The Polarizable Charge Equilibration Model for Transition-Metal Elements

Soonho Kwon, Saber Naserifar, Hyuck Mo Lee, and William A. Goddard

J. Phys. Chem. A, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpca.8b07290 • Publication Date (Web): 09 Nov 2018

Downloaded from <http://pubs.acs.org> on November 12, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

The Polarizable Charge Equilibration Model for Transition-Metal Elements

Soonho Kwon¹, Saber Naserifar², Hyuck Mo Lee^{1,*}, and William A. Goddard III^{2,*}

¹Department of Materials Science and Engineering, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

²Materials and Process Simulation Center, California Institute of Technology, Pasadena, California, 91125

*corresponding author, email: hyuckmolee@kaist.ac.kr, wag@wag.caltech.edu

ABSTRACT: The Polarizable Charge Equilibration (PQEq) method was developed to provide a simple but accurate description for the electrostatic interactions and polarization effects in materials. Previously, we optimized the 4 parameters per element for the main group elements. Here, we extend this optimization to the 24 *d*-block transition-metal (TM) elements, column 4 to 11 of the periodic table including Ti-Cu, Zr-Ag, and Hf-Au. We validate the PQEq description for these elements by comparing to interaction energies computed by quantum mechanics (QM). Since many materials applications involving TM are for oxides and other compounds that formally oxidize the metal, we consider a variety of oxidation states in 24 different molecular clusters. In each case, we compare interaction energies and induced fields from QM and PQEq along various directions. We find that the original χ and J parameters (electronegativity and hardness) related to the ionization of the atom remain valid, however we find that the atomic radius parameter needs to be close to the experimental ionic radii of the transition metals. This leads to a much higher spring constant to describe the atomic polarizability. We find that with these optimized parameters for PQEq provide accurate interactions energies compared to QM with charge distributions that depend in a reasonable way on the coordination number and oxidation states of the transition metals. We expect that this description of the electrostatic interactions for TM will be useful in molecular dynamics simulations of inorganic and organometallic materials.

1. Introduction

Transition metals (TM) play an essential role in numerous materials and biological applications including transition-metal nanoclusters in catalysis¹, catalytic reactions for organic synthesis², photonic and optoelectronic devices³, two-dimensional semiconductors⁴, polymerization⁵, magnetic refrigerants⁶, and metal-organic frameworks^{7, 8}. This diversity in applications of TMs arises from the unique properties of their valence *d*- and *f*- orbitals. In order to develop improved materials, it is valuable to use quantum mechanics (QM) to predict the structures and properties. However, the QM is limited to ~200 atoms per molecule or per periodic cell, and ~10-20 picoseconds of dynamics. This is not sufficient for designing nanoscale devices that may involve several distinct materials and their interfaces (a cell with 25 nm on a side may be 4 million atoms) and time scales should be at least nanoseconds. Thus, it is very valuable to develop force fields to use in molecular dynamics (MD) simulations to describe the structures, properties, and dynamics of practical sized TM systems.

The problem here is that TM containing materials lead to a range of coordination numbers, oxidation states, and electronic configurations depending on their compositions and local environment. In particular, the simulation results may depend sensitively on the partial charge and polarization on the TMs atoms.

In order to address this problem, we developed the Universal Force Field (UFF)⁹ in 1992 to provide generic parameters to describe the equilibrium structures of inorganics compounds based on physical principles and trends. UFF included generic descriptions of the bond, angle, and torsion valence interactions along with parameters for nonbonded the van der Waals interactions and charges based on the Charge Equilibration (QEq) method. An innovation with QEq was to distribute each charge over a region the size of the atom (originally a Slater orbital, now a Gaussian function). The parameters for QEq are the size of the atom (half the standard bond distance) and the electronegativity (χ) and hardness (J) derived from the atomic ionization potential (IP) and electron affinity (EA). However, no attempt was made to optimize these parameters.

We recently developed the polarizable charge equilibration methodology (PQEq)¹⁰ that includes self-consistent atomic charge transfer and polarization for use in MD simulations of materials. In PQEq, the charge on each atomic core is described by an atomic sized Gaussian function while the polarization is described by a Gaussian shaped shell connected to the core by a harmonic spring with force constant K . 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. An innovation with PQEq is describing both core charge and the shell charge as distributed charges, which avoids the singularities commonly found with point charge models. A second innovation was optimizing the parameters by comparing the polarization energy from QM and PQEq as point dipoles are brought into typical molecules containing the atoms.

PQEq uses four parameters per element to describe the charge and polarizability. The original PQEq paper provided default atomic parameters (denoted PQEq0) for all elements of the periodic table up to Nobelium ($Z=102$) based on available experimental atomic data. We previously optimized and validated the accuracy of PQEq for main group elements of the C, N, O, and F columns of the periodic table TM (H, C-F, Si-Cl, Ge-Br, Sn-I, Pb-At)^{10, 11}. These optimized values were denoted as PQEq1 and PQEq2.

In this paper, we optimize and validate the PQEq parameters for TMs to provide accurate descriptions of the dynamic charge and polarization for molecular dynamics (MD) and reactions. Here, we validate against QM the interaction energies for molecules involving the 24 TMs: Ti-Cu, Zr-Ag, Hf-Au.

2. Method

The complete description of PQEq can be found elsewhere^{10, 11}. Here, we summarize the key elements. PQEq describes charges on each atom as Gaussian functions, ρ_{ic} and ρ_{is} , with

- ρ_{ic} centered on the nuclear core (containing also the mass) with total charge of $q_i + 1$ and
- ρ_{is} allowed to polarize away from the nuclear core (containing zero mass) with fixed total charge (-1).

Thus, the total charge (core plus shell) on the atom is q_i . Both core and shell are described with 1s Gaussian functions having the same size of the atom (R_i) and they are connected by an isotropic harmonic spring with force constant K_s (see Figure 1). The Coulomb energy is expressed as (1)

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

where i and j represent atomic indices while k and l denote core (c) or shell (s). Here

- $r_{ik, jl}$ is the distance between the core (or shell) of the i -th atom with that of the j -th atom.
- χ_i^0 is the Mulliken electronegativity $[(IP+EA)/2]$ and
- J_{ii}^0 is the idempotential or hardness (IP-EA) of the i -th atom.

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 $C_{ik, jl}(r_{ik, jl}) q_{ik} q_{jl}$, where

$$C(r_{ik, jl}) = \frac{1}{r_{ik, jl}} \operatorname{erf} \left(\frac{\sqrt{\alpha_{ik} \alpha_{jl}}}{\alpha_{ik} + \alpha_{jl}} r_{ik, jl} \right), \quad (2)$$

where α_{ik} is the width of the Gaussian distribution, which is a function of covalent atomic radius (R_{ik}) and shielding (λ), $\alpha_{ik} = \lambda / 2R_{ik}^2$. The long-range Coulomb interactions become important in periodic system simulations where we must dampen the Coulomb interactions smoothly at the cutoff distance. For this purpose We use a 7th order taper function $T(r_{ik, jl})$ that matches through the third derivative in the energy at $R=0$ and at $R=\text{cutoff}$ ¹¹.

During the MD simulations, the PQEq step dynamically updates the atomic charges and shell positions in response to the electrostatic environment. The charges are updated by minimizing the energy equation (Equation 1) subject to the conditions that the total charge is conserved and that the chemical potentials ($\partial E_{\text{Coulomb}} / \partial q_i$) are equal for all atoms. We use the preconditioned-conjugate-gradient (PCG) method to reduce computational costs of adjusting the charges at each step while retaining the accuracy and stability of the results.¹² The shell relaxation was coupled with the PCG method to update the shell positions at the same time that charges are computed.

The optimum shell position is computed by balancing the electrostatic forces from all other atoms with the attractive harmonic force between the core and the shell of the atom (described by K_s).¹⁰

We started with the default PQEq0 parameters for all elements up to Nobelium ($Z=102$) from experimental ionization and electron affinity data and standard bond distances.¹⁰

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 (ρ_{ic}) and shells (ρ_{is}). The integral of the shell charge is -1 while the integral of the core charge is $q_i + 1$, so that the total charge is q_i . The interaction of shell and core is through a harmonic spring with force constant K . Cores and shells of different atoms interact with each other through standard Coulomb interactions.

3. Optimization of PQEq using QM polarization energy

To optimize the PQEq parameters for TM elements, we used cyclic structures based on common oxidation states of M . Thus for W we used the W_3O_9 cluster (Figure 2a) in which each W makes two $W=O$ oxo bonds and two $W-O-W$ bridging bonds, leading to W^{VI} . For Pt we used the Pt_6O_{12} cluster (Figure 2b) in which there are two $Pt-O-Pt$ chains between each Pt , leading to Pt^{IV} . For Ta we used the Ta_4O_{10} cluster (Figure 2c) in which each Ta has one $Ta=O$ oxo bond with $Ta-O-Ta$ bridges to each of the other three Ta . The full set of 24 oxide and fluoride structures are depicted in Figures S1 and S2 of the Supporting Information and provided in XYZ format with PQEq3 force field file(txt). Most structures were chosen by considering the stability of the geometric configurations. In addition, some halogen compounds such as Ag_4F_4 and Au_4F_4 having D_{2d} symmetry were chosen for extra analysis. We designed model clusters to have net charge of 0.0 and single spin state.

We probe each of the model clusters in our training set with an electric dipole described using a pair of ± 1 point charges separated by 1 Å (this also includes higher order multipoles). We scan the QM total energy by bringing the electric dipole toward the closest atom in the structure along various directions from distances as long as 10 Å down to 2 Å. A variety of scan directions were chosen to study the dependence of interaction energies on the orientation of the molecule with respect to the electric field.

For all DFT calculations, we used Jaguar code¹³ with the standard B3LYP hybrid functional¹⁴⁻¹⁸ using the LACVP (small core) basis set¹⁹ together with polarization functions²⁰⁻²³. We also included the D3 empirical van der Waals correction of Grimme *et al*^{24, 25}. For most cases, the total energy for d -block element leads to non-monotonic behavior due to non-electrostatic effects. Occasionally, this also leads to positive net interaction energies depending on the orientation of the molecular dipole. The nature of this occasional non-monotonic behavior in the QM energy curve was discussed in our previous papers^{10, 11}. To avoid such problems and to measure directly the dipole interaction energy, we introduced a new approach where we define the net dipole interaction energy (E_{net}^{QM}) as

$$E_{net}^{QM} = E^{QM} - E_{fix}^{QM}, \quad (3)$$

where E^{QM} is QM total energy for the fully converged wavefunction at the given dipole distance and E_{fix}^{QM} is single point QM total energy at the same distance using wavefunctions from the longest dipole distance. Therefore, the difference between E^{QM} and E_{fix}^{QM} arises purely from polarization due to the dipole interaction with the structure (i.e. E_{net}^{QM}). Similarly, the net interaction energy for PQEq is defined as

$$E_{net}^{PQEq} = E^{PQEq} - E_{fix}^{PQEq}, \quad (4)$$

where E_{net}^{PQEq} is the dipole net interaction energy for PQEq, E^{PQEq} is the PQEq total energy with fully equilibrated charge and shell positions, and E_{fix}^{PQEq} is the PQEq total energy at the same dipole distance but using the atomic charges and shell positions that were obtained at the longest dipole distance. Therefore, we validate and optimize the PQEq parameters by comparing E_{net}^{PQEq} directly with E_{net}^{QM} .

We obtained the Mulliken electronegativity, $\chi = (IP+EA)/2$, and the idempotential, $J=IP-EA$, from the most recent experimental ionization potential (IP) and electron affinities (EA) values for each TMs element²⁶⁻⁵⁵. These values are provided in Table S1 of the SI. In addition, for the atomic radius (R) we also start with half the experimental bond distance and for the spring force (K_s) constants we start with the literature polarization values. However, we find that R and K_s must be optimized for E_{pol}^{PQEq} to fit E_{pol}^{QM} (see below) for the TM oxides.

For optimization, we performed a full mapping of the parameters K_s and R to avoid getting trapped in local minima. The total error is defined as the weighted mean square error (MSE) given

$$Error = \sum_i \omega_i (E_{net}^{PQEq} - E_{net}^{QM})^2, \quad (5)$$

where ω_i is the weight. The mapping was performed such that the parameters were kept physically reasonable while minimizing the total error (see below). The new optimized parameter set is denoted PQEq3 whereas the default set from paper 1 is denoted as PQEq0^{10, 11}. We used the PQEq0 for oxygen and fluorine for all optimization. We found that PQEq1 shows negligible differences as shown for Pt and W in Figure S3.

3. Results

Net interaction energy. Figure 2 shows the result of electric dipole scans for (a) W_3O_9 , (b) Pt_6O_{12} , and (c) Ta_4O_{10} clusters. The scans were performed along four different directions for W_3O_9 and 2 different directions for Pt_6O_{12} and Ta_4O_{10} .

For the W_3O_9 cluster (with D_{3h} symmetry) the dipoles were scanned toward the center of mass of the cluster through W atom (a1 direction), along the axis connecting W with a bridging O bond (a2 direction), along the two-fold axis between bridging and terminal O atoms (a3 direction), and along the W=O bond (a4 direction). The a4 direction also corresponds to three-fold axis between two bridging and one terminal O atoms.

For Pt_6O_{12} , a1 indicates the in-plane direction that passes through a Pt atom and its 2nd nearest Pt atom and a2 is the out-of-plane direction toward the Pt atom.

For Ta_4O_{10} , the a1 and a2 directions are two- and three-fold directions, respectively.

The energies for the dipole scan were calculated by bringing the electric dipole from 10.0 Å (negligible interaction energy) to 2.0 Å, leading to the net interaction energies of 15 ~ 20 kcal/mol. The electric dipole scans for the other TMs are shown in Figure S1 in the Supplementary Information.

The total energy as the distance to the dipole is decreased is not monotonic for these cases is shown in Figures 2 (d-f). In contrast, the net polarization energy, shown in Figures 2 (g-i), lead to monotonic increases in the interaction as the distance of the dipole from the molecule decreases.

We found that optimizing the χ and J parameters had a negligible effect on the fit, and we kept them fixed at the experimental values. Thus, we optimized only the R and K_s values to minimize the total error in Equation 5. This optimization was performed by mapping R and K_s over a wide range of values. For example, Figure 3 shows the mapping for W, over the range of $R=0.5$ Å to 1.5 Å and $K_s=100$ to 700 kcal/mol/Å². We note that K_s is less sensitive than R above a specific lower limit. Based on this, we have tried to ensure that the K_s behaves in a reasonable way across the periodic table (See Figure 4).

Our results show that the optimum values of the atomic radii (R) are close to the standard ionic radii. Thus for W^{6+} our optimum $R=0.655$ Å is close to the standard ionic radius from crystal structure analysis of 0.42 Å. We will show that the optimum R for all others cases are similar to the ionic radius rather than our original default values based on the bond distances in the bulk metals.

With these much smaller R values it is necessary to adopt much larger spring force constants (K_s). For example, for W, R changes from 1.538 Å to 0.655 Å while K_s changes from 29.92 kcal/mol/Å² to 385 kcal/mol/Å² after optimization.

The final PQEq3 parameters for all TMs are given in Table S1 in the Supplementary Information.

This optimized parameter set (PQEq3) provides excellent agreement between PQEq and QM net interaction energies (see Figures 2 (g-i)). The average error for each electric dipole distance for most directions is less than 0.5 kcal/mol. A similar trend was found for all other TMs elements as shown in the Figure S1 of the Supporting Information.

Figure 2. The interaction energy as an electric dipole is brought up to the clusters computed by QM and PQEq for (a) W_3O_9 , (b) Pt_6O_{12} , and (c) Ta_4O_{10} . The structures for the clusters are shown in the left (a-c) where blue and green spheres represent positive (+1) head and negative (-1) tail of the electric dipole, respectively. The QM total energies (d-f) lead to non-monotonic behaviors for some of the directions, whereas the QM and PQEq net interaction energies (g-i) are always monotonic. The optimized PQEq provides excellent agreement with QM net interaction energy.

Figure 3. Contour plot of estimated total error versus the atomic radius, R , and the spring force constant, K_s for the W_3O_9 cluster model. The black dot indicates the value we selected.

Figure 4. Comparison of the optimum K for PQEq3 with the default values in PQEq0.

Partial Charge Calculations. PQEq represents the charge on each atom as a Gaussian function having the size of the atom. However, it is useful to compare PQEq charges with the partial point charges obtained from Mulliken population analysis (MPA) and from electrostatic potential (ESP) charges. We calculated MPA and ESP charges using several flavors of DFT including B3LYP, M06⁵⁶, and Perdew-Burke-Ernzerhof (PBE)⁵⁷ functionals with LACVP, LACVP**, LACVP++** basis sets. An example of these calculations is shown in Figure 5 for three selected cases. The figures for all other TMs are included in Figure S2 of the Supporting Information.

The magnitude of the optimized charges (PQEq3) are generally larger than for the default

parameters (PQEq0) (see Figure 5). For example, for W_3O_9 Figure 5(a), the PQEq3 charge is +4.0 for W atom, MPA leads to +1.80, and the PQEq0 charge is +0.76. The PQEq3 charges on bridging and terminal oxygen atoms are -1.7 and -1.4, respectively, while QM leads to -0.82 and -0.49 and PQEq0 leads to -0.24 and -0.26. All other cases are in Figure S2 of the Supporting Information.

It should be emphasized that PQEq3 parameters are *not* fitted to get match partial charges from QM; they are fitted to reproduce the QM net interaction energy.

Another important result is that the PQEq3 parameter set leads to reasonable distributions of partial atomic charges based on the coordination number and oxidation states of the atoms in the structure. For example, consider the Pt_6O_{12} and Ta_4O_{10} clusters shown in Figures 5 (b) and (c), respectively. Pt_6O_{12} has D_{6h} symmetry with 6 Pt and 12 O equivalent atoms. PQEq leads to similar +1.5 charge on all Pt and -0.27 charge on all O atoms. On the other hand, the Ta_4O_{10} cluster has T_d symmetry with 4 terminal Ta=O oxo bonds and 6 bridging O atoms. PQEq correctly distinguishes the atoms with different coordination numbers leading to -1.4 charge for the bridging O, and -1.0 for the terminal O atoms. We find similar behavior for PQEq for all other TMs (see Figure S2 of the Supporting Information).

Figure 5. Comparison of Partial charges from PQEq3 (optimized) and PQEq0 (default) with standard QM methods (MPA and ESP) in (a) W_3O_9 , (b) Pt_6O_{12} , and (c) Ta_4O_{10} clusters. The ESP (left) and MPA (right) charges are computed using several basis sets and DFT functionals, including B3LYP, M06, and PBE and LACVP, LACVP**, and LACVP***. The position of each atom for the corresponding ID is shown on the molecular structure schematic on the right.

4. Discussion

TMs lead to a variety of coordination environments with a variety of oxidation states experienced during chemical reactions and under structural deformations. Therefore, to accurately describe the interactions of TMs with other elements, it is necessary to have a model that can dynamically distinguish between these different modes of TMs.

To validate the ability of PQEq to describe such variations, we compared the computed net interaction energy (using electric dipole scan) of PQEq with that of QM. This provides a robust validation of the PQEq method since the QM energy provides an accurate description of the interactions. We see that the PQEq model with 1s-Gaussian functions, leads to an accurate description of the QM interaction energies.

The main difference between the PQEq3 and original PQEq0 parameters sets is in the atomic radius (R) value. As discussed above, the optimization results in values very close to the experimental effective ionic radii. Thus, $R = 0.641 \text{ \AA}$ for Ta^{5+} compares well with $R = 0.640 \text{ \AA}$ from experiment. The same trend was found for other TMs as shown Figure 6, where all PQEq3 atomic radii values are in the range of experimental ionic values. The experimental R values in Fig. 5 are estimated by averaging over the values taken from literature for the same oxidation states used in our oxide cluster models. These results show that to obtain a correct distribution of the charge density on each atom it is necessary to use TM radii close to the ionic radius rather than the covalent bond radius of PQEq0.

Using the ionic atomic radii requires much larger values for K , since the small ionic core is much harder to polarize than for the larger covalent metal-metal bonding based radii appropriate for delocalized conduction electrons. Thus the spring force constant (K_s) was optimized to ensure stability of the shells around the cores. This resulted in much larger K_s values than the original PQEq0 numbers. Table S2 of the Supplementary Information compares R and K_s values of PQEq0 and PQEq3 parameter sets

The correct response of the PQEq3 parameter set to the changes in electrostatic environment is shown by the electric dipole scans. The PQEq3 parameter set provides reasonable charge distribution on TMs and other elements of the structure consistent with the imposed electric fields at each distance of the electric dipole from the structure. Figure 7 shows the partial charge distribution in W_3O_9 (Figure 7a), Pt_6O_{12} (Figure 7b), and Ta_4O_{10} (Figure 7c) clusters at electric dipole distances ranging from $1 \text{ \AA}$ to $10 \text{ \AA}$ computed by QM (Figures 7d-7f), PQEq3 (Figures 7g-7i), and PQEq0 (Figures 7j-7l). When the electric dipole (with positive +1 head) approaches W1 in the W_3O_9 structure, the QM charge of W1 becomes less positive and the terminal oxygens attached to the W1 (O7, O10) become less negative. A similar trend was found for Pt_6O_{12} and Ta_4O_{10} cases although there is a bigger change in the magnitude of the partial charges.

We should emphasize again that the PQEq3 parameters were obtained solely by optimizing against the QM net interaction energies. No effort was made to fit standard MPA charges, which often depend sensitively on the QM basis set. Yet PQEq leads to quite reasonable partial charge distributions on the atoms.^{10, 11} For example, for the Pt_6O_{12} cluster in Figure 5 (b), the atomic charge of Pt atom changes from 0.67 using PBE-LACVP^{++**} level of QM to 1.2 for M06-LACVP^{**}.

Figure 6. Comparison of atomic radii of transition metals from the PQEq0 original parameter set (blue), PQEq optimized parameter set (red), and experimental ionic radii (black). The experimental values for each TM are obtained from averaging the ionic radii of the atom at the same oxidation states.

Figure 7. Partial charge distribution on (a) W_3O_9 , (b) Pt_6O_{12} , and (c) Ta_4O_{10} clusters at various points in electric dipole scan toward the TM atoms. QM (d-f), PQEq3 (g-i), and PQEq0 (j-l). Note

12

that the scales are quite different. The PQEq0 and PQEq3 plots use the same label as the QM plot. The position of each atom for the corresponding ID is shown on the molecular structure schematic on the left. Here the star case (10.0A) can be considered the free cluster charge. The trend that the oxo bonds have less negative charge than the bridging O is similar for PQEq3 and QM, but different with PQEq0. The QM and PQEq3 charges are generally about half the idealized ionic limit.

5. Conclusions

This paper opens up the application of PQEq model to the *d*-block transition metals. We optimized the PQEq3 parameter sets for 24 transition metal elements (from 4th to 11th columns of the periodic table) using 24 individual metal oxide cluster and halogen compound models. The PQEq3 parameter sets includes experimental values for the electronegativity (χ) and idempotential (J) based on the most recent IP and EA for atomic atoms. Only the atomic radius (R) and spring force (K_s) were optimized against QM interaction energy. The optimization of R results in values in the range of experimental TM ionic radii. These small values for R require substantially increased of K_s to maintain the stability of the shells around each core. The PQEq3 parameter set leads to partial charge distributions on the TMs that vary in reasonable ways as the coordination environment and oxidation state is changed. This suggests that PQEq will provide a reliable electrostatic description for simulating TM containing systems.

SUPPORTING INFORMATION

See Supporting Information for:

- Parameter set for PQEq, net interaction energy, charge distribution comparisons, comparison of atomic radii between experimental and PQEq values and comparison of R and K_s values before and after optimization for all 24 transition metal elements, effect of QM diffuse functionals on electric dipole polarization, and dielectric response and polarization scalability of PQEq model.
- PQEq3 electronic parameter file

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(Ministry of Science and ICT) (No. 2017R1E1A1A03071049). This work was supported as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC00014607. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant ACI-1548562.

REFERENCES

1. Aiken, J. D.; Finke, R. G. A Review of Modern Transition-Metal Nanoclusters: Their Synthesis, Characterization, and Applications in Catalysis. *J. Mol. Catal. A: Chem.* **1999**,

- 145, 1-44.
2. Prier, C. K.; Rankic, D. A.; MacMillan, D. W. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322-5363.
 3. Kalyanasundaram, K.; Grätzel, M. Applications of Functionalized Transition Metal Complexes in Photonic and Optoelectronic Devices. *Coord. Chem. Rev.* **1998**, *177*, 347-414.
 4. Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. Emerging Device Applications for Semiconducting Two-Dimensional Transition Metal Dichalcogenides. *ACS Nano* **2014**, *8*, 1102-1120.
 5. Buchmeiser, M. R. Homogeneous Metathesis Polymerization by Well-Defined Group Vi and Group Viii Transition-Metal Alkylidenes: Fundamentals and Applications in the Preparation of Advanced Materials. *Chem. Rev.* **2000**, *100*, 1565-1604.
 6. Tegos, O.; Brück, E.; Buschow, K.; De Boer, F. Transition-Metal-Based Magnetic Refrigerants for Room-Temperature Applications. *Nature* **2002**, *415*, 150-152.
 7. Czaja, A. U.; Trukhan, N.; Müller, U. Industrial Applications of Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1284-1293.
 8. Mueller, U.; Schubert, M.; Teich, F.; Puetter, H.; Schierle-Arndt, K.; Pastre, J. Metal–Organic Frameworks—Prospective Industrial Applications. *J. Mater. Chem.* **2006**, *16*, 626-636.
 9. Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *Journal of the American Chemical Society* **1992**, *114*, 10024-10035.
 10. Naserifar, S.; Brooks, D. J.; GoddardIII, W. A.; Cvicek, V. Polarizable Charge Equilibration Model for Predicting Accurate Electrostatic Interactions in Molecules and Solids. *J. Chem. Phys.* **2017**, *146*, 124117.
 11. Oppenheim, J. J.; Naserifar, S.; Goddard, W. A. 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. *J. Phys. Chem. A* **2018**, *122*, 639-645.
 12. Aktulga, H. M.; Pandit, S. A.; Duin, A. C. T. v.; Grama, A. Y. Reactive Molecular Dynamics: Numerical Methods and Algorithmic Techniques. *SIAM J. Sci. Comput.* **2012**, *34*, C1-C23.
 13. Bochevarov, A. D.; Harder, E.; Hughes, T. F.; Greenwood, J. R.; Braden, D. A.; Philipp, D. M.; Rinaldo, D.; Halls, M. D.; Zhang, J.; Friesner, R. A. Jaguar: A High-Performance Quantum Chemistry Software Program with Strengths in Life and Materials Sciences. *Int. J. Quantum Chem.* **2013**, *113*, 2110-2142.
 14. Slater, J. C. *Quantum Theory of Molecules and Solids Vol. 4, Vol. 4*, McGraw-Hill, New York; London, 1974.
 15. Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: A Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200-1211.
 16. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785-789.
 17. Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct

- Asymptotic Behavior. *Phys. Rev. A: At. Mol. Opt. Phys.* **1988**, *38*, 3098-3100.
18. Becke, A. D. Density-Functional Thermochemistry. Iii. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
19. Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *J. Chem. Phys.* **1985**, *82*, 299-310.
20. Dyall, K. G. Relativistic and Nonrelativistic Finite Nucleus Optimized Double Zeta Basis Sets for the 4p, 5p and 6p Elements. *Theor. Chem. Acc.* **1998**, *99*, 366-371.
21. Dyall, K. G. Relativistic Double-Zeta, Triple-Zeta, and Quadruple-Zeta Basis Sets for the 5d Elements Hf–Hg. *Theor. Chem. Acc.* **2004**, *112*, 403-409.
22. Dyall, K. G. Relativistic Double-Zeta, Triple-Zeta, and Quadruple-Zeta Basis Sets for the 4d Elements Y–Cd. *Theor. Chem. Acc.* **2007**, *117*, 483-489.
23. Dyall, K. G.; Gomes, A. S. P. Revised Relativistic Basis Sets for the 5d Elements Hf–Hg. *Theor. Chem. Acc.* **2009**, *125*, 97-100.
24. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (Dft-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
25. Goerigk, L.; Grimme, S. A Thorough Benchmark of Density Functional Methods for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670-6688.
26. Lindahl, A. O.; Andersson, P.; Diehl, C.; Forstner, O.; Klason, P.; Hanstorp, D. The Electron Affinity of Tungsten. *Eur. Phys. J. D* **2010**, *60*, 219-222.
27. Hotop, H.; Lineberger, W. C. Dye-Laser Photodetachment Studies of Au⁻, Pt⁻, PtN⁻, and Ag⁻. *J. Chem. Phys.* **1973**, *58*, 2379-2387.
28. Feigerle, C. S.; Corderman, R. R.; Bobashev, S. V.; Lineberger, W. C. Binding Energies and Structure of Transition Metal Negative Ions. *J. Chem. Phys.* **1981**, *74*, 1580-1598.
29. Hackett, P. A.; Humphries, M. R.; Mitchell, S. A.; Rayner, D. M. The First Ionization Potential of Zirconium Atoms Determined by Two Laser, Field-Ionization Spectroscopy of High Lying Rydberg Series. *J. Chem. Phys.* **1986**, *85*, 3194-3197.
30. James, A. M.; Kowalczyk, P.; Langlois, E.; Campbell, M. D.; Ogawa, A.; Simard, B. Resonant Two Photon Ionization Spectroscopy of the Molecules V₂, VNb, and Nb₂. *J. Chem. Phys.* **1994**, *101*, 4485-4495.
31. René, C. B.; Michael, S.; Harold, K. H. Infrared Laser Photodetachment of Transition Metal Negative Ions: Studies on Cr⁻, Mo⁻, Cu⁻ and Ag⁻. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 3885-3891.
32. Dyubko, S. F.; Efremov, V. A.; Gerasimov, V. G.; MacAdam, K. B. Millimetre-Wave Spectroscopy of Au I Rydberg States: S, P and D Terms. *J. Phys. B: At. Mol. Opt. Phys.* **2005**, *38*, 1107-1118.
33. MacAdam, K. B.; Dyubko, S. F.; Efremov, V. A.; Gerasimov, V. G.; Kutsenko, A. S. Laser-Microwave Spectroscopy of Cu I Atoms in S, P, D, F and G Rydberg States. *J. Phys. B: At. Mol. Opt. Phys.* **2009**, *42*, 165009.
34. Kessler, T.; Brück, K.; Baktash, C.; Beene, J. R.; Ch, G.; Havener, C. C.; Krause, H. F.; Liu, Y.; Schultz, D. R.; Stracener, D. W.; Vane, C. R.; Wendt, K. Three-Step Resonant Photoionization Spectroscopy of Ni and Ge: Ionization Potential and Odd-Parity Rydberg Levels. *J. Phys. B: At. Mol. Opt. Phys.* **2007**, *40*, 4413-4432.

35. Baig, M. A.; Rashid, A.; Iqbal, Z.; Hormes, J. High Resolution Absorption Spectrum of Palladium in the 4d Subshell Excitation Region. *J. Phys. B: At. Mol. Opt. Phys.* **1991**, *24*, 2295-2304.
36. Zygmunt, J. J.; Benoit, S. Rydberg Series and the First Ionization Potential of Platinum and Yttrium Atoms. *J. Phys. B: At. Mol. Opt. Phys.* **2000**, *33*, 1827-1841.
37. Rayner, D. M.; Mitchell, S. A.; Bourne, O. L.; Hackett, P. A. First-Ionization Potential of Niobium and Molybdenum by Double-Resonance, Field-Ionization Spectroscopy. *J. Opt. Soc. Am. B: Opt. Phys.* **1987**, *4*, 900-905.
38. Callender, C. L.; Hackett, P. A.; Rayner, D. M. First-Ionizationpotential of Ruthenium, Rhodium, and Palladium by Double-Resonance Ionization Spectroscopy. *J. Opt. Soc. Am. B: Opt. Phys.* **1988**, *5*, 614-618.
39. Page, R. H.; Gudeman, C. S. Completing the Iron Period: Double-Resonance, Fluorescence-Dip Rydberg Spectroscopy and Ionization Potentials of Titanium, Vanadium, Iron, Cobalt, and Nickel. *J. Opt. Soc. Am. B: Opt. Phys.* **1990**, *7*, 1761-1771.
40. Campbell-Miller, M. D.; Simard, B. First Ionization Potentials of Tungsten and Rhenium by Mass-Selected Double-Resonance Ionization Spectroscopy. *J. Opt. Soc. Am. B: Opt. Phys.* **1996**, *13*, 2115-2120.
41. Simard, B.; Kowalczyk, P.; James, A. M. First Ionization Potential of Tantalum by Mass-Selected Double-Resonance Field-Ionization Spectroscopy. *Phys. Rev. A: At. Mol. Opt. Phys.* **1994**, *50*, 846-849.
42. Colarusso, P.; Lebeault-Dorget, M.-A.; Simard, B. First Ionization Potentials of Osmium and Iridium Determined by Mass-Analyzed Double-Resonance Field-Ionization Spectroscopy. *Phys. Rev. A: At. Mol. Opt. Phys.* **1997**, *55*, 1526-1529.
43. Scheer, M.; Brodie, C. A.; Bilodeau, R. C.; Haugen, H. K. Laser Spectroscopic Measurements of Binding Energies and Fine-Structure Splittings of Co⁻, Ni⁻, Rh⁻, and Pd⁻. *Phys. Rev. A: At. Mol. Opt. Phys.* **1998**, *58*, 2051-2062.
44. Looock, H.-P.; Beaty, L. M.; Simard, B. Reassessment of the First Ionization Potentials of Copper, Silver, and Gold. *Phys. Rev. A: At. Mol. Opt. Phys.* **1999**, *59*, 873-875.
45. Norquist, P. L.; Beck, D. R.; Bilodeau, R. C.; Scheer, M.; Srawley, R. A.; Haugen, H. K. Theoretical and Experimental Binding Energies for the d⁷s² ⁴F Levels in Ru⁻, Including Calculated Hyperfine Structure and M1 Decay Rates. *Phys. Rev. A: At. Mol. Opt. Phys.* **1999**, *59*, 1896-1902.
46. Bilodeau, R. C.; Scheer, M.; Haugen, H. K.; Brooks, R. L. Near-Threshold Laser Spectroscopy of Iridium and Platinum Negative Ions: Electron Affinities and the Threshold Law. *Phys. Rev. A: At. Mol. Opt. Phys.* **1999**, *61*, 012505.
47. O'Malley, S. M.; Beck, D. R. Binding Energies of 4d⁶5s² States in Tc⁻. *Phys. Rev. A: At. Mol. Opt. Phys.* **2002**, *65*, 064502.
48. Matsuoka, L.; Hasegawa, S. Two-Color Resonance Ionization Spectroscopy of Rydberg States of Hafnium Atoms. *Phys. Rev. A: At. Mol. Opt. Phys.* **2006**, *74*, 062515.
49. Mattolat, C.; Gottwald, T.; Raeder, S.; Rothe, S.; Schwellnus, F.; Wendt, K.; Thörle-Pospiech, P.; Trautmann, N. Determination of the First Ionization Potential of Technetium. *Phys. Rev. A: At. Mol. Opt. Phys.* **2010**, *81*, 052513.
50. Chen, X.; Ning, C. Accurate Electron Affinity of Co and Fine-Structure Splittings of Co⁻ Via Slow-Electron Velocity-Map Imaging. *Phys. Rev. A: At. Mol. Opt. Phys.* **2016**, *93*, 052508.

- 1
2
3 51. Bilodeau, R. C.; Haugen, H. K. Experimental Studies of Os⁻: Observation of a Bound-
4 Bound Electric Dipole Transition in an Atomic Negative Ion. *Phys. Rev. Lett.* **2000**, *85*,
5 534-537.
6
7 52. Andersen, T. Atomic Negative Ions: Structure, Dynamics and Collisions. *Phys. Rep.* **2004**,
8 *394*, 157-313.
9 53. Schoenfeld, W. G.; Chang, E. S.; Geller, M.; Johansson, S.; Nave, G.; Sauval, A. J. High-
10 Excitation Rydberg Levels of Fe-I from the Atmos Solar Spectrum at 2.5 and 7 Mu-M.
11 *Astron. Astrophys.* **1995**, *301*, 593-601.
12 54. Liu, Y.; Gottwald, T.; Mattolat, C.; Wendt, K. Three-Photon Resonance Ionization of
13 Atomic Mn in a Hot-Cavity Laser Ion Source Using Ti: Sapphire Lasers. *J. Phys. B: At.*
14 *Mol. Opt. Phys.* **2015**, *48*, 115006.
15 55. Chen, X.; Luo, Z.; Li, J.; Ning, C. Accurate Electron Affinity of Iron and Fine Structures
16 of Negative Iron Ions. *Sci. Rep.* **2016**, *6*, 24996.
17 56. Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group
18 Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States,
19 and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class
20 Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215-241.
21 57. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple.
22 *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table of Contents (TOC) Image

177x113mm (300 x 300 DPI)

154x119mm (300 x 300 DPI)

275x187mm (300 x 300 DPI)

309x235mm (300 x 300 DPI)

272x166mm (300 x 300 DPI)

Table of Content (TOC)

59x44mm (300 x 300 DPI)