

Computation of Madelung Energies for Ionic Crystals of Variable Stoichiometries and Mixed Valencies and Their Application in Lithium-Ion Battery Voltage Modeling

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Electrostatic energy (Madelung energy) is a major constituent of the cohesive energy of ionic crystals. Several physicochemical properties of these materials depend on the response of their electrostatic energies to a variety of applied thermal, electrical, and mechanical stresses. In the present study, a method has been developed based on Ewald's technique to compute the electrostatic energy arising from ion–ion interactions in ionic crystals such as $\text{Li}_x\text{Mn}_2\text{O}_4$ with variable stoichiometries and mixed valencies. An interesting application of this method in computing the voltages of lithium ion batteries employing spinel cathodes is presented for the first time. The effect of including additional interaction terms such as the short-range and the multipolar was estimated and was found to necessitate only a fairly small change in the battery voltage. The advantages of the present method of computation over existing methods are also discussed.

Introduction

Electrostatic energy of ionic crystals^{1–3} is an important constituent of the cohesive energy⁴ of these crystals. Various physicochemical properties such as melting points, heats of fusion and evaporation, and activation energies for formation and diffusion of electronic and atomic point defects are related to the solid-state cohesion.⁵ Response of the lattice energy toward a variety of applied thermal, electrical, and mechanical stresses leads to piezoelectric, ferroelectric, and electrochromic properties of these materials. Madelung energy computations have also recently generated much interest.^{6–9} A Madelung model has been used to predict the dependence of the lattice parameter on the nanocrystal size.⁶ Three-dimensional systems periodic in one direction have been simulated using the Ewald summation method.^{2,7} Madelung constants were computed for a wide variety of ionic crystals, and it was further shown that structural phase transitions could also be probed within this framework.⁸ More recently, Madelung type long-range Coulomb interactions were shown to be important in fixing the optimal doping level, that is, the stoichiometry, in high-temperature superconductors.⁹

Electrostatic energies of simple ionic crystals of fixed stoichiometries and valencies such as CsCl, NaCl, and ZnS have already been calculated and reported as Madelung constants in the literature. This energy, however, is no more a constant for nonstoichiometric and multivalent compounds (e.g., VO_x , UO_{2+x} , Li_xCoO_2 , LiMn_2O_4 , Li_xWO_3 , Na_xWO_3 , TiO_x , and $\text{Li}_x\text{Mn}_{2-y}\text{M}_y\text{O}_4$ with dopant) as it varies with the stoichiometry as well as with the valency. A method has been developed in the present study to compute the electrostatic energy arising from ion–ion interactions in ionic crystals of variable stoichiometries and mixed valencies. A novel use of this method in computing the voltage of lithium ion batteries with electrodes of variable stoichiometries and valencies is presented with $\text{Li}_x\text{Mn}_2\text{O}_4$, a widely studied cathode material used in high-voltage lithium-ion batteries, as a specific example.

It must be pointed out that in addition to the long-range electrostatic interactions contained in the Madelung part, other interactions such as the short-range electron–electron repulsion and dipole–dipole and dipole–quadrupole interactions also contribute to the total energy of the crystal. The effect of these other interactions on the battery voltage was estimated and found to be not as significant as the major electrostatic component.

Ewald Method Applied to Ionic Crystals of Variable Stoichiometries and Mixed Valencies

In this section, Ewald's technique has been applied to compute the long-range electrostatic interactions in ionic crystals of variable stoichiometries and mixed valencies. Any ionic crystal may be specified by giving its crystallographic space group, the unit cell parameters (corresponding to the primitive, conventional, or super cells) and the corresponding basis (consisting of a set of ions). The electrostatic energy of ionic crystals is usually expressed as a sum of pairwise Coulombic terms given by

$$E_M = \sum_{(i,j)} \frac{z_i z_j}{r_{ij}} \quad (1)$$

where z_i and z_j are the valencies of the i th and j th ions and r_{ij} is the interionic distance. The sum runs over all ion pairs. To apply Ewald's method for crystals of variable stoichiometries and mixed valencies, the above sum is expressed in terms of contributions arising from several sublattices present in the crystal so that the stoichiometry and the valency can be tuned in each sublattice. Hence, the appropriate form for the energy will be

$$E_M = \frac{1}{2} \sum_{i_{\text{ref}}=1}^N E_{i_{\text{ref}}} \quad (2)$$

where N is the number of ions in the basis and is also the number of sublattices into which the crystal can be split. The factor $1/2$ removes the double counting of the pair interaction.

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Using Ewald's method, one can obtain the final expression

$$E_M = \frac{1}{2} \left[\sum_{\mathbf{g} \neq 0} S S^* f(\mathbf{g}) + \sum_{i=1}^N \lambda^2(i) F(G) + \sum_{j=1}^N \lambda(j) \sum_{i \neq j}^N \lambda(i) \bar{F}(G, \mathbf{r}_i^j) \right] \quad (3)$$

where

$$S = \sum_{i=1}^N \lambda(i) \exp(i\mathbf{g} \cdot \mathbf{r}_i)$$

S^* is the complex conjugate of S , G is the convergence factor, and $\mathbf{r}_i^j = \mathbf{r}_i - \mathbf{r}_j$.

The details of the derivation and the meaning of the symbols appearing in eq 3 are given in the Appendix. It must be noted that, though the Ewald method is well-known, its present application is new. Equation 3 is the most general form for the electrostatic energy in ionic crystals with variable stoichiometries and mixed valencies. It forms the basis of Madelung energy computations for systems with variable stoichiometries and valencies.

Choice of Unit Cells for Crystals with Sublattice Order and Sublattice Disorder vis-à-vis Variable Stoichiometries and Valencies

In the previous section, a method of arriving at a general formula for the electrostatic energy of any ionic crystal with variable stoichiometries and valencies was reported. Before proceeding toward computing the electrostatic energy, it is desirable to clarify the meaning of the $\lambda(i)$'s ($i = 1$ to N).

For regular stoichiometric ionic crystals such as NaCl, CsCl, and ZnS, these effective charges are integral quantities. In the case of nonstoichiometric or variable stoichiometric crystals, there arises a need to distinguish between crystals with sublattice order or sublattice disorder. For crystals with sublattice order, these effective charges will again be integral quantities whereas for crystals with sublattice disorder they will be fractional, reflecting the random distribution of ions and their valencies in the sublattices. For the computation, one can choose the primitive unit cell, the conventional unit cell, or even the super cell depending on the problem at hand. Choosing the primitive unit cell would certainly take the least computational time. However, though it can handle efficiently cases with sublattice disorder, it has obvious limitations for cases with sublattice ordering. Super cells may be required to deal efficiently with cases of sublattice ordering with variable stoichiometry and valence. At the end stoichiometries, namely, $x = 0$ and $x = 1$ of $\text{Li}_x\text{Mn}_2\text{O}_4$, there is no sublattice disorder. It is for the intermediate stoichiometries that one needs to encounter the question of sublattice order versus sublattice disorder. No particular Li sublattice order has been reported in the literature so far for the intermediate stoichiometries and, hence, a Li sublattice with disorder is employed in our work.

To clarify the above issues, a discussion using a specific crystal, for example, $\text{Li}_x\text{Mn}_2\text{O}_4$, will help. This is an oxide belonging to the class of spinels with space group $Fd3m$.¹⁰ The primitive basis has two lithium ions, eight oxide ions, and four manganese ions. The oxide ion valence can be considered fixed at 2− and the lithium ion valence at 1+. This crystal is a mixed-valent compound with respect to the oxidation state of the manganese ion. When the stoichiometry x of the spinel varies from 0 to 1, the valence of the Mn ion continuously varies from

a state of all 4+ to a mixed-valent state of 50% of 4+ and 50% of 3+. At this point, two cases arise: (i) spinel with sublattice ordering and (ii) spinel with sublattice disorder. For case i, the x value is restricted to 0, 0.5, and 1 if we choose the primitive basis for the energy computation, and for enlarging the scope of the computation to more values of x , one will have to move on from the primitive to conventional and even to super cells. For case ii, the primitive basis alone can handle all values of x .

Regarding the oxidation states of the atomic species (Li, Mn, and O), there is a general consensus¹¹ in this field that these ions do take the charge states assumed in this paper. However, the ultimate test would be the agreement with experiments. Mössbauer spectroscopy has also confirmed the proposed assignment of the oxidation states.¹² Quantum simulation is also expected to throw light on this question. However, it is beyond the scope of our work.

Details of the Computation and Results

A program was written to implement eq 3 for the computation of Madelung energy. Inputs to the program were as follows: space group of the spinel, cubic lattice constant and the atomic positions of the 14 ions in the primitive cell (four Mn, eight O, and two Li ions), convergence factor G set as 1 with a grid size of $10 \times 10 \times 10$ for both direct and reciprocal lattices, and the stoichiometry- and valency-dependent parameters, namely, the $\lambda(i)$'s, fixed as follows:

$$\lambda_1 = \lambda_2 = x$$

$$\lambda_3 = \lambda_4 = \lambda_5 = \lambda_6 = 4 - (x/2)$$

$$\lambda_7 = \lambda_8 = \dots = \lambda_{14} = -2$$

It may be further noted from eq 3 that the stoichiometry- and valency-dependent parameters, namely, the $\lambda(i)$'s, are products separable from a host of factors, which depend *only* on the crystal structure. These can be viewed as a set of generalized Madelung constants, which take the place of the single Madelung constant for conventional stoichiometric crystals.

Before applying it to cases of variable stoichiometry and valency, eq 3 was tested against conventional systems such as NaCl, CsCl, and ZnS. The Madelung energy calculated using eq 3 matched with the values reported in the literature¹ correct to five decimal places. When applied to the spinel $\text{Li}_x\text{Mn}_2\text{O}_4$, $\lambda(i)$'s are no more constant as for conventional systems but vary as a function of x . The result of applying eq 3 to compute the Madelung energy of this spinel as a function of x is presented in Figure 1. The figure is almost linear.

The program was executed on a 1.13-GHz Pentium III, and the total energy computation (for all values of x) took nearly 8 h. It is to be noted here that Ceder and co-workers used quantum ab initio methods to compute the total energy of layered oxides of lithium on a Cray C 90 Supercomputer, which is reported to take 1 h for one total energy calculation.^{13,14} The authors have computed total energies for *only* $x = 0$ and $x = 1$. For intermediate values of x , one need to do computation on superstructures, which requires computational speeds that are beyond the limits of present-day resources.

Discussion and Application to Lithium-Ion Battery Voltage Computation

The values of $x = 0$ and $x = 1$ in $\text{Li}_x\text{Mn}_2\text{O}_4$ correspond to the fully charged and the fully discharged states of the battery,

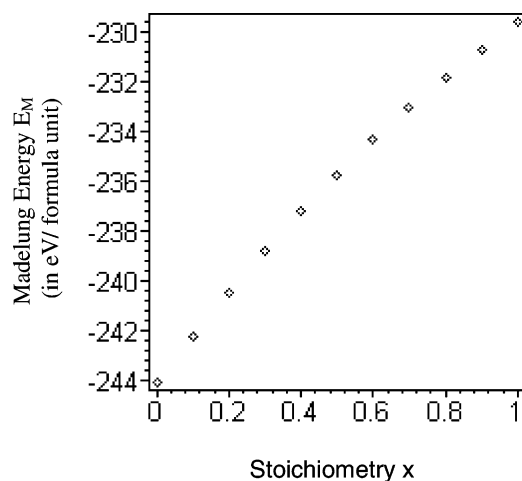
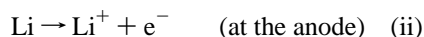
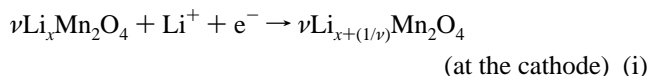


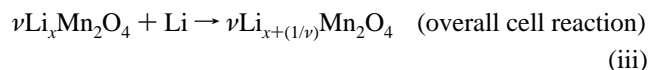
Figure 1. Madelung energy E_M (in eV/formula unit) versus the stoichiometry x .

respectively. In this section, the voltage of the battery system is modeled using the Madelung energies computed in the previous sections.

Battery System: $\text{Li}_x\text{Mn}_2\text{O}_4/\text{Li}^+$ Ion Carrying Electrolyte/Li Metal. The electrode reactions in this battery can be represented as



Adding eqs i and ii

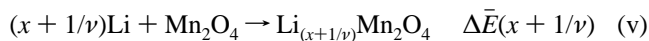
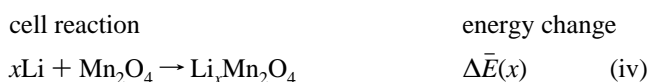


(note: for every ν moles of $\text{Li}_x\text{Mn}_2\text{O}_4$, 1 F passes through the circuit)

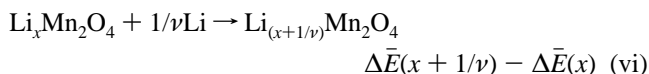
The battery voltage is given by¹⁵

$$V = -\Delta G/F \quad (4)$$

where ΔG is the free energy change accompanying eq iii. On neglecting volume and entropy effects,¹³ eq 4 can be rewritten as $V = -\Delta E/F$, where ΔE is the energy change of reaction iii. Before proceeding further, it must be remarked that the energy quantities must be normalized as per equivalent as pointed out by Vijh¹⁶ and Diggle.⁵ For example, the energy of formation per mole may be divided by the number of total valencies (either cationic or anionic) participating in the compound to obtain the energy of formation per equivalent.¹⁶ For $\text{Li}_x\text{Mn}_2\text{O}_4$, a division by 8 is required. For a convenient evaluation of ΔE for the reaction iii, the following steps may be considered:



Equation v – eq iv gives



Thus,

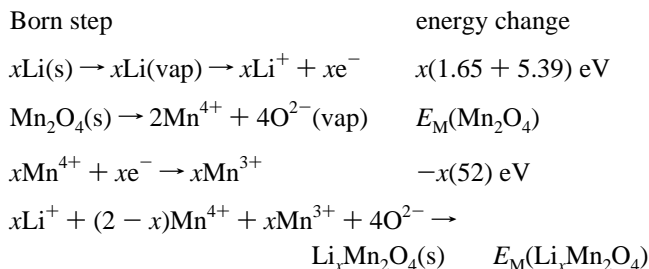
$$\begin{aligned} \Delta E &= \nu[\Delta\bar{E}(x + 1/\nu) - \Delta\bar{E}(x)] \\ &= [\Delta\bar{E}(x + 1/\nu) - \Delta G(x)]/(1/\nu) \\ &= d\Delta\bar{E}(x)/dx \quad (\text{for a differential change in } x) \end{aligned} \quad (5)$$

Hence, finally,

$$V = -(1/F) d[\Delta\bar{E}(x)]/dx \quad (6)$$

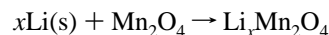
Equation 6 is the desired relation connecting the battery voltage V and the energy change $[\Delta\bar{E}(x)]$.

$\Delta\bar{E}(x)$ can be deduced as follows, by breaking reaction iv into elementary Born steps.



[The sublimation energy of lithium metal (1.65 eV), the ionization potential of lithium (5.39 eV), and the fourth ionization potential of manganese (52 eV) have been used in the steps above].

Adding all the Born steps and the corresponding energies, the net reaction and the net energy are given respectively as



and

$$\Delta\bar{E}(x) = (1/8)[x(1.65 + 5.39) - x(52) - E_M(\text{Mn}_2\text{O}_4) + E_M(\text{Li}_x\text{Mn}_2\text{O}_4)]$$

Now the battery voltage may be computed using eq 7:

$$V = -(1/F)[-5.62 + 0.125(dE_M/dx)] \quad (7)$$

If the Madelung energy E_M is a linear function of x , then the battery voltage will be independent of x . However, in general E_M may have a nonlinear dependence on x in which case the battery voltage itself may depend on stoichiometry x . Despite the slight nonlinearity evident in Figure 1, the following linear fit provides a good approximation to E_M .

$$E_M = 7.166(1.761x - 34.058) \text{ eV/formula unit}$$

Using eqs 5 and 6, the battery voltage turns out to be 4.042 V, which agrees well with the experimental value of 4.1 V^{10,17} [see below, however, for the influence of certain additional interactions]. This is the first time that a battery voltage has been related to the Madelung energies of the electrode materials. Owing to the near linearity of Figure 1, the voltage of $\text{Li}_x\text{Mn}_2\text{O}_4$ is expected to depend only weakly on stoichiometry. However, in general, the crystal energy may have severe nonlinearities in x , in which case the battery voltage will be strongly dependent upon the stoichiometry. Using quantum ab initio methods, Ceder et al.^{13,14} have computed average intercalation voltages for layered oxide systems. If the battery voltage is dependent upon x , this average method cannot capture the x dependence of the battery voltage. On the other hand, using the present method,

one can compute battery voltages for any value of x . In addition, one is able to visualize how the battery voltage can have a dependence on the stoichiometry x which is actually a measure of the state of the charge of the battery, because the battery voltage is linearly dependent upon the derivative of the total energy with respect to x .

Though the dominant contribution to the energy of an ionic crystal comes from the electrostatic or Madelung energy, a host of other terms such as the short-range electron–electron repulsion and the multipolar terms such as the dipole–dipole and dipole–quadrupole interactions do contribute to the total energy of the ionic crystal. However, the relative contributions of these additional interactions are expected to be of the order of 10% for the short-range electron–electron repulsion, ~1% for the dipole–dipole, and 0.1% for the dipole–quadrupole terms. We have computed the effects of the first two leading terms (beyond the Madelung part) on the battery voltage. It is found that though their contribution to the total energy can be nearly 11%, their influence on the battery voltage is minimal. On incorporating these corrections, the battery voltage becomes 3.9 V. Note further that the battery voltage is not directly proportional to the computed energy but to the first derivative of the energy with respect to stoichiometry. Hence, though the additional interaction terms may contribute significantly to the energy itself, they may not contribute so significantly to the first derivative. However, for computing other properties of crystals which depend directly on the energy itself, the additional interactions neglected in this paper may become very important, for example, in studying the relative stabilities of two similar crystalline phases of the same material.

Conclusion

The class of ionic crystals finds applications in several areas such as (i) ferroelectrics, (ii) piezoelectrics, (iii) electrochromic devices, (iv) nonlinear optical materials, and (v) advanced batteries and fuel cells. The ionic displacement in the crystal underlies the basic phenomenon in ferroelectrics and piezoelectrics. Hence, it will be of interest to follow the electrostatic energy of the crystal as a function of ionic displacements from the normal positions. This can be implemented in our program by varying the input parameters corresponding to the ionic coordinates. The electrostatic environment in the crystal will modify the local electronic energy levels at the sites of the guest or dopant ions and, hence, modify the electrochromic properties.

In batteries and fuel cells, extensive material search is for suitable electrode materials. Ionic oxides of varying structures (layered, spinel) constitute an important class of electrode materials. That the Madelung energy of these materials is directly relatable to the open circuit voltages of batteries is demonstrated in this paper. A method of computing the long-range ion–ion interactions was developed in this paper for ionic crystals of variable stoichiometry and valencies. An interesting application was to battery voltage computation for $\text{Li}_x\text{Mn}_2\text{O}_4$ -based lithium-ion batteries where the material stoichiometry x varies continuously during battery charging and discharging. In addition to stoichiometric changes, this method will be of use in studying the effect of doping on Madelung energies. Substitution of some of the host ions by hetero-ions is a widely practiced way of tuning material properties for different applications.

The present approach also offers a basis for investigating order–disorder transitions in nonstoichiometric and mixed-valent materials such as $\text{Li}_x\text{Mn}_2\text{O}_4$. In fact, a small voltage step is observed near $x = 0.5$ on the voltage-versus-state-of-charge

plot for this system which is usually attributed to the order–disorder transition, though detailed studies are not available. We plan to probe it in our future work.

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Appendix

Computation of $E_{i_{\text{ref}}}$. $E_{i_{\text{ref}}}$ is the energy of interaction of any chosen reference ion with its own Bravais relatives (see the following) and with other ions in the basis and their Bravais relatives. Let

$$\mathbf{r}_i = [x(i), y(i), z(i)] \quad i = 1 \rightarrow N$$

denote the atomic positions of the i th ion in the basis and $\lambda(i)$ ($i = 1 \rightarrow N$) denote the effective charge at the i th ion of the basis. Shift the origin of the coordinates (0, 0, 0) so that $\mathbf{r}_{i_{\text{ref}}} = (0, 0, 0)$. In this coordinate system

$$\mathbf{r}_i[x(i) - x(i_{\text{ref}}), y(i) - y(i_{\text{ref}}), z(i) - z(i_{\text{ref}})] = \mathbf{r}_i'$$

Now the interaction energy $E_{i_{\text{ref}}}$ can be written as

$$\begin{aligned} E_{i_{\text{ref}}} &= \sum_{\mathbf{l} \neq 0} [\lambda^2(i_{\text{ref}})/|\mathbf{l}|] + \sum_{i \neq i_{\text{ref}}} \sum_{\mathbf{l}} \lambda(i_{\text{ref}}) \lambda(i)/|\mathbf{l} + \mathbf{r}_i'| \\ &= \lambda^2(i_{\text{ref}}) \sum_{\mathbf{l} \neq 0} 1/|\mathbf{l}| + \lambda(i_{\text{ref}}) \sum_{i \neq i_{\text{ref}}} \lambda(i) \sum_{\mathbf{l}} 1/|\mathbf{l} + \mathbf{r}_i'| \quad (\text{i}) \end{aligned}$$

Bravais relatives of a given ion are here defined as the set of ions generated by Bravais translations acting on the chosen ion.

$$E_{i_{\text{ref}}} = \lambda(i_{\text{ref}}) \left[\left(\sum_{\mathbf{l} \neq 0} \lambda(i_{\text{ref}})/|\mathbf{l}| \right) + \left(\sum_{i \neq i_{\text{ref}}} \lambda(i) \sum_{\mathbf{l}} 1/|\mathbf{l} + \mathbf{r}_i'| \right) \right] \quad (\text{ii})$$

In the above equations, \mathbf{l} is the Bravais translation vector given by

$$\mathbf{l} = l_1 \mathbf{a} + l_2 \mathbf{b} + l_3 \mathbf{c}$$

where the vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} depend on the type of unit cell chosen.

Using Ewald's transformation, the summations appearing in eq ii can be expressed as

$$\sum_{\mathbf{l} \neq 0} 1/|\mathbf{l}| = \sum_{\mathbf{g}} f(\mathbf{g}) + F(G) \quad (\text{iii})$$

$$\sum_{\mathbf{l}} 1/|\mathbf{l} + \mathbf{r}_i'| = \sum_{\mathbf{g}} \exp(-i\mathbf{g} \cdot \mathbf{r}_i') f(\mathbf{g}) + \bar{F}(G, \mathbf{r}_i') \quad (\text{iv})$$

where

$$f(\mathbf{g}) = (\pi/\nu_c)(1/G^2) \exp[-(\mathbf{g}^2/4G^2)]/(\mathbf{g}^2/4G^2) \quad (\text{v})$$

$$F(G) = \sum_{\mathbf{l} \neq 0} (1/|\mathbf{l}|) \operatorname{erfc}\{G \cdot |\mathbf{l}|\} - 2G/\sqrt{\pi} \quad (\text{vi})$$

$$\bar{F}(G, \mathbf{r}_i') = \sum_{\mathbf{l}} (1/|\mathbf{l} + \mathbf{r}_i'|) \operatorname{erfc}\{G \cdot |\mathbf{l} + \mathbf{r}_i'|\} \quad (\text{vii})$$

In the above equations, G is a variable scalar parameter which is adjusted for fast convergence of the infinite sum, \mathbf{g} is the reciprocal lattice vector given by $\mathbf{g} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$ where vectors \mathbf{A} , \mathbf{B} , and \mathbf{C} are obtained from the vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} by the usual transformations. v_c is the unit cell volume given by $v_c = |\mathbf{a} \times \mathbf{b} \cdot \mathbf{c}|$.

$E_{i_{\text{ref}}}$ may now be written as

$$E_{i_{\text{ref}}} = \lambda(i_{\text{ref}}) \sum_{\mathbf{g}} f(\mathbf{g}) + \lambda(i_{\text{ref}}) F(G) + \sum_{\mathbf{g}} \left\{ \sum_{i \neq i_{\text{ref}}}^N \lambda(i) \exp(-i\mathbf{g} \cdot \mathbf{r}_i') \right\} f(\mathbf{g}) + \sum_{i \neq i_{\text{ref}}}^N \lambda(i) \bar{F}(G, \mathbf{r}_i') = \lambda(i_{\text{ref}}) \left[\sum_{\mathbf{g}} \{ \lambda(i_{\text{ref}}) + \sum_{i \neq i_{\text{ref}}}^N \lambda(i) \exp(-i\mathbf{g} \cdot \mathbf{r}_i') \} f(\mathbf{g}) + F(G) \lambda(i_{\text{ref}}) + \sum_{i \neq i_{\text{ref}}}^N \lambda(i) \bar{F}(G, \mathbf{r}_i') \right] \quad (\text{viii})$$

The coefficient of $f(0)$ in the first summation appearing in the eq viii is

$$\lambda(i_{\text{ref}}) + \sum_{i \neq i_{\text{ref}}}^N \lambda(i) = 0$$

due to the electroneutrality of the basis. Hence, the singularity arising from $f(\mathbf{g})$ for $\mathbf{g} = 0$ is removed.

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