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Energy correction for isolated impurities under periodic boundary conditions

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The Coulomb energy of aperiodic systems was investigated. To treat completely isolated disorder in infinite systems, energy correction for a supercell method is presented. We discuss a definition of the correction term, and then consider a direct approach taking into account interactions between charge distribution and an indirect approach based on a multipole expansion. In test calculations for isotropic-charged, anisotropic-charged, and neutral impurities, impurity energies independent of supercell sizes were obtained. The present energy correction can be applied to arbitrary systems and is expected to realize more practical simulations for aperiodic systems.

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I. INTRODUCTION

Computer simulations for complicated and large-sized systems, e.g., amorphous structures, liquid crystals, and polymers, are now increasingly sought for materials design, and molecular mechanics (MM) and molecular dynamics (MD) simulations are being applied as useful tools [1,2]. In many simulations for aperiodic systems, periodic boundary conditions are imposed to remove surface effects and construct infinite systems. This technique, a supercell method, is known as an expedient approach and widely applied both to *ab initio* and empirical calculations. For example, we can directly use well-developed schemes for periodic systems such as energy band calculation methods.

In order to simulate aperiodic systems containing local disorder, large supercells are required to diminish artificial interactions with impurities in the surrounding image cells. Unfortunately, it is quite difficult to treat sufficiently large-sized cells, because of the restrictions on computational time, and thus numerical inaccuracy depending on system sizes is an unavoidable problem in the supercell method. This problem becomes most serious in systems with long-range interactions typified by a Coulomb potential.

One of the skillful approaches to aperiodic systems is a Green-function method to calculate the electronic states of deep levels in semiconductors [3,4]. For more efficient calculations, an algorithm of empirical MM and MD simulations has been recently devised [5]. The aim of these schemes is to simulate isolated disorder in infinite systems directly.

When we focus our attention on the Coulomb energy, there is another approach in which we consider correction terms for the supercell method. Actually, the importance of the correction has been already pointed out for ionic systems [6,7]. In those studies, correction terms were given as monopole-monopole and monopole-quadrupole interactions, and impurity energies in some simple crystal lattices were analytically investigated.

In this paper, we discuss correction terms more precisely to deal with arbitrary systems where there is no constraint of crystal lattices and charge distribution. We consider two approaches: one is a direct method treating charge distribution, and the other is an indirect method based on a multipole expansion. Impurity energies of ionic systems have been investigated to ascertain the validity of the present scheme, and the energies independent of cell sizes were obtained.

This paper is organized as follows. In the next section, the formulation of the energy correction is described. To understand the physical meaning of the correction terms, a multipole expansion is also discussed. In Sec. III, test calculations for charged and neutral impurities are presented. We consider isotropic and anisotropic charge distribution for the charged impurities, and show that the three cases have essential differences in cell-size dependence. We also compare the two methods, i.e., the direct and the indirect approaches, for computational accuracy and efficiency. Finally, a short summary is given in Sec. IV.

II. FORMULATION

A. Definition

Our interest in this study is in the energy change due to local disorder which is introduced into an infinite host. Here, we regard the host as a periodic system such as perfect crystals. The energy change for the Coulomb interaction is given by

$$E_i=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho^a(\mathbf{r})\rho^a(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho^h(\mathbf{r})\rho^h(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{1}$$

The symbols $\rho^a(\mathbf{r})$ and $\rho^h(\mathbf{r})$ are the charge distribution in the aperiodic and the host systems, respectively. When impurity atoms are considered as the local disorder, $\rho^a(\mathbf{r})$ is defined by

$$\rho^a(\mathbf{r})=\rho^{\mathrm{imp}}(\mathbf{r})+\rho^{h'}(\mathbf{r}), \tag{2}$$

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where $\rho^{\mathrm{imp}}(\mathbf{r})$ is the charge distribution of the impurity atoms, and $\rho^{h'}(\mathbf{r})$ represents the charge distribution modified by lattice relaxation around the introduced impurity. All types of impurities, e.g., substitutional impurities, interstitial impurities, and defects, are described by Eq. (2). The energy change E_i is called the impurity energy, hereafter.

In the supercell method, the impurity energy is evaluated from

$$E_{\mathrm{SC}}=\frac{1}{2}\int_{\mathrm{cell}}d\mathbf{r}\int_{\mathrm{cell}}d\mathbf{r}'\sum_{\ell}\frac{\rho_{\mathrm{SC}}^{a}(\mathbf{r})\rho_{\mathrm{SC}}^{a}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_{\ell}|}-\frac{1}{2}\int_{\mathrm{cell}}d\mathbf{r}\int_{\mathrm{cell}}d\mathbf{r}'\sum_{\ell}\frac{\rho_{\mathrm{SC}}^{h}(\mathbf{r})\rho_{\mathrm{SC}}^{h}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_{\ell}|},\tag{3}$$

where $\rho_{\mathrm{SC}}^{a}(\mathbf{r})$ means the charge distribution of an aperiodic system under the periodic boundary condition, and is given by

$$\rho_{\mathrm{SC}}^{a}(\mathbf{r})=\rho_{\mathrm{SC}}^{\mathrm{imp}}(\mathbf{r})+\rho_{\mathrm{SC}}^{h'}(\mathbf{r})+\rho^{\mathrm{BG}}.\tag{4}$$

The background charge ρ^{BG} is required to keep the charge neutrality per cell. The vector $\mathbf{r}_{\ell}$ is the equilibrium position of the ℓth unit cell, and the summations in Eq. (3) are taken for all cells.

Whereas the impurity energy E_i is the energy change in the whole system, E_{SC} is the energy change per cell. Considering the cell size L, we obtain

$$\lim_{L\to\infty}E_{\mathrm{SC}}(L)=E_i.\tag{5}$$

Since the cell size is limited by computer capabilities, the supercell method needs a correction term to evaluate the impurity energy E_i. In fact, it has been shown that the E_{SC} of ionic systems has very slow asymptotic behavior with the cell-size dependence [5]. In this study, we define the correction energy as

$$\Delta E(L)=E_{\mathrm{SC}}(L)-E_i.\tag{6}$$

Here, we note that the following condition is assumed as a prerequisite for the correction term ΔE : the size of supercells is taken to be large enough to describe lattice relaxation caused by the impurity. Thus, the present correction aims to obtain the impurity energy of a system where the optimized relaxation structure has been embedded in the host system. This prerequisite is supported from the fact that the Coulomb forces acting on constituent atoms have rapid convergence concerning the cell-size dependence [5]. Since ΔE depends primarily on the lattice constant L, the correction term for the forces almost disappears in the differential. This fact brings about reliable results for crystal structures obtained by MM and MD simulations based on finite-sized supercells. The prerequisite is explicitly written by

$$\rho^{a}(\mathbf{r})\simeq[\rho_{\mathrm{SC}}^{\mathrm{imp}}(\mathbf{r})+\rho_{\mathrm{SC}}^{h'}(\mathbf{r})]\delta(\mathbf{r}-\mathbf{r}_{\mathrm{cell}})+\sum_{\ell\neq 0}\rho_{\mathrm{SC}}^{h}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_{\mathrm{cell}}-\mathbf{r}_{\ell}),\tag{7}$$

where $\mathbf{r}_{\mathrm{cell}}$ is the relative position in the unit cell and $\mathbf{r}_{\ell}=0$ for $\ell=0$. We also accept

$$\rho^{h}(\mathbf{r})=\sum_{\ell}\rho_{\mathrm{SC}}^{h}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_{\mathrm{cell}}-\mathbf{r}_{l})\tag{8}$$

for the host system which contains no local disorder.

Standing on Eqs. (7) and (8) and substituting Eqs. (1) and (3) into Eq. (6), the correction term is, finally, written as

$$\Delta E=\Delta E_{(1)}+\Delta E_{(2)}+\Delta E_{(3)}.\tag{9}$$

The three terms are given by

$$\Delta E_{(1)}=\frac{1}{2}\int_{\mathrm{cell}}d\mathbf{r}\int_{\mathrm{cell}}d\mathbf{r}'\sum_{\ell}\frac{[\rho^{\mathrm{imp}}(\mathbf{r})+\rho^{\mathrm{BG}}][\rho^{\mathrm{imp}}(\mathbf{r}')+\rho^{\mathrm{BG}}]}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_{\ell}|}-\frac{1}{2}\int_{\mathrm{cell}}d\mathbf{r}\int_{\mathrm{cell}}d\mathbf{r}'\frac{\rho^{\mathrm{imp}}(\mathbf{r})\rho^{\mathrm{imp}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},\tag{10}$$

$$\Delta E_{(2)}=\int_{\mathrm{cell}}d\mathbf{r}\int_{\mathrm{cell}}d\mathbf{r}'\sum_{\ell\neq 0}\frac{\rho^{\mathrm{imp}}(\mathbf{r})\rho^{\mathrm{rlx}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_{\ell}|}+\int_{\mathrm{cell}}d\mathbf{r}\int_{\mathrm{cell}}d\mathbf{r}'\sum_{\ell}\frac{\rho^{\mathrm{BG}}\rho^{h'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_{\ell}|},\tag{11}$$

$$\Delta E_{(3)}=\frac{1}{2}\int_{\mathrm{cell}}d\mathbf{r}\int_{\mathrm{cell}}d\mathbf{r}'\sum_{\ell\neq 0}\frac{\rho^{\mathrm{rlx}}(\mathbf{r})\rho^{\mathrm{rlx}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_{\ell}|},\tag{12}$$

where $\rho^{\mathrm{rlx}}(\mathbf{r})$, which is defined by

$$\rho^{\mathrm{rlx}}(\mathbf{r})=\rho^{h'}(\mathbf{r})-\rho^{h}(\mathbf{r}),\tag{13}$$

indicates the difference in charge distribution caused by the lattice relaxation. The subscript SC for the charge distribution is omitted in Eqs. (10)–(13) and hereafter.

Equations (10)–(12) give the interactions between the different cells, and $\Delta E_{(1)}$, $\Delta E_{(2)}$, and $\Delta E_{(3)}$ correspond to ρ^{imp}-ρ^{imp}, ρ^{imp}-ρ^{rlx}, and ρ^{rlx}-ρ^{rlx} interactions, respectively. The terms $\rho^{\mathrm{imp}}(\mathbf{r})\rho^{h}(\mathbf{r}')$ in $\Delta E_{(2)}$ and $\rho^{h'}(\mathbf{r})\rho^{h}(\mathbf{r}')$ in $\Delta E_{(3)}$ originate from the impurity energy E_i of the aperiodic system, because $\rho^{\mathrm{imp}}(\mathbf{r})+\rho^{h'}(\mathbf{r})$ of the cell $\ell=0$ interacts with $\rho^{h}(\mathbf{r})$ of the surrounding cells as shown in Eq. (7).

B. Multipole expansion

In this subsection, we discuss the physical meaning of the correction terms. According to the electromagnetism, the potential at $\mathbf{r}'(|\mathbf{r}'|\gg|\mathbf{r}|)$ given by the local charge distribution $\rho(\mathbf{r})$ around the origin O is generally described as the potential due to multipoles $\{M_{\alpha[\mu]}\}$ $(\mu=0,1,2,\ldots)$ positioned at O, where $M_{\alpha[\mu]}$, the μth-order multipole moment $M_{\alpha\beta\cdots}$, is defined by

$$M_{\alpha[\mu]}=\frac{(2\mu-1)!!}{\mu!}\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r}_{\alpha[\mu]},\tag{14}$$

with $(2\mu-1)!!=(2\mu-1)(2\mu-3)\cdots 1$ and $\mathbf{r}_{\alpha[\mu]}\equiv r_{\alpha}r_{\beta}\cdots$.

When the charge distribution $\rho^{a}(\mathbf{r})$ in each supercell is approximated by a set of $\{M_{\alpha[\mu]}\}$ $(\mu=0,\ldots,\mu_{\max})$ at $\mathbf{r}_O$, the correction term ΔE is given by interactions between these multipoles located in different cells as follows:

$$\Delta E=\sum_{\mu=0}^{\mu_{\max}}\sum_{\mu'=0}^{\mu_{\max}}\phi_{\mu\mu'}. \tag{15}$$

The multipole interaction $\phi_{\mu\mu'}$ is written by [8,9]

$$\phi_{\mu\mu'}=\frac{1}{2}\frac{(-1)^{\mu'}}{(2\mu-1)!!(2\mu'-1)!!}\sum_{\alpha[\mu]}\sum_{\alpha'[\mu']}M_{\alpha[\mu]}M_{\alpha'[\mu']}\times\left[\nabla_{\alpha[\mu]}\nabla_{\alpha'[\mu']}\sum_{\ell\neq 0}\frac{1}{|\mathbf{r}_{\ell}|}\right], \tag{16}$$

with $\nabla_{\alpha[\mu]}\equiv\partial^{\mu}/\partial r_{\alpha}\partial r_{\beta}\cdots$.

The multipole moment $M_{\alpha[\mu]}$ in Eq. (16) is given as

$$M_{\alpha[\mu]}=M_{\alpha[\mu]}^{\mathrm{imp}}+M_{\alpha[\mu]}^{\mathrm{rlx}}, \tag{17}$$

where $M_{\alpha[\mu]}^{X}$ $(X=\text{imp or rlx})$ is calculated from

$$M_{\alpha[\mu]}^{X}=\frac{(2\mu-1)!!}{\mu!}\int_{\mathrm{cell}}d\mathbf{r}\rho^{X}(\mathbf{r})(\mathbf{r}-\mathbf{r}_O)_{\alpha[\mu]}. \tag{18}$$

The position $\mathbf{r}_O$ is usually chosen to be in the center of the charge distribution $\rho^{\mathrm{imp}}(\mathbf{r})$. Generally, if $\rho(\mathbf{r})$ has the μth-order multipole moments $M_{\alpha[\mu]}$, $M_{\alpha[\mu+1]}$ depends on the choice of $\mathbf{r}_O$ which cannot be uniquely defined. We have checked that the ΔE obtained from Eq. (15) does not show serious dependence on $\mathbf{r}_O$ as long as it is centered around $\rho^{\mathrm{imp}}(\mathbf{r})$, because of the prerequisite $|\mathbf{r}|\ll|\mathbf{r}'|$ for the multipole expansion, where $|\mathbf{r}'|$ has the order of the cell size.

In the present study, multipoles up to the second-order are taken into account $(\mu_{\max}=2)$. We denote monopole (point charge), dipole, and quadrupole moments by Z, P_{α}, and $Q_{\alpha\beta}$, respectively. It has been numerically checked that higher-order multipole moments than quadrupoles contribute little to the correction energy, as discussed later. The monopole-monopole interaction is exceptionally calculated by

$$\phi_{ZZ}=\frac{1}{2}\int_{\mathrm{cell}}d\mathbf{r}\int_{\mathrm{cell}}d\mathbf{r}'\sum_{\ell}\frac{Z'(\mathbf{r})Z'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_{\ell}|} \tag{19}$$

instead of by Eq. (16), and $Z'(\mathbf{r})$ is defined as

$$Z'(\mathbf{r})=Z\delta(\mathbf{r}-\mathbf{r}_O)+\rho^{\mathrm{BG}}. \tag{20}$$

In the case of orthorhombic supercells, the multipole interaction $\phi_{\mu\mu'}$ with odd $\mu+\mu'$ becomes zero through the symmetry constraint. On the other hand, $\phi_{\mu\mu'}$ with even $\mu+\mu'$ has a nonzero value and, particularly for cubic cells with the lattice constant L, they are analytically written as

$$\phi_{ZZ}=-\frac{\lambda}{2}\frac{Z^2}{L}, \tag{21}$$

$$\phi_{ZQ}=\frac{4\pi}{9}\frac{Z\hat{Q}}{L^3}, \tag{22}$$

$$\phi_{PP}=-\frac{2\pi}{3}\frac{\hat{P}^2}{L^3}, \tag{23}$$

$$\phi_{QQ}=\frac{3.73\times 10^4}{18}\frac{1}{L^5}\left[\sum_{\alpha}2(Q_{\alpha\alpha})^2-\sum_{\alpha\neq\beta}\{2(Q_{\alpha\beta})^2+Q_{\alpha\alpha}Q_{\beta\beta}\}\right], \tag{24}$$

where we define $\hat{P}=|\mathbf{P}|$ and $\hat{Q}=\Sigma_{\alpha}Q_{\alpha\alpha}$. The correction term ϕ_{ZZ} is discussed in Ref. [6] and the factor λ is given as 2.8373, 3.6392, and 4.5848 for sc, bcc, and fcc lattices, respectively. The term ϕ_{ZQ} has been suggested in Ref. [7].

Here, let us make a comparison between Eqs. (9) and (15). As mentioned above, the three terms $\Delta E_{(1)}$, $\Delta E_{(2)}$, and $\Delta E_{(3)}$ correspond to the ρ^{imp}-ρ^{imp}, ρ^{imp}-ρ^{rlx}, and ρ^{rlx}-ρ^{rlx} interactions. Since $\rho^{\mathrm{rlx}}(\mathbf{r})$ never has a monopole, the leading terms of $\Delta E_{(1)}$, $\Delta E_{(2)}$, and $\Delta E_{(3)}$ are expected to be ϕ_{ZZ}, ϕ_{ZQ}, and ϕ_{QQ} for charged impurities [if $\rho^{\mathrm{rlx}}(\mathbf{r})$ has dipole moments, ϕ_{PP} becomes the leading term of $\Delta E_{(3)}$]. As for neutral impurities, ϕ_{PP} is expected to be the leading term of all three terms. The energy correction based on Eq. (9) where the charge distribution is directly taken into account is regarded as the calculation for an N-particle system. In contrast, the indirect approach given by Eq. (15) corresponds to a one-particle calculation, since only a set of multipoles is considered per cell.

C. Classical approach

It is straightforward to extend the present energy correction to classical calculations, considering the point charge $q\binom{s}{\ell}$ which has the following relations with the charge distribution $\rho(\mathbf{r})$:

$$\rho^{a}(\mathbf{r})=\sum_{s}^{N}\sum_{\ell}q^{a}\binom{s}{\ell}\delta\left[\mathbf{r}-\mathbf{r}^{a}\binom{s}{\ell}\right], \tag{25}$$

$$\rho^{h}(\mathbf{r})=\sum_{s}^{N}\sum_{\ell}q^{h}\binom{s}{\ell}\delta\left[\mathbf{r}-\mathbf{r}^{h}\binom{s}{\ell}\right], \tag{26}$$

$$\rho^{\mathrm{imp}}(\mathbf{r})=\sum_{\sigma}^{N_{\sigma}}\sum_{\ell}q^{\mathrm{imp}}\binom{\sigma}{\ell}\delta\left[\mathbf{r}-\mathbf{r}^{a}\binom{\sigma}{\ell}\right]. \tag{27}$$

The notation $\binom{s}{\ell}$ indicates the sth atom in the ℓth cell, and N and N_{σ} are the numbers of total atoms and impurity atoms per supercell, respectively. The atomic positions $\mathbf{r}^{a}\binom{s}{\ell}$ and $\mathbf{r}^{h}\binom{s}{\ell}$ are those in the aperiodic and the host systems.

In the classical approach, Eqs. (10)–(12) and Eq. (18) are replaced by the following expressions:

$$\Delta E_{(1)}=\frac{1}{2}\sum_{s}^{N}\sum_{s'}^{N}\sum_{\ell'}\frac{q_{\mathrm{BG}}^{\mathrm{imp}}\binom{s}{0}q_{\mathrm{BG}}^{\mathrm{imp}}\binom{s}{\ell'}}{\left|\mathbf{r}^{a}\binom{s}{0}-\mathbf{r}^{a}\binom{s'}{\ell'}\right|}-\frac{1}{2}\sum_{\sigma}^{N_\sigma}\sum_{\sigma'}^{N_\sigma}\frac{q^{\mathrm{imp}}\binom{\sigma}{0}q^{\mathrm{imp}}\binom{\sigma'}{0}}{\left|\mathbf{r}^{a}\binom{\sigma}{0}-\mathbf{r}^{a}\binom{\sigma'}{0}\right|},\tag{28}$$

$$\Delta E_{(2)}=\sum_{\sigma}^{N_\sigma}\sum_{s'}^{N}\sum_{\ell'\neq 0}\left[\frac{q^{\mathrm{imp}}\binom{\sigma}{0}q^{h}\binom{s'}{\ell'}}{\left|\mathbf{r}^{a}\binom{\sigma}{0}-\mathbf{r}^{a}\binom{s'}{\ell'}\right|}-\frac{q^{\mathrm{imp}}\binom{\sigma}{0}q^{h}\binom{s'}{\ell'}}{\left|\mathbf{r}^{a}\binom{\sigma}{0}-\mathbf{r}^{h}\binom{s'}{\ell'}\right|}\right]+\sum_{s}^{N}\sum_{s'}^{N}\sum_{\ell'}\frac{q^{\mathrm{BG}}q^{h}\binom{s'}{\ell'}}{\left|\mathbf{r}^{a}\binom{s}{0}-\mathbf{r}^{a}\binom{s'}{\ell'}\right|},\tag{29}$$

$$\Delta E_{(3)}=\frac{1}{2}\sum_{s}^{N}\sum_{s'}^{N}\sum_{\ell'\neq 0}\left[\frac{q^{h}\binom{s}{0}q^{h}\binom{s'}{\ell'}}{\left|\mathbf{r}^{a}\binom{s}{0}-\mathbf{r}^{a}\binom{s'}{\ell'}\right|}-2\frac{q^{h}\binom{s}{0}q^{h}\binom{s'}{\ell'}}{\left|\mathbf{r}^{a}\binom{s}{0}-\mathbf{r}^{h}\binom{s'}{\ell'}\right|}+\frac{q^{h}\binom{s}{0}q^{h}\binom{s'}{\ell'}}{\left|\mathbf{r}^{h}\binom{s}{0}-\mathbf{r}^{h}\binom{s'}{\ell'}\right|}\right],\tag{30}$$

with

$$q_{\mathrm{BG}}^{\mathrm{imp}}\binom{s}{\ell}=\begin{cases}q^{\mathrm{imp}}\binom{s_\sigma}{\ell}+q^{\mathrm{BG}} & \text{for impurity atoms} \quad (\sigma=1,\ldots,N_\sigma)\\ q^{\mathrm{BG}} & \text{otherwise,}\end{cases}\tag{31}$$

and

$$M_{\alpha[\mu]}^{\mathrm{imp}}=\frac{(2\mu-1)!!}{\mu!}\sum_{\sigma}^{N_\sigma}q^{\mathrm{imp}}\binom{\sigma}{0}\left[\mathbf{r}^{a}\binom{\sigma}{0}-\mathbf{r}_O\right]_{\alpha[\mu]},\tag{32}$$

$$M_{\alpha[\mu]}^{\mathrm{rlx}}=\frac{(2\mu-1)!!}{\mu!}\sum_{s}^{N}q^{h}\binom{s}{0}\left\{\left[\mathbf{r}^{a}\binom{s}{0}-\mathbf{r}_O\right]_{\alpha[\mu]}-\left[\mathbf{r}^{h}\binom{s}{0}-\mathbf{r}_O\right]_{\alpha[\mu]}\right\}.\tag{33}$$

In Eqs. (28)–(30), self-interactions are not included in the summations the same as in the integrations for $\rho(\mathbf{r})$.

III. TEST CALCULATIONS

In order to check the validity of the present energy correction, we have calculated the impurity energies of some ionic systems. As isolated impurity systems, NaCl alkali halides containing local defects are considered. The equilibrium structures have been determined by empirical MM simulations in which the interatomic potential of NaCl is given by the rigid-ion model

$$\psi(r_{ij})=\frac{e^2}{4\pi\varepsilon_0}\frac{q(i)q(j)}{r_{ij}}+A\exp\left[-B\frac{r_{ij}}{R(i)+R(j)}\right].\tag{34}$$

The constants A and B in the Born-Mayer-type potential are fixed at 1822 eV and 12.364, respectively [10]. The potential parameters, $q(i)=1$ and $R(i)=1.85$ Å for Na ions; $q(i)=-1$ and $R(i)=1.85$ Å for Cl ions, are determined so as to realize an fcc crystal structure with the experimental lattice constant of 5.63 Å. The convergence criteria of the MM calculations are set for when the maximum force becomes 0.01 times that in the initial structure. We apply the Ewald method to lattice sums both in the MM calculations and in the energy correction.

The numerical results for three typical cases, isotropic-charged impurity (point defect), anisotropic-charged impurity, and neutral impurity, are presented in this section. Because of the long-range Coulomb interaction, the electrostatic energy sensitively depends on the lattice relaxation, even if its deviation under different simulation conditions is less than 1% of the nearest-neighbor interatomic distance. To check clearly the cell-size dependence, the same relaxation structure is embedded in different sized supercells and their impurity energies are compared in this study. The relaxation structure was optimized by using a small-sized supercell in order to attain a comparison with larger-sized supercells. We should note again that the purpose of the present correction is to obtain the impurity energy of a system where all the surrounding image cells are replaced by the host system as shown in Eq. (7), and that the energy sensitively depends on the lattice relaxation. Therefore, we also have to carefully choose the size of supercells to optimize relaxation structures before the energy correction.

In this section, the impurity energies of the three cases are discussed, and the correction terms given by Eqs. (9) and (15) are compared to each other. For convenience, we will call the two approaches based on Eqs. (9) and (15), methods I and II, respectively.

A. Case I: Isotropic-charged impurity

As the simplest example, an NaCl system containing a point defect is discussed. First, the electrostatic impurity energy corrected by method I is shown as a function of the cell size in Fig. 1(a). The direct results of the supercell method E_{SC} (crosses) shows very slow convergence with increase in the size of the supercells. In contrast to E_{SC}, the corrected energies (open diamonds) give the constant value $E_i=5.32$ eV, independent of cell sizes. The ratio $\Delta E/E_i$ is about 15% for the supercell with 216 constituent ions. We have ascertained that this impurity energy of 5.32 eV agrees with the result obtained by the algorithm for aperiodic systems [5], which means that method I gives the impurity energy of a completely isolated state.

The contributions from each term of method I are also shown in Fig. 1(a). The impurity energies corrected only by the first term are plotted as open circles, and those corrected up to the second term are open squares. The first term $\Delta E_{(1)}$ overcorrects the impurity energy and the second term $\Delta E_{(2)}$ compensates for it. The contributions from the three terms to the total correction energy show the relation $\Delta E_{(1)}>\Delta E_{(2)}>\Delta E_{(3)}$. In this case I, the correction is done well by considering only $\Delta E_{(1)}$ and $\Delta E_{(2)}$ for all cell sizes except for the 216-ion supercell. This result comes about since the third term $\Delta E_{(3)}$, which is given as the ρ^{rlx}-ρ^{rlx} interaction, contributes little to the total correction energy, because the point defect does not strongly affect the lattice relaxation, and ρ^{rlx}, the change in charge distribution caused by the relaxation,

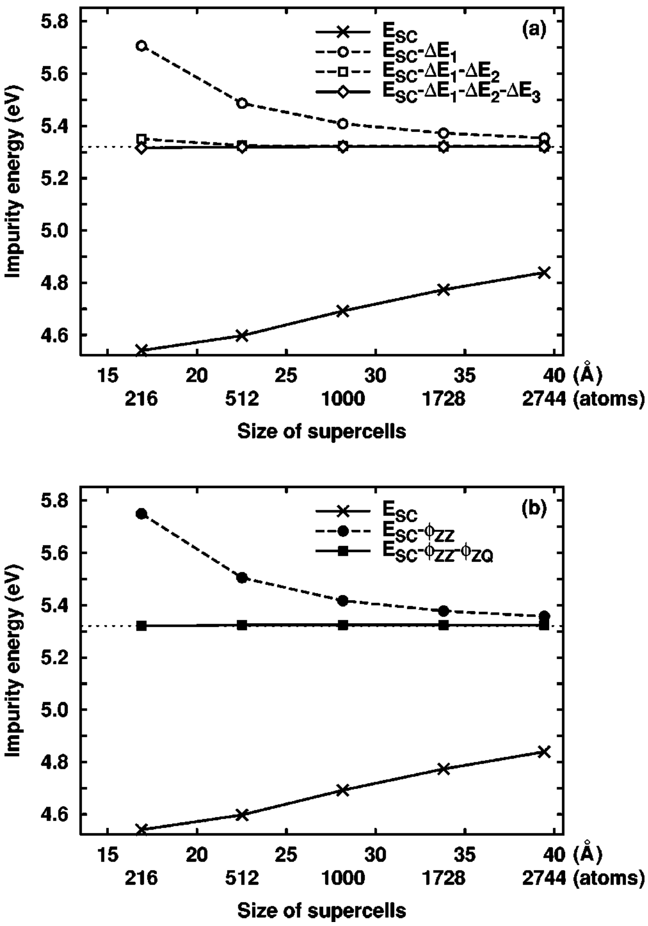

FIG. 1. Coulomb energies of the isotropic-charged impurity (case I) obtained by method I (a) and by method II (b). Crosses are the results of the supercell method. Open diamonds show the impurity energies corrected fully by method I, and open circles and open squares show those corrected by $\Delta E_{(1)}$ and $\Delta E_{(1)}+\Delta E_{(2)}$, respectively. Closed circles and closed squares for method II are the impurity energies corrected by the multipole interactions ϕ_{ZZ} and $\phi_{ZZ}+\phi_{ZQ}$.

consequently remains small. The 216-ion supercell, however, has a non-negligible contribution from $\Delta E_{(3)}$, which indicates that the correction for the smaller-sized supercells needs consideration up to the higher-order terms.

Secondly, the impurity energy obtained by method II is shown in Fig. 1(b). Satisfactory correction is achieved for all the cell sizes by considering ϕ_{ZZ} and ϕ_{ZQ} (closed squares). The monopole-quadrupole interaction ϕ_{ZQ} compensates for the energy which is overcorrected by the monopole-monopole interaction ϕ_{ZZ} (closed circles). The multipole moments calculated for case I are given in Table I. This system has only a monopole for M^{imp}. The obtained moments M^{rlx} correspond to the fact that the point defect in a host system with homogeneous charge distribution brings isotropic lattice relaxation and, in particular, no dipole moments appear. Because of the quadrupole moment Q^{rlx}, the quadrupole-quadrupole interaction ϕ_{QQ} also exists in this system. We have checked that ϕ_{QQ} is negligibly small compared to ϕ_{ZZ} and ϕ_{ZQ}. The corrected energy in Fig. 1(b) which is not inferior to that in Fig. 1(a) suggests that method II is effective for simple cases such as a point defect.

TABLE I. Multipole moments calculated for the three cases.

	Case I		Case II		Case III	
	imp	rlx	imp	rlx	imp	rlx
Z (e)	1.0		1.0		0.0	
$\hat{P}$ (e Å)	0.0	0.0	13.7	-6.4	14.1	-6.5
$\hat{Q}$ (e Å^2)	0.0	102.9	212.0	33.2	0.0	9.6

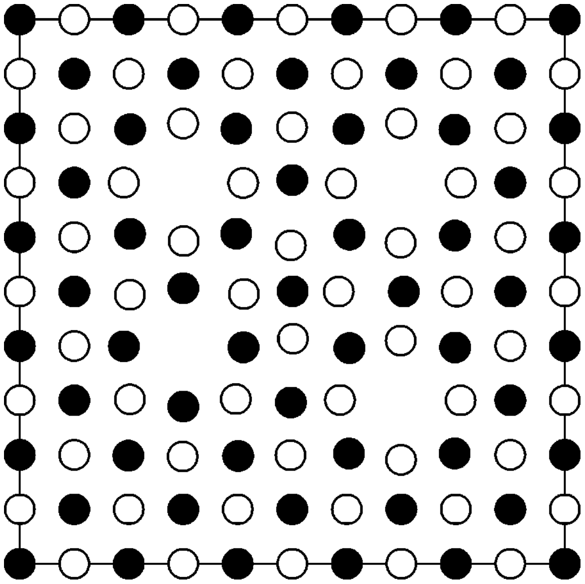

FIG. 2. Cross section of the equilibrium structure of case II. Open and closed circles are Na and Cl ions. A line indicates a 1000-ion supercell where four ions, one Na and three Cl ions, are missing.

Finally, we compare the two methods. Figure 1 shows that the three terms of method I, $\Delta E_{(1)}$, $\Delta E_{(2)}$, and $\Delta E_{(3)}$, are mainly derived from the multipole interactions Z^{imp}-Z^{imp}, Z^{imp}-Q^{rlx}, and Q^{rlx}-Q^{rlx}, respectively. As mentioned above, the lower-order term in method I makes the larger contribution to the total correction energy. This is explained from the fact that the three terms have the cell-size dependence L^{-1}, L^{-3}, and L^{-5}.

B. Case II: Anisotropic-charged impurity

Anisotropic charge distribution is now considered as the second example. The equilibrium structure of an NaCl system containing four defects is shown in Fig. 2. The multipole moments of this system are given in Table I. Case II has the dipole moments P^{imp} and P^{rlx} which do not exist in case I. To make an easy comparison with the other cases by scaling the monopole-monopole interaction, we have obtained $Z^{\mathrm{imp}}=1$ by substituting a divalent anion for the central Cl$^-$ ion in the cell.

The result of method I is given in Fig. 3(a). Compared with Fig. 1(a), the contribution from the third term $\Delta E_{(3)}$ to the total correction energy increases remarkably. In case II, where a large relaxation occurs as shown as the multipole moments P^{rlx} and Q^{rlx}, it is consequently important to take account of $\Delta E_{(3)}$ which is given as the ρ^{rlx}-ρ^{rlx} interaction.

Figure 3(b) shows the impurity energy calculated by method II. Since dipole and quadrupole moments exist in

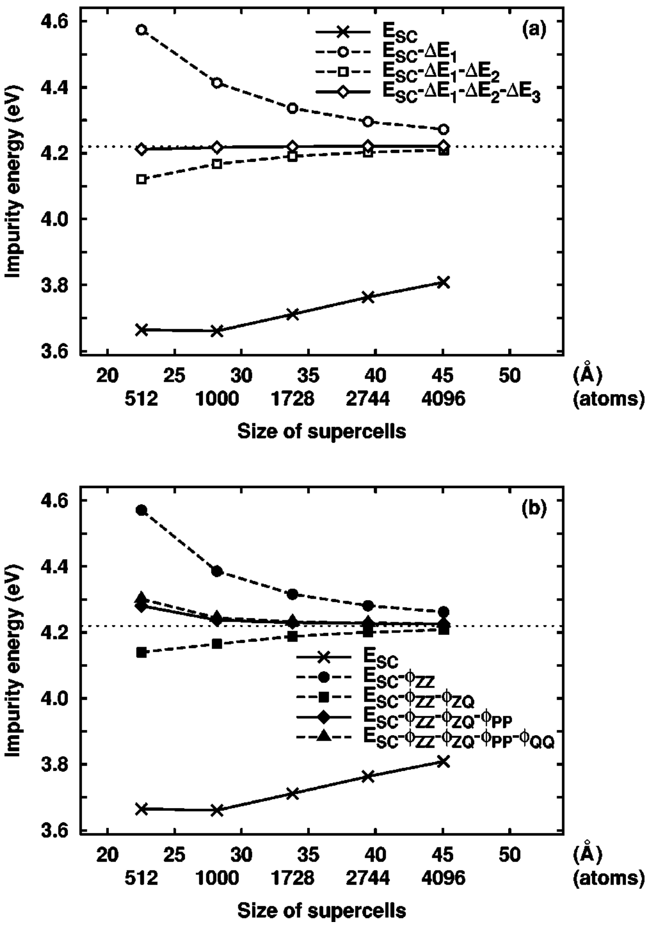

FIG. 3. Coulomb energies of the anisotropic-charged impurity (case II) obtained by method I (a) and by method II (b). Closed diamonds and closed triangles for method II are the impurity energies corrected by the multipole interactions $\phi_{ZZ}+\phi_{ZQ}+\phi_{PP}$ and $\phi_{ZZ}+\phi_{ZQ}+\phi_{PP}+\phi_{QQ}$. The other symbols and the scale of the vertical axis for E/E_i are the same as Fig. 1.

this case, the higher-order multipole interactions, particularly ϕ_{ZQ} and ϕ_{PP}, play an important role. In contrast to them, the contribution from ϕ_{QQ} is still small, as in case I. An accurate impurity energy was not obtained for the 512-ion supercell. This result means that higher-order multipoles than the quadrupole are required for a supercell of this size, where the cell size is relatively determined from a comparison with the relaxation region. With respect to large-sized supercells, method II gives a good correction when L^{-1} and L^{-3} multipole interactions are taken into account. Method II is expected to be combined with MM and MD simulations owing to its one-particle calculations, for example, it enables us to perform the energy correction at each MM and MD simulation step. From the viewpoint of computational accuracy, the energy correction by ϕ_{ZZ}, ϕ_{ZQ}, and ϕ_{PP} (closed diamonds) seems to be available for this purpose.

From Fig. 3, it can be seen that $\Delta E_{(1)}$, $\Delta E_{(2)}$, and $\Delta E_{(3)}$ in method I are derived from the multipole interactions Z^{imp}-Z^{imp}, Z^{imp}-Q^{rlx}, and P^{rlx}-P^{rlx}, respectively. The difference from case I is the third term. A large contribution from $\Delta E_{(3)}$ in Fig. 3(a) is attributed to the dipole-dipole interaction with the L^{-3} cell-size dependence. Case II shows that method I is required to consider up to the third term for systems having dipole moments, even in the calculation using large-sized supercells.

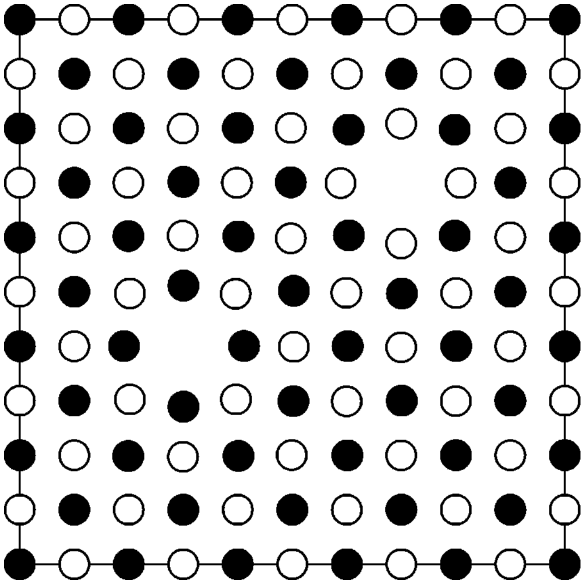

FIG. 4. Cross section of the equilibrium structure of case III. The line indicates a 1000-ion supercell where two ions are missing as a Schottky defect.

C. Case III: Neutral impurity

In the last example, a Schottky defect shown in Fig. 4 was considered as the neutral impurity. Although the net charge per cell does not appear, this system has a dipole moment as M^{imp} and dipole and quadrupole moments as M^{rlx}. Their calculated moments are listed in Table I.

Figure 5 shows the results obtained by methods I and II. Whereas the ratio $\Delta E/E_i$ for the smallest-sized supercell is about 15% in case I and 13% in case II, it is only 2% in case III. This result is obvious because the monopole-monopole and the monopole-quadrupole interactions are unable to exist for the neutral impurity. However, if the impurity has the dipole moment, the dipole-dipole interaction gives the L^{-3} cell-size dependence to the correction energy. Figure 5 shows that the neutral impurity also needs the correction term, although it is not as large as that of the charged impurities.

From the comparison between methods I and II, the three terms of method I are found to come from the multipole interactions P^{imp}-P^{imp}, P^{imp}-P^{rlx}, and P^{rlx}-P^{rlx}. The results of cases II and III seem to suggest that the relation $\mathbf{P}^{\mathrm{rlx}} \approx -\frac{1}{2}\mathbf{P}^{\mathrm{imp}}$ is satisfied in the present test calculations. This relation leads to $\Delta E_{(2)} \simeq -\Delta E_{(1)}$, which is the reason $\Delta E_{(1)}$ and $\Delta E_{(2)}$ cancel each other (i.e. crosses and open squares overlap) in Fig. 5(a). Since the total correction energy is attributed only to the dipole-dipole interaction, the cancellation prevents the correction energy from having a large contribution, in spite of the long-range L^{-3} interaction. In cases where a host system has a heterogeneous charge distribution such as a molecular crystal, and thus the lattice relaxation enhances $\mathbf{P}^{\mathrm{imp}}+\mathbf{P}^{\mathrm{rlx}}$, the correction energy could have a more important contribution even for the neutral impurity.

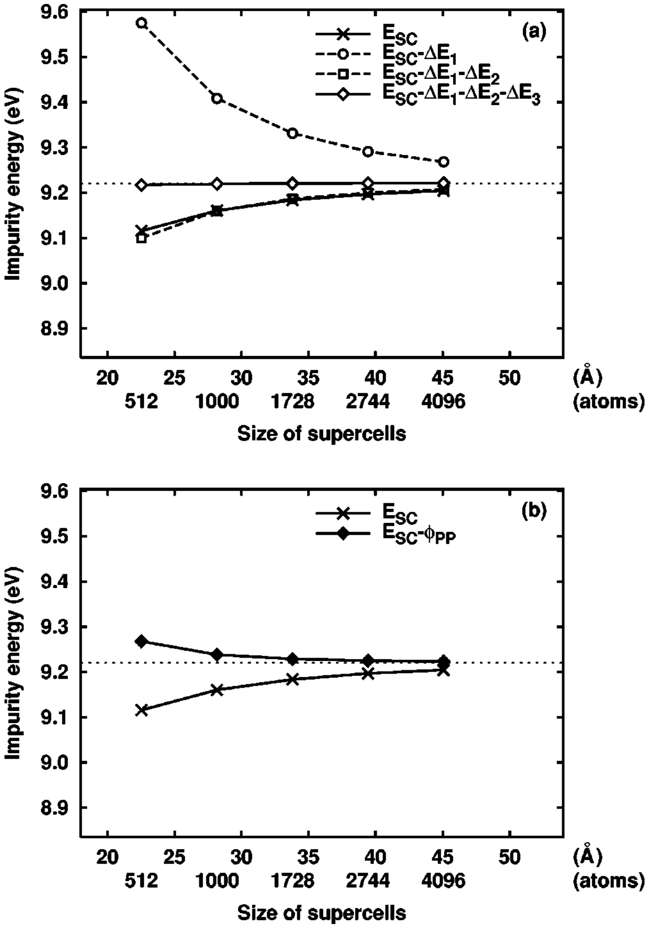

FIG. 5. Coulomb energies of the neutral impurity (case III) obtained by method I (a) and by method II (b). Closed diamonds for method II are the impurity energies corrected by the dipole-dipole interaction ϕ_{PP}. The other symbols have the same meanings as Figs. 1 and 3. The vertical axis is enlarged three times the scale of Figs. 1 and 3 for E/E_i.

IV. CONCLUSIONS

In this paper, we investigated the Coulomb energy of isolated impurities. Due to the periodic boundary condition, the supercell method contains interactions with impurities in the surrounding image cells. To exclude these artificial interactions and obtain the energy of a completely isolated state, the correction terms were presented. We discussed the two approaches: one calculates directly interactions between the charge distribution as the three terms, and the other describes the charge distribution based on a multipole expansion, where multipole moments up to second order are considered, in this study.

In the test calculations, we considered the three typical cases: isotropic-charged, anisotropic-charged, and neutral impurities. From the results obtained, the following characteristics have been found for the two approaches. For the energy correction given in the definition (method I), (i) the impurity energy can be evaluated for arbitrary sized cells, if the supercells are large enough to describe the relaxation region, (ii) the three terms contribute to the total correction energy as $\Delta E_{(1)} > \Delta E_{(2)} > \Delta E_{(3)}$, and (iii) consideration up to the third term is required for systems having dipole moments and for small-sized supercells, where the cell size is relatively determined from a comparison with the relaxation region. As for the energy correction based on the multipole expansion (method II), (i) its one-particle calculation attains a more efficient correction than method I, which is regarded as an *N*-particle calculation, (ii) it is indispensable for computational accuracy to consider up to the L^{-3} interactions: monopole-monopole, monopole-quadrupole, and dipole-dipole, and (iii) satisfactory correction is likely to be achieved for isotropic-charged impurities and large-sized supercells. With respect to the cell-size dependence, charged and neutral impurities have the leading terms of L^{-1} and L^{-3} interactions, respectively.

The present energy correction can be efficiently applied to arbitrary systems by considering the two approaches, and is expected to realize more practical computer simulations for aperiodic systems. Applications in which MM and MD calculations are combined with the energy correction are now required for further important study.

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