Atomic Charges in Highly Ionic Diatomic Molecules

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Supporting Information

ABSTRACT: Atomic charges were investigated as functions of detectable atomic and molecular constants at equilibrium structures. It was found based upon the variation idea that atomic charges in highly ionic molecules can be expressed as a function of molecular dipole moments, polarizabilities of free cations, and polarizabilities of free neutral atoms of the corresponding anions. The function can be given in the form of classical Rittner’s relationship (J. Chem. Phys. 1951, 19, 1030). For the ground states of alkali halide molecules, the predicted atomic charges are close to an elementary charge e and the predicted dipole moments are in good agreement with the observed values; for spin-restricted high-ionic systems such as the lowest 3Σ electronic states of BN, AlN, GaN, BP, AlP, GaP, BAs, AlAs, and GaAs molecules, the predicted atomic charges are also near 1e and in good agreement with the results of natural population analysis at MRCI/cc-pvqz and HF/6-311+G(3df) levels. Polarizabilities for the lowest quintet states of B⁺, Al⁺, Ga⁺, N⁺, P⁺, and As⁺ ions were also obtained based upon high-level ab initio computations. Atomic charges from other related methods are also investigated for comparison. The results demonstrate that high-quality atomic charges can be obtained with detectable variables, such as molecular dipole moment, vibrational frequency, as well as polarizabilities of the related free atoms and ions.

1. INTRODUCTION

Atomic charges are also known as the polarized partial charges in molecular systems. With atomic charges, theoretical insights can be obtained for mapping atomic activities or atomic properties in molecules. Atomic charges are therefore important in fields of molecular science and have attracted the interest of many related researchers.1−9 Among various definitions for atomic charges,10−26 a large amount of them are defined based upon the electron population analysis or the partition of electron density from ab initio or density functional computations, such as Mulliken population analysis,10 natural population analysis (NPA),11 Bader’s quantum theory of atoms in molecules (AIM),1 and so on.12,13 Atomic charges are also defined based on computational physical observables such as dipole moment15,16 or electrostatic potential17−19 and a set of fitted empirical parameters. Though it is hard to detect atomic charges directly and accurately with present experimental techniques, people believe that they are intrinsically related to detectable properties such as dipole moment, polarizabilities, internuclear separations, and so on.27

Atomic charges defined based upon pure experimental variables are of special significance for the investigation of connections between different physical variables in molecular systems. In addition, high-quality atomic charges with computed detectable variables may also be used as an important reference to evaluate the quality of related theoretical studies. The simplest form of empirical atomic charges is the point charge model, from which the atomic charges can be estimated with \( q = \mu_d / R_e \) for general diatomic systems, where \( \mu_d \) is the dipole moment and \( R_e \) is the equilibrium internuclear distance. For high-ionic systems, a classical consideration for the relationship between atomic charges and detectable physical variables was given by Rittner,28 in which the polarizabilities of species in the molecules were used to consider the effects from static polarization. Recently, Hou and Bernath29 presented another relationship, in which the zero point energy or the harmonic vibrational frequency was introduced to consider the influences of polarization effects.

As expected, different definitions or different parameterizations may give different predictions for atomic charges. However, for highly ionic systems, unphysical results were often obtained with high quality observed and/or computed data. For example, for the well-known complete ionic systems such as the Rb and Cs halides, the atomic charges from the observed dipole moments and equilibrium internuclear separations (\( q = \mu_d / R_e \)) are less than 0.8e (e.g., 0.70e−0.75e); such data mean that the percent ionicities for these compounds are less than 80%, which is far lower than the expectations (~100%) for complete ionic species.

For alkali halide molecules, the original Rittner model and its truncated form (T-Rittner)28,30−33 had been used to investigate molecular spectral properties such as binding energies, molecular spectroscopic constants, and so on with experimentally detectable variables, based on the assumption...
that the molecules were completely ionized, that is, the atomic charges were 1e. However, for a large part of the molecules, the predicted atomic charges with the same relationships were far larger than the expected values. To improve the quality of predictions, the above-mentioned Rittner relationships had been widely investigated, including the assumption of the polarizabilities for species in molecules were functions of the potentials between ions in molecules and so on. This made the polarizabilities of species in molecules not detectable; therefore, the corresponding atomic charges were not functions of complete experimental variables. It can be easily found that the original Rittner relationship and the previously modified model cannot present consistent results between atomic charges and the corresponding experimentally/theoretically determined high-quality physical variables (including the polarizabilities of free species). The main purpose of the present work is to address such a problem.

In this work, analytic functions for atomic charges, especially the Rittner relationships, were reinvestigated and modified so that the predicted atomic charges were consistent with the related experimental and/or computed physical variables. The modified models were tested with the ground states of alkali halides and extended to the theoretically determined spin-restricted high-ionic systems such as the lowest nonet states of BN, AlN, GaN, BP, AlP, GaP, BAs, AlAs, and GaAs molecules. The results were also compared with data from other related methods, including pure ab initio NPA and/or AIM charges.

2. RESULTS AND DISCUSSION

2.1. Theoretical Considerations. From the classical Rittner relationship for dipole moment (in atomic units)

\[ \mu_q = e R_e - e R \left( \alpha_A^+ + \alpha_B^- \right) + 4 R \left( \alpha_A^+ \alpha_B^- \right) \]

where \( \alpha_A^+ \) and \( \alpha_B^- \) are the polarizabilities of the corresponding cations and anions in highly ionic molecules \( A^+B^- \).

On the basis of a perturbation treatment, Brumer and Karplus obtained an approximate form of eq 1, known as "T-Rittner" relationship for dipole moment

\[ \mu_q \approx e R_e - e \left( \alpha_A^+ + \alpha_B^- \right)/R_e \]

where \( \alpha_A^+ \) and \( \alpha_B^- \) are the polarizabilities of the corresponding neutral atoms \( A \) and \( B \) and \( \alpha_A^+ \) and \( \alpha_B^- \) are the polarizabilities of the free cation \( A^+ \) and free anion \( B^- \). At last, we find that \( \alpha_A^+ \) and \( \alpha_B^- \) are the simplest functional (i.e., \( \lambda = 0 \)) which can give reasonable predictions for highly ionic systems. Therefore, a more accurate Rittner-type relationship can be expressed as

\[ q \approx \mu_d \left[ R_e - R_e \left( \alpha_A^+ + \alpha_B^- \right) + 4 R \left( \alpha_A^+ \alpha_B^- \right) \right]/R_e \]

Similar modification can be made to the truncated form of Rittner relationship. Equations 2, 4, and 5 are used to calculate the atomic charges in typical high-ionic systems and are compared with the results from the relationship given by Hou and Bernath, which is also a function of detectable physical variables

\[ q = \mu_d \sqrt{\rho \mu k} \]

where \( k = 137.87436 \) for reduced mass \( \mu_k \) in atomic mass units (amu), \( \mu_d \) in Debye (D), \( \omega_A \) (harmonic vibrational frequency) in cm\(^{-1} \), \( R_e \) in \( \text{Å} \), and \( \rho \) in cm\(^{-3} \). Details on eq 6 can be found in ref 29. Because \( \mu k \omega_A^4 \) is also the force constant of the molecule, the atomic charge from eq 6 is also a function of molecular force constant. Note for convenience to application that the right-hand sides of eqs 2, 4, and 5 need to be divided by a conversion factor, 4.8032, so that the units of related variables are similar to those in eq 6.

2.2. Computational Results. The above-mentioned relationships are tested with two sets of typical high-ionic systems. One is the ground states of alkali halide molecules, which are well-known high-ionic molecules based on literature ionic polarizabilities, such discrepancies (+20 to +40% for lithium halides) are possibly introduced neither by the theoretical polarizabilities nor by the experimental \( R_e \) and \( \mu_d \). They are typical kind of systematic errors.

To solve the above problem, the atomic/ionic polarizabilities of species in molecules were taken as functions of atomic charges, such as \( \alpha_A^+ = \alpha_A^0 + \lambda (\alpha_A^0 - \alpha_A^-) \) and \( \alpha_B^- = \alpha_B^0 - \lambda (\alpha_A^0 - \alpha_B^-) \), where \( \lambda (0 \leq \lambda \leq 1) \) is a variation parameter, with conditions \( \alpha_A^0 \leq \alpha_A^+ \leq \alpha_A^- \) and \( \alpha_B^- \geq \alpha_B^0 = \alpha_B^- \) where \( \alpha_A^0 \) and \( \alpha_B^- \) are the polarizabilities of the corresponding neutral atoms \( A \) and \( B \) and \( \alpha_A^0 \) and \( \alpha_B^- \) are the polarizabilities of the free cation \( A^+ \) and free anion \( B^- \). Therefore, a more accurate Rittner-type relationship can be expressed as

\[ q \approx \mu_d \left[ R_e - R \left( \alpha_A^+ + \alpha_B^- \right) + 4 R \left( \alpha_A^+ \alpha_B^- \right) \right]/R_e \]

where \( R \) is a constant related to units only. \( k = 137.87436 \) for reduced mass \( \mu_k \) in atomic mass units (amu), \( \mu_d \) in Debye (D), \( \omega_A \) (harmonic vibrational frequency) in cm\(^{-1} \), \( R_e \) in \( \text{Å} \), and \( \rho \) in cm\(^{-3} \). Details on eq 6 can be found in ref 29. Because \( \mu k \omega_A^4 \) is also the force constant of the molecule, the atomic charge from eq 6 is also a function of molecular force constant. Note for convenience to application that the right-hand sides of eqs 2, 4, and 5 need to be divided by a conversion factor, 4.8032, so that the units of related variables are similar to those in eq 6.
on the knowledge of general chemistry. Another set is spin-
restricted theoretical high-ionic systems, the lowest Σ states of
BN, AlN, GaN, BP, AlP, GaP, BAs, AlAs, and GaAs molecules
(hereafter BN-group molecules), for which the ab initio
computations present complete ionic characters. Atomic
charges from observed \(^{34,35}\) and/or computed molecular
constants \((ω_0, R_0, μ_e)\) and free atomic/ionic polarizabilities \(^{34}\)
are used in Rittner and T-Rittner relationships. In eq 6, the
atomic masses of the most abundant isotopes from ref 36 are
used to calculate the corresponding reduced masses. The
atomic charges obtained with eqs 2 and 4–6 are compared
with theoretical atomic charges from Hartree–Fock (HF) and
the internally contracted multiconfiguration reference config-
uration interaction (MRCI)\(^ {37–39}\) calculations. The MRCI
computations were performed with Molpro;\(^ {40,41}\) the HF
computations were performed with Gaussian.\(^ {32}\) The 6–
311+G(3df) and cc-pvqz basis sets\(^ {43–51}\) embedded in the
suites were used.

Atomic charges computed with ab initio methods include
AIM (calculated with Gaussian), NPA, and Mulliken charges.
The above-mentioned analytic relationships, including the
point charge model, the original Rittner, T-Rittner, and the
modified Rittner forms in the present work, are investigated
with both theoretical and experimental data (if available). All
the detailed results are presented in Supporting Information
(Tables S1–S4). For clarity, only AIM and NPA charges are
compared in the text with those from eqs 2 and 4–6.

2.2.1. Ground States of Alkali Halides. Atomic charges for
the ground states of alkali halide molecules are given in Figure
1 and are compared with the NPA charges from MRCI/cc-
pvqz computations. All the observed data are taken from ref 34
except the dipole moments for CsBr and CsI, which are taken
from the database of NIST Webbook.\(^ {35}\) The polarizabilities
for free atoms and ions of halides and alkali elements used in this
work, which are recommended by ref 34, are listed in Table 1.
Except that for the iodine atom, no experimental polariz-
abilities for other species in Table 1 are available to us.

Table 1. Polarizabilities Used for Dipole Moments and
Atomic Charges in the Ground-State Alkali Halide
Molecules

| atoms | \(α/Å^3\) \(^{34}\) | anions | \(α^*/Å^3\) \(^{34}\) | cations | \(α/Å^3\) \(^{34}\) |
|-------|-----------------|-------|-----------------|---------|-----------------|
| F     | 0.557           | F\(^-\) | 1.04            | Li\(^+\) | 0.029           |
| Cl    | 2.18            | Cl\(^-\) | 3.66            | Na\(^+\) | 0.179           |
| Br    | 3.05            | Br\(^-\) | 4.77            | K\(^+\) | 0.83            |
| I     | 5.35\(^a\)      | I\(^-\) | 7.1             | Rb\(^+\) | 1.4             |
|       |                 |       |                 | Cs\(^+\) | 2.42            |

\(^a\)Observed data, with uncertainty 25%. The recommended theoretical value was 4.7 Å\(^3\)\(^{35}\) the uncertainty was also 25%. In the present work, the value 5.35 Å\(^3\) was used.

The results in Figure 1 show that the original Rittner model
(shown with “●”) gives relatively large predictions \((q \gtrsim
1.1e)\) for Na, K, Rb, and Cs halides and too large predictions
\((q \gtrsim 1.2e)\) for lithium halides. Compared with the original Rittner model, the T-Rittner model (shown with “▲”) seems to provide better predictions, but only for part of the molecules (K, Rb, and Cs halides) the atomic charges are highly improved. For Li and Na halides, only slight improvements are achieved. Equation 5, in which the polarizability of anions in the original Rittner model is reduced to polarizability of the corresponding free atom, can provide far better predictions (shown with “◆”) for all alkali halides. Such results show that the quality of the predicted atomic charges can be highly improved by the modification of polarizabilities of the anions in highly ionic molecules. For some of the light species, the NPA charges (shown with “★”) from MRCI/cc-pvqz computations are also listed for comparison. Compared with the charges from eqs 2 and 4, it is clear that the charges (eq 5) are close to the NPA data. The differences to the NPA charges are not larger than 0.1e for LiF, LiCl, LiBr, NaF, NaCl, and NaBr molecules. Note that eq 6 also presents high-quality predictions (“◼”) with observed molecular constants \(ω_0, R_0, μ_e\) for all alkali halides, except lithium halides, the predicted atomic charges from eqs 5 and 6 are in good agreement. For lithium halides except LiI (basis set not available for I), eq 6 gives better predictions to the NPA data. As expected, the point charge model (the data are shown with “●”) gives predictions lower than expectation.

Figure 2 gives the predicted dipole moments with different
approaches, including analytic relationships, such as the point
charge model and the Rittner-type model, and the ab initio
results at HF/6-311+G(3df) (indicated with “●”). The original
Rittner model (shown with “○”) and the present modified Rittner model (shown with “◆”) models, the atomic charges are assumed 1e, and polarizabilities are taken from Table 1. Dipole moments from ab initio approaches at HF/6-311+G(3df) (“★”) and MRCI/cc-pvqz (“▲”) levels, and results from the point charge model with experimental \(R_e\) (taken from ref 34) and atomic charges taking 1e (”◆”) and the NPA charges (“■”) at the HF/6-311+G(3df) level, respectively, are also present for comparison.
data (" □ "). Compared with the ab initio results, the quality for predictions from eq 5 is similar to the MRCI/cc-pvqz (" ▾ ") and HF/6-311+G(3df) (" ○ ") results for light lithium and sodium halides and better than predictions for potassium halides at the HF/6-311+G(3df) (" ○ ") level.

For predictions from eq 5, the percentage error in average is 2.2% for all of the 20 alkali halide molecules. Note the largest of the errors is −6.8% (of LiI). From the data given in ref 34, such a largest error is most possibly introduced from the uncertainty (25%) of the observed polarizability (5.35 Å³) for the free iodine atom. For heavy atoms, it is also very difficult to obtain accurate predictions from ab initio computation; the uncertainty was also 25% for the recommended computational data (4.7 Å³) for this atom. The value used at present is the observed data 5.35 Å³; when it is reduced to 5.0 Å³, the error is decreased to −2.8%. For other molecules, the predictions are excellently good.

The mean percentage errors of the original Rittner model and the T-Rittner model are 12 and 7.7%, respectively. These data indicate that the modified model (eq 5) in the present work can give far better predictions than the other two similar models. The results of the predicted dipole moments also indicate that the relationship (eq 5) is self-consistent.

The predicted atomic charges with the modified T-Rittner model (q = μi/[Ri − (αR + αq)/Ri²]) using the same polarizabilities as those in eq 5 are given in Table S1, which show that the predictions of atomic charges are lower than expectation for highly ionic molecules such as CsF (0.91e), CsCl (0.92e), and CsBr (0.90e), whereas the present atomic charges (eq 5) are more close to an elementary charge, CsF (0.96e), CsCl (0.97e), and CsBr (0.95e). These predictions indicate that such a modified T-Rittner relationship is not superior to eq 5.

The results of the predicted atomic charges and dipole moments with the modified T-Rittner model also demonstrate that the truncation of the original Rittner model cannot essentially improve the quality of the corresponding predictions.

The predicted dipole moments with eq 5 are also compared with the results from the original and T-Rittner models (eqs 1 and 3) using polarizabilities from literature empirical approaches, such as the Seitz–Ruffa (SR)32,33 and the Wilson–Curtis–Coker (for short, “Coker”)35–36 models. The results are given in Figure 3. The results show that the eq 5 data (shown with “ □○”), are generally better than those from SR and/or Coker polarizabilities. The averages of the differences (|δq|ave) to the observed dipole moments are 0.26 and 0.25 D for the predicted data from the SR polarizabilities32 with the original Rittner (shown with “ □”) and T-Rittner (shown with “△”) models, respectively. For predictions from the Coker polarizabilities,32 the |δq|ave are 0.45 and 0.33 D for the Rittner (shown with “ ▽”) and T-Rittner (shown with “ ▽”) models, respectively. For the predictions with the polarizabilities of (αR, αq), the modified Rittner model (eq 5) gives |δq|ave = 0.21 D, which is clearly better than the best of other predictions. The maximum of the deviations of predictions with eq 5 is 0.52 D, which is also less than the largest deviations of other predictions (ranges from 0.64 to 0.90 D). Details are given in Table S2 in Supporting Information.

Such a comparison demonstrates that the present scheme is not only simple but also of high quality in predictions; therefore, it is more efficient than other similar models.

Figure 3. Comparison between predicted dipole moments for the ground states of alkali halides from Rittner-type models with different polarizabilities. Squares (“ □”), and triangles up (“ △”), indicate results from the SR polarizabilities32 with original (eq 1) and T-Rittner (eq 3) models, respectively. Solid triangles left (“ ▽”), and triangles down (“ ▽”), indicate results from the Coker polarizabilities32 with the original Rittner and T-Rittner models, respectively. Circles (“ ○”), results from the modified Rittner relationship (eq 5) with free-state polarizabilities of cations and atoms collected in ref 34. Stars (" ▾"), experimental data are similar to those in Figure 2. Note that both the SR and Coker polarizabilities were taken from ref 32, which were functions of other physical variables, and are listed in Table S2 in Supporting Information for comparison.

Note that eq 2, etc., hold at R6e > 4(αR αq)28 For all cases tested here, this condition is satisfied. For eq 5, because αq > αR > 0, the above condition is also well satisfied.

Note in addition that systematic comparison is also made between atomic charges predicted with observed and computed molecular constants at HF/6-311+G(3df) and MRCI/cc-pvqz levels. For both eqs 5 and 6, the predicted atomic charges from theoretical molecular constants are consistent with the predictions from experimental constants. Details are presented in Table S3.

2.2.2. Lowest Nonet States of the First Nine N- and B-Group Molecules. On the basis of high-level ab initio computations, we find that the lowest nonet states of BN-group molecules (BN, AlN, GaN, BP, AIP, GaP, BAs, AlAs, and GaAs) are also high-ionic systems. Because there are no observed data available for such systems, systematically comparisons are made at MRCI/cc-pvqz and HF/6-311+G(3df) theoretical levels. Detailed results are presented in Table S4 in Supporting Information.

On the basis of the NPA, the dominant configurations of the valence electrons are nsnp1np1np1 for both the cations in the N-group (N⁺, P⁺, As⁺) and the anions in the B-group (B⁻, Al⁻, Ga⁻) in the lowest 3Σ states of BN-group molecules. The nonet spin states of the molecules require that the corresponding cations and anions in the molecules should be in their largest spin states, that is, quintet states for configurations of nsnp1np1np1; at the same time, the lowest energy states of the molecules also require that the related ions in the molecules should be in their lowest energy states. This means that the states of the species in these BN-group molecules are in their lowest ionic quintet states not the ground atomic states. For such quintet states, the polarizabilities are not available to us at present. Therefore, the polarizabilities of the lowest quintet states of N⁺, P⁺, As⁺, B⁻, Al⁻, and Ga⁻ ions are computed and used in the calculation of...
atomic populations also give atomic charges similar to the NPA data, which are also listed in Table S4 for comparison.

All the data used in eqs 2 and 5 include polarizabilities $\alpha$ of all related species, and the equilibrium distances $R_e$, dipole moments $\mu_d$, and harmonic vibrational frequencies $\omega$ were calculated at HF/6-311+G(3df) and MRCI/cc-pvqz levels, respectively. Note that the corresponding polarizabilities at the MRCI/cc-pvqz theoretical level (with all electrons correlated) were computed using a finite field approach (with the field set to be 0.0001 a.u.) with Molpro. The obtained polarizabilities of the corresponding ions and atoms (B, Al, Ga, B$^+$, Ga$^+$, N$^+$, P$^+$, As$^+$) are given in Table 2 and are used in eqs 2 and 5.

The atomic charges from MRCI/cc-pvqz and HF/6-311+G(3df) computations for these nonet-state molecules are given in Figures 4 and 5, respectively. As expected, the relationship (eq 5) ("▲") gives atomic charges close to these NPA charges. The differences between them are less than about 0.05e. Similar to those of alkali halides, the atomic charges from the original Rittner model (eq 2) ("▼") are larger than 1.0e, which seem too high compared with the NPA data. The charges (eq 6) ("●") are slightly smaller than the NPA charges but are far better than the predictions from the point charge model ("○"). The consistency to the NPA results demonstrates that eq 5 can give reliable predictions for the $^9\Sigma$ states of BN-group molecules at the MRCI/cc-pvqz level.

The atomic charges at the HF/6-311+G(3df) theoretical level are presented in Figure 5. At this level, the AIM data ("○") are also obtained. From this figure, it is clear that the predictions from eq 5 ("▲") are also in good agreement with NPA charges (shown with "●")$; \delta \leq 0.05e$; compared with the AIM data, the discrepancies are about 0.1e. For eq 6, the predictions ("●") are in excellent agreement with the AIM data, the discrepancies are less than 0.03e. For eq 2, the predicted atomic charges are too large; for GaAs, GaP, and GaN, the predicted atomic charges are larger than 2e, which are obviously wrong. It is clear that the quality of eq 5 is far better than eq 2. Results in this figure show that at the HF/6-311+G(3df) level, both eqs 5 and 6 can provide high-quality predictions for the atomic charges of highly ionic systems investigated in this work.

For all the nine high-spin BN-group molecules, results in Figures 4 and 5 demonstrate that the predictions from eq 5 are highly improved than those from the original Rittner model eq 2. The data from eq 5 are comparable to the NPA charges at MRCI and HF levels. For the predictions from eq 6, they are

| Table 2. Calculated Polarizabilities (in Å$^3$) for the Ground States of B, Al, and Ga Atoms and the Lowest Quintet States of B$^+$, Al$^+$, Ga$^+$, N$^+$, P$^+$, and As$^+$ Ions |
|---------------------------------|------------------|------------------|
|                                 | ground-state atoms | the lowest quintet cations and anions |
|                                | HF/6-311+G(3df)   | MRCI/cc-pvqz$^*$ | HF/6-311+G(3df) | MRCI/cc-pvqz$^*$ |
| B                               | 3.124            | 3.050            | B$^+$           | 8.371            | 4.622            |
| Al                              | 8.137            | 9.185            | Al$^+$          | 17.744           | 14.476           |
| Ga                              | 7.934            | 8.876            | Ga$^-$          | 23.786           | 13.637           |

$^*$Computations were performed with a finite field approach embedded in Molpro, with the dipole field set to be 0.0001 a.u.

Figure 4. Comparison between ab initio charges (AIM and NPA) and the atomic charges from analytical formulae with computed variables ($\mu_d$, $\omega$, $R_e$) at the HF/6-311+G(3df) level. The atomic and ionic polarizabilities are taken from Table 2.
highly consistent with the AIM charges from HF computations, which were demonstrated to be stable with respect to the levels of theory, such as HF, DFT, and MP2 (the AIM charges at the MRCI level are not computed in this study).

2.3. Discussion. The classical method, for example, the original Rittner model eq 2, cannot provide satisfactory predictions for either atomic charges or dipole moments; this can be seen from the results for the ground states of alkali halide molecules. In the original Rittner model, it is reasonable for the prediction of dipole moments with the atomic charges assuming to be unit charge for such typical complete systems. However, the predicted atomic charges are not consistent with this assumption; which are systematically larger than 1e. Such results therefore demonstrate that there is something wrong with the use of the original Rittner model eq 2. On the basis of the qualities of the calculated dipole moments and the observed internuclear distances, it is easy to find that the trouble mainly lies in the polarizabilities used. The main reason lies in the fact that the polarizabilities for the corresponding free ions are not suitable for the bonded ions in molecules at equilibriums. This is why the predicted atomic charges are abnormally high ($q > 1.3e$) for molecules such as LiCl, LiBr, and LiI.

To seek a better relationship for improving the quality of the polarizabilities for bonded ions in highly ionic molecules, various functional and approaches have been tested. Finally, we found that when supposing the polarizabilities of bonded species ($\alpha_A^{\text{ff}}$ and $\alpha_B^{\text{ff}}$, $0 < q \leq 1$) as functions of a free adjustable parameter, $\lambda$, in forms of $\alpha_A^{\text{ff}} = \alpha_A + \lambda(\alpha_A - \alpha'^{\text{free}})$ and $\alpha_B^{\text{ff}} = \alpha_B + \lambda(\alpha_B - \alpha'^{\text{free}})$, where $0 \leq \lambda \leq 1$, and high-quality results can be obtained at $\lambda = 0$. Then the following approximations are obtained for the polarizabilities of species in highly ionic molecules: (1) bonded cation $\approx$ free cation and (2) bonded anion $\approx$ free atom. The results of eq 5 for the lowest states of the nonet BN-group molecules demonstrate that it is also suitable for spin-restricted highly ionic systems under high-level computations, such as MRCI/cc-pvqz.

For the BN-group molecules, the excellent agreement between the data (eq 6) and the AIM charges indicates that such an analytical expression for atomic charges in molecules also presents a close connection with experimentally detectable variables, such as $\omega_A$, $\mu_A$ for spin-restricted highly ionic diatomic states. The agreement to NPA and/or AIM data demonstrates that the qualities of predictions from eq 6 are also acceptable. The agreement between the results from eqs 5 and 6 also indicates that eq 5 can provide high-quality predictions among empirical relationships for high-ionic, high-spin species.

The differences between the results of eqs 2 and 5 indicate that the polarizabilities of species in molecules will influence the quality of the predicted atomic charges; therefore, the quality of the atomic/anion polarizabilities is important for obtaining high-quality predictions. The ab initio results presented in Table 2 show that the basis sets also influence the quality of the computed atomic/ion polarizabilities; therefore, additional efforts are needed, in general, to obtain high-quality atomic polarizabilities in theoretical computations. For highly ionic systems, the relationship of eq 5 may also be used to investigate the atomic polarizabilities.

For alkali halides, the excellent agreement between observed dipole moments and the predicted data from eq 5 was reached, except LiI; for this molecule, the discrepancy was relatively high, $-6.8\%$ ($\delta \approx -0.5$ D). From ref 34, we find that the estimated uncertainties were 25% for the polarizabilities of the iodine atom for both experimental (5.35 A³) and calculated (4.7 A³) data recommended in ref 34. When taking the error of the predicted dipole moment for LiI to be zero, the estimated polarizability for the free I atom is 4.75 A³, which is nearly identical to the recommended theoretical value 4.7 A³. In the same way, the polarizabilities for the I atom are estimated from NaI, KI, RbI, and CsI; interestingly, the average of all these five predictions (including that from LiI) is 5.33 A³, which is nearly similar to the recommended observed value. Using the same approach, the obtained mean polarizabilities for atoms F, Cl, and Br are 0.66, 2.40, and 3.41 (in A³), respectively. These data are similar to the recommendations (F = 0.557, Cl = 2.18, Br = 3.05 (in A³); see in Table 1) for free atoms in ref 34 and/or the polarizabilities32 for related anions in molecules (see in Table S2). These results also demonstrate that the relationship (eq 5) can be used as a simple approximation for investigating the polarizabilities of atoms in high-ionic systems with detectable molecular constants.

As to the molecules studied here, we find that the nonet states of BN-group molecules are high-ionic, high-spin, and relative stable species with large dipole moments. In addition, the populations of atomic charges of the atoms/ions in the molecules are inversely compared with the ground-state species, that is, the B-group species have negative charges (i.e., B⁺, Al⁺, and Ga⁺), whereas the N-group elements have positive charges (i.e., N⁺, P⁺, and As⁺). These special properties are quite different from those of normal molecules in their ground electronic states; therefore, they may have special significance for the investigation of molecular properties under electric and/or magnetic fields for special purpose.

All the results for 29 highly ionic molecules studied in this work, including the singlet states of 20 alkali halide molecules and the nonet states of the first nine BN-group spin-excited $^3\Sigma$ molecules, demonstrate that eq 5 can provide predictions close to results from high-quality ab initio and/or other empirical approaches. The results for the BN-group molecules demonstrate that eq 5 is also suitable for spin-restricted highly ionic states.

Keep in mind that eq 2, etc., hold at $R_e \gg 4(\alpha_A^{\text{ff}})$. This condition is not satisfied, the predictions with those relationships may not be qualified. The results for the ground state of CO are present as examples. As known, CO is not a typical ionic system. However, according to Pauling,56,59 it was expressed as a mixture of some resonance Lewis structures, in which two typical ionic structures were involved.

One may wonder if the Rittner-type relationships work or not. Tests on this molecule can be made according to two different lines: (1) treat the molecule as a general molecule using the polarizabilities of the corresponding ground-state atoms and the observed molecular dipole moment and (2) treat the molecule as a mixture of two highly ionic species (the corresponding ionic resonance Lewis structures) using the related atom’s and cation’s polarizabilities to estimate the atomic charges for the molecular “mixture”. For the ground state of CO, the related data from ref 34 are as follows: $R_e = 1.12823$ Å; $\mu_e = 0.1098$ D; $\omega_A = 2169.81$ cm$^{-1}$; $\mu_A = 6.857143$ amu; $\alpha(C) = 1.76$ A³ and $\alpha(O) = 0.802$ A³. For the lowest states of C⁺ and O⁺ cations, $\alpha(C^+) = 0.942$ A³ and $\alpha(O^+) =$
0.391 Å³, which are calculated at the HF/6-311+G(3df) level, are used to calculate the atomic charges with eq 5 for the two resonance ionic structures. 

On the basis of the partition ratio given in eq 7 (eq 1 in ref 58), the atomic charges are \(|q| \approx 0.4e\) (suppose the atomic charges are zero for nonionic resonance structures). According to line 2, the dipole moments for the point charge model give \(|e| = \frac{0.0056e}{0.0206e} \approx 0.274S D\) from eq 5, the atomic charges \(q = 0.0206e\) respectively, using the polarizabilities for atomic carbon and atomic oxygen. The dipole moments are also in excellent agreement with the observed molecular constants and polarizabilities of related free cations \((\text{eq } 6)\). For spin-restricted highly ionic states, such as resonance ionic structures. This indicates that the present model is not suitable for both the ionic resonance structures of CO ground state discussed here.

3. CONCLUSIONS

For highly ionic diatomic molecules, the present improved Rittner model (eq 5) for both dipole moments and atomic charges is demonstrated to be self-consistent with the molecular constants and polarizabilities of related free cations and free atoms. For alkali halides, the predicted atomic charges are close to an elementary charge; the predicted dipole moments are also in excellent agreement with the observed dipole moments. For spin-restricted highly ionic states, such as the lowest nonet states of BN, AlN, GaN, etc., the predicted atomic charges are in good agreement with the NPA and/or AIM charges at MRCI/cc-pVQZ and HF/6-311+G(3df) levels. The predicted atomic charges with such a modified model for most of the species (except some lithium halides) are also comparable to the predictions from vibrational frequencies and dipole moments at equilibrium structures. All the results demonstrate that high-quality atomic charges can be obtained with experimentally detectable variables.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02370.

Predicted atomic charges and dipole moments and detailed ab initio data for comparison (PDF)

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Notes

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REFERENCES

1. Bader, R. F. W. Atoms in Molecules: A Quantum Theory; Oxford University Press: Oxford, 1990; pp 1–438.
2. Coppens, P. X-ray Charge Densities and Chemical Bonding; Oxford University Press: Chester, England, 1997; pp 1–384.
3. Popelier, P. L. A. Atoms in Molecules: An Introduction; Prentice Hall: Harlow, U.K., 2000; pp 1–188.
4. Matta, C.; Boyd, R. J. Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design; Wiley: Weinheim, 2007; pp 1–514.
5. Huibers, P. D. T. Quantum-Chemical Calculations of the Charge Distribution in Ionic Surfactants. Langmuir 1999, 15, 7546–7550.
6. Dunnington, B. D.; Schmidt, J. R. Generalization of Natural Bond Orbital Analysis to Periodic Systems: Applications to Solids and Surfaces via Plane-Wave Density Functional Theory. J. Chem. Theory Comput. 2012, 8, 1902–1911.
7. Vanpoucke, D. E. P.; Oláh, J.; De Proft, F.; Van Speybroeck, V.; Roos, G. Convergence of Atomic Charges with the Size of the Enzymatic Environment. J. Chem. Inf. Model. 2015, 55, 564–571.
8. Wells, B. A.; De Bruin-Dickason, C.; Chaffee, A. L. Charge Equilibration Based on Atomic Ionization in Metal–Organic Frameworks. J. Phys. Chem. C 2014, 119, 456–466.
9. Yang, X.; Lei, H.; Gao, P.; Thomas, D. G.; Mobley, D. L.; Baker, N. A. Atomic Radius and Charge Parameter Uncertainty in Biomolecular Solvation Energy Calculations. J. Chem. Theory Comput. 2018, 14, 759–767.
10. Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. J. Chem. Phys. 1955, 23, 1833–1840.
11. Reed, A. E.; Weinstock, R. B.; Weinhold, F. Natural Population Analysis. J. Chem. Phys. 1985, 83, 735–746.
12. Huzinaga, S.; Sakai, Y.; Miyoshi, E.; Narita, S. Extended Mulliken electron population analysis. J. Chem. Phys. 1990, 93, 3319–3325.
13. Wiberg, K. B.; Rablen, P. R. Comparison of atomic charges derived via different procedures. J. Comput. Chem. 1993, 14, 1504–1518.
14. Zhang, P.; Bao, P.; Gao, J. Dipole Preserving and Polarization Consistent Charges. J. Comput. Chem. 2011, 32, 2127–2139.
15. Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. SM6: A Density Functional Theory Continuum Solvation Model for Calculating Aqueous Solvation Free Energies of Neutrals, Ions, and Solute-Water Clusters. J. Chem. Theory Comput. 2005, 1, 1133–1152.
16. Marenich, A. V.; Jerome, S. V.; Cramer, C. J.; Truhlar, D. G. Charge Model 5: An Extension of Hirshfeld Population Analysis for the Accurate Description of Molecular Interactions in Gaseous and Condensed Phases. J. Chem. Theory Comput. 2012, 8, 527–541.
17. Chemical Applications of Atomic and Molecular Electrostatic Potentials; Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1984; pp 1–467.
18. Singh, U. C.; Kollman, P. A. An approach to computing electrostatic charges for molecules. J. Comput. Chem. 1984, 5, 129–145.
19. Besler, B. H.; Merz, K. M.; Kollman, P. A. Atomic charges derived from semiempirical methods. J. Comput. Chem. 1990, 11, 431–439.
20. No, K. T.; Cho, K. H.; Jhon, M. S.; Scheraga, H. A. An Empirical Method To Calculate Average Molecular Polarizabilities from the Dependence of Effective Atomic Polarizabilities on Net Atomic Charge. J. Am. Chem. Soc. 1993, 115, 2005–2014.
21. Yakovenko, O.; Oliferenko, A. A.; Bdhola, V. G.; Palyulin, V. A.; Zefirov, N. S. Kirchhoff Atomic Charges Fitted to Multipole Moments: Implementation for a Virtual Screening System. J. Comput. Chem. 2008, 29, 1332–1343.
(22) Storer, J. W.; Giesen, D. J.; Cramer, C. J.; Truhlar, D. G. Class IV charge models: A new semiempirical approach in quantum chemistry. J. Comput.-Aided Mol. Des. 1995, 9, 87–110.

(23) De Proft, F.; Van Alsenoy, C.; Peeters, A.; Langenaeker, W.; Geerlings, P. Atomic charges, dipole moments, and Fukui functions using the Hirshfeld partitioning of the electron density. J. Comput. Chem. 2002, 23, 1198–1209.

(24) Heinz, H.; Suter, U. W. Atomic Charges for Classical Simulations of Polar Systems. J. Phys. Chem. B 2004, 108, 18341–18352.

(25) Mullay, J. Simple Method for Calculating Atomic Charge in Molecules. J. Am. Chem. Soc. 1986, 108, 1770–1775.

(26) Zhao, D.-X.; Zhu, Z.-W.; Zhang, C.; Yang, Z.-Z. A model of atoms in molecules based on potential acting on one electron in a molecule: I. Partition and atomic charges obtained from ab initio calculations. Int. J. Quantum Chem. 2018, 118, No. e25610.

(27) Bader, R. F. W.; Matta, C. F. Atomic Charges Are Measurable Quantum Expectation Values: A Rebuttal of Criticisms of QTAIM Charges. J. Chem. Phys. 2011, 135, 103105.

(28) Rittner, E. S. Binding Energy and Dipole Moment of Alkali Halide Molecules. J. Chem. Phys. 1951, 19, 1030–1035.

(29) Hati, S.; Datta, B.; Datta, D. Polarizability of an Ion in a Contracted Multi-Reference Configuration Interaction Method. J. Chem. Phys. Lett. 1984, 108, 5735–5740.

(30) Brumer, P.; Karplus, M. Perturbation theory and ionic models for alkali halide systems. I. Diatomics. J. Chem. Phys. 1973, 88, 3903–3918.

(31) Kumar, M.; Kaur, A. J.; Shanker, J. Spectroscopic constants of alkali halides and hydrides using modified T-Rittner model. J. Chem. Phys. 1986, 84, 5735–5740.

(32) Kumar, M.; Shanker, J. Electronic polarizabilities, potential functions, and spectroscopic constants for diatomic molecules of alkali halides and alkali hydrides. J. Chem. Phys. 1992, 96, 5289–5297.

(33) De Proft, F.; Van Alsenoy, C.; Peeters, A.; Langenaeker, W.; Stefanov, B. B.; Liu, B.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pope, J. A. Gaussian 03, Revision E.01; Gaussian, Inc.: Wallingford, CT, 2007.

(34) Chalasani, V. K.; Shanker, J. Electronic polarizabilities and dipole moments for alkali halides. J. Phys. Chem. 1995, 109, 7667–7676.

(35) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. 1980, 72, 6536–6548.

(36) Wang, M.; Audi, G.; Wapstra, A. H.; Kondev, F. G.; Kurkjian, F.; Stoyer, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Self-Consistent Molecular Orbital Methods. 20. Basis set for correlated wave-functions. J. Chem. Phys. 1980, 72, 650–654.

(37) Neill, D. P.; Palmieri, P.; Peng, D.; Pople, J. A. Self-Consistent Chemical Models for Use in Quantum Molecular Calculations. J. Chem. Phys. 1981, 75, 1209–1215.

(38) Wilson, A. K.; Woon, D. E.; Sanderson, E. K.; Pople, J. A. Systematically Convergent Correlation Consistent Basis Sets for Molecular Core–Valence Correlation Effects: The Third-Room Atoms Gallium through Krypton. J. Phys. Chem. A 2007, 111, 11383–11393.

(39) Seitz, F. Interpretation of the Properties of Alkali Halide-Thallium Phosphors. J. Chem. Phys. 1938, 6, 150–162.

(40) Politzer, P. A. Theory of the Electronic Polarizabilities of Ions in Crystals: Application to the Alkali Halide Crystals. Phys. Rev. 1963, 130, 1412–1423.

(41) Coker, H. The electronic strain polarizability constants of the alkali halides. J. Chem. Phys. Solids 1979, 40, 1079–1088.

(42) Wilson, J. N.; Curtis, R. M. Dipole polarizabilities of ions in alkali halide crystals. J. Phys. Chem. 1970, 74, 187–196.

(43) Sangachin, A. A. S.; Shanker, J. Electronic polarizabilities and dipole moments for alkali halides. J. Chem. Phys. 1989, 90, 1061–1066.

(44) Barone, V.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dauprêch, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. J.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision E.01; Gaussian, Inc.: Wallingford, CT, 2007.

(45) McLean, A. D.; Chandler, G. S. Contracted Gaussian basis sets for molecular calculations. J. Chem. Phys. 1980, 72, 6536–6548.

(46) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. 20. Basis set for correlated wave-functions. J. Chem. Phys. 1980, 72, 650–654.

(47) Bader, R. F. W.; Matta, C. F. Atomic Charges Are Measurable Quantum Expectation Values: A Rebuttal of Criticisms of QTAIM Charges. J. Chem. Phys. 2011, 135, 103105.

(48) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. 1989, 90, 1007–1023.