Extension of the Polarizable Charge Equilibration Model to Higher Oxidation States with Applications to Ge, As, Se, Br, Sn, Sb, Te, I, Pb, Bi, Po, and At Elements

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ABSTRACT: We recently developed the Polarizable Charge Equilibration (PQEq) model to predict accurate electrostatic interactions for molecules and solids and optimized parameters for H, C, N, O, F, Si, P, S, and Cl elements to fit polarization energies computed by quantum mechanics (QM). Here, we validate and optimize the PQEq parameters for other *p*-block elements including Ge, As, Se, Br, Sn, Sb, Te, I, Pb, Bi, Po, and At using 28 molecular structures containing these elements. For elements in the Se column of the periodic table, we now include molecules with higher oxidation states: III and V for the As column, IV and VI for the Se column, -I, III, and V for the Br column. We find that PQEq predicts polarization energies in excellent agreement with QM.

1. Introduction

Accurately describing electrostatic interactions at the atomic level is crucial in characterizing and developing complex materials to meet economic and environmental imperatives. These interactions are included automatically in Quantum Mechanics (QM) calculations, but QM is limited to 100s of atoms for 10s of picoseconds and we want to simulate thousands or millions of atoms for 100s of nanoseconds or larger. Thus, we must replace the QM by force fields, where the first step is to specify partial atomic charges. Usually this is done by extracting point charges from QM on small molecules, which raises issues of how to define the point charges (Mulliken approximation or by fitting the electrostatic potentials) and of how to allow the charges to change or polarize during the molecular dynamics (MD).

Previous studies have shown that describing the electrostatic energy and polarization effects are important for *p*-block elements, specifically in peptide and protein systems. Polarization has been shown to be a major component in the solvation of a protein and necessary to find the correct folded structure¹. The inclusion of polarization in molecular mechanics (specifically the SIBFA procedure) has been shown to demonstrate the stabilization of peptides chains of N-methylformamide into α -helices and β -sheets². Other polarizable force fields used for peptide and protein modeling include NEMO³, PROSA⁴⁻⁵, POSSIM⁶, and SDFP⁷. Polarization methods have also been successful capturing the binding energy of potassium cations to benzene due to the high polarizability of benzene⁸.

Recently, we proposed the new polarizable charge equilibration scheme (PQEq) that includes self-consistent atomic charge transfer and polarization for use in MD simulations of materials⁹, hereafter denoted as Paper I. We attach Gaussian-shaped charges to the atomic cores along with a Gaussian shaped polarizable shell connected to the core by a harmonic spring force. The net atomic charge and shell position adjust instantaneously in response to the electrostatic environment of the system to achieve a constant chemical potential across all atoms of the system. We provided atomic parameters of the model for all elements of the periodic table up to Nobelium (atomic no. = 102) based on experimental atomic data. In order to validate the accuracy of PQEq, we used the QM interaction energy as dipoles are brought into the atoms of model molecules, showing that the PQEq model leads to interaction energies very close to QM for molecules involving the H, C, N, O, F, Si, P, S, and Cl elements. We also adjusted these parameters to fit QM calculations on model molecules.

In this paper, we extend and validate the accuracy of the PQEq model for reproducing the QM interaction energy for molecules involving Ge, As, Se, Br, Sn, Sb, Te, I, Pb, Bi, Po, and At.

2. Polarizable Charge Equilibration (PQEq) Method

The PQEq model is based on a combination of charge equilibration (QEq)¹⁰ with the Drude oscillator model¹¹⁻¹⁴. In this model, each atom, *i*, is partitioned into two charged regions (core and shell). The core (ρ_{ic}) includes all the mass of the atom plus a Gaussian function ρ_i with a variable total charge ($q_i + 1$). The shell (ρ_{is}) is massless and consists of a Gaussian function ρ_{is} with a fixed total charge (-1). The shell and core of an atom are connected by an isotropic harmonic spring with force constant K_s (see [Figure 1](#)). Thus the total charge (core plus shell) on *i*-th atom is q_i . The Coulombic energy is expressed as

$$E_{Coulomb}(\{\vec{r}_{ic}, \vec{r}_{is}, q_i\}) = \sum_i^N \left[\chi_i^0 q_i + \frac{1}{2} J_{ii}^0 q_i^2 + \frac{1}{2} K_s r_{ic, is}^2 \right] + \sum_{ik>jl} T(\vec{r}_{ik, jl}) C_{ik, jl}(\vec{r}_{ik, jl}) q_{ik} q_{jl}, \quad (1)$$

where i and j are the atomic indices and k and l represent the core (c) or shell (s). $r_{ik, jl}$ is the distance between the i -th atom's core or shell with the j -th atom's core or shell. $\chi_i^0 = (\text{IP} + \text{EA})/2$ is the Mulliken electronegativity and $J_{ii}^0 = (\text{IP} - \text{EA})$ is the idempotential (hardness) or electron capacity of the i -th atom (IP and EA are the valence averaged atomic ionization potential and electron affinity). The second sum is the pairwise shielded Coulomb interaction energy between all cores and shells. The electrostatic energy between two Gaussian charges is given by $C_{ik, jl}(\vec{r}_{ik, jl}) q_{ik} q_{jl}$, where

$$C_{ik, jl}(\vec{r}_{ik, jl}) = \frac{1}{r_{ik, jl}} \text{erf} \left(\sqrt{\frac{\alpha_{ik} \alpha_{jl}}{\alpha_{ik} + \alpha_{jl}}} r_{ik, jl} \right), \quad (2)$$

where α_{ik} , the width of the distribution given by $\alpha_{ik} = \lambda / 2R_{ik}^2$. Here, R_{ik} is the covalent atomic radius in Å units and λ is a parameter that converts the overlap of two Gaussian charges to the effective shielding. In the case of $\vec{r}_{ik} = \vec{r}_{jl}$, $C_{ik, jl}$ is equal to

$$C_{ik, jl}^0 = \lim_{r \rightarrow 0} C_{ik, jl}(\vec{r}) = \frac{2}{\sqrt{\pi}} \sqrt{\frac{\alpha_{ik} \alpha_{jl}}{\alpha_{ik} + \alpha_{jl}}}, \quad (3)$$

so that the Gaussian shielding present in PQEq results in a finite Coulombic interaction energy in the limit of zero interatomic distance. The Coulombic interaction is screened using a taper function, which has a finite range. We use a 7-*th* order taper function as

$$T(\vec{r}_{ik, jl}) = \sum_{\alpha=0}^7 \text{Tap}_{\alpha} \left(\frac{r_{ik, jl}}{r_{\text{cut}}} \right)^{\alpha}, \quad (4)$$

where r_{cut} is a cutoff length defined in the input file (see below) and $\text{Tap}_7 = 20$, $\text{Tap}_6 = -70$, $\text{Tap}_5 = 84$, $\text{Tap}_4 = -35$, $\text{Tap}_3 = 0$, $\text{Tap}_2 = 0$, $\text{Tap}_1 = 0$, and $\text{Tap}_0 = 1$. Eq. (1) can be expanded to give the total electrostatic energy as

$$E_{Coulomb}(\{\vec{r}_{ic}, \vec{r}_{is}, q_i\}) = \sum_i^N \left[\chi_i^0 q_i + \frac{1}{2} J_{ii}^0 q_i^2 + \frac{1}{2} K_s r_{ic, is}^2 \right] + \sum_{i>j} \left[T(\vec{r}_{ic, jc}) C(\vec{r}_{ic, jc}) q_{ic} q_{jc} - T(\vec{r}_{ic, js}) C(\vec{r}_{ic, js}) q_{ic} Z_j - T(\vec{r}_{is, jc}) C(\vec{r}_{is, jc}) q_{jc} Z_i + T(\vec{r}_{is, js}) C(\vec{r}_{is, js}) Z_i Z_j \right] \quad (5)$$

In PQEq, the atomic charges q_i are variables that change dynamically in time. When atomic positions are updated during the MD simulation, the PQEq subroutine updates charge distribution q^N by minimizing $E_{Coulomb}$ subject to the conditions that the chemical potentials ($\partial E / \partial q_i$) are equal for all of the atoms (which provides $N-1$ conditions where N is the number of atoms) and that the total charge is conserved,

$$\sum_i (q_{ic} + q_{is}) = \sum_i q_i = Q, \quad (6)$$

where Q is the total charge of the system. We use Lagrange multipliers to guarantee this constraint as the charges are optimized,

$$g_i \equiv -\frac{\partial E_{Coulomb}}{\partial q_i} = -\mu, \quad (7)$$

where μ is the electrochemical potential. We solve this equation iteratively using the preconditioned-conjugate-gradient (PCG) method, which dramatically reduces computational costs while retaining stability and accuracy for various model systems¹⁵⁻¹⁶. We coupled the PCG method with shell relaxation (see below) to calculate the PQEq charges while updating the shell position. The shell position for each atom is obtained by balancing the effect of the electrostatic field due to all external atoms with intra-atomic interactions involving only the core and its shell.

$$F_{intra} = -\frac{\partial}{\partial r_{is}} \left(\frac{1}{2} K_s r_{ic, is}^2 \right), \quad (8)$$

$$F_{external} = -\frac{\partial}{\partial r_{is}} \left\{ \sum_{ik > jl} T(\vec{r}_{ik, jl}) C_{ik, jl}(\vec{r}_{ik, jl}) q_{ik} q_{jl} \right\}. \quad (9)$$

We solve Eqs. 7 and 8 to find the optimal position of shells (r_{is}) using a single iteration of the Newton-Raphson method. We assume here that the shell is massless, so that it relaxes instantaneously to its zero-force position, with no inertial delay. The parameters for PQEq are derived from valence averaged experimental ionization and electron affinity data and standard bond distances for all elements up to Nobelium (atomic no. =102).

Figure 1. The components of the PQEq model for a system with two atoms. Spherical 1s Gaussian charge distributions are used to describe both cores and shells. The core (ρ_{ic}) contains a variable (ρ_i) and fixed (ρ_{iZ}) charge distributions while shell (ρ_{is}) has only the fixed charge distribution. The interaction of shell and core is described through a harmonic spring

force. Cores and shells of different atoms interact with each other through Coulombic interactions.

3. PQEq validation using QM interaction energy

In order to validate how well PQEq matches the QM for Ge, As, Se, Br, Sn, Sb, Te, I, Pb, Bi, Po, and At, we chose a set of 28 molecular structures selected to include common oxidation states of each elements. Since selenium, tellurium, and polonium may exist in several oxidation states, each was sampled in an oxo and in a dioxo structure to include both the +2 and +4 oxidation states. Bromine, iodine, and astatine were sampled in cyclohexane-based structures and hypervalent interhalogen structures to include the -1, +3, and +5 oxidation states. Most structures were based upon a cyclohexane structure with either a carbon or a hydrogen replaced by the element of interest. In addition, some interhalogen compounds such as BrF₃ and BrF₅ were examined since bromo-cyclohexane does not polarize easily and halogens have common hypervalent examples.

Then, for each of these molecules we probe with a pair of ± 1.0 pair charges separated by 1 Å to examine the interaction with dipole and higher order multipoles. These scans were performed along several unique axes to sample different electrostatic environments around each element. In addition, the scan axes were selected to avoid close contacts with the nearby atoms. The scan directions that resulted in less than 2 kcal/mol change in interaction energy were excluded. We also avoided scanning directions that could lead to very close interaction of the dipole with nearby atoms. In addition, to avoid non-electrostatic interactions (due to Pauli principle repulsion), we scan only down to about 2.5-3.0 Å, which we find to be close to the inflection point (attractive forces) of the electrostatic potential curve. These considerations resulted in a total of 56 scans for the 28 molecular structures. The change of QM electric dipole energy with the distance for each case is shown in Figure S1 of the Supplementary Materials and for several selected cases in Figure 2a-o.

4. Results

Training Set. For elements in column 14 (Ge, Sn, Pb), atoms were placed in cyclohexane-based structures with either one, three, or six carbons replaced by the element of interest. Dipole probes were scanned along an H-X bond, along the two-fold axis between H-X bonds, or along a C-X bond (where X represents a generic *p*-block element).

For column 15 (As, Sb, Bi), atoms were placed in cyclohexane-based structures where a carbon and a hydrogen were replaced by the element of interest and an oxygen, respectively. Dipole probes were scanned along the H-X bond and along the two-fold axis between the H-X and O-X bonds. Additionally, cacodylic acid, (CH₃)₂AsOOH, was scanned along the two-fold axis between the both O-As bonds, along the oxo bond, along the oxo-alcohol-methyl three-fold axis, and along a C-As bond.

For column 16 (Se, Te, Po), atoms were placed in cyclohexane-based structures with a carbon replaced by the element of interest with either one or two oxo bonds rather than hydrogens. Dipole probes were scanned along the O-X bonds or along the two-fold axis between the oxo groups.

For column 17 (Br, I, At), atoms were placed in either cyclohexane-based structures with a hydrogen replaced by an element of interest, in a XF₃ structure, or in a XF₅ structure. Dipole

probes were scanned along X-C and X-F bonds, the two-fold axis in XF_3 , and the three-fold axis in XF_5 . See Figure 2 and the Supporting Information for more details on each dipole scan.

Electric Dipole Energy. Dipoles were scanned towards each molecular structure along various directions and at incremental steps, the energy of the system was calculated via QM and PQEq. Figure 2 shows examples of such dipole electrostatic interaction energy curves for each element of interest. Supporting Information contains scans for all other directions. Dipoles were scanned along a bond, along a two-fold axis, or along a three-fold axis. In order to calculate the QM interaction energies, we used the Schrodinger Jaguar¹⁷ software with a B3LYP¹⁸ DFT functional and either

- the LACVP¹⁹ large core relativistic effective potential (in which Ge, As, Se and Br have 4, 5, 6 and 7 explicit electrons, respectively) along with the 6-31G basis set for the H,C,O atoms or
- the ERMLER2²⁰ small core relativistic effective potential (in which Ge, As, Se and Br have 22, 23, 24 and 25 explicit electrons, respectively) with the 6-31G**++ basis set for H, C, O atoms that includes diffuse (++) and polarization functions (**). This was test only for Po and At.

The inclusion of diffuse functions had little impact on the interaction energies. For example, Figure 3 shows that the inclusion of the diffuse functions does not significantly alter the dipole electrostatic interaction energy curve for germanium in a cyclohexane-based structure.

Then, the χ and J parameters from PQEq1⁹ were optimized (minimizing the difference between PQEq and QM) for all p -block elements were optimized, using the 28 molecular structures described above. We use an optimization strategy similar to that in paper I. That means using constrained conjugate gradient (CG) with a cost function $\left(\frac{E_{QM}-E_{PQEq}}{E_{QM}}\right)^2$, to ensure the final optimized parameters follow the physical meaning and general trend of the periodic table, while ensuring agreement with QM. The new optimized parameter set is called PQEq2 to avoid confusion with the PQEq and PQEq1 parameter sets that were obtained in paper I.

Figure 2. Electrostatic interaction energies of an electric dipole approaching the molecule from various directions computed by QM (black) and PQEq (red and blue). Cases are presented for atoms types of: (a) Ge, (b) Sn, (c) Pb, (d) As, (e) Sb, (f) Bi, (g) Se, (h) Te, (i) Po, (j, m) Br, (k, n) I, and (l, o) At. The inset of each subfigure shows the molecular structure configuration with the scan direction (blue +1, green -1) of the electric dipole.

Figure 3. Comparison of QM electrostatic interaction energies of an electric dipole approaching germanium in a cyclohexane-based structure using LACVP with (black) and without (blue) diffuse functions. There is no significant difference in the QM energy curves.

Partial Charge Calculation. The partial charge of atoms in the molecular structures was calculated via PQEq, PQEq2, Mulliken population analysis (MPA), and electrostatic potential (ESP) to ensure that the computed charges by QEq method are consistent with our chemical intuition. When computing MPA and ESP charges, the DFT hybrid functionals, B3LYP, M06²¹, and PBE²² were used with LACVP, LACVP**, and LACVP+++ (or the ERMLER2 equivalent for molecular structures with astatine and polonium). An example partial charge calculation is depicted in Figure 4a-d. Partial charge calculations for each molecule in the training set are supplied in the SI as Figure S2.

Figure 4. Partial charge comparison between PQEq, PQEq2, and various QM methods (MPA and ESP) in (a) germinane, (b) arsinane 1-oxide, (c) selenane 1-oxide, and (d) bromine pentafluoride molecules. The ESP (left) and MPA (right) charges were computed using several basis sets and DFT functionals including B3LYP, M06, and PBE and LACVP, LACVP**, and LACVP++*. The PQEq and PQEq2 charges are plotted in each figure for a better comparison. The position of each atom for the corresponding ID is shown on the molecular structure schematic on the right.

5. Discussion

We find an excellent agreement between the electrostatic interaction energy computed by PQEq and QM.

The non-monotonic behavior present in some dipole scans, such as Figure 2e and Figure 5, is due to non-electrostatic effects along the scan. We have found that some directions lead to positive energies (depending on the molecular dipole). We have found the best convention is to orient the dipole such that the total interaction energy is negative at larger distances. In this case, the polarization energy is monotonic and negative down to near the van der Waals radius. We consider that the shorter distances are not just probing the polarization involving the target atom, but more complex interactions with all atoms.

Figure 5. Non-monotonic behavior in the energy curve.

We calculate the polarization energy by subtracting the total QM energy for each distance from the QM energy at the longest distance. For the *p*-block elements, using the total QM energy appears to be accurate enough and provide a monotonic behavior for most cases.

We have found that the QM dipole electrostatic interaction energy curve is fairly insensitive to the method used to compute it. We have tested the method used in this experiment B3LYP/LACVP***++ (or ERMILER equivalent), against M06 and HFS²³ and without the use of diffuse functionals. The results are shown in Figure S5 of the SI.

For some cases such as Figures 2k and 2o, the trends from PQEq2 differ slightly from those of the original PQEq set and depend on the oxidation number of the element. We constrained the optimization to preserve the ordering of χ and J along the rows and columns of the periodic table. For halogens, the χ and J parameters depend on the oxidation number but we see that the original values of χ and J for PQEq work quite well.

It should be mentioned that we do not constrain the χ and J parameters for hydrogen because the Mulliken definition electronegativity, which is implicit in QEq makes H far too electronegative. The reason is that the experiment electron affinity for of H⁻ (EA~0.7 eV) leads

to a size of $\sim 6\text{\AA}$ for H^- . This is not appropriate for moving charge onto the H in a molecule, where the H atom has a size $< 1\text{\AA}$. Thus, the EA used in PQEq should be negative. However, it is not well defined, so we let the hydrogen parameters float freely. As a result of this free parameter, the PQEq2 parameters for Ge and Sn are more electronegative than H and therefore the partial charge calculation shows more negative charge on Ge and Sn atoms compared to H, as seen in Figure 6a-b. Our main criteria for validation is the interaction energy comparison, which we find a good agreement for all cases.

Figure 6. Partial charge comparison between PQEq, PQEq2, and various QM (see caption of Figure 4) in (a) hexagerminane, and (b) hexastannane molecules. The computed partial charges for Ge and Sn are smaller (more negative) than H atom when PQEq2 parameter set is used. The reason is H parameters are let to float freely during PQEq 2 parameter set optimization.

6. Conclusions

The current paper represents an additional step toward validation and extension of the PQEq model to all elements of the periodic table. Here, we validated the accuracy of PQEq for Ge, As, Se, Br, Sn, Sb, Te, I, Pb, Bi, Po, and At elements. Again we find that original PQEq parameters obtained from standard atomic ionization energies, standard covalent radii, and literature atomic polarizabilities provide electrostatic interaction energies in good agreement with QM.

These validations were performed by comparing the electrostatic interaction energies as an electric dipole is brought up to the molecule for 28 molecules (56 cases) involving above atoms. We also provide the PQEq2 parameter set in which the atomic parameters (χ and J) were optimized against QM polarization energy, leading to some improvements. We also show that PQEq and PQEq2 result in reasonable partial charge distribution for all of the 28 molecules.

SUPPLEMENTARY MATERIALS

See Supplementary Materials for:

- PQEq database of test molecules, PQEq2 optimized parameters, polarization energy comparison, charge comparison
- PQEq2 electronic parameter files
- Geometries of all 28 molecular structures used in the training set in XYZ file format
- Electrostatic interaction dipole scans for additional oxidation states
- Tests of electrostatic interaction dipoles using different DFT functionals and diffuse functions

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TOC Graphic

The components of the PQEq model for a system with two atoms. Spherical 1s Gaussian charge distributions are used to describe both cores and shells. The core (ρ_{ic}) contains a variable (ρ_i) and fixed (ρ_{iZ}) charge distributions while shell (ρ_{is}) has only the fixed charge distribution. The interaction of shell and core is described through a harmonic spring force. Cores and shells of different atoms interact with each other through Coulombic interactions.

170x106mm (300 x 300 DPI)

Electrostatic interaction energies of an electric dipole approaching the molecule from various directions computed by QM (black) and PQEq (red and blue). Cases are presented for atoms types of: (a) Ge, (b) Sn, (c) Pb, (d) As, (e) Sb, (f) Bi, (g) Se, (h) Te, (i) Po, (j, m) Br, (k, n) I, and (l, o) At. The inset of each subfigure shows the molecular structure configuration with the scan direction (blue +1, green -1) of the electric dipole.

190x232mm (300 x 300 DPI)

Comparison of QM electrostatic interaction energies of an electric dipole approaching germanium in a cyclohexane-based structure using LACVP with (black) and without (blue) diffuse functions. There is no significant difference in the QM energy curves.

66x46mm (300 x 300 DPI)

Partial charge comparison between PQEq, PQEq2, and various QM methods (MPA and ESP) in (a) germinane, (b) arsinane 1-oxide, (c) selenane 1-oxide, and (d) bromine pentafluoride molecules. The ESP (left) and MPA (right) charges were computed using several basis sets and DFT functionals including B3LYP, M06, and PBE and LACVP, LACVP**, and LACVP++*. The PQEq and PQEq2 charges are plotted in each figure for a better comparison. The position of each atom for the corresponding ID is shown on the molecular structure schematic on the right.

222x272mm (300 x 300 DPI)

Non-monotonic behavior in the energy curve.

66x46mm (300 x 300 DPI)

Partial charge comparison between PQEq, PQEq2, and various QM (see caption of Figure 5) in (a) hexagerminane, and (b) hexastanninane molecules. The computed partial charges for Ge and Sn are smaller (more negative) than H atom when PQEq2 parameter set is used. The reason is H parameters are let to float freely during PQEq 2 parameter set optimization.

2275x1234mm (72 x 72 DPI)

TOC

82x44mm (300 x 300 DPI)