A new definition of atomic charges based on a variational principle for the electrostatic potential energy
TaiSung Lee, Darrin M. York, and Weitao Yang

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INTRODUCTION

The concept of net atomic charges in molecules is fundamental to chemistry. For instance, atomic charge has been used to describe the processes of electronegativity equalization and charge transfer in chemical reactions, and to model the electrostatic potential outside molecular surfaces.

Atomic charges have been defined based on population analysis, partitioning of the molecular density into atomic densities, electronegativity equalization techniques, electrostatic potential fitting procedures, and generalized atomic polar tensors. However, no single definition of atomic charge has universal applicability. Consequently, one must choose a definition of atomic charge that is best suited to represent a given set of properties.

Frequently atomic charges are derived from experimental data or electronic structure calculations for the purpose of providing an empirical representation of the electrostatic field used in molecular simulations. The most commonly employed methods for deriving charges for this purpose involve least-squares fitting of the electrostatic potential at a given set of fitting points, and does not rely on an arbitrary set of fitting points as do conventional electrostatic potential fitting procedures. The dipole moments and electrostatic potentials calculated from atomic charges obtained from this method agree well with those from self-consistent-field calculations. The new method also provides a spherical-atom potential model that may be useful in future generation molecular simulation force fields.

THEORY

Here we develop a definition of atomic charge based on the optimal representation of the molecular density by a superposition of spherical atomic densities. The atomic charge is determined from the corresponding spherical-atom model density by quadrature.

Given an electron density \( \rho \), consider the quantity \( U \) as a functional of the trial potential \( \tilde{\phi} \).

\[
U(\tilde{\phi}) = \frac{1}{8\pi} \int \tilde{\phi}(\mathbf{r}) \nabla^2 \tilde{\phi}(\mathbf{r}) d\mathbf{r} + \int \tilde{\phi}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}.
\]

A necessary condition for \( U \) to take on a maximum value with respect to variations in the trial potential is

\[
\frac{\delta U}{\delta \tilde{\phi}(\mathbf{r})} = \frac{1}{4\pi} \nabla^2 \tilde{\phi}(\mathbf{r}) + \rho(\mathbf{r}) = 0.
\]

Hence, the trial potential \( \tilde{\phi} \) that maximizes \( U \) is a solution of the Poisson equation for the input density \( \rho \). This principle has been used by Luty et al. to solve the Poisson equation.

It can be shown that maximizing \( U \) is equivalent to minimizing the Dirichlet functional \( F \) defined as

\[
F(\phi) = \frac{1}{8\pi} \int \phi(\mathbf{r}) \nabla^2 \phi(\mathbf{r}) d\mathbf{r} + \int \phi(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}.
\]

This principle has been used by Luty et al. to solve the Poisson equation.

It can be shown that maximizing \( U \) is equivalent to minimizing the Dirichlet functional \( F \) defined as

\[
A new definition of atomic charges based on a variational principle for the electrostatic potential energy

Tai-Sung Lee
Department of Chemistry, Duke University, Durham, North Carolina 27708-0354

Darrin M. York
Department of Chemistry, Duke University, Durham, North Carolina 27708-0354 and North Carolina Supercomputing Center, MCNC, Research Triangle Park, North Carolina 27709-12889

Weitao Yang
Department of Chemistry, Duke University, Durham, North Carolina 27708-0354

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A unique definition of atomic charges in molecules is presented based on a variational principle involving the electrostatic potential energy. The method requires only the electron density as input, and does not rely on an arbitrary set of fitting points as do conventional electrostatic potential fitting procedures. The definition is based on the construction of spherical-atom model potentials, and hence is ideal for use in molecular simulations.

**TABLE I.** Exponents used in the Slater-type basis functions.

<table>
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<tr>
<th>Atom</th>
<th>H</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Cl</th>
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<tbody>
<tr>
<td>Exponent ( n_A )</td>
<td>2.66</td>
<td>2.07</td>
<td>3.58</td>
<td>4.27</td>
<td>4.91</td>
<td>5.64</td>
<td>6.29</td>
<td>6.71</td>
<td>1.71</td>
</tr>
</tbody>
</table>

\( ^a \)Unit: a.u.
\[ F = \int \left[ \mathbf{E}(\mathbf{r}) - \mathbf{\tilde{E}}(\mathbf{r}) \right]^2 d\mathbf{r}, \]

where \( \mathbf{E}(\mathbf{r}) \) and \( \mathbf{\tilde{E}}(\mathbf{r}) \) are the input and model electric fields, respectively. Since it is the electric field, not the potential, that determine the electrostatic force on an atom, this interpretation of the atomic charge definition may have particular relevance for molecular dynamic simulations. This principle has been previously employed to model electron densities using cone functions, Gaussian functions, and atomic orbitals.22,23

Here we model the potential by a set of spherical functions centered at the nuclear positions. Consider the trial potential \( f \) of the form,

![Graphs and Figures]

FIG. 1. The results of atomic charges (△) and \( U (\bigcirc) \) with respect to number of basis functions.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>ESPD</th>
<th>PM</th>
<th>PMTD</th>
</tr>
</thead>
<tbody>
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<td>BH</td>
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<td>-0.195</td>
<td>-0.266</td>
<td>-0.266</td>
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<tr>
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<td>Li</td>
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<td>0.721</td>
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<tr>
<td>LiF</td>
<td>Li</td>
<td>0.773</td>
<td>0.797</td>
<td>0.797</td>
</tr>
<tr>
<td>CO</td>
<td>C</td>
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<td>-0.047</td>
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<td>CO₂</td>
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<tr>
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<td>0.402</td>
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<tr>
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<td>H</td>
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<td>-0.447</td>
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<tr>
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<td>0.495</td>
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<td>H</td>
<td>H(carbon)</td>
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<td>0.070</td>
<td>0.069</td>
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<table>
<thead>
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<th>Molecule</th>
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<th>PM</th>
<th>SCF density</th>
<th>Experiment</th>
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<td>0.51</td>
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<td>2.18</td>
<td>2.32</td>
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<tr>
<td>LiF</td>
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<td>0.101</td>
<td>0.094</td>
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<td>H₂O</td>
<td>0.740</td>
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<td>HF</td>
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<td>0.719</td>
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<tr>
<td>NH₃</td>
<td>0.611</td>
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<td>0.576</td>
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<td>0.589</td>
<td>0.55</td>
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<tr>
<td>CH₃OH</td>
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<td>0.639</td>
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</tr>
<tr>
<td>NH₂CHO</td>
<td>1.42</td>
<td>1.41</td>
<td>1.42</td>
<td>1.47</td>
</tr>
</tbody>
</table>

[a] Unit: a.u.
\[ \tilde{\phi}(\mathbf{r}) = \sum_{A,n} C_{n}^{A} f_{n}^{A}(|\mathbf{r} - \mathbf{R}_{A}|) , \]  

where the index \( A \) sums over different atoms and \( n \) sums over spherical functions \( f_{n}^{A}(r) \) centered at the nuclear position \( \mathbf{R}_{A} \). In this basis, the functional \( U \) can be rewritten

\[ U = \frac{1}{8\pi} \sum_{A,n} \sum_{A',n'} C_{n}^{A} C_{n'}^{A'} \left( f_{n}^{A} \nabla^2 f_{n'}^{A'} \right) + \sum_{A,n} C_{n}^{A} \left( f_{n}^{A} |\rho| \right) . \]

Maximization of Eq. (4) under the normalization constraint

\[ \int -\frac{1}{4\pi} \nabla^2 \tilde{\phi}(\mathbf{r}) d\mathbf{r} = \int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N , \]

where \( \tilde{\rho} \) is the model density associated with the trial potential \( \tilde{\phi} \) and \( N \) is the total number of electrons, leads to the matrix equation,

\[ \mathbf{H} \rho - \mathbf{\gamma D} = 0 , \]

where

\[ (C)_{A,n} = C_{n}^{A} , \]

\[ (H)_{A,A',n,n'} = \frac{1}{4\pi} \left( f_{n}^{A} \nabla^2 f_{n'}^{A'} \right) , \]

\[ (\rho)_{A,n} = \left( f_{n}^{A} |\rho| \right) . \]  

The forgoing formulation of atomic charge can be easily extended to include higher multipoles. By including functions of corresponding higher multipoles in the expansion Eq. (3), it would certainly improve the representation of the electrostatic potential. However, the set of atomic charges and multipoles obtained should be used together and we lose the simple point charge model typically employed in molecular simulations. The main focus of this paper is to find the best possible atomic point charges. To serve this purpose, we should have only the atomic spherical functions in the expansion. We will next demonstrate that the atomic charges obtained this way are in general superior to ESPD charges for the representation of the electrostatic potential.

A related approach was taken by Koster et al.\(^\text{24}\) to model molecular electrostatic potential. Their focus was on the approximation of the molecular electrostatic potential. First

<table>
<thead>
<tr>
<th>Set 1(^a)</th>
<th>F</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
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<tr>
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<td>1.4×10^{-6}</td>
<td>1.3×10^{-7}</td>
<td></td>
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<tr>
<td>Set 2(^b)</td>
<td>2.3×10^{-6}</td>
<td>1.9×10^{-7}</td>
<td>1.5×10^{-7}</td>
</tr>
<tr>
<td>1.2 R_{VDW}</td>
<td>6.2×10^{-6}</td>
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<td>1.0×10^{-6}</td>
</tr>
<tr>
<td>2.0 R_{VDW}</td>
<td>2.3×10^{-8}</td>
<td>2.3×10^{-8}</td>
<td>2.7×10^{-8}</td>
</tr>
<tr>
<td>2.0 R_{VDW}+6.0</td>
<td>5.3×10^{-11}</td>
<td>5.8×10^{-11}</td>
<td>5.8×10^{-11}</td>
</tr>
<tr>
<td>2.0 R_{VDW}+12.0</td>
<td>1.4×10^{-10}</td>
<td>4.4×10^{-11}</td>
<td>4.4×10^{-11}</td>
</tr>
</tbody>
</table>

\(^a\)Set 1 is the set of concentric surfaces obtained from the scaled van der Waals surface (scaling factor 1.2, 1.4, 1.6, and 1.8).

\(^b\)Set 2 is the set of concentric surfaces obtained from the scaled van der Waals surface (scaling factor 1.4, 1.6, 1.8, and 2.0).
they obtained the atomic multipoles (atomic charges and dipoles) from their multipole moment analysis (MMA), then they determined the approximate electrostatic potential by solving the Poisson equation, Eq. (2), for each atom, so that the potential has the exact asymptotic behavior both at the nuclei and at the large distance. Our approach is different in determining the atomic multipoles (atomic charges here) from solution of the Poisson equation, because the Poisson equation is solved for the entire molecule rather for the constituent atoms.

**COMPUTATIONAL METHODOLOGY**

In the present work, we used the deformation density as input to Eq. (1), which is the difference between the molecular electron density and the sum of the spherical atomic densities of the free atoms centered at the corresponding nuclear positions. Equations (1) to (9) apply equally to the deformation density and the charges given by Eq. (10) are the net atomic charges. The use of the deformation density facilitates faster convergence of the calculated charges with respect to the number of basis functions used in the expansion in Eq. (3). However, both procedures give essentially the same converged atomic charges (Table II).

The short-range behavior of the electrostatic potential was modeled using Slater-type basis functions [Eq. (11a)], and the long-range behavior was modeled by a “long-range” basis function [Eq. (11b)] with correct $1/r$ asymptotic behavior,

$$f_n^l(r) = N_0^{l+1} r^{n-1} e^{-\lambda r},$$  

(11a)
\[ N_0^{(n)} = \sqrt{\frac{(2 \times \lambda_A)^{2n+1}}{4 \pi (2n + 2)!}}, \quad n = 1 \ldots N; \]
\[ f_0^A(r) = \frac{1}{r} (1 - e^{-\lambda_A r}), \quad (11b) \]

where \( N_0^{(n)} \) is the normalization constant and the \( \lambda_A \) are positive parameters. Similar basis functions have been used by Koster et al.\(^{24} \) in the approximation of electrostatic potentials.

For this choice of basis, the atomic charges \( \{q_A\} \) are determined by the coefficients of the long-range basis functions,

\[ q_A = \sum_n C_n^A \int \frac{1}{4 \pi} \nabla^2 f_n^A \, dr = -C_0^A. \quad (12) \]

The exponents \( \{\lambda_A\} \) were determined empirically for each atom type by inputting the spherical atomic density of an isolated atom and optimizing the exponent by calculating the atomic charge on this atom, which should equal to the atomic number. The results are listed in Table I. The exponents do not affect the atomic charges significantly. For example, the exponent of the H atom in the HF molecule can\(^{25} \) range functions changing from 0.4013 to 0.4014. The exponents for the long-range functions \( \{\lambda_A\} \) had little effect on the overall results, and were taken to be twice the corresponding \( \{\lambda_A\} \) values.

A total of 15 Slater-type functions were used to model the short-range potential. This was adequate to provide stable convergence of \( U \), and in most cases stable charges (Fig. 1). For exceptional cases such as CH\(_4\), converged charge results cannot be obtained; however, this is not a significant limitation, as will be discussed later.

The matrix elements \( \rho_{A,n} \) were calculated numerically with three-dimensional multilcenter quadrature; the rest of the matrix elements in Eq. (6) were integrated analytically.\(^{25} \) The electron density and related properties of various test molecules were determined with a self-consistent-field (SCF) program based on the conventional Kohn–Sham density-functional theory,\(^{26} \) with a numerical basis. Basis functions used in the SCF calculations were obtained from numerical solutions of the isolated atoms, similar to that of Delley.\(^{27} \) A basis set of 3s, 2p, and 1d functions was used for hydrogen atoms, and a basis set of 4s, 3p, and 2d functions was used for all other atoms.

RESULTS

Table II compares ESPD charges to those determined from the present method. The ESPD results were obtained by a least-squares fit to the SCF electrostatic potential on the set of four scaled van der Waals surfaces (scaling factors 1.2, 1.4, 1.6, and 1.8) (Ref. 28) at a density of 80 points per square angstrom. Overall, the two methods give similar charges.

It is known that dipole moments calculated by density-functional theory, in most cases, agree more closely with experiment than those obtained from Hartree–Fock calculations.\(^{29} \) For example, the Hartree–Fock results predict the wrong sign for the dipole moment of the CO molecule, whereas density-functional theory gives the correct sign.\(^{29,30} \) Table III shows the dipole moments from density-functional theory SCF calculations are very close to experimental results, and the simple charge model can reproduce the dipole moments and give the correct sign for each molecule. In addition, our method gives better agreement with the SCF results than the ESPD charges.

The choice of fitting points above has been employed elsewhere,\(^{17} \) but is somewhat arbitrary. Table IV demonstrates the dependence of ESPD charges on the choice of fitting points. The present method circumvents the ambiguity associated with choosing a set of fitting points by use of three-dimensional integrations in the construction of the necessary matrix elements.

The present method has the advantage that it not only gives charges, but also determines a spherical potential model representation for each atom. Table V compares the variance of the calculated electrostatic potential from the SCF potential for CO\(_2\) at the fit points described above. In general, the spherical model potential gives the best agreement with the SCF potential, whereas the potential of different point charge models are very similar to one another.

In the case of CH\(_4\), we have obtained a converged value for the functional \( U \), but we cannot obtain stable atomic charges (Fig. 1). This can be explained by the fact that the atomic charge is a long-range phenomena, and with our method the charge is determined by the coefficient of the long-range (asymptotic \( 1/r \)) basis function. The electrostatic potential around CH\(_4\), however, is short-range since it has vanishing monopole, dipole, and quadrupole moments. This is illustrated in Fig. 2. The electrostatic potential for CH\(_4\) is very small in the region outside the van der Waals radius, and is not significantly affected by varying the charge. Thus, the atomic charges do not have much meaning in this case, which is reflected by the large variance in the computed values. Nevertheless, the convergence of the functional \( U \), in spite of the fluctuation in the atomic charge in this case, indicates the convergence of the calculated spherical model potential.

To examine the necessity of using the spherical potential model in place of the point charge model, we examine the interaction energy, defined as the difference between the total energy of the interacting system and the total energy of isolated molecules. The electrostatic interaction energy is defined as the classical electrostatic energy component of the total interaction energy for a system composed of point-charged nuclei and fixed electronic densities.\(^{31} \) In general, the electrostatic interaction energy is modeled by a simple point charge model.\(^{32} \) We calculated the electrostatic interaction energy by using the point charge model and the spherical potential model for comparison.

Figure 3 is a typical bimolecular interaction energy curve.\(^{31} \) For molecular simulations, the electrostatic interaction energy will not be important in the core repulsive region where molecules have small probability of occupying. Figures 4 and 5 show the interaction energy and the electrostatic interaction energy between two HF molecules in different orientations. In the head-on case (Fig. 4), the point charge
model can describe the electrostatic interaction energy well in the range \( r > 4.3 \) a.u. outside the core repulsive region. Thus the point charge model is acceptable in this case.

In the “stacked” case (Fig. 5), however, the point charge model poorly represents the electrostatic interaction energy outside the core repulsive region \( (r > 3.7 \) a.u.). In the range of \( r = 3.7 - 5.5 \) a.u., the spherical potential model gives significantly better results.

**DISCUSSION**

We have presented a new method for determining atomic charges in molecules. The results show the charges obtained from this method are similar to ESPD charges that are widely used for determining parameters in molecular simulations. Unlike the electrostatic potential fitting procedures, the method described here does not rely on arbitrary fitting points. Hence, this method is unique, and can be used as an alternative to obtain atomic charges for molecular simulations. This method has the additional advantage that it depends only on the electron density. Since the electron density is an observable quantity and can be obtained by experiments, this method can be used to calculate charges directly from experimental data.

It has been shown that certain methods based on population analysis or partitioning of the molecular density result in accurate molecular dipole moments, but require atomic dipole or multipole contributions. The present method is designed to give the best possible spherical-atom representation of the electric field, and has been demonstrated to give accurate molecular dipole moments without requiring higher order multipole terms. As a further demonstration of the quality of the spherical atom model potential, we have included higher order angular momentum \( p \)-type functions in Eq. (3), and repeated calculations for the CO molecule. In-

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**FIG. 3.** A typical interaction energy curve for a two-molecule system.

**FIG. 4.** The comparison of interaction energy curves for head-on HF case. Solid line, electrostatic interaction energy from the SCF density. Short dash, electrostatic interaction energy from the ESPD point charge model. Long dash, electrostatic interaction energy from the spherical potential model. Dot–dash, total interaction energy from SCF calculations. The total interaction energy curve indicates the range of \( r > 4.3 \) a.u. is important for simulations. In this range the point charge model is good enough to reproduce the electrostatic potential. All units are atomic units.
Inclusion of $p$-type functions does not significantly change the atomic charges. The spherical model and spherical model with $p$-type function give very similar atomic charges $\approx 0.0473$ and $0.0472$ for C, respectively, and molecular dipole moments $0.1007$ a.u. and $0.1006$ a.u., respectively. In the present method the spherical component is highly dominant with little contribution from the atomic dipoles $4.3 \times 10^{-4}$ a.u. for C and $4.4 \times 10^{-4}$ a.u. for O. Thus the atomic charges and other higher order moments derived from our model should be considered as a set of empirical parameters designed to best reproduce the electrostatic potential and they may not be suitable for other interpretations.

Finally, the method presented provides a prescription for determining spherical-atom potential models for atoms in molecules. In some cases, the point charge model is inadequate to describe the interaction energy between molecules. The description of the interaction energy is much improved when the spherical atom potential models are used (e.g., stacked HF case in Fig. 5). Such models may prove useful in future generation force fields that abandon the point charge description of atoms. Moreover, the method is not restricted to spherical-atom models, but can be generalized to other functional forms to include atomic polarization effects. When nonspherical functions are used, one will obtain a more accurate description of the electrostatic potentials but more parameters beside atomic charges will be needed.

**ACKNOWLEDGMENTS**

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