PHYSICAL REVIEW B VOLUME 6, NUMBER 4 15 AUGUST 1972

Electrostatic Potentials for Semi-Infinite and Lamellar Cubic Lattices Containing Several Different Kinds of Ions Per Unit Cell

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(Received 4 April 1972)

The electrostatic potential for a square planar lattice of positive, unit, point charges neutralized by a uniform-negative-background charge is developed and numerically tabulated. By stacking up such planes, potentials are constructed for infinite, semi-infinite, and lamellar-neutralized, simple-cubic lattices of positive point charges; numerical results are presented. The relation between potentials obtained by smearing out the neutralizing charge over all space and by confining the neutralizing charge to lattice planes is explicitly exhibited. Using $SrTiO_3$, a perovskite, as a specific example, it is shown how the tabulated potentials given here may be used to obtain the electrostatic potential on the surface of and within a complex cubic crystal containing several kinds of ions per unit cell. The methods for obtaining the potentials above the crystal surface or in the presence of vacancies and impurities are briefly indicated.

I. INTRODUCTION

Many of the physical properties of ionic crystals depend upon the electrostatic or Madelung potentials. The importance of such potentials in estimating cohesive energies and compressibilities is well known.[1] Seitz[2] suggested a simple method for calculating the energy bands of ionic crystals based on the Madelung potentials some time ago. More recently this approach was utilized by Kahn and Leyendecker[3] in the calculation of the energy bands of $SrTiO_3$. A similar scheme has been used by Levine and Mark[4] to calculate the intrinsic electronic surface states of zinc-blende crystals such as CdS. In extending the Seitz model to the calculation of surface states on ionic crystals, it is necessary to know how the electrostatic Madelung potentials are modified by the crystal surface or surfaces. The required potentials for complicated cubic crystals such as the perovskites, containing three kinds of ions per unit cell, are presented here.

II. STATEMENT OF THE PROBLEM

As Hund has shown,[5] it is convenient to introduce the electrostatic potential $\Phi_H(x, y, z)$ due to an infinite simple-cubic lattice with spacing a of positive, unit, point charges neutralized by a spatially smeared-out, uniform background of negative charge. The bulk electrostatic potential for a complex, cubic, ionic crystal containing several kinds of ions per unit cell can then be represented as a linear combination of Hund's potentials displaced from one another by a fraction of a lattice spacing and with each term being weighted according to the charge on the ionic sublattice it represents.[5,6] The sum of the weighting charges must of course be zero to maintain over-all charge neutrality. Extended tables of Hund's potentials have been published[7] permitting numerical evaluation of the bulk Madelung constants of complex crystals, virtually by inspection.

In order to obtain the same kind of representation for the electrostatic potential of a complex semi-infinite crystal lattice or slab containing several different kinds of ions per unit cell, we introduce the electrostatic potential $\psi(x, y, z)$. Here $\psi(x, y, z)$ is the electrostatic potential due to an infinite, plane, square lattice with spacing a of positive, unit, point charges located in the plane $z = 0$ and neutralized by a uniform background of negative charge confined to the plane $z = 0$. With the aid of this potential, we shall construct the required electrostatic potentials for semi-infinite lattices and slabs.

III. ELECTROSTATIC POTENTIAL OF A NEUTRALIZED PLANE LATTICE

Consider the potential due to a neutralized plane lattice of positive point charges e and side a at a distance z above the plane. The potential satisfies Poisson's equation

$$\nabla^2 \psi = -4\pi\rho(\vec{r}\,') , \tag{3.1}$$

where the neutralized charge density is given by

$$\rho(\vec{r}\,') = \delta(z') \frac{e}{a^2} \sum_{n_1=-\infty}^{\infty} \sum_{\substack{n_2=-\infty \\ n_1^2+n_2^2>0}}^{\infty} e^{(2\pi i/a)(n_1 x' + n_2 y')} . \tag{3.2}$$

The absence of the constant term from the Fourier-series expansion (3.2) implied by the restriction $n_1^2 + n_2^2 > 0$ guarantees that the average charge density in the (x, y) plane is zero and corresponds to the requirement of charge neutrality.

The well-known solution of Poisson's equation

$$\psi(\vec{\mathrm{r}}) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\rho(x', y', z')\cdot dx'dy'dz'}{[(x'-x)^2+(y'-y)^2+(z'-z)^2]^{1/2}} \tag{3.3}$$

then gives

$$\psi(\vec{\mathrm{r}}) = \frac{e}{a^2} \sum_{\substack{n_1=-\infty \\ n_1^2+n_2^2>0}}^{\infty} \sum_{n_2=-\infty}^{\infty} I(n_1, n_2) e^{(2\pi i/a)(n_1 x + n_2 y)} , \tag{3.4}$$

where

$$I(n_1, n_2) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{dx'dy' \exp\{(2\pi i/a)[n_1(x'-x)+n_2(y'-y)]\}}{[(x'-x)^2+(y'-y)^2+z^2]^{1/2}} . \tag{3.5}$$

The double integral in (3.5) can be evaluated[8] to yield

$$I(n_1, n_2) = \frac{a e^{-(2\pi/a)|z|(n_1^2+n_2^2)^{1/2}}}{(n_1^2+n_2^2)^{1/2}} , \tag{3.6}$$

and thus

$$\psi(x, y, z) = \frac{e}{a} \times \sum_{\substack{n_1=-\infty \\ n_1^2+n_2^2>0}}^{\infty} \sum_{n_2=-\infty}^{\infty} \frac{e^{(2\pi i/a)(n_1x+n_2y)} e^{-(2\pi/a)|z|(n_1^2+n_2^2)^{1/2}}}{(n_1^2+n_2^2)^{1/2}} \tag{3.7}$$

is the desired plane-lattice potential.

IV. NEUTRALIZED-BULK, HALF-SPACE, AND SLAB POTENTIALS OBTAINED BY SUPERPOSING NEUTRALIZED PLANE-LATTICE POTENTIALS

Consider the set of neutralized plane lattices shown in Fig. 1 with the origin of coordinates on the neutral plane $z=0$. The bulk potential $\Phi_B(x, y, z)$ at a distance z from the neutral plane at $z=0$ and due to all of the neutral planes is given by

$$\Phi_B(x, y, z) = \sum_{n=-\infty}^{\infty} \psi(x, y, na-z) . \tag{4.1}$$

The function $\Phi_B(x, y, z)$, like Hund's potential $\Phi_H(x, y, z)$, represents the potential due to a neutralized, infinite, cubic lattice of positive point charges. It differs from Hund's potential in that the the neutralizing, uniform, negative background is confined to the lattice planes instead of being smeared out three dimensionally. We can explicitly exhibit the difference between Φ_B and Φ_H as follows. Hund's potential satisfies

$$\nabla^2\Phi_H = -4\pi\rho_H(\vec{\mathrm{r}}') , \tag{4.2}$$

where

$$\rho_H(\vec{\mathrm{r}}') = \frac{e}{a^3} \sum_{\substack{n_1=-\infty \\ n_1^2+n_2^2+n_3^2>0}}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty} \exp[(2\pi i/a) \times (n_1x'+n_2y'+n_3z')] . \tag{4.3}$$

The corresponding potential Φ_B, due to the infinite set of neutralized planes, satisfies

$$\nabla^2\Phi_B = -4\pi\rho_p(\vec{\mathrm{r}}') , \tag{4.4}$$

where

$$\rho_p(\vec{\mathrm{r}}') = \frac{e}{a^2}\left(\sum_{n_3=-\infty}^{\infty} \delta(z'+n_3 a)\right) \times \sum_{\substack{n_1=-\infty \\ n_1^2+n_2^2>0}}^{\infty} \sum_{n_2=-\infty}^{\infty} \exp[(2\pi i/a)(n_1x'+n_2y')] . \tag{4.5}$$

With the aid of the identity

$$\sum_{n_3=-\infty}^{\infty} \delta(z'+n_3 a) = \frac{1}{a} \sum_{n_3=-\infty}^{\infty} e^{(2\pi i/a)n_3 z'} , \tag{4.6}$$

one obtains

$$\rho_H(\vec{\mathrm{r}}') - \rho_p(\vec{\mathrm{r}}') = \frac{e}{a^3} \sum_{\substack{n_3=-\infty \\ n_3\neq 0}}^{\infty} e^{(2\pi i/a)n_3 z'} . \tag{4.7}$$

Define $\psi_\delta(x, y, z)$ by

$$\nabla^2\psi_\delta(x, y, z) = -4\pi[\rho_H(\vec{\mathrm{r}}') - \rho_p(\vec{\mathrm{r}}')] , \tag{4.8}$$

and note that the solution of (4.8) can be obtained by inspection and is

$$\psi_\delta(x, y, z) = \frac{e}{\pi a} \sum_{\substack{n_3=-\infty \\ n_3\neq 0}}^{\infty} n_3^{-2} e^{(2\pi i/a)n_3 z} . \tag{4.9}$$

The series (4.9) can be summed by recognizing it as the Fourier-series expansion of a parabola giving

$$\psi_\delta(x, y, z) = 2\pi(e/a)\left[\tfrac{1}{6} - (z/a) + (z/a)^2\right] \quad \text{for } 0 \le z \le a . \tag{4.10}$$

As a consequence of (4.2), (4.4), and (4.8) we find

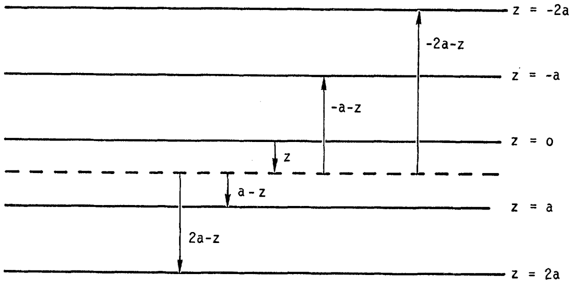

FIG. 1. Parallel, neutral planes with the origin of coordinates on the neutral plane at $z=0$.

TABLE I. Plane potential ψ, half-space potential Φ_S, and bulk potential Φ_B due to neutralized plane arrays of positive, unit, point charges. Coordinates x, y, and z are measured in units of the lattice spacing a.

$x\ y\ z$	$\psi(x,y,z)$	$\Phi_S(x,y,z)$	$x\ y\ z$	$\Phi_B(x,y,z)$
0 0 0	-3.90026	-3.892377	0 0 0	-3.884495
$\frac{1}{2}$ 0 0	-1.14236	-1.142745	$\frac{1}{2}$ 0 0	-1.143129
$\frac{1}{2}$ $\frac{1}{2}$ 0	-1.61554	-1.622629	$\frac{1}{2}$ $\frac{1}{2}$ 0	-1.629719
0 0 $\frac{1}{2}$	-0.2135052147	0.427339	0 0 $\frac{1}{2}$	-0.427666
$\frac{1}{2}$ 0 $\frac{1}{2}$	-0.02945678794	-0.0589182	$\frac{1}{2}$ 0 $\frac{1}{2}$	-0.0589227
$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$	-0.1388498088	-0.278018	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$	-0.278337
0 0 1	0.007870915027	-3.884506		
$\frac{1}{2}$ 0 1	-0.0003843006292	-1.143129		
$\frac{1}{2}$ $\frac{1}{2}$ 1	-0.007074306709	-1.629703		
0 0 $\frac{3}{2}$	$+0.0003274160392$	0.427665		
$\frac{1}{2}$ 0 $\frac{3}{2}$	$-4.589392926\times10^{-6}$	-0.0589228		
$\frac{1}{2}$ $\frac{1}{2}$ $\frac{3}{2}$	-0.0003181851391	-0.278337		
0 0 2	1.400352958×10^{-5}	-3.884492		
$\frac{1}{2}$ 0 2	$-5.410926463\times10^{-8}$	-1.143129		
$\frac{1}{2}$ $\frac{1}{2}$ 2	$-1.389521375\times10^{-5}$	-1.629717		

$$\Phi_B(x, y, z) = \Phi_H(x, y, z) - \psi_6(x, y, z) . \tag{4.11}$$

This explicitly shows the relation between Φ_B and Φ_H and will be useful in numerical calculations to be given below.

Referring to Fig. 1, the potential at a distance z below the free surface $z=0$ of a semi-infinite lattice of neutral planes located at $z=0$, a, $2a$, ... is given by

$$\Phi_S(x, y, z) = \sum_{n=0}^{\infty} \psi(x, y, na - z) \quad \text{for} \quad 0 \leq z \leq a . \tag{4.12}$$

For the case of a slab of $N+1$ neutral planes, (4.12) holds with the sum running from $n=0$ to $n=N$. On the neutral-plane surface $z=0$ of a semi-infinite lattice

$$\Phi_S(x, y, 0) = \psi(x, y, 0) + \sum_{n=1}^{\infty} \psi(x, y, na) , \tag{4.13}$$

while on a neutral plane $z=0$ in the infinite bulk lattice

$$\phi_B(x, y, 0) = \psi(x, y, 0) + 2\sum_{n=1}^{\infty} \psi(x, y, na) , \tag{4.14}$$

since $\psi(x, y, z) = \psi(x, y, -z)$. We can therefore express the half-space potential on the surface as

$$\Phi_S(x, y, 0) = \tfrac{1}{2}\psi(x, y, 0) + \tfrac{1}{2}\Phi_B(x, y, 0) . \tag{4.15}$$

Similarly, consider the point $z = \frac{1}{2}a$ midway between the $z=0$ neutral plane and the neutral plane at $z=a$. We have

$$\Phi_B(x, y, \tfrac{1}{2}a) = 2\psi(x, y, \tfrac{1}{2}a) + 2\sum_{n=1}^{\infty} \psi(x, y, na + \tfrac{1}{2}a) \tag{4.16}$$

and

$$\Phi_S(x, y, \tfrac{1}{2}a) = 2\psi(x, y, \tfrac{1}{2}a) + \sum_{n=1}^{\infty} \psi(x, y, na + \tfrac{1}{2}a) , \tag{4.17}$$

so that

$$\Phi_S(x, y, \tfrac{1}{2}a) = \psi(x, y, \tfrac{1}{2}a) + \tfrac{1}{2}\Phi_B(x, y, \tfrac{1}{2}a) . \tag{4.18}$$

Equation (4.18) shows that the half-space potential at one-half a lattice spacing below the surface consists of the contribution from the surface layer plus one-half of the bulk potential. Similar arguments using Fig. 1 show that the potential at a distance $(-a \leq z \leq 0)$ above the boundary surface of a semi-infinite lattice is given by

$$\Phi_S^-(x, y, z) = \psi(x, y, z) + \sum_{n=1}^{\infty} \psi(x, y, na - z) . \tag{4.19}$$

For $z = -\frac{1}{2}a$, Eqs. (4.19) and (4.1) give

$$\Phi_S^-(x, y, -\tfrac{1}{2}a) = \tfrac{1}{2}\Phi_B(x, y, -\tfrac{1}{2}a) , \tag{4.20}$$

showing that the potential one-half a lattice spacing above the surface of a half-space is just one-half of the bulk value at that point. We can also derive the following recursion relation from Fig. 1:

$$\Phi_S(x, y, Na + z) = \psi(x, y, Na + z) + \Phi_S[x, y, (N-1)a + z] , \tag{4.21}$$

where $0 \leq z \leq a$. To summarize, $\Phi_S(x, y, z)$ is the electrostatic potential inside a neutralized, semi-infinite, simple-cubic lattice of positive, unit, point charges at a distance $z \geq 0$ from vacuum-crystal interface.

V. NUMERICAL RESULTS

For $z > 0$, the series expansion (3.7) for ψ is rapidly convergent. On the plane $z=0$, (3.7) can be summed by the Ewald technique.[1] However, one can avoid this step by using the representation

$$\psi(x, y, 0) = \Phi_H(x, y, 0) - 2\sum_{n=1}^{\infty} \psi(x, y, na) - \frac{e\pi}{3a} , \tag{5.1}$$

obtained from (4.1), (4.10), and (4.11), together with tabulated values[7] of $\Phi_H(x, y, 0)$. Table I presents numerical results; for the potential $\psi(x, y, z)$ due to a neutralized plane of positive, unit, point charges, for the half-space potential $\Phi_S(x, y, z)$ due to a semi-infinite array of such planes, and for the bulk potential $\Phi_B(x, y, z)$ due to a completely infinite array of such planes. The x, y, and z coordinates in Table I are measured in units of the lattice spacing a, and the self-potential $\psi(0, 0, 0)$ of a neutralized plane array is seen to satisfy the identity

$$\psi(0, 0, 0) = 2\psi(\tfrac{1}{2}, 0, 0) + \psi(\tfrac{1}{2}, \tfrac{1}{2}, 0) . \tag{5.2}$$

Table II contains further values of the plane potential out to five lattice spacings above the neutral plane $z=0$. The series (4.1) and (4.12) for Φ_B and Φ_S converge very rapidly, and in practice only a few planes need be summed to obtain Φ_B or Φ_S accurate to several decimal places.

VI. APPLICATIONS

As a specific example of some applications of the potential functions derived above to complex

TABLE II. Plane potential ψ due to a neutralized planar array of positive, unit, point charges continued to five lattice spacings above the plane.

$x\ y\ z$	$\psi(x,y,z)$
$0\ 0\ \frac{5}{2}$	$+6.034\,436\,757\times10^{-7}$
$\frac{1}{2}\ 0\ \frac{5}{2}$	$-6.366\,723\,772\times10^{-10}$
$\frac{1}{2}\ \frac{1}{2}\ \frac{5}{2}$	$-6.021\,701\,476\times10^{-7}$
$0\ 0\ 3$	$2.605\,713\,765\times10^{-8}$
$\frac{1}{2}\ 0\ 3$	$-7.488\,621\,61\times10^{-12}$
$\frac{1}{2}\ \frac{1}{2}\ 3$	$-2.604\,215\,862\times10^{-8}$
$0\ 0\ \frac{7}{2}$	$1.125\,795\,447\times10^{-9}$
$\frac{1}{2}\ 0\ \frac{7}{2}$	$-8.772\,528\,237\times10^{-14}$
$\frac{1}{2}\ \frac{1}{2}\ \frac{7}{2}$	$-1.125\,618\,553\times10^{-9}$
$0\ 0\ 4$	$4.864\,723\,425\times10^{-11}$
$\frac{1}{2}\ 0\ 4$	$-7.030\,017\,103\times10^{-16}$
$\frac{1}{2}\ \frac{1}{2}\ 4$	$-4.864\,449\,598\times10^{-11}$
$0\ 0\ \frac{9}{2}$	$2.102\,163\,972\times10^{-12}$
$\frac{1}{2}\ 0\ \frac{9}{2}$	$3.486\,362\,612\times10^{-16}$
$\frac{1}{2}\ \frac{1}{2}\ \frac{9}{2}$	$-2.101\,417\,955\times10^{-12}$
$0\ 0\ 5$	$9.081\,638\,675\times10^{-14}$
$\frac{1}{2}\ 0\ 5$	$1.108\,789\,684\times10^{-16}$
$\frac{1}{2}\ \frac{1}{2}\ 5$	$-9.059\,405\,548\times10^{-14}$

crystals having several different kinds of ions per unit cell, consider the perovskite lattice of strontium titanate shown in Fig. 2.

Choosing the origin (0, 0, 0) at a cube center and measuring distances in units of the cube edge a, the ions of a typical cube are located as follows:

$$\mathrm{Ti}^{+4} \text{ at } (0,0,0)\ ,$$

$$\mathrm{O}^{-2} \text{ at } (\pm\tfrac{1}{2},0,0),\ (0,\pm\tfrac{1}{2},0),\ (0,0,\pm\tfrac{1}{2})\ ,$$

$$\mathrm{Sr}^{+2} \text{ at } (\pm\tfrac{1}{2},\pm\tfrac{1}{2},\pm\tfrac{1}{2})\ ,$$

corresponding to a titanium ion at the cube center, oxygen ions at the cube faces, and strontium ions at the eight cube corners, respectively. The bulk potential in an infinite $\mathrm{SrTiO_3}$ crystal is, according to the method of Hund[5] and Tosi,[6]

$$\begin{aligned}\Phi^{B}_{\mathrm{SrTiO_3}}(x,y,z) = {} & g(\mathrm{Ti})\Phi_B(x,y,z) - g(\mathrm{O})\Phi_B(x-\tfrac{1}{2},y,z) \\ & - g(\mathrm{O})\Phi_B(x,y-\tfrac{1}{2},z) - g(\mathrm{O})\Phi_B(x,y,z-\tfrac{1}{2}) \\ & + g(\mathrm{Sr})\Phi_B(x-\tfrac{1}{2},y-\tfrac{1}{2},z-\tfrac{1}{2})\ , \qquad (6.1)\end{aligned}$$

where $g(\mathrm{Ti})$, $g(\mathrm{O})$, and $g(\mathrm{Sr})$ are charges on the titanium, oxygen, and strontium ions, respectively, and over-all charge neutrality

$$g(\mathrm{Ti}) - 3g(\mathrm{O}) + g(\mathrm{Sr}) = 0 \qquad (6.2)$$

is maintained.

The electrostatic potentials at the various ionic sites in $\mathrm{SrTiO_3}$ may be obtained from (6.1) and Table I. For example, the potential at a titanium site in the bulk crystal is obtained by setting $x=$ $x=y=z=0$ in (6.1), using Table I, and noting that the bulk potentials in (6.1) are even in their arguments. Numerical results are shown in Table III. For convenience in preparing the tables, the lattice spacing a, which in this example represents the oxygen-oxygen distance in $\mathrm{SrTiO_3}$, was set equal to 1. In terms of arbitrary a, the electrostatic potential at a titanium site in the bulk crystal is, referring to Table III,

$$\Phi_{\mathrm{Ti}}(\mathrm{bulk}) = -12.377\,456/a\ . \qquad (6.3)$$

The numerator in (6.3) is the Madelung constant at the titanium site in an infinite $\mathrm{SrTiO_3}$ crystal. To convert (6.3) to eV, note that charge is measured

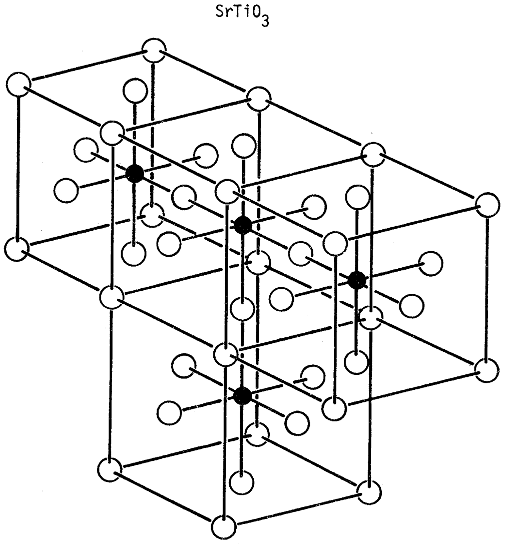

FIG. 2. $\mathrm{SrTiO_3}$ lattice: oxygen ions at cube faces; strontium ions at cube corners; titanium ions at center of cubes; cube edge = O-O distance = a.

TABLE III. Electrostatic potentials as functions of depth at the ionic sites in semi-infinite $\mathrm{SrTiO_3}$ lattices. Type-I lattice bounded by an (001) plane containing Ti and O, type-II lattice bounded by an (001) plane containing Sr and O.

$\Phi_{\mathrm{Ti}}(\mathrm{bulk}) = -12.377\,456$	$\Phi_{\mathrm{O}}(\mathrm{bulk}) = 6.455\,912$
$\Phi^{\mathrm{SI}}_{\mathrm{Ti}}(0) = -11.704\,528$	$\Phi^{\mathrm{SII}}_{\mathrm{O}}(0) = 5.512\,676$
$\Phi^{\mathrm{SII}}_{\mathrm{Ti}}(\frac{1}{2}) = -12.409\,238\,04$	$\Phi^{\mathrm{SI}}_{\mathrm{O}}(\frac{1}{2}) = 6.484\,524\,010$
$\Phi^{\mathrm{SI}}_{\mathrm{Ti}}(1) = -12.376\,217\,18$	$\Phi^{\mathrm{SII}}_{\mathrm{O}}(1) = 6.454\,633\,567$
$\Phi^{\mathrm{SII}}_{\mathrm{Ti}}(\frac{3}{2}) = -12.377\,508\,38$	$\Phi^{\mathrm{SI}}_{\mathrm{O}}(\frac{3}{2}) = 6.455\,961\,588$
$\Phi^{\mathrm{SI}}_{\mathrm{Ti}}(2) = -12.377\,452\,15$	$\Phi^{\mathrm{SII}}_{\mathrm{O}}(2) = 6.455\,905\,791$
$\Phi_{\mathrm{O}}(\mathrm{bulk}) = 6.455\,912$	$\Phi_{\mathrm{Sr}}(\mathrm{bulk}) = -5.387\,208$
$\Phi^{\mathrm{SI}}_{\mathrm{O}}(0) = 6.459\,036$	$\Phi^{\mathrm{SII}}_{\mathrm{Sr}}(0) = -4.978\,324$
$\Phi^{\mathrm{SII}}_{\mathrm{O}}(\frac{1}{2}) = 6.459\,036$	$\Phi^{\mathrm{SI}}_{\mathrm{Sr}}(\frac{1}{2}) = -5.415\,896\,083$
$\Phi^{\mathrm{SI}}_{\mathrm{O}}(1) = 6.455\,905\,580$	$\Phi^{\mathrm{SII}}_{\mathrm{Sr}}(1) = -5.386\,005\,639$
$\Phi^{\mathrm{SII}}_{\mathrm{O}}(\frac{3}{2}) = 6.455\,905\,580$	$\Phi^{\mathrm{SI}}_{\mathrm{Sr}}(\frac{3}{2}) = -5.387\,260\,022$
$\Phi^{\mathrm{SI}}_{\mathrm{O}}(2) = 6.455\,905\,147$	$\Phi^{\mathrm{SII}}_{\mathrm{Sr}}(2) = -5.387\,204\,225$

in units of $e = 4.8 \times 10^{-10}$ esu and

$$\Phi_{\mathrm{Ti}}(\mathrm{eV}) = -12.377\,456(e^2/a) = -45.644 \text{ eV} . \quad (6.4)$$

Next, consider the electrostatic potential on the surface of and within a semi-infinite strontium titanate lattice. We see from Fig. 2 that there are, for example, two types of (001) neutral surfaces, type-I surfaces containing titanium and oxygen ions and type-II neutral surfaces containing strontium and oxygen ions. Correspondingly, there are two types of potential functions for $\mathrm{SrTiO_3}$ half-spaces terminated by (001) planes. Taking the plane $z = 0$ as the boundary surface, these are (where $z \geqslant 0$)

$$\begin{aligned}\Phi^{\mathrm{SI}}_{\mathrm{SrTiO_3}}(x, y, z + \tfrac{1}{2}) = {} & g(\mathrm{Sr})\Phi_S(x - \tfrac{1}{2}, y - \tfrac{1}{2}, z) \\ & - g(\mathrm{O})\Phi_S(x, y, z) + g(\mathrm{Ti})\Phi_S(x, y, z + \tfrac{1}{2}) \\ & - 2g(\mathrm{O})\Phi_S(x - \tfrac{1}{2}, y, z + \tfrac{1}{2}) \quad (6.5)\end{aligned}$$

for the potential at a depth of $(z + \frac{1}{2})$ lattice spacings below a type-I (Ti-O) (001) boundary surface and

$$\begin{aligned}\Phi^{\mathrm{SII}}_{\mathrm{SrTiO_3}}&(x, y, z + \tfrac{1}{2}) \\ &= g(\mathrm{Ti})\Phi_S(x, y, z) - 2g(\mathrm{O})\Phi_S(x - \tfrac{1}{2}, y, z) \\ &\quad + g(\mathrm{Sr})\Phi_S(x - \tfrac{1}{2}, y - \tfrac{1}{2}, z + \tfrac{1}{2}) - g(\mathrm{O})\Phi_S(x, y, z + \tfrac{1}{2}) \quad (6.6)\end{aligned}$$

for the potential at a depth of $(z + \frac{1}{2})$ lattice spacings below a type-II (Sr-O) (001) boundary surface. With the aid of these expressions, we can derive expressions for the potentials on the type-I and type-II boundary surfaces themselves. For example, to determine the potential on a type-I (Ti-O) surface, we note that such a surface is located one-half a lattice spacing below a type-II (Sr-O) surface. Thus, we need only remove this topmost (Sr-O) layer to obtain the potential on the surface of a half-space with a type-I (Ti-O) boundary, i.e.,

$$\begin{aligned}\Phi^{\mathrm{SI}}_{\mathrm{SrTiO_3}}&(x, y, 0) \\ &= \Phi^{\mathrm{SII}}_{\mathrm{SrTiO_3}}(x, y, \tfrac{1}{2}) - g(\mathrm{Sr})\psi(x - \tfrac{1}{2}, y - \tfrac{1}{2}, \tfrac{1}{2}) \\ &\quad + g(\mathrm{O})\psi(x, y, \tfrac{1}{2}) . \quad (6.7)\end{aligned}$$

Using (6.6), this can be written as

$$\begin{aligned}\Phi^{\mathrm{SI}}_{\mathrm{SrTiO_3}}(x, y, 0) = {} & g(\mathrm{Ti})\Phi_S(x, y, 0) - 2g(\mathrm{O})\Phi_S(x - \tfrac{1}{2}, y, 0) \\ & + g(\mathrm{Sr})[\Phi_S(x - \tfrac{1}{2}, y - \tfrac{1}{2}, \tfrac{1}{2}) - \psi(x - \tfrac{1}{2}, y - \tfrac{1}{2}, \tfrac{1}{2})] \\ & - g(\mathrm{O})[\Phi_S(x, y, \tfrac{1}{2}) - \psi(x, y, \tfrac{1}{2})] , \quad (6.8)\end{aligned}$$

and from (4.18) it follows that

$$\begin{aligned}\Phi^{\mathrm{SI}}_{\mathrm{SrTiO_3}}&(x, y, 0) \\ &= g(\mathrm{Ti})\Phi_S(x, y, 0) - 2g(\mathrm{O})\Phi_S(x - \tfrac{1}{2}, y, 0) \\ &\quad + \tfrac{1}{2}[g(\mathrm{Sr})\Phi_B(x - \tfrac{1}{2}, y - \tfrac{1}{2}, \tfrac{1}{2}) - g(\mathrm{O})\Phi_B(x, y, \tfrac{1}{2})] . \quad (6.9)\end{aligned}$$

A similar argument for $\Phi^{\mathrm{SII}}_{\mathrm{SrTiO_3}}(x, y, 0)$ gives

$$\begin{aligned}\Phi^{\mathrm{SII}}_{\mathrm{SrTiO_3}}&(x, y, 0) \\ &= g(\mathrm{Sr})\Phi_S(x - \tfrac{1}{2}, y - \tfrac{1}{2}, 0) - g(\mathrm{O})\Phi_S(x, y, 0) \\ &\quad + \tfrac{1}{2}[g(\mathrm{Ti})\Phi_B(x, y, \tfrac{1}{2}) - 2g(\mathrm{O})\Phi_B(x - \tfrac{1}{2}, y, \tfrac{1}{2})] . \quad (6.10)\end{aligned}$$

The physical interpretation of these expressions is straightforward. For example, Eq. (6.9) states that the potential on the surface of a type-I $\mathrm{SrTiO_3}$ half-space consists of the contribution from a pure-(Ti-O)-lattice half-space corrected by one-half the bulk contribution from the Sr-O sublattice, one-half a lattice spacing away. Numerical results for the potentials as functions of depth in type-I and type-II $\mathrm{SrTiO_3}$ half-spaces at the various ionic sites are shown in Table III which was obtained using (6.5–6.6), (6.9–6.10), and Table I. Above the surface of the crystal the potential falls off rapidly. At a titanium site one-half a lattice spacing above the surface $\Phi_{\mathrm{Ti}}(0, 0 - \frac{1}{2}) = -0.672\,924/a$ compared to the bulk value (6.3). It should be observed that vacancies and impurities can be easily incorporated by subtracting out from the half-space potentials those Coulomb contributions coming from the particular ions one wishes to convert to vacancies. Impurity ions may be added on in the same fashion.

One should note that the relations derived above between potentials near the surface of a complex cubic crystal and the potentials for neutralized planar arrays will hold only if the ionic lattice on the exposed crystal surface is charge neutral. When such is not the case, the resulting electric field from the lattice will cause a readjustment of electrons near the surface, violating, thereby, the assumption that the neutralizing background is uniform.

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