A New Method Applicable to Study Solid Compounds with Multiple Polyhedral Structures (Postprint)

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Abstract

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Full Text

A New Method for Studying Solid Compounds with Multiple Polyhedral Structures

Zhenlian Chen and Jun Li*

We propose a new direct summation method, termed the polyhedron method, for calculating Madelung energy. This method computes sums of electrostatic interactions over sets of neutral polyhedron unit pairs rather than conventional ion pairs, yielding the Madelung constant in matrix form. With robust and rapid convergence, the polyhedron method is generally applicable to compounds containing multiple polyhedral building blocks and diverse polyhedral connection modes.

Matrix analysis suggests that face-sharing between octahedral pairs and edge-sharing between tetrahedral pairs can be electrostatically stable, contrary to Pauling' s third rule. Furthermore, the complex matrix calculation of Madelung energies offers a unique advantage for high-throughput evaluation of enormous cation distribution configurations in a given lattice. This approach is applicable to studying solid solution composites, polymorphism, and defect structures, including but not limited to intermediate phases of delithiated cathode compounds, charge order or antisite defects, and extensive magnetic ordering.

Introduction

Coordination polyhedra are fundamental building blocks of complex compounds that help elucidate the nature of chemical bonding, including crystal field splitting, d-electron configurations, and d-p orbital overlaps.[1–3] The stacking of these building blocks—their network—forms the crystal framework and determines material properties. For a given close-packed anion sublattice, the cation distribution governs the connectivity of polyhedra. Studies of these polyhedral structures not only provide insights into complex phenomena such as phase transitions but also enable simple yet high-throughput design of compounds that can be doped with different elements to modify their physical and chemical properties.[4–7] For instance, solid-solution designs represent a major approach for achieving better electrochemical performance in lithium-ion cathode compounds.[8–10] During delithiation and lithiation processes, the intermediate delithiated phases of cathode compounds often involve energetic competition between occupation and vacancy on Li sites, accompanied by charge ordering of transition metal ions in mixed valence states.

Although significant progress has been made in predicting crystal structures from chemical composition alone, two major challenges persist in materials design.[11–16] The first is the combinatorial complexity of the search strategy; the second is the energy landscape of global minimization. A close-packed anion sublattice with cations occupying interstitial sites (octahedral and/or tetrahedral) provides a foundational platform for constructing new solid compounds.[1] Within such an anion sublattice, only a finite number of cation distributions are permitted by geometric constraints and energy filtering criteria.[17] The design process becomes straightforward: first, all possible polyhedral units can be generated combinatorially; then, non-repeating cation distribution configurations can be filtered and grouped through rapid energy calculations. The objective of the present work is to employ Madelung energy (ME) calculations as an efficient filtering algorithm for exploring the global energy landscape. When coupled with first-principles calculations, detailed structural modifications and material properties can be obtained for selected candidates without loss of generality. This approach is physically grounded in the fact that ME represents the electrostatic energy under the point-charge hypothesis, reflecting the overall distribution of all elements in a chemical compound. As a major contributor to lattice cohesive energy, ME also provides a basis for understanding various physical and chemical properties, including piezoelectricity, electrochromism, and even protein folding.[18–23]

Despite advances in supercomputing for computational chemistry, the calculation of ME remains essentially unchanged since the proposal of Ewald Summation. It remains time-consuming and highly inefficient for evaluating vast numbers of ionic configurations. The Madelung constant (MC), defined as the ratio between the electrostatic energy due to periodic images and that due to an isolated ion pair, must be calculated for every possible structure, regardless of whether integral transformation or direct summation methods are employed.[24–

29] The fundamental difficulty lies in the definition of MC, which depends on the lattice, ion coordinates, and valence states of ions.

Here, based on Pauling' s rules of electrostatic valence and treating ionic crystalline structures as periodic stacking of coordinating polyhedra,[1] we have developed a new method—the polyhedron method—to calculate MC. This method counts Coulomb interactions between polyhedron pairs rather than ion pairs, resulting in rapidly robust convergence without requiring mathematical tricks to handle lattice summation boundary conditions, and is straightforward to implement. Notably, the expression for MC adopts a matrix form that directly correlates electrostatic potential with polyhedral structure. The matrix is a function of lattice and ion coordinates only, excluding valence states of ions. This facilitates high-throughput calculation of MEs for all cation distributions within the same anion sublattice.

Methods

Description of the Polyhedron Method

A. Construction of Neutral Polyhedron Unit. The core implementation of the polyhedron method is the construction of neutral polyhedron unit (NPU), illustrated here with the example of ionic crystal NaCl shown in Figure 1a. In this case, a full point charge (+1) is assigned to the central Na cation, while a fractional charge (-1/6) is assigned to each coordinating Cl anion. The neutrality of the unit guarantees that the network assembled by NaCl octahedral NPUs remains neutral, and the construction of NPU can be generally and easily implemented for any complex compound within the point charge approximation.

B. Representation of MM and ME. Figure 1c gives the set of Coulombic interactions among all ionic pairs between an NPU pair with parameters shown in Figure 1b. The Coulombic interaction U_{ij} between NPU-i in the center cell and NPU-j in L cell (L = $l_1\mathbf{a}_1 + l_2\mathbf{b}_1 + l_3\mathbf{c}$, where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are the unit cell vectors) is:

$$U_{ij} = q_i q_j \sum_{m=1}^{N_j} \frac{1}{|\mathbf{r}_{ijL} + \mathbf{r}_m|} + \sum_{n=1}^{N_i} \frac{1}{|\mathbf{r}_{ijL} - \mathbf{r}_n|} + \sum_{n=1}^{N_i}\sum_{m=1}^{N_j} \frac{1}{|\mathbf{r}_{ijL} - \mathbf{r}_n + \mathbf{r}_m|}$$

where $\mathbf{r}_{ijL} = \mathbf{r}_{ij} + \mathbf{L}$.

Because the neutrality of the polyhedron unit radically removes net point charge oscillation in lattice summation, the summation of U_{ij}^L over lattice L is now unconditionally convergent to a definite physical result for any given numerical threshold, whereas it is conditionally convergent in the original format (the specified condition to obtain a definite result is shown in Appendices A and B). A matrix form independent of the point charge can be obtained:

$$M_{ij} = \sum_{L} U_{ij}^{L}$$

No boundary condition, no special lattice cut-off, even number of ions arrangement along expanding edge, charge compensation on the summation boundary, or average over nanoparticle is employed in the polyhedron method.[24,27–30] The convergence of each matrix element M_{ij} is solely determined by the geometric combination of NPUs in the context of periodic arrays. Note that the matrix (Madelung Matrix, MM) differs from the conventional definition of MC, which refers to individual ions depending on point charge assignment in compounds and is inconvenient for multicomponent complex crystals.[27] It should be noted that MM has units of reciprocal distance, different from the unit-less MC; only cations within the unit cell enter the matrix index because the calculation entity is the whole NPU group, not individual ions as implemented in conventional MC approaches.

For a generic compound with an array of cationic charges $\mathbf{Q} = (q_1, q_2, ..., q_n)$ per unit cell, ME is calculated through the quadratic form of MM:

$$E_M = \frac{1}{2}\mathbf{Q}^T\mathbf{M}\mathbf{Q}$$

where $\mathbf{Q}^T$ is the transpose of cationic array $\mathbf{Q}$ and the factor 1/2 removes double counting of NPU pairs. Once the matrix is calculated, ME for arbitrary cationic distribution within that structure family can be evaluated in a high-throughput manner by matrix algebra, providing calculation efficiency for charge ordering determination for cations with variable valence states and materials of variable stoichiometry. The conventional MC α can be transformed from ME by $\alpha = 2E_M/N_f R$ or $\alpha = 2E_M/N_f a$ (N_f is the number of formula units in the unit cell), referred to bond length R or lattice constant a, respectively.

C. Calculation Procedure of NaCl as Example. Here, we use the conventional NaCl unit cell (with four formula units per cubic cell) to illustrate the complete procedure of the Polyhedron Method. Four NPUs are constructed on the four Na sites, as shown in Figure 2a, giving a 4×4 MM. Since the four NPUs are equivalent, all diagonal elements ($M_{ii}, i = 1, 4$) and non-diagonal elements ($M_{ij}, i \neq j$) are identical, respectively. The two polyhedral building blocks relating to distinct elements M_{11} and M_{12} are shown in Figure 2b. The interactions contributing from the center cube to M_{11}, M_{12} are:

$$U_{CC} = 0; \quad U_{CA} = \frac{1}{d}; \quad U_{AA} = \frac{1}{\sqrt{2}d}$$

where d (2.8201 Å) is the Na-Cl ionic bond length. Then:

$$M_{11} = \frac{1}{2}(U_{CC} + U_{AA}) = \frac{1}{2}\left(0 + \frac{1}{\sqrt{2}d}\right) = \frac{1}{2\sqrt{2}d}$$

$$M_{12} = U_{CA} = \frac{1}{d}$$

Three-dimensional cell expansion along unit cell vectors from the center cell is shown in Figure 2c, and the summation is over nL cells, $(n+1)\times(n+1)\times(n+1)$ cubes at summation length nL ($n = 0, 1, ...$; L is a symbol representation of the length of unit cell vectors). The evolutions of calculated values of matrix elements and conventional MC at summation length nL are listed in Table 1. At summation length $2L$, the values of MM reach the preset converging threshold (cf. Table 2) and give the conventional MC 1.7476 by the conversion:

$$E_M = \begin{pmatrix}1 & 1 & 1 & 1\end{pmatrix}\begin{pmatrix}-0.7056 & -0.1779 & -0.1779 & -0.1779\\ -0.1779 & -0.7056 & -0.1779 & -0.1779\\ -0.1779 & -0.1779 & -0.7056 & -0.1779\\ -0.1779 & -0.1779 & -0.1779 & -0.7056\end{pmatrix}\begin{pmatrix}1\\1\\1\\1\end{pmatrix} = -0.35253$$

$$\alpha = 1.7476$$

Notably, Table 1 shows the contribution from the $2L$ shell has become small on the order of 10^{-4} Å^{-1} for both diagonal and non-diagonal elements. Here, nL shell means all cubes located between nL and $(n-1)L$ length. At summation length $2L$, that is, $4d$, the $2L$ cell consists of $5 \times 5 \times 5 \times 8 = 1000$ ions, in contrast to $8L$, that is, $16d$ or 27000 ions required in Baker' s scheme (cf. Table 3 in Ref. 29), which was the shortest length to give the value 1.7476 by direct MC calculation in literature to our best knowledge.

Solid-Solution Configurations Construction

We take spinel $LiMn_2O_4$ as an example to illustrate the determination of cation distributions using ME as a high-throughput filter. The flow chart is shown in Figure 3. In spinel $LiMn_2O_4$, Mn exhibits variable valence states, Mn^{3+} and Mn^{4+}. In $Fd\bar{3}m$ unit cell, there are 16 Mn ions on octahedral sites and 8 Li ions on tetrahedral sites, generating a 24×24 MM. When one picks 8 octahedral sites for Mn^{3+} ions among the 16 octahedral sites, the combinatorial gives $C(16, 8) = 12870$ configurations. Each can be represented by a cationic array **Q** (e.g., $[1, 1, 1, 1, 1, 1, 1, 1, 3, 3, 3, 3, 3, 3, 3, 3, 4, 4, 4, 4, 4, 4, 4, 4]$, where the first eight entries are for Li ions and the remaining 16 for Mn ions). Then by comparing MEs calculated for the 12,870 configurations using eq. (3), 25 distinct configurations are obtained in a high-throughput manner. Thus, this method can be generally applied to other solid solutions of elements even in identical nominal valence states or antiferromagnetic order, as long as elements or spin orientations

are assigned to different pseudo-valence states, which need not have chemical meaning but help identify or classify geometric patterns of cation distributions. Detailed chemical bonding effects can be captured by subsequent first-principles calculations.

Applications

General Applicability of the Polyhedron Method

The neutrality of the polyhedron unit ensures the polyhedron method is a robust approach to MC calculations, regardless of Bravais lattice type, unlike other reported direct summation methods which are mostly applicable to cubic compounds.[27–29] Systematic calculations of ME for various compounds, such as the often-studied cubic NaCl and CsCl, wurtzite ZnO, perovskites $SrTiO_3$ (undistorted, cubic) and $LaMnO_3$ (distorted, orthogonal), and rhombohedral cathode $LiCoO_2$, all reach flat values within numerical precision of 0.1% at a summation length not longer than $2L$. Digital precision is slightly structure-dependent but ME always converges monotonically, as seen in Table 2. The accuracy of all converged MEs at the converging threshold is better than chemical accuracy. From the perspective of highly efficient and high-throughput energy filtering, we do not pursue further accuracy and precision in the calculation of MC for structure prediction beyond the point-charge hypothesis.

Physical Insight of Polyhedral Connection

What MM describes is the Coulomb interaction between polyhedral building blocks, analogous to Pauling' s structural characteristics of coordination compounds, especially relating to his third rule about polyhedral combination. Figure 4 shows the stacking of all octahedral and tetrahedral interstitial sites within cubic close-packing (AB stacking) and hexagonal close-packing (ABC stacking) oxygen sublattices, with one cation-oxygen octahedra layer sandwiched between two cation-oxygen tetrahedra layers. There could be nine connection modes: corner-, edge-, and face-sharing between tetrahedron and/or octahedron in AB close-packing oxides; whereas six modes exist: corner- and edge-sharing between octahedron-octahedron pairs, face-sharing between tetrahedron-tetrahedron pairs, and corner-, edge-, and face-sharing between octahedron-tetrahedron pairs in ABC stacking. The MM elements for these modes (values given in Table 3) can be calculated from a hexagonal supercell of six layers with lattice parameters $a = 3a_0$ and $c = 4\sqrt{3}a_0$, where $a_0 = 0.707$ Å. When the six stacking layers of oxygen are ABABAB, the cation-oxygen polyhedral sequences are AAAAAA and ABBAABBAABBA for octahedra and tetrahedra, respectively; for ABCABC stacking, the sites are ABCABC and ABCABCABCABC for octahedra and tetrahedra, respectively. For the six polyhedral connection modes in ABC stacking, the distances between cation centers of polyhedra are the same as those in AB stacking, except for octahedron-octahedron corner-sharing, for which the distance is 1.00 Å and 0.91 Å in ABC and AB stacking, respectively.

One finds that with tetrahedra, face-sharing is often electrostatically unstable. Especially, the tetrahedron-tetrahedron face-sharing pair even gives a positive value, confirming Pauling' s speculation that face-sharing tends to decrease the stability of crystals with low coordination number.[1] However, for octahedron-octahedron pairs, face-sharing gives a value extremely close to edge-sharing and more negative than corner-sharing; among all polyhedron pairs, edge-sharing gives values more negative than corner-sharing. This indicates Pauling' s third rule is partially incorrect and supports that edge-sharing between tetrahedra can stabilize structures such as β-BeO, dumortierite $Al_7BO_3(SiO_4)_3O_3$, Li_5FeO_4 and Li_6CoO_4, and face-sharing between octahedra can stabilize 2H-$BaMnO_3$.[33–36] The physical root is that the collective Coulomb attraction between anions of NPU-j and the cation in NPU-i surpasses cation-cation Coulomb repulsion for most connection modes except for face-sharing between tetrahedron pairs, but this was ignored in Pauling' s speculation.

Charge Order Determination in Coupling with First-Principles Calculations

Now, we use spinel $LiMn_2O_4$ again to demonstrate that, in coupling with first-principles calculations, the polyhedron method can provide deeper insights into the physical and chemical properties of complex compounds. There are four configurations with high symmetry (by ISOTROPY analysis[37]) of $P\bar{4}m2$, $P4_{322}$, $Imma$, and $Cmm2$ among the twenty-five distinct configurations according to MEs. In the $Fd\bar{3}m$ lattice, all MnO_6 octahedra are indistinguishable, so the major contributions—intra-NPU interactions of all MnO_6 units—are the same. The ME for Mn^{3+}-Mn^{4+} charge order is always lower than the referenced $Mn^{[3.5+]}$ configuration (cf. Table 4). This is due to the quadratic ruling in Coulomb energy [referring to eq. (3)], i.e., sum of squares ($3^2 + 4^2$) vs. square of average (2×3.5^2). This simple rule indicates charge orders always electrostatically stabilize a compound with mixed valences if differences in NPUs surpass other electronic repulsion effects.

In Mn^{3+}-Mn^{4+} charge-order configurations, charge disproportion forms on oxygen ions because each oxygen ion is shared by one LiO_4 tetrahedron with three MnO_6 octahedra. In the $P\bar{4}m2$ configuration, three Mn^{3+} or three Mn^{4+} ions share one oxygen ion, giving a valence disproportion of 1/2 and a nominal oxygen valence of $-(2-1/2)$ or $-(2+1/2)$. In contrast, two Mn^{3+} and one Mn^{4+} or two Mn^{4+} and one Mn^{3+} share one oxygen ion in the other three configurations, reducing the valence disproportion of oxygen to 1/6, as shown in Figure 5. In the $P\bar{4}m2$ configuration, the valence disproportion is so strong that it tends toward an average valence state after relaxation, whereas the other three configurations all favor clear Mn^{3+}-Mn^{4+} charge orders. These features are well revealed in magnetic moment patterns, as seen in Table 4. Total energies of the three charge-order configurations are again lower than that of the $P\bar{4}m2$ configuration. The atomistic difference among the three Mn^{3+}-Mn^{4+} charge-order configurations lies in the pattern of $Mn^{[3+]}O_6/Mn^{[4+]}O_6$ combinations—that is,

the nearest Mn-Mn connections (cf. Figure 5)—and gives rise to small differences in MEs as well as in total energies. The proximity of energies suggests various charge-order configurations may coexist in $LiMn_2O_4$; the charge order may be local rather than global, as demonstrated in long first-principles structural relaxations showing partially charge-ordered states in $Fddd$ supercells with 504 ions per cell.[44] This awaits further experimental verification.

Conclusions

Based on the construction of NPU, a new direct summation method is proposed to calculate MEs for complex crystal compounds. Due to screening effects of NPUs, the convergence of lattice summation becomes rapidly robust and generally applicable. The MC is expressed in a matrix form and each matrix element accounts for the group interaction between NPU pairs. The matrix quantitatively characterizes connection modes among polyhedral building blocks. This justifies Pauling' s third rule and validates that face-sharing between octahedra and edge-sharing between tetrahedra can be electrostatically stable. The matrix form also benefits comprehensive and systematic ME calculations for solid materials with variable stoichiometry and mixed valence states.

It offers a new strategy to study atomistic details of solid solutions and polymorphisms (such as A_2BSiO_4 silicates with cations A, B, and Si on tetrahedral sites in AB stacking oxygen lattice), charge order, or even spin-polarized systems, for example, anti-ferromagnetic order. This may guide the search for charge-pairing mechanisms in very challenging solid compounds and provide a new strategy to study complicated processes for compounds with variable valence metal ions, including intercalation cathodes of lithium-ion batteries.

Appendix A

Mathematical Proof of Unconditional Convergence of Lattice Summation of U^L Due to NPU Construction

Due to NPU construction, net point-charge interactions are screened off between NPUs, and eq. (1) can be rewritten as sum of interactions between dipolar pairs:

$$U_{ij}^L = q_i q_j \sum_{m=1}^{N_j} \sum_{n=1}^{N_i} \left(\frac{1}{|\mathbf{r}_{ijL} + \mathbf{r}_m - \mathbf{r}_n|} - \frac{1}{|\mathbf{r}_{ijL} + \mathbf{r}_m|} - \frac{1}{|\mathbf{r}_{ijL} - \mathbf{r}_n|} + \frac{1}{r_{ijL}} \right)$$

where $u_L = q_i q_j$. When $r_{ijL} \gg r_m, r_n$, $\frac{1}{|\mathbf{r}_{ijL}+\mathbf{r}_m|} \approx \frac{1}{r_{ijL}} - \frac{\mathbf{r}_m \cdot \mathbf{r}_{ijL}}{r_{ijL}^3}$, $\frac{1}{|\mathbf{r}_{ijL}-\mathbf{r}_n|} \approx \frac{1}{r_{ijL}} + \frac{\mathbf{r}_n \cdot \mathbf{r}_{ijL}}{r_{ijL}^3}$, and $\frac{1}{|\mathbf{r}_{ijL}+\mathbf{r}_m-\mathbf{r}_n|} \approx \frac{1}{r_{ijL}} - \frac{(\mathbf{r}_m-\mathbf{r}_n)\cdot \mathbf{r}_{ijL}}{r_{ijL}^3}$.

The first three terms in eq. (A2) are dipolar contributions and the last term includes all other higher multipolar terms with smaller contributions. The dipole terms vanish after merging:

$$\sum_{m=1}^{N_j}\sum_{n=1}^{N_i}(\mathbf{r}_m - \mathbf{r}_n) = 0$$

Then:

$$U_{ij}^{L} \approx q_i q_j \sum_{m=1}^{N_j}\sum_{n=1}^{N_i}\frac{(\mathbf{r}_m - \mathbf{r}_n)\cdot \mathbf{r}_{ijL}}{r_{ijL}^3} \approx \frac{1}{r_{ijL}^3}$$

That means U_{ij}^{L} attenuates to the third order or higher order of reciprocal distance between the centers. Therefore, the lattice summation of U_{ij}^{L} should converge monotonically, scaling as $1/r_{ijL}^2$ because the number of polyhedra increases with cell expansion scaling as r_{ijL}^2. In other words, for any given converging threshold Δ, one can find a suitable summation length nL satisfying $|(E_M^{nL} - E_M^{(n-1)L})/E_M^{nL}| < \Delta$. This confirms the convergence of the polyhedron method is mathematically robust, in contrast to the conditional convergence of classical MC schemes. If the symmetry of the polyhedra is high, higher multipolar terms such as quadrupolar terms may also be counteractive so as to achieve much faster convergence than dipole convergence.

Appendix B

Independence of Convergence on Cell Expansion and Lattice Shape

The neutrality of the polyhedron unit is a strong physical imposition on the group summation that drives the convergence of the polyhedron method, insensitive to boundary condition—that is, the scheme of cell expansion in sphere or cube and lattice shape in cubic or triclinic.

Figure B1 shows four cases using NaCl as an example for sphere and cube cell expansion with primitive cell (PC) and conventional cell (CC). All cases reach convergence within $5L$ with error smaller than 10^{-4}. This is in contrast to conventional direct summation methods, which are divergent for sphere lattice expansion in the calculation of MC for NaCl without correction terms.[25] In conventional methods, whether ions (cations or anions) are on the boundary is determined by their pair distance to the reference ion.[45] In contrast, in the polyhedron method, the determination condition is the pair distance between the center cations of the polyhedron unit and the reference unit. In fact, coordinated anions are on the boundary. For example, shown in Figure B1b, the Cl ions coordinated to the 12 cations (forming an icosahedron) seen in the upper atomic model are on the boundary of the $1L$ summation with PC using sphere expansion.

While the value of ME using sphere expansion with rhombohedral PC deviates far from the convergent value at summation length of $1L$, it converges rapidly to

the same definite physical result after $5L$. That deviation arises from the group of cations, which is determined by the lattice constant in our calculations. In sphere expansion with PC, the radius of $1L$ length is 3.9882 Å and only nearest cation neighbors are included, whereas at least second nearest cation neighbors are counted in the other three cases.

Appendix A has shown that the polyhedron method will obtain a definite result, which is independent of the boundary scheme of cell expansion and lattice shape. However, this does not exclude numeric deviation before convergence is reached. The numeric deviation of the polyhedron method depends on the symmetry of the polyhedron units and the lattice. The latter determines the networking of the polyhedra on the boundary, similar to other direct summation methods. This deviation is different in nature from the convergence difficulty in other direct summation methods, in which convergence difficulties or errors mainly come from correction terms on the boundary. Recent works showed such difficulties also exist in the well-developed Ewald summation.[46]

Keywords: Madelung energy • polyhedral connection • crystal structure prediction • charge order • direct summation method

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A new method is proposed to study electrostatic interactions among polyhedral building blocks in complex crystals within the point-charge approximation. By counting group interactions between neutral polyhedron unit pairs,

the Madelung constant is obtained in matrix form, revealing the geometric correlations among interstitial sites in the lattice. Distinct cationic distributions can be classified according to Madelung energies via high-throughput matrix algebra.

Note: Figure translations are in progress. See original paper for figures.