Molecular geometry-dependent atomic charge calculation with modified charge equilibration method

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Abstract

We have improved a modified charge equilibration (MQEq) method for calculating the geometry-dependent distribution of atomic charges. In this paper, Ohno-Klopman, Ohno and DasGupta-Huzinaga equations are adopted to express the shielding effect, and the calculated atomic charges with these MQEq methods are in good agreement with those by the HF/6-31G(d,p) calculations for several organic molecules. These MQEq methods would be useful to estimate the charge distribution for large molecules.

Key Words: charge equilibration method, QEq, atomic charge, Ohno-Klopman equation key words

Area of Interest: Molecular Computing
1. Introduction

In the classical force field approach, a non-bonded interaction is represented by the following formula:

\[ E_{\text{non-bonded}} = E_{\text{short+middle}} + E_{\text{ex}} \]  

(1)

A serious problem is that the conventional molecular mechanics and the molecular dynamics simulations use the fixed charges that cannot represent the relaxation of charge distribution. The atomic charges depend upon varied molecular geometry, which is essential to evaluate the appropriate electrostatic energies, for biomolecular simulation such as receptor-ligand docking.

In 2001, Nakano et al. proposed the modified charge equilibration (MQEq) method [1] for calculating the geometry-dependent distribution of atomic charges with the aid of Nishimoto-Mataga equation [2]. It is not necessary in their method to iterate simultaneous equations for evaluating charge equilibration in contrast to the original QEq method [3]. The MQEq charge is in good agreement with the Mulliken charge obtained by the HF/STO-3G level of theory [1]. On the other hand, Oda and Hirono introduced an atom type for a QEq/PD method [4], and appropriate atomic charges were obtained for various molecules [5,6] with the use of Ohno-Klopman equation [7, 8]. In this study, we compare the Ohno-Klopman [7, 8], Ohno [7], and DasGupta-Huzinaga [9] equations to calculate the Coulomb shielding effect with the Nishimoto-Mataga [2] equation that was employed in the previous paper [1]. We apply various MQEq methods to several organic molecules and some polypeptides, and compare the results with the atomic charges obtained through ab initio MO calculations. Through these calculations, we assess the validity of various MQEq methods.

2. Method

In the original QEq method [3], the electrostatic energy is expressed as a sum of intra-atomic contributions and inter-atomic interactions between pairs of atoms:

\[ E_{\text{ex}} = \sum_{i=1}^{N} \left( E_{i}^{0} + \chi_{i}^{0} q_{i} + \frac{1}{2} J_{i}^{0} q_{i}^{2} \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} J_{ij} q_{i} q_{j} , \]  

(2)

where \( N \) is the number of atoms, \( q_{i} \) is an atomic charge and \( E_{i}^{0} \) is the energy of the isolated neutral atom at the ground state. In this work, the Ohno-Klopman (OK) (Eqs. (3) and (4)), Ohno (O) (Eqs. (3) and (5)), DasGupta-Huzinaga (DH) (Eqs. (6) and (7)) equations are used to calculate the Coulomb integrals instead of the Nishimoto-Mataga (NM) (Eqs. (6) and (8)) equation that was used in the previous paper [1],

\[ J_{ij} = \frac{1}{\sqrt{R_{ij}^{2} + \gamma_{ij}}} \]  

(3)
where \( \gamma_{ij} \) is the ionization potential, \( \chi \) is the electron affinity, and \( R_{ij} \) is the distance between the \( i \)-th atom and the \( j \)-th atom. In the following calculations, we used the atomic parameters \( \chi^0 \) and \( J^0_{ii} \) in the literature [3] that are independent of molecules.

We find a set of atomic charges giving a stationary point regarding the electrostatic energy with constraints for the total charge of the system and the subsystems.

\[
\sum_{i=1}^{N_{i}} \sum_{j=1}^{N_{j}} Q_{ij} = \sum_{i=1}^{N_{i}} Q_{total} - \sum_{i=1}^{N_{i}} q_i = 0, \quad (11)
\]

\[
Q_{total} = \sum_{i=1}^{N_{i}} \sum_{j=1}^{N_{j}} Q_{ij} = \sum_{i=1}^{N_{i}} q_i, \quad (12)
\]

where \( N_{mol} \) is the number of the subsystems and \( N_0 = 0 \). Without loss of generality, the I-th subsystem consists of atoms \( N_{i-1} + 1 \) to \( N_{i} \). We consider the following functional \( L \) with multipliers \( \lambda_i \),

\[
L = E_{es} + \sum_{i=1}^{N_{i}} \lambda_i \left( Q_{total} - \sum_{i=1}^{N_{i}} q_i \right). \quad (13)
\]

The derivative of the \( L \) to \( q_i \) is

\[
\frac{\partial L}{\partial q_i} = \frac{\partial E_{es}}{\partial q_i} - \lambda_i = \chi_i^0 + J^0_{ii} q_i + \sum_{j \neq i} J_{ij} q_j - \lambda_i = 0 \quad \text{for } i \in I \quad (14)
\]

Eqs. (12) and (14) give the dense asymmetric simultaneous linear equations:

\[
C\mathbf{q} = \mathbf{D}, \quad (15)
\]

where

\[ C_{(N_j+1)j} = \begin{cases} 1 & \text{for } j \in I \\ 0 & \text{for } j \notin I \end{cases} \]  

(16)

\[ C_j = J_{(N_j+1)j} - J_{ij} \quad \text{for } i \in I \text{ and } i \neq N_j + 1 \]

and

\[ D_{N_j+1} = Q_{\text{total}}^j \]

(17)

\[ D_j = \chi_j^0 - \chi_{N_j+1}^0 \quad \text{for } i \in I \text{ and } i \neq N_j + 1 \]

Since the Ohno-Klopman, Ohno, DasGupta-Huzinaga and Nishimoto-Mataga equations do not contain the atomic charges, \( q_i \), it is not necessary to iterate the simultaneous equations for evaluating a charge equilibration.

Atomic charge calculations were carried out for the following molecules: formaldehyde, acetaldehyde, formamide, formic acid, acetic acid, propane, methylamine, methanol, ethanol, toluene, phenol, and three (\( \alpha \)-helix, \( \beta \)-strand and extended) conformers of polyalanine with five residues, (Ala)\(_5\). Molecular structures of small molecules were taken from the HF/6-31G(d,p) optimized geometries. Three conformers of (Ala)\(_5\) were modeled with the Accelrys InsightII molecular modeling system [10]. The Hartree-Fock-Roothaan [11] calculation with STO-3G [12] and 6-31G(d,p) [13-15] basis sets were performed for those organic molecules and the three conformers of (Ala)\(_5\). The Mulliken [16], the CHELPG [17], the Merz-Singh-Kollman (MSK) [18, 19] and the original QEq charges were calculated using the Gaussian98 program package [20].

3. Results and Discussion

Table 1 shows the standard deviation of the QEq and MQEq atomic charges from some reference charges of the small organic molecules including the H, C, N, and O atoms. The MQEq (NM) atomic charges are in good agreement with the Mulliken charges obtained by the HF/STO-3G calculations, while the MQEq(OK, O, and DH) charges are close to the Mulliken, the CHELPG and the MSK charges at the HF/6-31G(d,p) level of theory.

Milner-White [21] discussed the electronic character of formamide that is a model of peptide bond. The classical formula of peptide bond has the two resonance formulas as shown in Figure 1, in one of which the nitrogen atom has a positive charge (b).

![Resonance structure of peptide bond.](image)

**Figure 1.** Resonance structure of peptide bond.

It is shown that the partial charge of the nitrogen of amides is negative rather than positive from the resonance forms by the quantum mechanical calculations [22]. As shown in Table 2, the MQEq(NM) charges for formamide are in good agreement with the HF/STO-3G charges. The three MQEq(OK,O,DH) charges are very close to the CHELPG and the MSK charges with the strong polar character at the HF/6-31G(d,p) level of theory, but the HF/STO-3G charge does not describe the polar amide bond.
Table 1. Standard deviation of QE and MQE atomic charges of several organic molecules from the reference charges.

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Table 2. Calculated atomic charges of formamide.

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</tbody>
</table>

To confirm the capability of the MQEq(OK,O,DH) method for the polypeptide system, we calculated the charge distribution of the three (α-helix, β-strand and extended) conformers of (Ala)_5. Table 3 shows the standard deviation of atomic charges of the three conformers of (Ala)_5. It is found that the peptide bond’s heavy atoms (N and O) are very polar from the HF/6-31G(d,p) calculations. The MQEq(NM) charges are in good agreement with the HF/STO-3G charges for the peptide. Since the HF/STO-3G charge does not describe the strong polar character, the MQEq(NM) method should not be adopted for the peptide molecule. On the other hand, the MQEq(OK) charges are close to the Mulliken, the CHELPG and the MSK charges at the HF/6-31G(d,p) level of theory. Thus the MQEq(OK) method is appropriate for atomic charge calculations of biomolecules.

Table 3. Standard deviation of QEq and MQEq atomic charges from the reference charges on the α-helix, β-strand, and extended conformers of (Ala)_5.

<table>
<thead>
<tr>
<th>α-helix</th>
<th>HF/STO-3G</th>
<th>HF/6-31G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mulliken</td>
<td>Mulliken</td>
</tr>
<tr>
<td>MQEq(NM)</td>
<td>0.06</td>
<td>0.28</td>
</tr>
<tr>
<td>QEq</td>
<td>0.16</td>
<td>0.13</td>
</tr>
<tr>
<td>MQEq(OK)</td>
<td>0.25</td>
<td>0.06</td>
</tr>
<tr>
<td>MQEq(O)</td>
<td>0.27</td>
<td>0.07</td>
</tr>
<tr>
<td>MQEq(DH)</td>
<td>0.29</td>
<td>0.08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>β-strand</th>
<th>HF/STO-3G</th>
<th>HF/6-31G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mulliken</td>
<td>Mulliken</td>
</tr>
<tr>
<td>MQEq(NM)</td>
<td>0.06</td>
<td>0.27</td>
</tr>
<tr>
<td>QEq</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>MQEq(OK)</td>
<td>0.24</td>
<td>0.07</td>
</tr>
<tr>
<td>MQEq(O)</td>
<td>0.26</td>
<td>0.08</td>
</tr>
<tr>
<td>MQEq(DH)</td>
<td>0.29</td>
<td>0.09</td>
</tr>
</tbody>
</table>
Table 3. (continued)

<table>
<thead>
<tr>
<th>extended</th>
<th>HF/STO-3G Mulliken</th>
<th>HF/6-31G(d,p) CHELPG</th>
<th>MKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MQEq(NM)</td>
<td>0.07 0.28 0.33 0.33</td>
<td>MQEq(OK) 0.25 0.07 0.23 0.22</td>
<td>MQEq(O) 0.27 0.08 0.17 0.15</td>
</tr>
</tbody>
</table>

Figure 2 shows shielded Coulomb potentials between two carbon atoms ($J_{C-C}$). As shown in Figure 2, the screening effect strengthens in order of OK, DH, and NM. A similar tendency was seen about nitrogen and oxygen atom pairs (Figure 3 and 4). The difference of this screening effect is one of the reasons for the above results.

![Figure 2. Shielded potentials between two carbon atoms. Abbreviation is as follows; OK: Ohno-Klopman, DH: DasGupta-Huzinaga, NM: Nishimoto-Mataga, 14.338/R: unshielded Coulomb potential.](image-url)
Figure 3. Shielded potentials between two nitrogen atoms. Abbreviation is as follows; OK: Ohno-Klopman, DH: DasGuputa-Huzinaga, NM: Nishimoto-Mataga, 14.338/R: unshielded Coulomb potential.

Figure 4. Shielded potentials between two oxygen atoms. Abbreviation is as follows; OK: Ohno-Klopman, DH: DasGuputa-Huzinaga, NM: Nishimoto-Mataga, 14.338/R: unshielded Coulomb potential.
4. Concluding Remarks

Since the calculated atomic charges with the MQEq (Ohno-Klopman, Ohno, and DasGupta-Huzinaga) methods are in good agreement with those using the HF/6-31G (d,p) calculations for the small organic molecules and peptides, it would be useful to calculate the protein’s electrostatic potential and an electric field with these methods, appropriately accounting for polarization effects. In addition, the MQEq calculation is faster than the original QEq procedure since the simultaneous linear equations do not need to be solved iteratively. It is also remarked that analytical gradient of electrostatic energy which can be calculated easily in the MQEq method is crucial to perform the geometry optimization and molecular dynamics simulations. Furthermore, by introducing explicit atom types and the parameter optimization of $\chi_A^\alpha$ and $J_A^\alpha\alpha$ with MSK charges obtained by MP2 calculations, the MQEq method is expected to allow the more accurate calculation of atomic charges. Such studies are in progress.

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References

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