which the diagonal terms of the square matrix are based on approximations and experiments, the significant errors occur in some regions. Furthermore, the explicit charges cause unrealistically attractive force towards atoms in the cluster. Derenzo and co-workers have proposed the use of point charge arrays in which their positions are at the lattice sites which are subsequently improved compared to the previous method (Derenzo *et al.* 2000). In consideration of the efficiency of the point charge scheme, it was shown that placing the point charges on the lattice site gave more accurate results than those on surface and required only a relatively low computational resource (Duangsrikaew *et al.* 2003). However, the fact that this work was tested in the system of ionic molecules such as NaCl, which is a periodic molecule but having a small unit-cell, cannot resolve the bottleneck in applying the point charge method to several systems of zeolites. Attempts to find solutions that will give accurate results for all systems have been made in subsequent works but, as yet, there is not in applicable for the bulk complex molecules like zeolites.

To study the adsorption of a sizable molecule in a zeolite possessing large pore size and hundreds of atoms per single unit cell, inclusion of long range Coulomb interaction is conspicuously inevitable. The adsorbed molecule like pyridine has been investigated experimentally in various zeolites (Parillo *et al.* 1993). This was

discussed in other works which reported that the proton of the bridging hydroxyl group of the zeolite is transferred to pyridine molecule resulting in a pyridinium cation-zeolite anion ($PyH^+ \ldots Z^-$) (Florian *et al.* 1995; Parrillo *et al.* 1995; Kubelkova *et al.* 1995; Lee *et al.* 1996; Savitz *et al.* 1998; Daniell *et al.* 2001; Mihalyi and Beyer 2001; Ehresmann *et al.* 2002; Savitz *et al.* 1999; Kresnawahjuesa *et al.* 2002).

MATERIALS AND METHODS

We created a method to generate a set of point charges able to represent the long range electrostatic potential of any zeolite influence on atoms in the cluster cut from the zeolite's lattice. The method was then converted into the program using Matlab as the code. The program was later run to generate a set of point charges for the particular zeolite applied for investigating cluster calculation. We tested it to prove that it is able to represent correctly the electrostatic potential of the infinite crystal lattice of the zeolite.

The program was applied to generate a set of point charges for H-Faujasite zeolite to investigate the adsorption of pyridine on its Brønsted acid site. As discussed in previous works, the use of the two-layered ONIOM embedded by point charges is effective, we combined our complete set of point charges with the quantum chemical calculation using the ONIOM approach in which the quantum cluster high level is treated with the DFT and the extended framework representing short range interaction is done with the UFF force field.

Part A. Generating a set of point charges

As we cut a small number of significant atoms referred to as a cluster applied for quantum chemical calculations from the infinite crystal lattices of a zeolite, the remaining unlimited atoms are transformed into a finite number of point charges to compensate the indispensable absent impact on the cluster. Our aim is to get an acceptably correct electrostatic potential at any position inside the significantly particular space in which the interaction between cluster atoms and adsorbed molecules take place. The electrostatic potential at any point is based on the formula "V = Q/r" where Q is an electronic charge of an atom in a molecule and r is a distance between a point charge and the considered position. Regarding this term as applied for the periodic molecules, efforts to cope with their slowly convergent result have been continuously developed to reach a more accurate and faster approach. The well-known technique commonly used is the Ewald summation method which has been

proven to be one of the high efficiency methods. As most zeolites are periodic molecules, the site potential resulting from infinite atoms could be calculated with the Ewald summation formula as shown in Equation 1.

$$V_r = \sum_{n=1}^{N} q_n \sum_{i_1=i_{\min}}^{i_{\max}} \sum_{i_2=i_{\min}}^{i_{\max}} \sum_{i_3=i_{\min}}^{i_{\max}} \frac{erfc\left(\alpha \left| r - r_{n,i_1,i_2,i_3} \right|\right)}{\left| r - r_{n,i_1,i_2,i_3} \right|} \tag{1}$$

$$+ \frac{1}{\pi V} \sum_{n=1}^{N} q_n \sum_{m_1=m_{\min}}^{m_{\max}} \sum_{m_2=m_{\min}}^{m_{\max}} \sum_{m_3=m_{\min}}^{m_{\max}} \frac{\exp\left(-\pi^2 \left| \mathrm{f}_{m_1,m_2,m_3} \right|^2 / \alpha^2\right)}{\left| \mathrm{f}^2_{m_1,m_2,m_3} \right|^2} \times \cos\left[2\pi \mathrm{f}_{m_1,m_2,m_3} \cdot (\mathrm{r} - \mathrm{r}_{n,0,0,0})\right]$$

The first term is the electrostatic poetential at any position due to the infinite array of charge q_i and position r_i, each shielded by a Gaussian charge distribution $\exp[-\alpha(r - r_i)^2]$ having charge $-q_i$. Due to the shielding, this spatial sum converges rapidly.

The second term is the electrostatic potential at any position due to the infinite array of Gaussian charge distributions described above. Since this sum is over a complete, periodic array of identical Gaussian distributions, it can be evaluated in the Fourier (reciprocal lattice) space, where the sum is over a single Gaussian and converges rapidly.

These two terms are combined to compute the electrostatic potential at any position.

The Cartesian space coordinates $r_{n,i1,i2,i3} = (x_{n,i1,i2,i3}, y_{n,i1,i2,i3}, z_{n,i1,i2,i3})$ of the *n*th ion in the (i_1, i_2, i_3) unit cell can be computed from the fractional unit cell coordinates (u_{n1}, u_{n2}, u_{n3}) and the three unit cell translation vectors a_j, where

$a_j = (a_{jx}, a_{jy}, a_{jz}), \qquad j = 1, 2, 3,$

$r_{n,i1,\,i2,\,i3} = (u_{1,n} + i_1)a_1 + (u_{2,n} + i_2)a_2 + (u_{3,n} + i_3)a_3$

The sums of the real space are carried out over non-negligible terms. The index n varies over the ions of the unit cell, and the indices i_1, i_2, and i_3 describe the periodic translation of the unit cell along its principal axis.

The sums of the reciprocal space are carried out over all reciprocal lattice points for which the exponential is non-negligible. The unit cell volume is given by $V=a_1\cdot(a_2 \times a_3)$ and the coordinates in inverse lattice space are given by

$$f_{m_1,m_2,m_3} = \begin{bmatrix} m_1 & m_2 & m_3 \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{bmatrix}$$

The three reciprocal vectors are given by

$b_j = (b_{j1}\ b_{j2}\ b_{j3})$,

where $b_1 = a_2 \times a_3/V$, $b_1 = a_1 \times a_3/V$, $b_1 = a_1 \times a_2/V$

The relative convergence rates for the real space sums and the reciprocal lattice sums are controlled by α. For large values of α the Gaussian charge distribution is narrow and the inverse lattice sum converges more slowly. For small values of α the Gaussian charge distribution is wide and the real space sum converges more slowly. It is important that the summation limits for these sums are sufficiently large to guarantee convergence. When this condition is met, the sum V_r is independent of the value of α.

The results calculated by the Ewald summation method is shown in the unit of electron charge/Å. To convert the electrostatic potential from electron charge/Å to Volt, we multiply the results in the code program with 14.39976.

The first procedure to transform the impact of infinite atomic charges regarding the long range electrostatic potential at any sites inside the cluster space is that we position the grid points throughout this space. The center of the space is calculated by averaging locations of every atom in the cluster region that will be treated in the quantum cluster calculation. These inputs of xyz coordinate, a cluster and adsorbed molecules, are used to create the spherical significant space built to

cover at least all of atoms that will be treated quantum chemically. The size of this sphere is designed to be large enough so that adsorbed molecules can move freely inside without being attracted to any near charge. However, too huge a cluster region leads to the regression of accuracy.

Trialing different values to attain the optimal and practical interval between the neighbor grid points, we have agreed to use the satisfactory distance of 0.5 to 0.7 Å. The amount of grid points is determined by the size of the cluster region, that is, the larger the cluster region, the greater the amount of grid points. These grid points are used as test points for which we optimize the magnitudes of charges to satisfy potentials at all of these points (Figure 2). Compared to a previous work launching the SCREEP method for investigating the adsorption of molecules in a zeolite (Vollmer *et al.* 1999), this scheme is far more effective as the SCREEP method used only one essential point, the Brønsted acid site, as the test point to correct the electrostatic potential reproduced by surface and explicit charges, whereas others positions inside quantum cluster region were neglected.

The site potential at every grid point is then calculated using the Ewald summation with the default parameters which have been tested to give acceptable accuracy. Discussed widely in previous works, atomic charges suitable to zeolites for cluster calculations should be half formal charges of atoms. The R_{cut}, the limited distance from the central unit cell to truncate the periodically calculated results, is determined directly varying on the size of the zeolite's unit cell. For example, a large molecule such as Faujasite zeolite having 576 atoms per single unit cell with the xyz dimension of 24.5 Å, the Rcut ,as we have tested different sizes, should not be less than 80 Å. The results we get could be said to be the infinite electrostatic potential of such a zeolite.

The next step is positioning point charges. In this work, as discussed earlier, we place our point charges on the ideal atomic positions of the lattice. Yet, as point charges close to the quantum region can easily cause the problems of unrealistically attractive force, possibly resulting in eccentric results of geometries and energies, we

place our point charges only in a region defined by a minimal distance to the center of the quantum region and a maximal distance that determines the number of point charges. No single point charge is placed at the site closer to the cluster's center than this minimal distance. Such minimal distance is adjustable in accordance with the size of the probe molecules in the QM region. For a sizable molecule, for example, it must be broader than that for a relatively small molecule to avoid unrealistically strong attractive force influencing on atoms in the QM part. However, the larger the minimal distance, the more error in the electrostatic potential reproduced by point charges. The suitable one as we recommended, is approximately 10 – 15 Å. Conversely, the maximal distance is not as strict as the minimal one. It is employed only to determine the total number of point charges as we place them on the atomic lattice sites. In case of a large amount of point charges, we just lengthen this maximal distance. Consequently, the farther atomic positions in the range of such spherical radius will be included. A greater number of point charges give less error of electrostatic potential in QM region than a smaller one.

This finite number of point charges is further divided into an inner and an outer zone as shown in Figure 3. Point charges in the inner zone are not optimized and have values of half the formal charges of the zeolite atoms. Such 'effective' charges $Q_{Si} = +2$ and $Q_O = -1$ seem to be more realistic for a supermolecule like zeolite than the formal charges. Point charges in the outer zone are optimized. They are defined by ΔQ which is the vector of deviations from the values $Q_{Si} = +2$ and $Q_O = -1$ that are generated to reproduce the electrostatic potential from atoms beyond those in this zone as shown in Equation 2. The reason behind optimizing point charges in the outer zone and not in the inner zone is because charges in the inner zone are more influential on atoms in QM part than the farther ones based on the electrostatic potential formula, $V = Q/r$. As a result, it is reasonable to fix the charge values in the inner zone and optimize the charge values only in the outer zone. The inner zone is defined by the radius from the center of the QM region, which is 15 – 20 Å, varying directly on the size of probe molecules.

$$Q'_{outer} = Q_{outer} + \Delta Q \quad (2)$$

ΔQ is derived in the following way: The electrostatic potential from the infinite crystal is calculated at the grid points using the Ewald method. Then the electrostatic potential from the zeolite cluster and from the point charges in both zones are subtracted from it according to Equation 3.

$$V_{outside} = V_{ewald} - V_{cluster} - V_{inner/outer} \quad (3)$$

We find the ΔQ that reproduces $V_{outside}$ by solving the matrix of simultaneous linear equations shown in Equation 4.

$$A \bullet \Delta Q = V_{outside} \quad (4)$$

$V_{outside}$ is a column matrix having m rows, m being the number of grid points. A is the distance matrix having m rows and n (the number of charges in the outer zone) columns. Its elements are defined as $A_{ij} = 1/|R_i - R_j|$. R_i is the position of grid point i and R_j is the position of charge j.

The system of equations described in Equation 4 contains also the four equations needed to guarantee the overall neutrality of charges and vanishing dipole moments along x, y and z .

We now have a complete set of charges consisting of the point charges in the inner zone and the optimized point charges in the outer zone and their respective positions which allow us to add the crystal potential to the quantum region. This set of point charges can be applied for the cluster calculation to investigate the adsorption of molecules on a zeolite.

Regarding the code program, the flowcharts of generating point charges are shown in Figure 4 to Figure 7. Also, the inputs required to obtain the complete set of point charges can be summarized as follows:

1) The unit cell of the periodic molecule such as zeolites, the matrix possessing the first three columns of xyz coordinates of every atom in a single unit cell with its atomic charge as the fourth column.
2) The 3 x 3 matrix of translation vector of such the unit cell.
3) A cluster, having 4 columns like the unit cell showing the xyz coordinate of the cluster atoms with their atomic charge excluding the hydrogen boundary atoms.
4) Atomic positions of all atoms in the cluster including probe molecules.
5) The radius to determine the number of point charges
6) The radius to determine the minimal distance from the center which has no point charges in this space.
7) The radius to determine the number of fixed value charges which are not optimized.
8) The number to determine the fineness of grid points.
9) R_{cut} for the Ewald summation, both for real and reciprocal space.

Part B. Applying point charges for cluster calculation using ONIOM approach

We applied the method described in part A. ('e-ONIOM', see Figure 8) to the adsorption of pyridine on H-Faujasite zeolite and compare it to two simpler models: Model A is a small 5T bare cluster model [≡SiO(H)Al(SiO)2OSi≡] as shown in Figure 9, employed to represent only the Brønsted acid site of zeolite.

In model B, the effect of the extended framework which results in the short-range forces over the active site of H-FAU zeolite, is included in the second model by means of the ONIOM method. This model is enlarged up to 84T tetrahedra and consists of two parts - the central cluster of the 5T Brønsted acid site treated quantum chemically on a high level and the remaining low-level part which is treated with the UFF force field (Figure 10).

Model C is our e-ONIOM model (Figure 11) that includes the long-range electrostatic contributions via a set of finite number of point charges as elucidated above. This set of point charges is used together with the ONIOM model (Figure 9) described earlier.

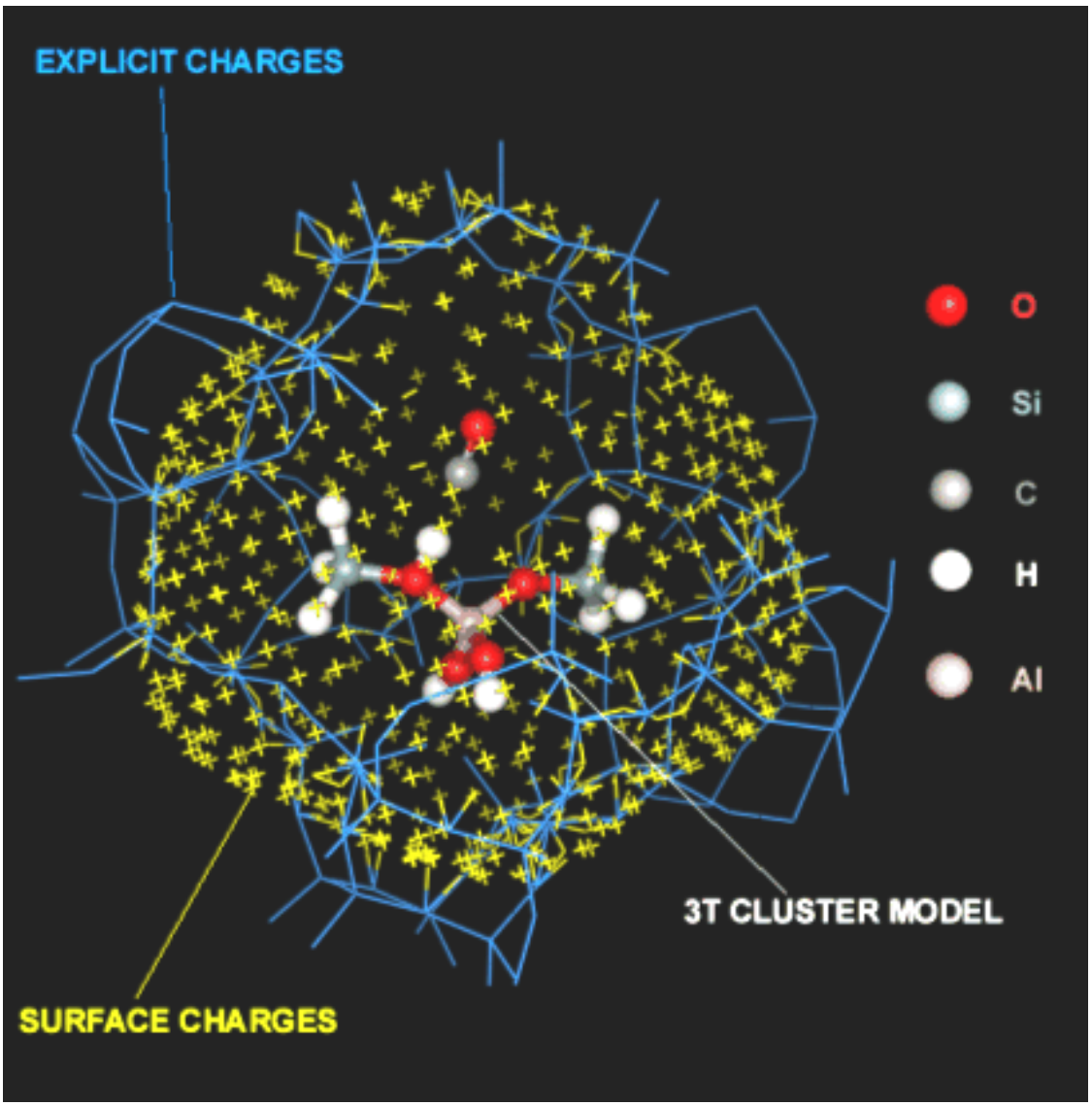


Figure 1 The use of SCREEP in the embedded cluster calculation

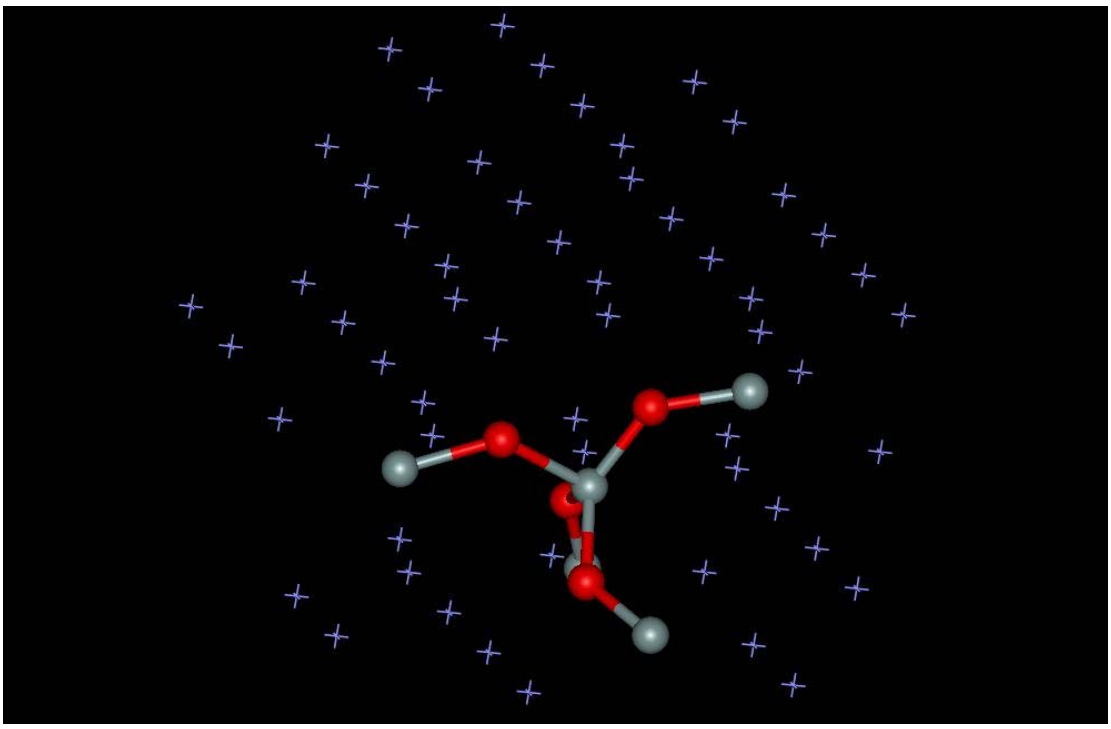


Figure 2 Creating grid points in quantum cluster region

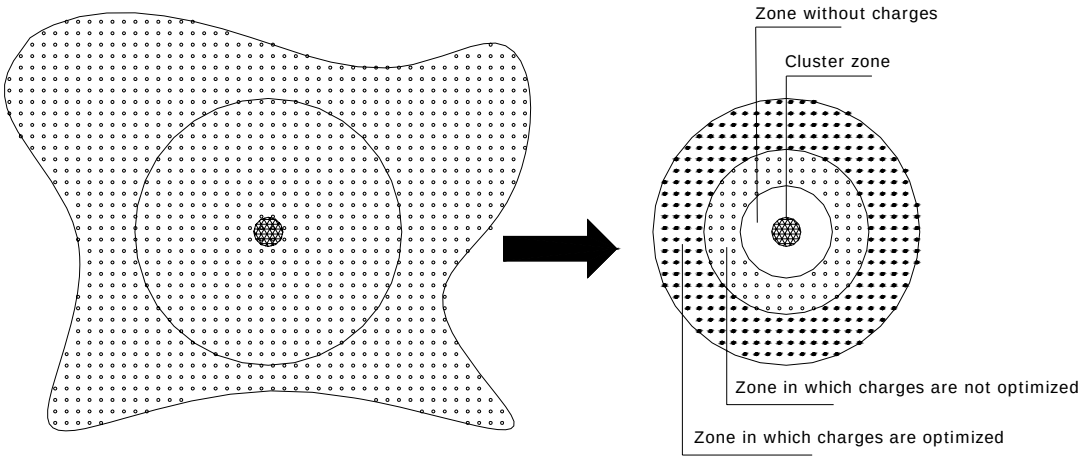


Figure 3 The method of positioning point charges and dividing them into 2 zones, the inner and outer zone.

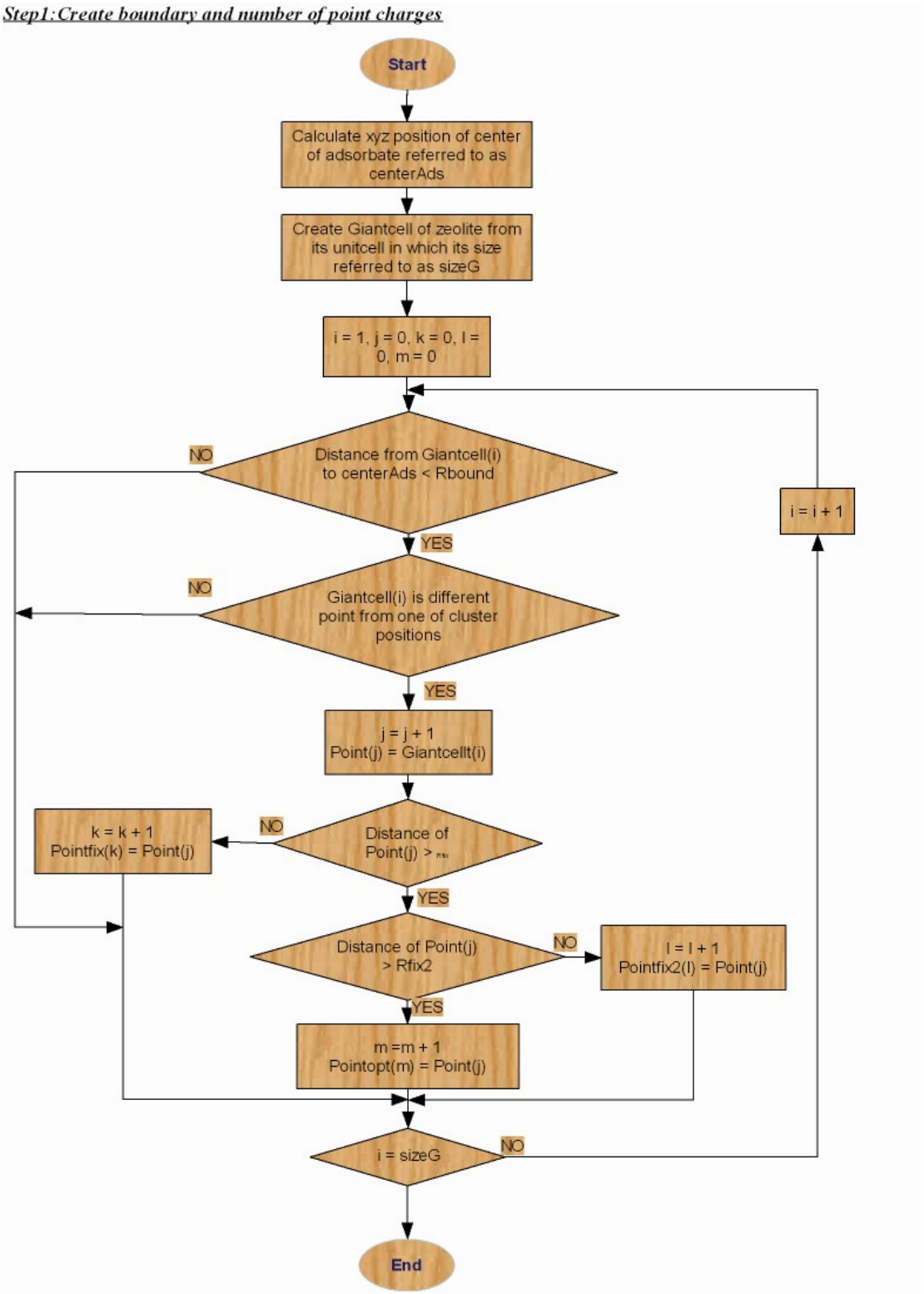


Figure 4 Flow chart of step 1: Create boundary and number of point charges

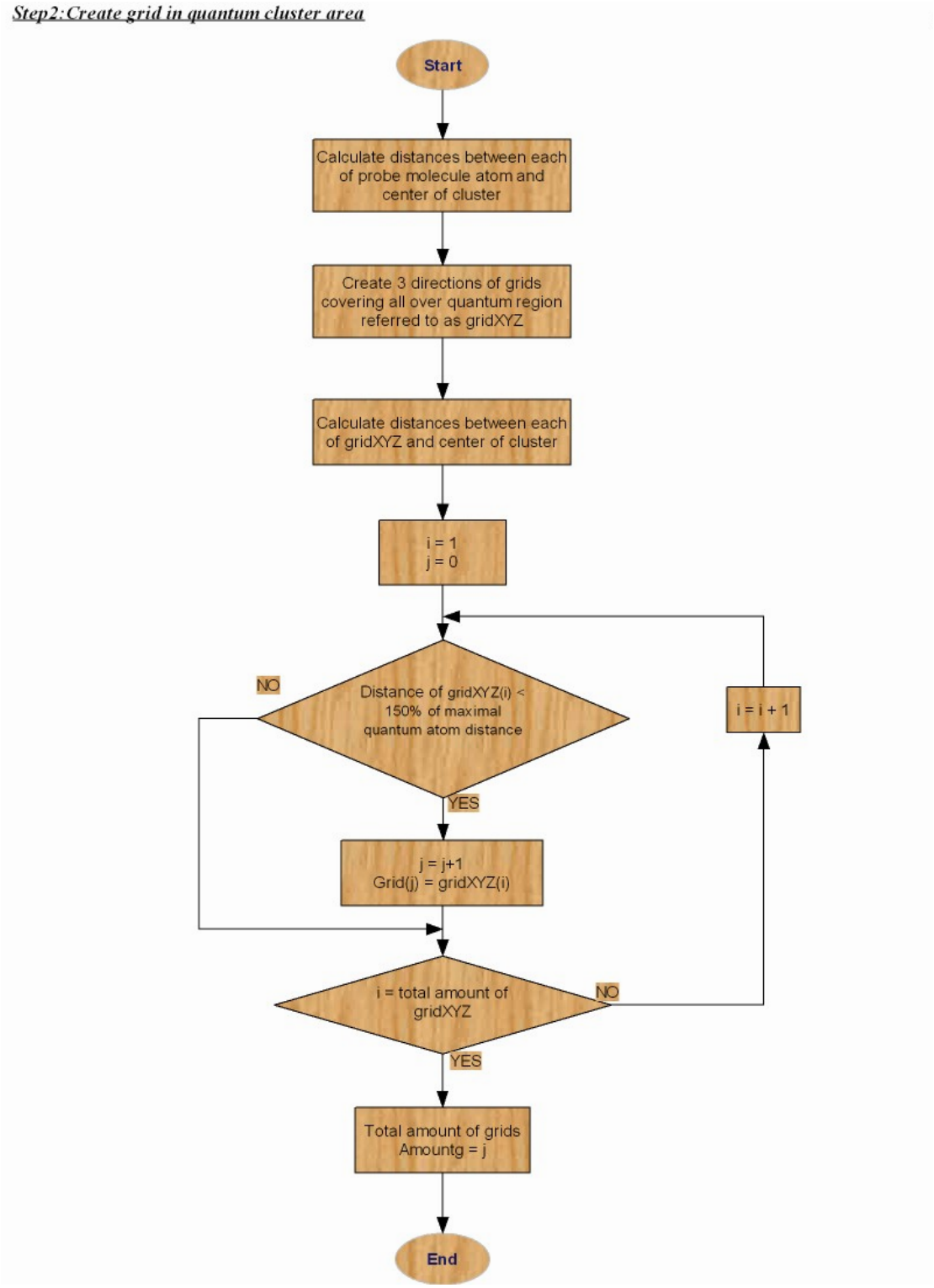


Figure 5 Flow chart of step 2: Create grids in quantum cluster area

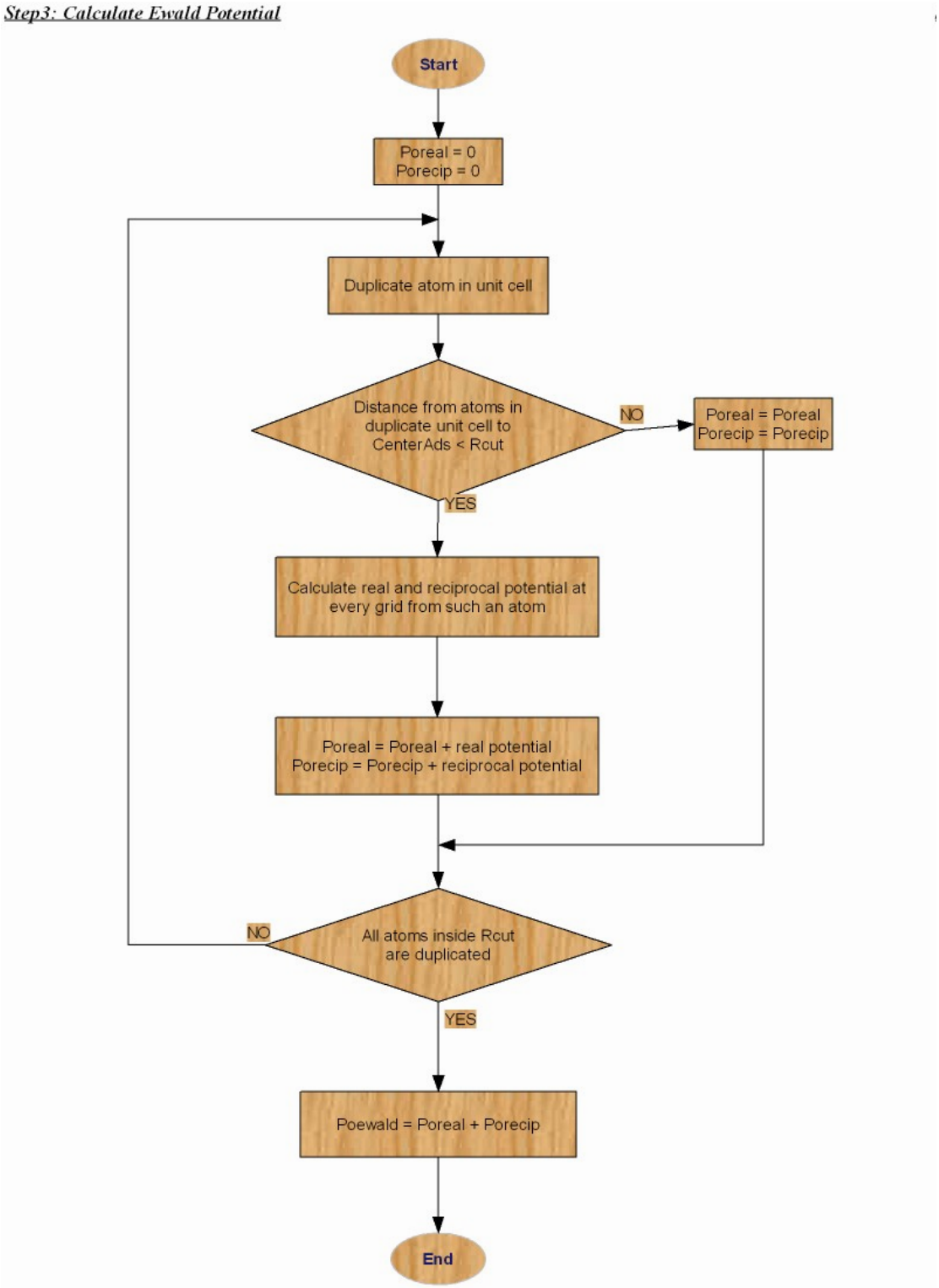


Figure 6 Flow chart of step 3: Calculate Ewald potential

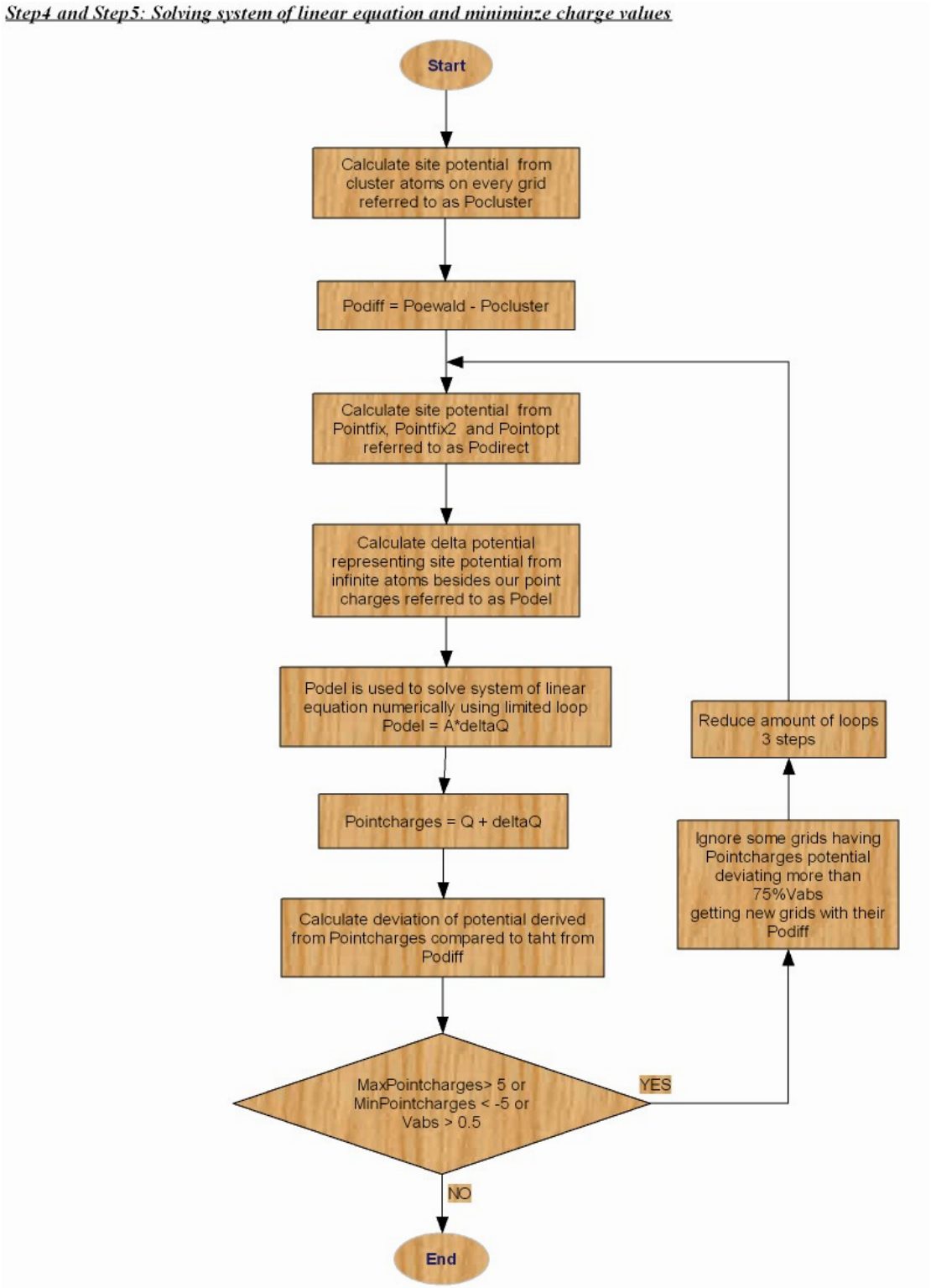


Figure 7 Flow chart of step 4 and step 5: Solving system of linear equation and minimizing charge values

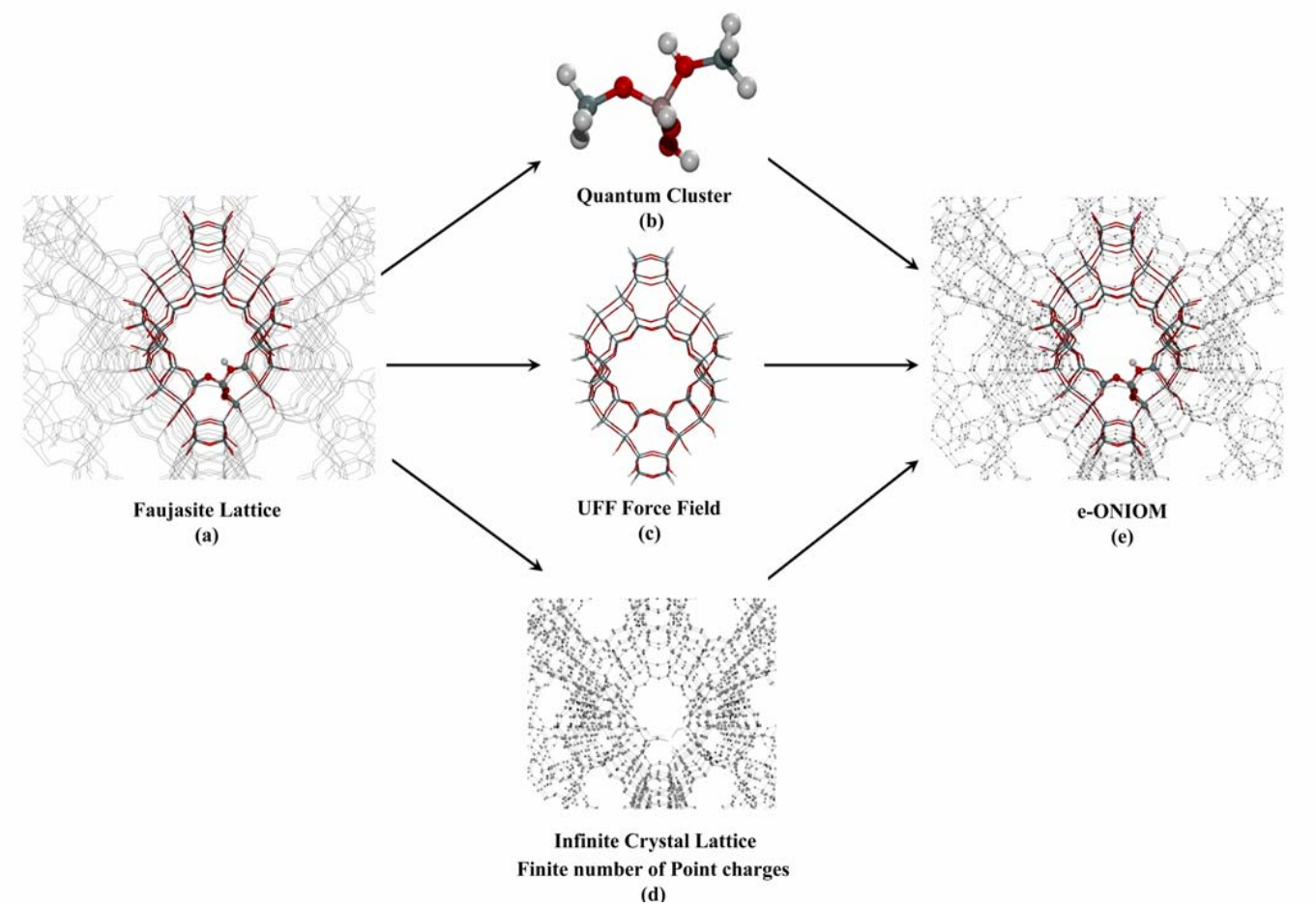


Figure 8 Schematic diagram of the embedded ONIOM method. The periodic structure of the FAU framework (a) was subdivided into three layers: the innermost one is the QM region (b: middle); the next layer is the UFF part (c), and the outermost one is a set of point charges (d). The complete embedded ONIOM is shown in (e).

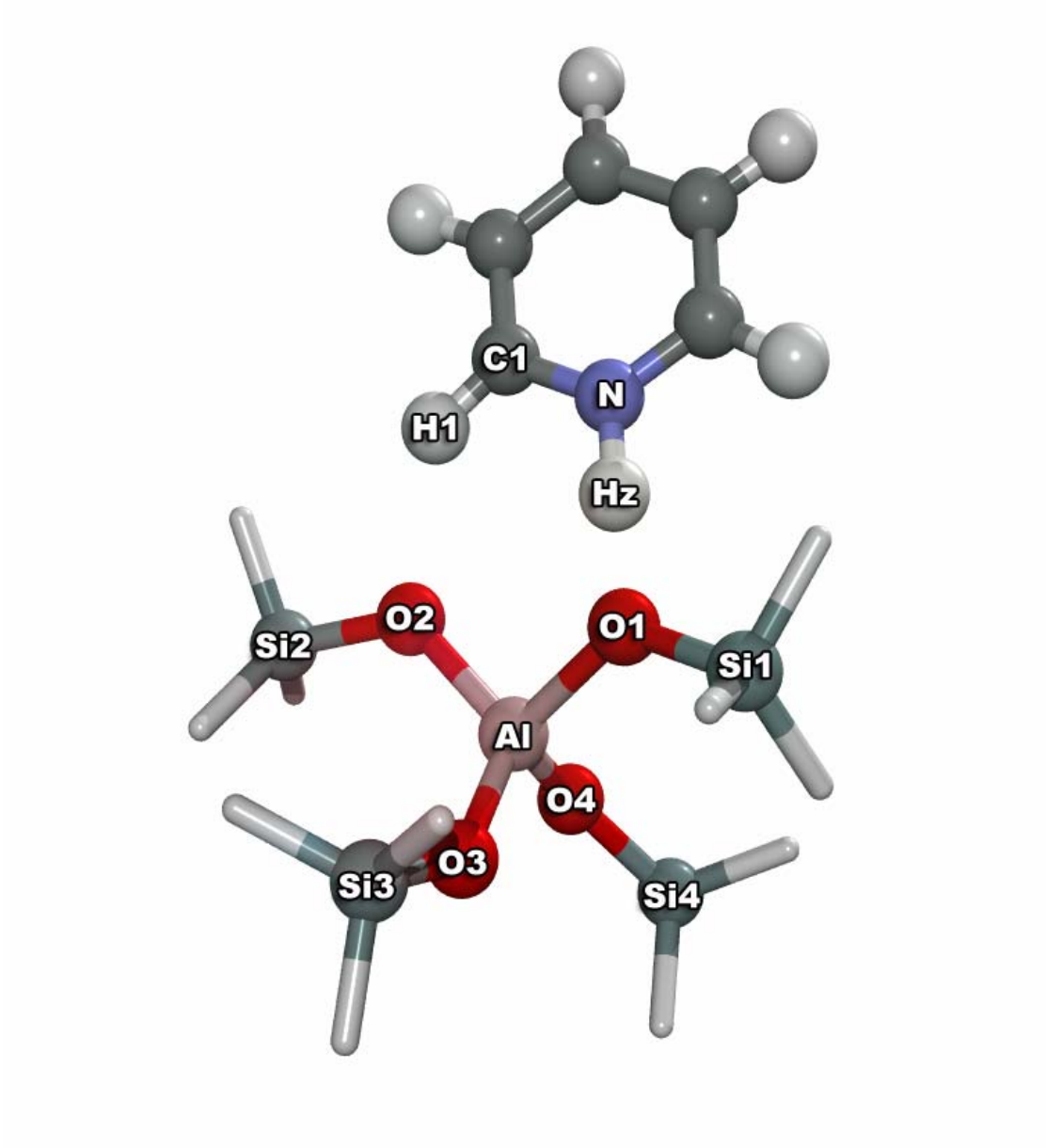


Figure 9 Presentation of pyridine interacted with the 5T bare cluster model of H-FAU zeolite (model A).

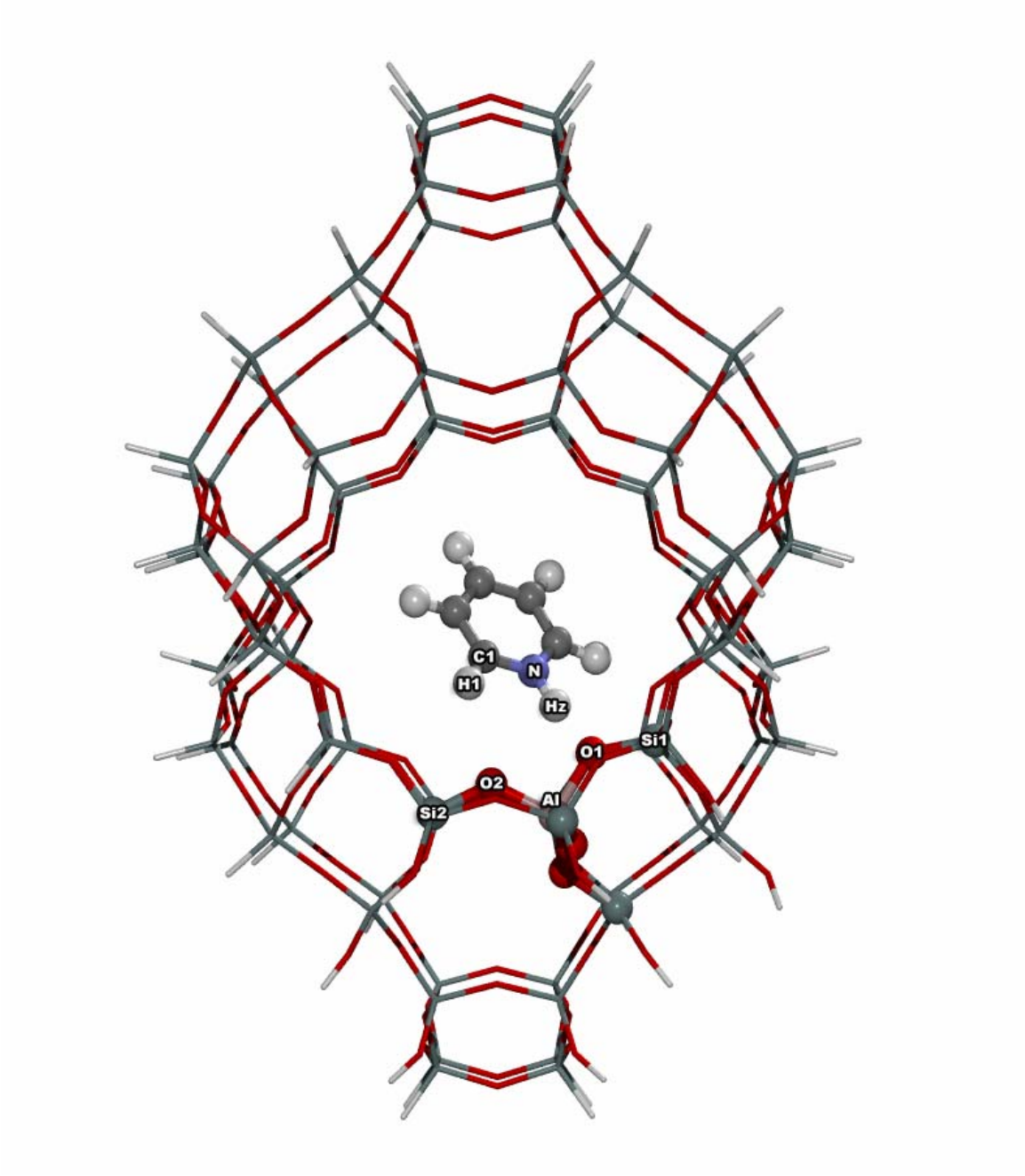


Figure 10 Presentation of pyridine interacted with the ONIOM 84T (5T:UFF) model of H-FAU zeolite (model B).

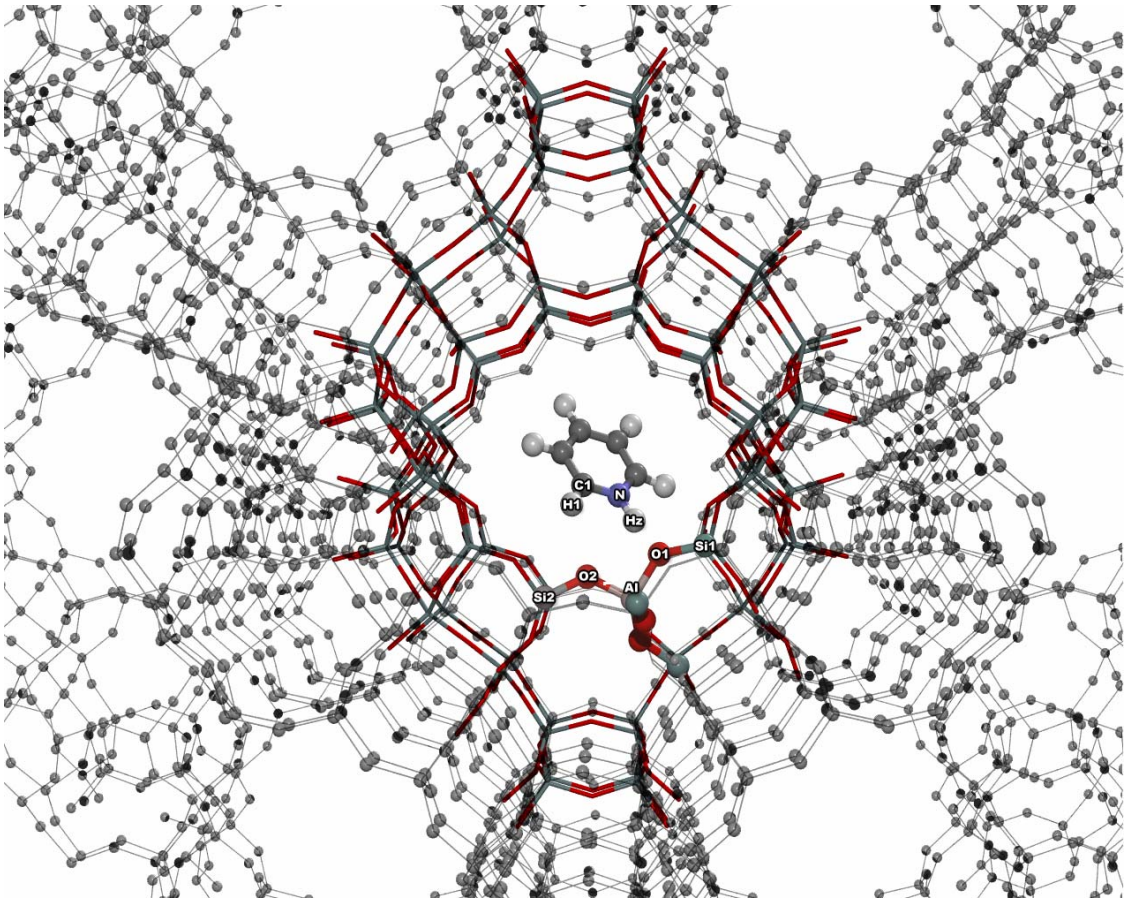


Figure 11 Presentation of pyridine interacted with the embedded ONIOM 84T (5T:UFF) model of H-FAU zeolite (model C).

RESULTS AND DISCUSSION

1. Geometries of the zeolite models

The geometrical parameters of the zeolite models are given in Table 1. They show that the long-range electrostatic forces have not much effect on the geometry of H-FAU. For example, the O1-Hz distance is 0.968 Å in the 5T cluster model, 0.970 Å in the ONIOM model and 0.971 Å in the e-ONIOM model. Accurate experimental structural data for H-FAU are not known. The Al-H distance in ZSM5 zeolite has been measured (2.46 Å)(Hunger *et al*., 1992; Kenaston *et al*, 1994). In H-FAU, results in the calculation exhibit Al-H distances of 2.398 Å, 2.334 Å and 2.338 Å for models A-C, respectively. This is consistent with the fact that H-FAU is less acidic than ZSM5.

2. Interaction of Pyridine with H-FAU zeolite

2.1 Structures

Several experimental and theoretical studies of pyridine (Py) interacting with various zeolites reported that the proton of the bridging hydroxyl group of zeolite is transferred to the pyridine molecule resulting in a pyridinium cation-zeolite anion ($PyH^+\cdots Z^-$) ion-pair complex. In addition, protonation of pyridine by the proton at the Brønsted acidic site of H-FAU occurs upon adsorption. This changes the geometries of both pyridine and, especially, also of FAU. In the models A, B and C, the O1-Hz distances in the $PyH^+\cdots Z^-$ ion-pair complex are 0.484 Å, 0.512, Å and 0.617 Å larger than without pyridine, respectively. These differences are typical for the formation of an ion pair. The N-Hz distances in the ion-pair complex are 1.109 Å, 1.098 Å and 1.073 Å for the three models, respectively. In isolated pyridinium, PyH^+, the N-H distance is 1.017 Å. For all models, the O1-Hz bonds get longer upon adsorption of pyridine (0.968 vs. 1.452 Å, 0.970 vs. 1.482 Å and 0.971 vs. 1.588 Å for models A, B and C). The O1-Al distance gets shorter because the zeolite O1 is more basic than in the isolated H-FAU (1.889 vs. 1.788 Å, 1.834 vs. 1.743 Å and 1.825 vs. 1.732 Å for

models A, B and C) while the O2-Al bonds become longer. Ehresmann *et al.* studied the proton transfer from H-ZSM-5 to various bases by means of Al MAS NMR experiments and ab-initio calculations. They found that, if the zeolite is deprotonated, the environment around Al is nearly perfectly tetrahedral but becomes distorted when it is not. We checked this by calculating the differences between the four Al-O distances and find that our results agree with their findings as well. After the proton moves to pyridine, the differences are much smaller for all models than before.

The O1-Hz bond distances are 1.452, 1.482 and 1.588 Å for the 5T cluster, the ONIOM and the e-ONIOM model, respectively. Therefore it seems that in the e-ONIOM model the ion pair is more favored, while the complex in the 5T cluster model still has some hydrogen-bond character. This is also indicated by its other geometrical features. It has the shortest O1-Hz bond, the longest N-Hz bond (see above) and the shortest O1-N distance of the three models.

2.2 Vibrational frequencies

In our calculations, we obtain the frequency of the OH stretching vibration in protonated zeolite at 3798 cm^{-1} and the NH stretching frequency in isolated pyridinium at 3569 cm^{-1}. In the $PyH^{+}\cdots Z^{-}$ ion-pair complex the frequency of the proton vibrating along N-O is 2077 cm^{-1} for model A which resembles more a normal hydrogen bonded complex. This frequency increases to 2248 cm^{-1} in model B and to 2588 cm^{-1} in model C. Due to the H-O hydrogen bond, this value is much lower than in isolated PyH^{+}. It is in good agreement with the reported experimental value of ~2600 cm^{-1} for the N-H stretching mode (Rappe *et al.*, 1992).

2.3 Energetics

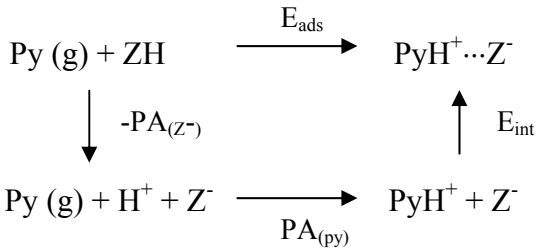
As expected, the interaction energy is stronger if the ion pair character is more pronounced. The adsorption of pyridine on H-FAU can be described by a thermodynamic cycle. First, a proton at the Brønsted acid site of H-FAU zeolite is abstracted giving an isolated proton (H^{+}) and an isolated zeolite anion (Z^{-}). Then, the

pyridine base attracts this proton to form a pyridinium cation (PyH^+). Finally, PyH^+ interacts with Z^- via a hydrogen bonded $PyH^+\cdots Z^-$ ion-pair complex (see scheme 1.). The adsorption energy of this $PyH^+\cdots Z^-$ ion pair complex is, therefore,

$$E_{ads} = E_{int} + PA_{(py)} - PA_{(Z^-)} \quad (5)$$

The proton affinity of pyridine, $PA_{(Py)}$, is -235.61 kcal/mol. For the competing $PA_{(Z^-)}$, we see that the 5T cluster has a somewhat smaller proton affinity (-307.26 kcal/mol) than the ONIOM model (-300.79 kcal/mol). The value for the e-ONIOM model is -331.50 kcal/mol. The difference between this number and the value from the ONIOM model can be explained by the negative electrostatic potential near O1 (-0.3 a.u.) generated by the point charges.

Scheme1



The adsorption energies of all models are shown in Table 2. The experimental adsorption energy of pyridine on H-FAU is -43.1 ± 1 kcal/mol . For the 5T cluster, the adsorption energy of pyridine on zeolite, E_{ads}, is -20.40 kcal/mol which is much lower than the experimental value. The 84T ONIOM model which includes the van der Waals interactions arising from confinement effects of the pore structure gives an adsorption energy of -33.67 kcal/mol, somewhat lower than the experimental value. The e-ONIOM model gives an adsorption energy of -42.78 kcal/mol, in perfect agreement with the experimental data.

Table 1 Gemotrical parameters of pyridine adsorbed on H-FAU (Distances in Å and angles in degree).

Parameters	Zeolite anion (Z^-)	5T cluster		ONIOM		e-ONIOM	
		isolated	complex	isolated	complex	isolated	complex
O1-Hz	-	0.968	1.452	0.970	1.482	0.971	1.588
Al-O1	1.727	1.889	1.788	1.834	1.743	1.825	1.732
Al-O2	1.717	1.702	1.731	1.665	1.688	1.664	1.689
Al-O3	1.728	1.684	1.707	1.642	1.667	1.643	1.669
Al-O4	1.751	1.701	1.720	1.673	1.693	1.677	1.701
RMSD[a]	0.014	0.784	0.097	0.766	0.088	0.765	0.083
Al-Hz	-	2.398	2.720	2.334	2.678	2.338	2.757
N- O1	-	-	2.561	-	2.579	-	2.659
N-Hz	-	-	1.109	-	1.098	-	1.073
<Al-O1-Si1	129.8	129.3	126.2	128.1	126.3	128.1	126.1
<N-Hz-O1	-	-	178.7	-	176.2	-	175.0

[a]Root mean square of the standard deviation of the four Al-O distances.

Table 2 Proton affinity of zeolite, $PA_{(ZO^-)}$, interaction energy, E_{int}, and adsorption energy, E_{ads}, of pyridine on H-FAU (Energies in kcal/mol).

	5T cluster	ONIOM	e-ONIOM
$PA_{(ZO^-)}$	-307.26	-300.79	-331.50
E_{int}	-95.69	-102.36	-142.08
E_{ads}	-24.04	-37.18	-46.19
E_{ads}^{BSSE}	-20.40	-33.67	-42.78
Experiment	**-43.1 ± 1**		

CONCLUSION

The new method was implemented to reproduce the electrostatic potential generated by an infinite crystal lattice in the region of a quantum cluster. It is represented via a set of finite numbers of point charges which are positioned at the ideal lattice site of zeolites. The disadvantages from previous works have been improved to avoid the problems often taking place in many systems of embedded cluster calculations resulting in considerable errer of geometries and energies and other properties investigated. The unrealistic attractive forces due to charges near quantum region are removed defined by the minimal distance and are compensated by point charges farther than such a distance. In addition, placing point charges at ideal lattice site based on the unit cell and translation vector of particular periodic molecule results in the relatively accurate electrostatic potential inside cluster region. Grid points throughout the cluster region are used to fit the values of finite generated point charges giving electrostatic potential towards the correct Madelung potential calculated with Ewald summation method. Furthurmore, the idea of employing fixed charges without optimization referred to as the charge-fixed zone assisted the process of optimization to obtain statisfoctorily correct results, as the charges near quantum region shows more effect on atoms in cluster than the farther ones. Moreover, Using Matlab program as the tools is totally effective due to its several different mathematical functions as well as its capability of fast execution.

The method was then applied to the problem of the adsorption of pyridine on H-FAU zeolite which are not practical in previous other cluster calculation methods and periodic calculations. The results are clearly shown that the adsorption energy is in much better agreement to the experimental data than that without incoprating this set of point charges as environment. Other results such as structures and vibrational frequencies are satisfactorily consistent to the results from experiments. The method is easy to use together with existing quantum chemical codes and requires nearly no additional CPU-time. Moreover, unnecessary to generate the new one again, this set of point charges can be applied for other problems of the adsorption of molecules in the same zeolite with the same cluster.

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APPENDIX

Appendix A.

Input data, as matlab codes, to generate a set of point charges for investigating pyridine adsorbed on H-Faujasite zeolite using ONIOM 84T(5T:UFF).

```
% INPUT DATA OF 5T-FAU to find Ewald Potential on any grid point

function[ucell,trans,cluster,Quantumclus,Adsorb,Rbound,Rfix,Rfix2,num
p,RcutReal,RcutRecip] = FAU_12T

%1. "ucell" is a matrix of atomic xyz coordinates in single unit cell
in which the first, second and third column is x y and z
respectively, and the fourth column is charge

%2. "tran" is a 3x3 matrix of particular zeolite's translation vector

%3. "cluster" is a matrix of atomic xyz coordinates in a quantum
cluster which has only atoms of Si and O; the first 3 columns are
coordinates and the 4th column is charge

%4. "Quantumclus" is a matrix of atomic positions in xyz coordinates
of all atoms(a zeolite and probe molecules) that would be treated
quantum chemically

%5. "Adsorb" is a matrix of atomic positions of probe molecules

%6. "Rbound" is the radius from center of quantum region to the
circle boundary in which charges are located; this value determines
an amount of optimized charges in this system.

%7. "Rfix" is the radius from center of quantum region to the circle
boundary in which no single charge is located(recommended 10-18A
varying directly to the size of probe molecule)

%8. "Rfix2" is the radius from center of quantum region to the circle
boundary in which charges are not optimized(recommended 15-25A)

%9. "nump" is the value indicating the fineness of grids; the higher
value, the finer grid (recommended 10-15)

%10. "RcutReal" is the Rcut of Real space in calculating Ewald
summation(recommended 60-100)

%11. "RcutRecip" is the Rcut of Reciprocal space in calculating Ewald
summation(recommended 45-80)

ucell       = [
                22.950   3.039   0.871     2
                 0.000  21.681   2.577    -1
                24.180  24.180   3.412    -1
                 1.836   1.836  23.390    -1
                 1.713   1.713   7.790    -1
                19.501   3.026  13.000     2
                18.194   8.641  14.706    -1
                18.271   6.142  15.541    -1
                16.358   4.228  11.261    -1
```

```
16.480   4.352  19.919    -1
 7.372  15.168  17.323     2
 6.064   9.552  15.616    -1
 6.142  12.051  14.781    -1
 4.228  13.965  19.062    -1
 4.352  13.842  10.403    -1
10.821  15.155   5.194     2
12.129  20.771   3.488    -1
12.051  18.271   2.653    -1
13.965  16.358   6.932    -1
13.842  16.480  22.532    -1
 0.871  22.950   3.039     2
 2.577   0.000  21.681    -1
 3.412  24.180  24.180    -1
23.390   1.836   1.836    -1
 7.790   1.713   1.713    -1
13.000  19.501   3.026     2
14.706  18.194   8.641    -1
15.541  18.271   6.142    -1
11.261  16.358   4.228    -1
19.919  16.480   4.352    -1
17.323   7.372  15.168     2
15.616   6.064   9.552    -1
14.781   6.142  12.051    -1
19.062   4.228  13.965    -1
10.403   4.352  13.842    -1
 5.194  10.821  15.155     2
 3.488  12.129  20.771    -1
 2.653  12.051  18.271    -1
 6.932  13.965  16.358    -1
22.532  13.842  16.480    -1
 3.039   0.871  22.950     2
21.681   2.577   0.000    -1
24.180   3.412  24.180    -1
 1.836  23.390   1.836    -1
 1.713   7.790   1.713    -1
 3.026  13.000  19.501     2
 8.641  14.706  18.194    -1
 6.142  15.541  18.271    -1
 4.228  11.261  16.358    -1
 4.352  19.919  16.480    -1
15.168  17.323   7.372     2
 9.552  15.616   6.064    -1
12.051  14.781   6.142    -1
13.965  19.062   4.228    -1
13.842  10.403   4.352    -1
15.155   5.194  10.821     2
20.771   3.488  12.129    -1
18.271   2.653  12.051    -1
16.358   6.932  13.965    -1
16.480  22.532  13.842    -1
21.233   4.757  11.258     2
18.115   5.986   8.717    -1
20.029   7.900  12.997    -1
19.906   7.778   4.339    -1
21.219   1.308  23.387     2
 0.078   0.078  20.846    -1
22.422  22.422   0.868    -1
```

22.545	22.545	16.468	-1
9.104	13.437	19.065	2
5.986	12.207	21.605	-1
7.900	10.293	17.326	-1
7.778	10.416	1.725	-1
9.090	16.885	6.936	2
12.207	18.115	9.476	-1
10.293	20.029	5.196	-1
10.416	19.906	13.854	-1
16.885	6.936	9.090	2
18.115	9.476	12.207	-1
20.029	5.196	10.293	-1
19.906	13.854	10.416	-1
13.437	19.065	9.104	2
12.207	21.605	5.986	-1
10.293	17.326	7.900	-1
10.416	1.725	7.778	-1
1.308	23.387	21.219	2
0.078	20.846	0.078	-1
22.422	0.868	22.422	-1
22.545	16.468	22.545	-1
4.757	11.258	21.233	2
5.986	8.717	18.115	-1
7.900	12.997	20.029	-1
7.778	4.339	19.906	-1
19.065	9.104	13.437	2
21.605	5.986	12.207	-1
17.326	7.900	10.293	-1
1.725	7.778	10.416	-1
6.936	9.090	16.885	2
9.476	12.207	18.115	-1
5.196	10.293	20.029	-1
13.854	10.416	19.906	-1
11.258	21.233	4.757	2
8.717	18.115	5.986	-1
12.997	20.029	7.900	-1
4.339	19.906	7.778	-1
23.387	21.219	1.308	2
20.846	0.078	0.078	-1
0.868	22.422	22.422	-1
16.468	22.545	22.545	-1
1.308	21.219	23.387	2
0.000	2.577	21.681	-1
4.757	21.233	11.258	2
6.064	15.616	9.552	-1
5.986	18.115	8.717	-1
7.900	20.029	12.997	-1
7.778	19.906	4.339	-1
16.885	9.090	6.936	2
18.194	14.706	8.641	-1
18.115	12.207	9.476	-1
20.029	10.293	5.196	-1
19.906	10.416	13.854	-1
13.437	9.104	19.065	2
12.129	3.488	20.771	-1
12.207	5.986	21.605	-1
10.293	7.900	17.326	-1
10.416	7.778	1.725	-1

```
23.387   1.308  21.219     2
21.681   0.000   2.577    -1
11.258   4.757  21.233     2
 9.552   6.064  15.616    -1
 8.717   5.986  18.115    -1
12.997   7.900  20.029    -1
 4.339   7.778  19.906    -1
 6.936  16.885   9.090     2
 8.641  18.194  14.706    -1
 9.476  18.115  12.207    -1
 5.196  20.029  10.293    -1
13.854  19.906  10.416    -1
19.065  13.437   9.104     2
20.771  12.129   3.488    -1
21.605  12.207   5.986    -1
17.326  10.293   7.900    -1
 1.725  10.416   7.778    -1
21.219  23.387   1.308     2
 2.577  21.681   0.000    -1
21.233  11.258   4.757     2
15.616   9.552   6.064    -1
18.115   8.717   5.986    -1
20.029  12.997   7.900    -1
19.906   4.339   7.778    -1
 9.090   6.936  16.885     2
14.706   8.641  18.194    -1
12.207   9.476  18.115    -1
10.293   5.196  20.029    -1
10.416  13.854  19.906    -1
 9.104  19.065  13.437     2
 3.488  20.771  12.129    -1
 5.986  21.605  12.207    -1
 7.900  17.326  10.293    -1
 7.778   1.725  10.416    -1
 3.026  19.501  13.000     2
 6.142  18.271  15.541    -1
 4.228  16.358  11.261    -1
 4.352  16.480  19.919    -1
 3.039  22.950   0.871     2
15.155  10.821   5.194     2
18.271  12.051   2.653    -1
16.358  13.965   6.932    -1
16.480  13.842  22.532    -1
15.168   7.372  17.323     2
12.051   6.142  14.781    -1
13.965   4.228  19.062    -1
13.842   4.352  10.403    -1
 7.372  17.323  15.168     2
 6.142  14.781  12.051    -1
 4.228  19.062  13.965    -1
 4.352  10.403  13.842    -1
10.821   5.194  15.155     2
12.051   2.653  18.271    -1
13.965   6.932  16.358    -1
13.842  22.532  16.480    -1
22.950   0.871   3.039     2
19.501  13.000   3.026     2
18.271  15.541   6.142    -1
```

```
16.358  11.261   4.228    -1
16.480  19.919   4.352    -1
 5.194  15.155  10.821     2
 2.653  18.271  12.051    -1
 6.932  16.358  13.965    -1
22.532  16.480  13.842    -1
17.323  15.168   7.372     2
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19.062  13.965   4.228    -1
10.403  13.842   4.352    -1
13.000   3.026  19.501     2
15.541   6.142  18.271    -1
11.261   4.228  16.358    -1
19.919   4.352  16.480    -1
 0.871   3.039  22.950     2
22.950  15.168  13.000     2
 0.000   9.552  14.706    -1
24.180  12.051  15.541    -1
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 1.713  13.842  19.919    -1
19.501  15.155   0.871     2
18.194  20.771   2.577    -1
18.271  18.271   3.412    -1
16.358  16.358  23.390    -1
16.480  16.480   7.790    -1
 7.372   3.039   5.194     2
 6.064  21.681   3.488    -1
 6.142  24.180   2.653    -1
 4.228   1.836   6.932    -1
 4.352   1.713  22.532    -1
10.821   3.026  17.323     2
12.129   8.641  15.616    -1
 0.871  10.821  15.168     2
 2.577  12.129   9.552    -1
 3.412  12.051  12.051    -1
23.390  13.965  13.965    -1
 7.790  13.842  13.842    -1
13.000   7.372  15.155     2
14.706   6.064  20.771    -1
17.323  19.501   3.039     2
15.616  18.194  21.681    -1
14.781  18.271  24.180    -1
19.062  16.358   1.836    -1
10.403  16.480   1.713    -1
 5.194  22.950   3.026     2
 3.488   0.000   8.641    -1
 2.653  24.180   6.142    -1
 6.932   1.836   4.228    -1
22.532   1.713   4.352    -1
 3.039  13.000  10.821     2
21.681  14.706  12.129    -1
24.180  15.541  12.051    -1
 1.836  11.261  13.965    -1
 1.713  19.919  13.842    -1
 3.026   0.871   7.372     2
 8.641   2.577   6.064    -1
 6.142   3.412   6.142    -1
 4.228  23.390   4.228    -1
```

```
 4.352   7.790   4.352    -1
15.168   5.194  19.501     2
 9.552   3.488  18.194    -1
15.155  17.323  22.950     2
20.771  15.616   0.000    -1
18.271  14.781  24.180    -1
16.358  19.062   1.836    -1
16.480  10.403   1.713    -1
21.233  16.885  23.387     2
18.115  18.115  20.846    -1
20.029  20.029   0.868    -1
19.906  19.906  16.468    -1
21.219  13.437  11.258     2
 0.078  12.207   8.717    -1
22.422  10.293  12.997    -1
22.545  10.416   4.339    -1
 9.104   1.308   6.936     2
 5.986   0.078   9.476    -1
 7.900  22.422   5.196    -1
 7.778  22.545  13.854    -1
 9.090   4.757  19.065     2
16.885  19.065  21.219     2
18.115  21.605   0.078    -1
20.029  17.326  22.422    -1
19.906   1.725  22.545    -1
13.437   6.936  21.233     2
 1.308  11.258   9.090     2
 0.078   8.717  12.207    -1
22.422  12.997  10.293    -1
22.545   4.339  10.416    -1
 4.757  23.387   9.104     2
 5.986  20.846   5.986    -1
 7.900   0.868   7.900    -1
 7.778  16.468   7.778    -1
19.065  21.233   1.308     2
21.605  18.115   0.078    -1
17.326  20.029  22.422    -1
 1.725  19.906  22.545    -1
 6.936  21.219   4.757     2
 9.476   0.078   5.986    -1
 5.196  22.422   7.900    -1
13.854  22.545   7.778    -1
11.258   9.104  16.885     2
23.387   9.090  13.437     2
20.846  12.207  12.207    -1
 0.868  10.293  10.293    -1
16.468  10.416  10.416    -1
 1.308   9.090  11.258     2
 0.000  14.706   9.552    -1
 4.757   9.104  23.387     2
 6.064   3.488  21.681    -1
 5.986   5.986  20.846    -1
 7.900   7.900   0.868    -1
 7.778   7.778  16.468    -1
16.885  21.219  19.065     2
18.194   2.577  20.771    -1
18.115   0.078  21.605    -1
20.029  22.422  17.326    -1
```

```
19.906  22.545   1.725    -1
13.437  21.233   6.936     2
12.129  15.616   8.641    -1
23.387  13.437   9.090     2
21.681  12.129  14.706    -1
11.258  16.885   9.104     2
 9.552  18.194   3.488    -1
 6.936   4.757  21.219     2
 8.641   6.064   2.577    -1
 9.476   5.986   0.078    -1
 5.196   7.900  22.422    -1
13.854   7.778  22.545    -1
19.065   1.308  21.233     2
20.771   0.000  15.616    -1
21.605   0.078  18.115    -1
17.326  22.422  20.029    -1
 1.725  22.545  19.906    -1
21.219  11.258  13.437     2
 2.577   9.552  12.129    -1
21.233  23.387  16.885     2
15.616  21.681  18.194    -1
18.115  20.846  18.115    -1
20.029   0.868  20.029    -1
19.906  16.468  19.906    -1
 9.090  19.065   4.757     2
14.706  20.771   6.064    -1
 9.104   6.936   1.308     2
 3.488   8.641   0.000    -1
 5.986   9.476   0.078    -1
 7.900   5.196  22.422    -1
 7.778  13.854  22.545    -1
 3.026   7.372   0.871     2
 6.142   6.142   3.412    -1
 4.228   4.228  23.390    -1
 4.352   4.352   7.790    -1
 3.039  10.821  13.000     2
15.155  22.950  17.323     2
18.271  24.180  14.781    -1
16.358   1.836  19.062    -1
16.480   1.713  10.403    -1
15.168  19.501   5.194     2
 7.372   5.194   3.039     2
 6.142   2.653  24.180    -1
 4.228   6.932   1.836    -1
 4.352  22.532   1.713    -1
10.821  17.323   3.026     2
22.950  13.000  15.168     2
19.501   0.871  15.155     2
18.271   3.412  18.271    -1
16.358  23.390  16.358    -1
16.480   7.790  16.480    -1
 5.194   3.026  22.950     2
 2.653   6.142  24.180    -1
 6.932   4.228   1.836    -1
22.532   4.352   1.713    -1
17.323   3.039  19.501     2
14.781  24.180  18.271    -1
19.062   1.836  16.358    -1
```

```
10.403   1.713  16.480    -1
13.000  15.155   7.372     2
 0.871  15.168  10.821     2
10.821   3.039  13.000     2
12.129  21.681  14.706    -1
12.051  24.180  15.541    -1
13.965   1.836  11.261    -1
13.842   1.713  19.919    -1
 7.372   3.026   0.871     2
 6.064   8.641   2.577    -1
19.501  15.168   5.194     2
18.194   9.552   3.488    -1
22.950  15.155  17.323     2
 0.000  20.771  15.616    -1
24.180  18.271  14.781    -1
 1.836  16.358  19.062    -1
 1.713  16.480  10.403    -1
13.000  22.950  15.168     2
14.706   0.000   9.552    -1
15.541  24.180  12.051    -1
11.261   1.836  13.965    -1
19.919   1.713  13.842    -1
 0.871  19.501  15.155     2
 2.577  18.194  20.771    -1
 3.412  18.271  18.271    -1
23.390  16.358  16.358    -1
 7.790  16.480  16.480    -1
 5.194   7.372   3.039     2
 3.488   6.064  21.681    -1
17.323  10.821   3.026     2
15.616  12.129   8.641    -1
15.168   0.871  10.821     2
 9.552   2.577  12.129    -1
12.051   3.412  12.051    -1
13.965  23.390  13.965    -1
13.842   7.790  13.842    -1
15.155  13.000   7.372     2
20.771  14.706   6.064    -1
 3.039  17.323  19.501     2
21.681  15.616  18.194    -1
24.180  14.781  18.271    -1
 1.836  19.062  16.358    -1
 1.713  10.403  16.480    -1
 3.026   5.194  22.950     2
 8.641   3.488   0.000    -1
 9.104   4.757  23.387     2
 9.090   1.308  11.258     2
12.207   0.078   8.717    -1
10.293  22.422  12.997    -1
10.416  22.545   4.339    -1
21.233  13.437   6.936     2
21.219  16.885  19.065     2
 0.078  18.115  21.605    -1
22.422  20.029  17.326    -1
22.545  19.906   1.725    -1
 4.757   6.936  21.219     2
 1.308  19.065  21.233     2
 0.078  21.605  18.115    -1
```

22.422	17.326	20.029	-1
22.545	1.725	19.906	-1
13.437	23.387	9.090	2
12.207	20.846	12.207	-1
10.293	0.868	10.293	-1
10.416	16.468	10.416	-1
16.885	11.258	9.104	2
6.936	9.104	1.308	2
19.065	9.090	4.757	2
23.387	21.233	16.885	2
20.846	18.115	18.115	-1
0.868	20.029	20.029	-1
16.468	19.906	19.906	-1
11.258	21.219	13.437	2
8.717	0.078	12.207	-1
12.997	22.422	10.293	-1
4.339	22.545	10.416	-1
13.437	21.219	11.258	2
12.129	2.577	9.552	-1
16.885	21.233	23.387	2
18.194	15.616	21.681	-1
4.757	9.090	19.065	2
6.064	14.706	20.771	-1
1.308	9.104	6.936	2
0.000	3.488	8.641	-1
0.078	5.986	9.476	-1
22.422	7.900	5.196	-1
22.545	7.778	13.854	-1
11.258	1.308	9.090	2
9.552	0.000	14.706	-1
23.387	4.757	9.104	2
21.681	6.064	3.488	-1
20.846	5.986	5.986	-1
0.868	7.900	7.900	-1
16.468	7.778	7.778	-1
19.065	16.885	21.219	2
20.771	18.194	2.577	-1
6.936	13.437	21.233	2
8.641	12.129	15.616	-1
9.090	23.387	13.437	2
14.706	21.681	12.129	-1
9.104	11.258	16.885	2
3.488	9.552	18.194	-1
21.219	6.936	4.757	2
2.577	8.641	6.064	-1
0.078	9.476	5.986	-1
22.422	5.196	7.900	-1
22.545	13.854	7.778	-1
21.233	19.065	1.308	2
15.616	20.771	0.000	-1
15.155	19.501	0.871	2
15.168	22.950	13.000	2
3.026	10.821	17.323	2
3.039	7.372	5.194	2
24.180	6.142	2.653	-1
1.836	4.228	6.932	-1
1.713	4.352	22.532	-1
19.501	17.323	3.039	2

```
22.950   5.194   3.026     2
24.180   2.653   6.142    -1
 1.836   6.932   4.228    -1
 1.713  22.532   4.352    -1
10.821   0.871  15.168     2
 7.372  13.000  15.155     2
17.323  15.155  22.950     2
 5.194  15.168  19.501     2
 0.871   3.026   7.372     2
 3.412   6.142   6.142    -1
23.390   4.228   4.228    -1
 7.790   4.352   4.352    -1
13.000   3.039  10.821     2
10.821  15.168   0.871     2
12.129   9.552   2.577    -1
12.051  12.051   3.412    -1
13.965  13.965  23.390    -1
13.842  13.842   7.790    -1
 7.372  15.155  13.000     2
 6.064  20.771  14.706    -1
19.501   3.039  17.323     2
18.194  21.681  15.616    -1
22.950   3.026   5.194     2
 0.000   8.641   3.488    -1
13.000  10.821   3.039     2
14.706  12.129  21.681    -1
15.541  12.051  24.180    -1
11.261  13.965   1.836    -1
19.919  13.842   1.713    -1
 0.871   7.372   3.026     2
 2.577   6.064   8.641    -1
 5.194  19.501  15.168     2
 3.488  18.194   9.552    -1
17.323  22.950  15.155     2
15.616   0.000  20.771    -1
15.168  13.000  22.950     2
 9.552  14.706   0.000    -1
12.051  15.541  24.180    -1
13.965  11.261   1.836    -1
13.842  19.919   1.713    -1
15.155   0.871  19.501     2
20.771   2.577  18.194    -1
 3.039   5.194   7.372     2
21.681   3.488   6.064    -1
 3.026  17.323  10.821     2
 8.641  15.616  12.129    -1
 9.104  16.885  11.258     2
 9.090  13.437  23.387     2
12.207  12.207  20.846    -1
10.293  10.293   0.868    -1
10.416  10.416  16.468    -1
21.233   1.308  19.065     2
21.219   4.757   6.936     2
 4.757  19.065   9.090     2
 1.308   6.936   9.104     2
13.437  11.258  21.219     2
12.207   8.717   0.078    -1
10.293  12.997  22.422    -1
```

```
                10.416   4.339  22.545    -1
                16.885  23.387  21.233     2
                 6.936  21.233  13.437     2
                19.065  21.219  16.885     2
                23.387   9.104   4.757     2
                11.258   9.090   1.308     2
                 8.717  12.207   0.078    -1
                12.997  10.293  22.422    -1
                 4.339  10.416  22.545    -1
                13.437   9.090  23.387     2
                12.129  14.706  21.681    -1
                16.885   9.104  11.258     2
                18.194   3.488   9.552    -1
                 4.757  21.219   6.936     2
                 6.064   2.577   8.641    -1
                 1.308  21.233  19.065     2
                 0.000  15.616  20.771    -1
                11.258  13.437  21.219     2
                 9.552  12.129   2.577    -1
                23.387  16.885  21.233     2
                21.681  18.194  15.616    -1
                19.065   4.757   9.090     2
                20.771   6.064  14.706    -1
                 6.936   1.308   9.104     2
                 8.641   0.000   3.488    -1
                 9.090  11.258   1.308     2
                14.706   9.552   0.000    -1
                 9.104  23.387   4.757     2
                 3.488  21.681   6.064    -1
                21.219  19.065  16.885     2
                 2.577  20.771  18.194    -1
                21.233   6.936  13.437     2
                15.616   8.641  12.129    -1
                15.155   7.372  13.000     2
                15.168  10.821   0.871     2
                 3.026  22.950   5.194     2
                 3.039  19.501  17.323     2
                19.501   5.194  15.168     2
                22.950  17.323  15.155     2
                10.821  13.000   3.039     2
                 7.372   0.871   3.026     2
                17.323   3.026  10.821     2
                 5.194   3.039   7.372     2
                 0.871  15.155  19.501     2
                13.000  15.168  22.950     2
                                             ];

trans       = [
                24.258    0.000   0.000
                0.000    24.258   0.000
                0.000     0.000  24.258
                                        ];

cluster     = [
                7.372   13.000  15.1550    2
                9.104   11.258  16.8850    2
                7.372   15.155  13.0000    2
                8.641   12.129  15.6160   -1
```

```
                7.790   13.842  13.8420   -1
                6.142   12.051  14.7810   -1
                6.932   13.965  16.3580   -1
                7.372   15.168  17.3230    2
                5.194   10.821  15.1550    2
                                             ];
Quantumclus = [
                7.358500    13.016100    15.013000
                9.052600    11.281600    16.776500
                7.433900    15.187000    13.015400
                8.766200    12.058100    15.387300
                8.086700    13.948800    13.808600
                6.077400    12.094700    14.475700
                6.741100    13.794500    16.383700
                7.286900    15.013300    17.245200
                5.214900    10.921600    15.124600
                6.064000     9.552000    15.616000
                8.641000    14.706000    18.194000
                6.142000    15.541000    18.271000
                4.228000    11.261000    16.358000
                7.900000    10.293000    17.326000
                9.476000    12.207000    18.115000
                6.142000    14.781000    12.051000
                4.352000    10.403000    13.842000
                6.932000    16.358000    13.965000
                7.790000    16.480000    16.480000
                8.641000    15.616000    12.129000
                0.416000    10.416000    16.468000
                9.719223    12.004579    14.253239
                0.476434    11.945928    13.460688
                0.845603    13.086981    12.854017
                1.826065    13.065990    11.870223
                2.418999    11.848399    11.532350
                2.011172    10.677052    12.176918
                1.022492    10.758436    13.145991
                0.642634     9.898609    13.683853
                2.448524     9.715761    11.933920
                3.190182    11.809539    10.768984
                2.112496    13.989654    11.381134
                0.308310    13.967662    13.181924
                                                 ];

Adsorb      = [
                0.476434    11.945928    13.460688
                0.845603    13.086981    12.854017
                1.826065    13.065990    11.870223
                2.418999    11.848399    11.532350
                2.011172    10.677052    12.176918
                1.022492    10.758436    13.145991
                0.642634     9.898609    13.683853
                2.448524     9.715761    11.933920
                3.190182    11.809539    10.768984
                2.112496    13.989654    11.381134
                0.308310    13.967662    13.181924
                                                 ];

Rbound=38;
Rfix=15;
```

```
Rfix2=18;
nump=13;
RcutReal=65;
RcutRecip=55;
```

Appendix B

Matlab codes to calculate ewald potential and generate a set of point charges.

```
%Step1:Create boundary of point charges
q=[ucell(:,4)];
Amountq=size(q);Amountq=Amountq(1,1);
AmountQuant=size(Quantumclus);AmountQuant=AmountQuant(1,1);
CenterQ=sum(Quantumclus)/AmountQuant;
AmountAds=size(Adsorb);AmountAds=AmountAds(1,1);
if AmountAds == 0
    CenterAds=CenterQ;
else
CenterAds=sum(Adsorb)/AmountAds;
end
sizecluster=size(cluster);sizecluster=sizecluster(1,1);
Center=sum(cluster(:,1:3))/sizecluster;
AddX=[(-1+round(-Rbound/trans(1,1))) (1+round(Rbound/trans(1,1)))];
AddY=[(-1+round(-Rbound/trans(2,2))) (1+round(Rbound/trans(2,2)))];
AddZ=[(-1+round(-Rbound/trans(3,3))) (1+round(Rbound/trans(3,3)))];
Addblock=0;Giantcell=[];
for S=AddX(1,1):AddX(1,2)
    for T=AddY(1,1):AddY(1,2)
        for U=AddZ(1,1):AddZ(1,2)
            Pluspoint=[ones(Amountq,1)*S*trans(1,1)
ones(Amountq,1)*T*trans(2,2) ones(Amountq,1)*U*trans(3,3)];
            Giantcell=[Giantcell
                       (ucell(:,1:3)+Pluspoint) q];
            Addblock=Addblock+1;
        end
    end
end
 sizeG=size(Giantcell); sizeG=sizeG(1,1);
 a=0;Point0=[];
 for s=1:sizeG
     if ((Giantcell(s,1)-CenterQ(1,1))^2+(Giantcell(s,2)-
CenterQ(1,2))^2+(Giantcell(s,3)-CenterQ(1,3))^2) < Rbound^2
         a=a+1;
         Point0(a,:)=Giantcell(s,:);
     end
 end
sizeP=size(Point0);
%Seperate cluster from Point0
Point=[];Equal=[];Closed=[];Far=[];
b=0;c=0;d=0;
for s=1:sizeP
    a=0;
    for t=1:sizecluster
        Far(s,t)=((Point0(s,1)-cluster(t,1))^2+(Point0(s,2)-
cluster(t,2))^2+(Point0(s,3)-cluster(t,3))^2)^.5;
        if (Far(s,t)==0) | (Far(s,t)<0.75)
            c=c+1;
            Equal(c,:)=Point0(s,:);
        else
            a=a+1;
        end
    end
```

```
    if (a==sizecluster) & (min(Far(s,:)) > 2.1)
        b=b+1;
        Point(b,:)=Point0(s,:);
    elseif (a==sizecluster) & (min(Far(s,:)) <= 2.1)
        d=d+1;
        Closed(d,:)=Point0(s,:);
    end
end
Point=[Closed(:,1:3) Closed(:,4)/2;Point];
Amounteq=size(Equal);Amounteq=Amounteq(1,1);
Amountcl=size(Closed);Amountcl=Amountcl(1,1);
Amountch=size(Point);Amountch=Amountch(1,1);
%Seperate the points which are fixed charges and optimized charges
a=0;Pointfix=[];b=0;Pointopt=[];Dist=zeros(Amountch,1);c=0;Pointfix2=
[];
for s=1:Amountch
    Dist(s,1)=((Point(s,1)-CenterAds(1,1))^2+(Point(s,2)-
CenterAds(1,2))^2+(Point(s,3)-CenterAds(1,3))^2)^.5;
    if Dist(s,1) < Rfix
       a=a+1;
       Pointfix(a,:)=Point(s,:);Distfix(a,1)=Dist(s,1);
   elseif Dist(s,1) >= Rfix & Dist(s,1) < Rfix2
        c=c+1;
        Pointfix2(c,:)=Point(s,:);Distfix2(c,1)=Dist(s,1);
    else
        b=b+1;
        Pointopt(b,:)=Point(s,:);Distopt(b,1)=Dist(s,1);
    end
end
Amountfix=size(Pointfix);Amountfix=Amountfix(1,1);
Amountfix2=size(Pointfix2);Amountfix2=Amountfix2(1,1);
Amountopt=size(Pointopt);Amountopt=Amountopt(1,1);

a=0;PointH=[];
for s=1:Amountcl
    for t=1:sizecluster
        if (((Closed(s,1)-cluster(t,1))^2 + (Closed(s,2)-
cluster(t,2))^2 + (Closed(s,3)-cluster(t,3))^2)^.5) < 1.5
            a=a+1;
            PointH(a,:)=cluster(t,:);
        end
    end
end

%Step2:Creat grid in quantum cluster area
FarQuant=[];
for s=1:AmountQuant
    FarQuant(s,1)=((CenterQ(1,1)-Quantumclus(s,1))^2+(CenterQ(1,2)-
Quantumclus(s,2))^2+(CenterQ(1,3)-Quantumclus(s,3))^2)^.5;
end
MaxXYZ=max(Quantumclus); MinXYZ=min(Quantumclus);
Length=MaxXYZ-MinXYZ;
Widthmax=1.5*Length;
Interv=max(Widthmax)/nump;
Upper=MaxXYZ+Widthmax/4; Lower=MinXYZ-Widthmax/4;
numpX=1+round(Widthmax(1,1)/Interv);
numpY=1+round(Widthmax(1,2)/Interv);
numpZ=1+round(Widthmax(1,3)/Interv);
```

```
GridX=linspace(Lower(1,1),Upper(1,1),numpX);
GridY=linspace(Lower(1,2),Upper(1,2),numpY);
GridZ=linspace(Lower(1,3),Upper(1,3),numpZ);
a=0;b=0;Grid=[];FarGrid=[];
for Sx=1:(numpX)
    for Sy=1:(numpY)
        for Sz=1:(numpZ)
            a=a+1;
            FarGrid(a,1)=(((GridX(Sx)-CenterQ(1,1))^2+(GridY(Sy)-
CenterQ(1,2))^2+(GridZ(Sz)-CenterQ(1,3))^2)^0.5);
            if FarGrid(a,1)<(1.5*max(FarQuant))
                b=b+1;
                Grid(b,1)=GridX(Sx);
                Grid(b,2)=GridY(Sy);
                Grid(b,3)=GridZ(Sz);
            end
        end
    end
end
Amountg=size(Grid); Amountg=Amountg(1,1);

%STEP3:Calculate Ewald Potential
%REAL
alpha=0.1;
lmax=round(RcutReal/trans(1,1))+1;
mmax=round(RcutReal/trans(2,2))+1;
nmax=round(RcutReal/trans(3,3))+1;
%Calculate Ewald Potential
Poreal=zeros(Amountg,1);
CenterU=sum(ucell(:,1:3))/Amountq;
for l=-lmax:lmax
for m=-mmax:mmax
for n=-nmax:nmax
    CenterCell=CenterU+l*trans(1,:)+m*trans(2,:)+n*trans(3,:);
    if ((CenterCell(1,1)-CenterQ(1,1))^2+(CenterCell(1,2)-
CenterQ(1,2))^2+(CenterCell(1,3)-CenterQ(1,3))^2)^.5 < (RcutReal+25)
        Cell=l*trans(1,:)+m*trans(2,:)+n*trans(3,:);
        Cellpoint=zeros(Amountq,4);
        Cellpoint(:,4)=ucell(:,4);
        for s=1:Amountq
            Cellpoint(s,1:3)=ucell(s,1:3)+Cell;
        end
        R=zeros(Amountg,3*Amountq);
    %Real Potential
        for s=1:Amountg
        for t=1:Amountq
            AbsR=((Cellpoint(t,1)-Grid(s,1))^2+(Cellpoint(t,2)-
Grid(s,2))^2+(Cellpoint(t,3)-Grid(s,3))^2)^0.5;
        if AbsR < RcutReal

        if AbsR ~= 0

Poreal(s,1)=Poreal(s,1)+Cellpoint(t,4)*erfc(alpha*AbsR)/AbsR;
        end
        end
        end
        end
    end
```

```
    14.39976*Poreal(1:3,1)
    [l m n]
end
end
end
Poreal=14.39976*Poreal;

%RECIPROCAL
lmax=round(RcutRecip/trans(1,1))+1;
mmax=round(RcutRecip/trans(2,2))+1;
nmax=round(RcutRecip/trans(3,3))+1;

V=dotvector(trans(1,:),crossvector(trans(2,:),trans(3,:)));
u=crossvector(trans(2,:),trans(3,:))/V;
v=crossvector(trans(3,:),trans(1,:))/V;
w=crossvector(trans(1,:),trans(2,:))/V;
%Calculate Ewald Potential
Porecip=zeros(Amountg,1);Poewald=zeros(Amountg,1);
CenterU=sum(ucell(:,1:3))/Amountq;
for l=-lmax:lmax
for m=-mmax:mmax
for n=-nmax:nmax
    CenterCell=CenterU+l*trans(1,:)+m*trans(2,:)+n*trans(3,:);
    if ((CenterCell(1,1)-CenterQ(1,1))^2+(CenterCell(1,2)-
CenterQ(1,2))^2+(CenterCell(1,3)-CenterQ(1,3))^2)^.5 < (RcutRecip+25)
        Cell=l*trans(1,:)+m*trans(2,:)+n*trans(3,:);
        Cellpoint=zeros(Amountq,4);
        Cellpoint(:,4)=ucell(:,4);
        for s=1:Amountq
            Cellpoint(s,1:3)=ucell(s,1:3)+Cell;
        end
        R=zeros(Amountg,3*Amountq);


    %Reciprocal Potential
        f=[l m n]*[u;v;w];
        Absf=(f(1,1)^2 + f(1,2)^2 +f(1,3)^2)^0.5;
        if (l == 0)&(m == 0)&(n == 0)
            Porecip=Porecip;
        else
            SubPorecip=zeros(Amountg,1);
            for s=1:Amountg
            for t=1:Amountq
            if ((Cellpoint(t,1)-Grid(s,1))^2+(Cellpoint(t,2)-
Grid(s,2))^2+(Cellpoint(t,3)-Grid(s,3))^2)^0.5 < RcutRecip
                R(s,t*3-2)=Grid(s,1)-Cellpoint(t,1);
                R(s,t*3-1)=Grid(s,2)-Cellpoint(t,2);
                R(s,t*3)=Grid(s,3)-Cellpoint(t,3);
            if [R(s,t*3-2) R(s,t*3-1) R(s,t*3)] ~= [0 0 0]

SubPorecip(s,1)=SubPorecip(s,1)+Cellpoint(t,4)*cos(2*pi*dotvector(f,[
R(s,3*t-2) R(s,3*t-1) R(s,3*t)]));
            end
            end
            end
            end
            Porecip=Porecip+SubPorecip*exp(-
pi^2*Absf^2/alpha^2)/Absf^2;
```

```
        end
        [l m n]
        14.39976/pi/V*Porecip(1:3,1)
    end
end
end
end
Porecip=14.39976/pi/V*Porecip;
Poewald=Poreal+Porecip;

%Step4: Calculate Pocluster, Podiff and Podel and solve linear
equation
%Calculate cluster potential
Pocluster=zeros(Amountg,1);
for s=1:Amountg
    for t=1:Amounteq
        Rcluster=((Grid(s,1)-Equal(t,1))^2+(Grid(s,2)-
Equal(t,2))^2+(Grid(s,3)-Equal(t,3))^2)^0.5;
        if Rcluster ~= 0
        Pocluster(s,1)=Pocluster(s,1)+Equal(t,4)/Rcluster;
        end
    end
    for t=1:Amountcl
        RClosed=((Grid(s,1)-Closed(t,1))^2+(Grid(s,2)-
Closed(t,2))^2+(Grid(s,3)-Closed(t,3))^2)^0.5;
        if RClosed ~= 0
        Pocluster(s,1)=Pocluster(s,1)+0.5*Closed(t,4)/RClosed;
        end
    end
end
Pocluster=14.39976*Pocluster;
%Find Podiff
Podiff=Poewald-Pocluster;
%Find Direct Potential from Points
sumQ=sum(Pointfix2(:,4))+sum(Pointopt(:,4));
Podirect=zeros(Amountg,1);
for s=1:Amountg
    for t=1:Amountfix2
        Podirect(s,1)=Podirect(s,1)+Pointfix2(t,4)/((Grid(s,1)-
Pointfix2(t,1))^2+(Grid(s,2)-Pointfix2(t,2))^2+(Grid(s,3)-
Pointfix2(t,3))^2)^0.5;
    end
    for tt=1:Amountopt
        Podirect(s,1)=Podirect(s,1)+Pointopt(tt,4)/((Grid(s,1)-
Pointopt(tt,1))^2+(Grid(s,2)-Pointopt(tt,2))^2+(Grid(s,3)-
Pointopt(tt,3))^2)^0.5;
    end
end
Podirect=14.39976*Podirect;
%find Podel and solving linear equation
B=zeros(Amountg+4,Amountopt);
for s=1:Amountg
    for t=1:Amountopt
        B(s,t)=1/((Grid(s,1)-Pointopt(t,1))^2+(Grid(s,2)-
Pointopt(t,2))^2+(Grid(s,3)-Pointopt(t,3))^2)^.5;
    end
end
for t=1:Amountopt
```

```
    B(Amountg+1,t)=Pointopt(t,1);
    B(Amountg+2,t)=Pointopt(t,2);
    B(Amountg+3,t)=Pointopt(t,3);
end
B(Amountg+4,:)=ones(1,Amountopt);
sumM=zeros(1,3);

for s=1:Amountfix2
    sumM=sumM+Pointfix2(s,1:3)*Pointfix2(s,4);
end
for s=1:Amountopt
    sumM=sumM+Pointopt(s,1:3)*Pointopt(s,4);
end
sumM=14.39976*sumM;
sumQ=14.39976*sumQ;
Podel=Podiff-Podirect;Podel=[Podel;-sumM(1,1);-sumM(1,2);-sumM(1,3);-
sumQ];
Loop=75;
delta=1/14.39976*(lsqr(B,Podel,0.00000001,Loop));
Pointcharges=[Pointfix2;Pointopt(:,1:3) Pointopt(:,4)+delta];
AmountP=Amountfix2+Amountopt;
%Calculate deviation
Porecal=zeros(Amountg,1);
for s=1:Amountg
    for t=1:AmountP

Porecal(s,1)=Porecal(s,1)+14.39976*Pointcharges(t,4)/((Grid(s,1)-
Pointcharges(t,1))^2+(Grid(s,2)-Pointcharges(t,2))^2+(Grid(s,3)-
Pointcharges(t,3))^2)^0.5;
    end
end
Vabs=0;
for s=1:Amountg
    Vabs=abs(Podiff(s,1)-Porecal(s,1))+Vabs;
end
Vabs=Vabs/Amountg;
Vrms=0;
for s=1:Amountg
    Vrms=((Podiff(s,1)-Porecal(s,1)))^2 + Vrms;
end
Vrms=(Vrms/Amountg)^.5;

%Step5:Fit Podiff and minimize charges by reiterating linear equation
while (Vabs > 0.5) | (max(Pointcharges) > 5) | (min(Pointcharges) < -
5)
Podiffnew=[];Gridnew=[];a=0;
for s=1:Amountg
    if abs(Porecal(s,1)-Podiff(s,1)) < 1.75*Vabs
        a=a+1;
        Gridnew(a,:)=Grid(s,:);
        Podiffnew(a,1)=Podiff(s,1);
    end
end

Grid=Gridnew;
Amountg=size(Grid);Amountg=Amountg(1,1);
Podiff=Podiffnew;
```

```
%Find Direct Potential from Points
sumQ=sum(Pointfix2(:,4))+sum(Pointopt(:,4));
Podirect=zeros(Amountg,1);
for s=1:Amountg
    for t=1:Amountfix2
        Podirect(s,1)=Podirect(s,1)+Pointfix2(t,4)/((Grid(s,1)-
Pointfix2(t,1))^2+(Grid(s,2)-Pointfix2(t,2))^2+(Grid(s,3)-
Pointfix2(t,3))^2)^0.5;
    end
    for tt=1:Amountopt
        Podirect(s,1)=Podirect(s,1)+Pointopt(tt,4)/((Grid(s,1)-
Pointopt(tt,1))^2+(Grid(s,2)-Pointopt(tt,2))^2+(Grid(s,3)-
Pointopt(tt,3))^2)^0.5;
    end
end
Podirect=14.39976*Podirect;
B=zeros(Amountg+4,Amountopt);
for s=1:Amountg
    for t=1:Amountopt
        B(s,t)=1/((Grid(s,1)-Pointopt(t,1))^2+(Grid(s,2)-
Pointopt(t,2))^2+(Grid(s,3)-Pointopt(t,3))^2)^.5;
    end
end
for t=1:Amountopt
    B(Amountg+1,t)=Pointopt(t,1);
    B(Amountg+2,t)=Pointopt(t,2);
    B(Amountg+3,t)=Pointopt(t,3);
end
B(Amountg+4,:)=ones(1,Amountopt);
sumM=zeros(1,3);

for s=1:Amountfix2
    sumM=sumM+Pointfix2(s,1:3)*Pointfix2(s,4);
end
for s=1:Amountopt
    sumM=sumM+Pointopt(s,1:3)*Pointopt(s,4);
end
sumM=14.39976*sumM;
sumQ=14.39976*sumQ;
Podel=Podiff-Podirect;Podel=[Podel;-sumM(1,1);-sumM(1,2);-sumM(1,3);-
sumQ];
if max(Pointcharges) > 5 | min(Pointcharges) < -5
   Loop = Loop - 3;
end
delta=1/14.39976*(lsqr(B,Podel,0.00000001,Loop));
Pointcharges=[Pointfix2;Pointopt(:,1:3) Pointopt(:,4)+delta];
AmountP=Amountfix2+Amountopt;
%Calculate deviation
Porecal=zeros(Amountg,1);
for s=1:Amountg
    for t=1:AmountP

Porecal(s,1)=Porecal(s,1)+14.39976*Pointcharges(t,4)/((Grid(s,1)-
Pointcharges(t,1))^2+(Grid(s,2)-Pointcharges(t,2))^2+(Grid(s,3)-
Pointcharges(t,3))^2)^0.5;
    end
end
Vabs=0;
```

```
for s=1:Amountg
    Vabs=abs(Podiff(s,1)-Porecal(s,1))+Vabs;
end
Vabs=Vabs/Amountg;
Vrms=0;
for s=1:Amountg
    Vrms=((Podiff(s,1)-Porecal(s,1)))^2 + Vrms;
end
Vrms=(Vrms/Amountg)^.5;
Amountg
Loop
end
```

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