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Abstract. The Madelung potentials of an arbitrary volume point in 11 cubic crystals are presented in terms of rapidly convergent series of the McDonald function. Atomic potentials, orbital splittings and polarization energy are calculated for ^4A_u fullerene anions C_{60}^{3-} in three different fullerite cubic lattices doped by alkali metals for various orientations of the C_{60} cage.

1. Introduction

The relative stability of crystalline phases of doped fullerides is currently attracting attention and is determined by the energy differences of the order of 0.1 eV per cation [1]. Already the simple purely electrostatic treatment in [1] ensures a correct qualitative description which has been confirmed by further quantum-mechanical semiempirical consideration [2]. This approach includes calculation of the Madelung energy of the corresponding ionic crystal phase of point charges and a separate evaluation of the energy of the isolated fullerene anion. However, because of the small energy differences involved and the large size of the fullerene anions, inclusion of the lattice polarization effects seems to be necessary. Interest in the alterations in the electronic structure of molecular ions entering the crystal lattice is also characteristic of the theory of donor–acceptor crystals of the TTF TCNQ type (see e.g. [3]).

For theoretical estimation of the lattice influence on a molecular ion, a reliable method is needed to calculate the electrostatic crystal potential at an arbitrary point in the crystal volume. It should be mentioned that usually an accuracy of 0.1–0.01 eV is enough for the Madelung energy [4, 5]. However, if the potential is used for the further calculation of molecular wavefunctions, greater accuracy is needed. In particular, as will be shown in section 3, differences in the polarization energies of fullerene anions are only a few hundredths of an electronvolt for different orientations in the cubic crystals. Therefore, for reliable estimation of these differences in total energies and for determination of the optimal orientation, a much higher accuracy of the potential is required. It is essential that the partly filled t_{1u} threefold degenerate one-electron level of C_{60} does not split in some arrangements of fullerene anions in the cubic lattices while in others it does, and this is important for interpretation of the superconductivity of the doped fullerides.

Recently a convenient method for calculation of the potential geometrical factors with an accuracy of 10^{-5}–10^{-6} has been proposed for the cubic lattice sites [6]. In section 2 we simplify and generalize this scheme for an arbitrary point in the crystal. In section 3 the method is applied to fullerene anions.

2. Construction of the geometrical factors of cubic crystals from the geometrical factors of the standard system

We start from the expression for the potential $V(\rho, z)$ at a point with cylindrical coordinates ρ, z that is created by a system of alternating charges $\pm q$ situated at a distance d from each other with the origin of the coordinate system at $+q$ [6]; ρ and z are measured in units of d:

$$V(\rho, z) = \frac{q}{d}\varphi(\rho, z) = \frac{q}{d}\sum_{k=1}^{\infty}(-1)^k[\rho^2 + (k+z)^2]^{-1/2}.$$ (1)

The sum is expressed as

$$\varphi(\rho, z) = 4\sum_{l=1}^{\infty}K_0[\pi(2l-1)\rho]\cos[\pi(2l-1)z]$$ (2)

where $K_0(x)$ is the modified cylindrical function of the zeroth order (the MacDonald function).

In [6], three systems of parallel lines of the above type have been considered which intersect the orthogonal plane at vertices of a square net with period r:

$$r = ud.$$ (3)

It should be mentioned that, for construction of the potentials of cubic lattices, in fact it is possible to retain a single system (denoted in [6] by M) in which the charges in the orthogonal plane alternate, while along the 'vertical' lines their signs are constant. If the potential of M at a point (x, y, z) is

$$V(x, y, z) = g(x, y, z; u)q/d$$ (4)

then the geometrical factor $g(x, y, z; u)$ is

$$g(x, y, z; u) = \frac{4}{u}\sum_{s,t=-\infty}^{\infty}(-1)^s\sum_{l=1}^{\infty}K_0\left[(2l-1)\pi\sqrt{(x-s)^2 + \left(\frac{z-t}{u}\right)^2}\right]\cos[(2l-1)\pi y].$$ (5)

On account of the symmetry and periodicity of system M (figure 1), $g(x, y, z; u)$ fulfils the identities

$$g(-x, y, z; u) = g(x, -y, z; u) = g(x, y, -z; u) = g(x, y, z; u)$$

$$g(x \pm 1, y, z; u) = g(x, y \pm 1, z; u) = g(x, u, z \pm 1; u) = -g(x, y, z; u)$$ (6)

$$g(x, y, z; u) = g(y, x, z; u).$$

These mean that calculation of a potential in an arbitrary point of the crystal volume is reduced to determination of the electric field inside the prism AFEMNL (figure 1). The
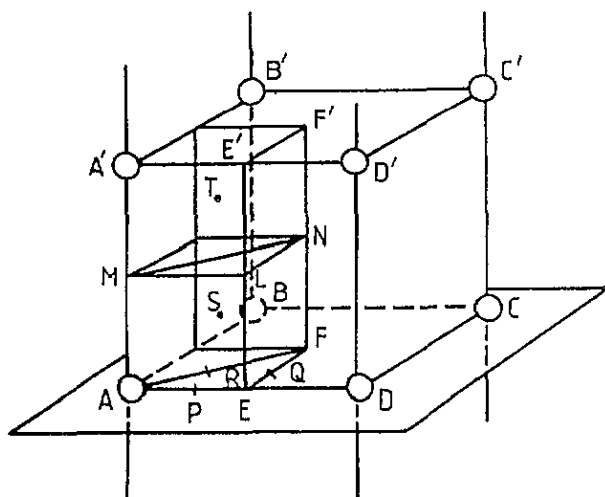
Figure 1. The main points of the cubic wall.

conditions (6) impose some identities on the MacDonald function which are not considered here.

The possibility of restricting the choice of the system M can be illuminated by decomposition of the NaCl lattice into two systems M mutually displaced by $\frac{1}{2}R$ along the z axis where R is the lattice constant. The elementary charges placed in the origins of each system are opposite. Symbolically this decomposition may be written as

$$L_A^{(-)}(R, u) = M_A\left(R, \tfrac{1}{2}u\right) - M_M\left(R, \tfrac{1}{2}u\right) \tag{7}$$

where L and M designate specific periodic point charge distributions. The arguments at M are the corresponding constants d and u whereas the subscript indicates the position of the origin according to figure 1. As a result, it immediately follows for the geometrical factor $h(x, y, z; u)$ of the NaCl lattice that

$$2h(x, y, z; u) = g(x, y, \tfrac{1}{2}z; \tfrac{1}{2}u) - g(x, y, \tfrac{1}{2}(z+1)/\tfrac{1}{2}u). \tag{8}$$

On the other hand, the second system $L^{(+)}(d, u)$ used of alternating planes of identical charges within the plane can also be formed from two M-systems rotated by $45°$ around the axis x, which is directed along the basis straight lines of alternating charges. In two cases $u = 1$ and $u = 2$ which are needed for construction of the cubic crystal potentials we have

$$L_{A,z}^{(+)}(d, 1) = M_{A,x}\left(d, \sqrt{2}\right) + M_{E,x}\left(d, \sqrt{2}\right)$$

$$L_{A,z}^{(+)}(d, 2) - L_{E,z}^{(+)}(d, 2) = M_{A,x}(2d, \tfrac{1}{2}) \tag{9}$$

$$L_{A,z}^{(+)}(d, 2) + L_{E,z}^{(+)}(d, 2) = M_{A,x}\left(2d, 1/\sqrt{2}\right) + M_{E,x}\left(2d, 1/\sqrt{2}\right)$$

where the second subscript denotes the direction of the constituting lines of alternating charges in the corresponding system. From these the geometrical factors $f(x, y, z; u)$ of the $L^{(+)}$-system are

$$f(x, y, z; 1) = g\left(\tfrac{1}{2}(y+z), \tfrac{1}{2}(z-y), x; \sqrt{2}\right) + g\left(\tfrac{1}{2}(y+z-1), \tfrac{1}{2}(z-y+1), x; \sqrt{2}\right)$$

$$4f(x, y, z; 2) = g\left(y + \tfrac{1}{2}z, \tfrac{1}{2}z - y, x; 1/\sqrt{2}\right) + g\left(y + \tfrac{1}{2}(z-1), \tfrac{1}{2}(z+1)y, x; 1/\sqrt{2}\right) \tag{10}$$

$$+ g\left(2y, z, x; \tfrac{1}{2}\right)$$

and also

$$g\left(x, y, z; \tfrac{1}{2}\right) = 2f\left(\tfrac{1}{2}x, z, y; 2\right) - 2f\left(\tfrac{1}{2}(x-1), z, y; 2\right). \tag{11}$$

Equations (8) and (10) allow one to calculate the electrostatic potential at an arbitrary point of any cubic crystal in terms of the rapidly convergent series (5) (except in the close vicinity of lattice sites for large u). The results of [6] for the site potentials are particular cases of equations (8), (10) and (11). For large u it is convenient to use directly the factor $f(x, y, z; u)$ which can be calculated by means of

$$f(x, y, z; u) = \sum_{s,t=-\infty}^{\infty} \sum_{l=1}^{\infty} K_0\left[\pi(2l-1)u\sqrt{(x-s)^2 + (y-t)^2}\right] \cos[\pi(2l-1)z]. \tag{12}$$

With these preliminaries, construction of the potential for cubic crystals is very simple and reduces to decomposition of the real crystal into systems M (or $L^{(+)}$). In fact, suitable constructions have already been used in [6]. They are shown in the third column of table 1. It is convenient to start with the NaCl, perovskite and CsCl systems. The subsequent systems are formed from those already mentioned which are properly shifted (their origins are given according to figure 1) and compressed. It seems that there is no need for special comments for the third column. Maybe it is worthwhile to mention only that the equation for the zincblende lattice ZnS is a consequence of

$$L_A(\mathrm{ZnS}) + L_S(\mathrm{NaCl}) = L'_A(\mathrm{ZnS}) \qquad L_A(\mathrm{ZnS}) + L'_A = L\left(\mathrm{CaF}_2\right) \tag{13}$$

where $L'(\mathrm{ZnS})$ denotes the ZnS lattice with full and empty small cubes interchanged. The lattice compositions containing fullerene (C_{60}) have been described in [2, 6].

When the lattice has been built, equations (8), (10) and (11) act and give the fourth column in table 1 where the geometrical factor $v(x, y, z)$ of a corresponding lattice is given. The potential in terms of $v(x, y, z)$ is

$$V(x, y, z) = (eq/R)v(x, y, z) \tag{14}$$

where q is the smallest charge on lattice sites in units of electron charge $-e$. The values of q are given in the second column. The origin of the coordinate system is at A and an ion of charge kq of the same sign as that of q is located at A. The integer constant k is determined by the lattice structure. For instance, it is equal to 2 for Ca in CaF_2, to 1 for Zn in ZnS, to 3 for C_{60} in A15, to 2 for Bi in $BaBiO_3$, etc.

3. The molecular ion as an element of a crystal lattice

To illustrate the above method, we shall calculate the polarization energy of a molecular ion which appears from the non-zero gradient of the crystal field in a cubic lattice. Clearly this energy increment is important only if the volume of the molecular ion is large, i.e. the case of doped fullerides. As was mentioned in the introduction, the relative stability of different crystal phases of C_{60} doped by alkali metals is satisfactorily described by the sum of the free anion C_{60}^{x-} energy E and the Madelung energy of this anion [1]:

$$E - kqe^2v(0, 0, 0)/R \tag{15}$$

Table 1. Geometrical factors of cubic lattices.

Number	Crystal	Lattice composition	Geometrical factor $v(x,y,z)^a$
1	NaCl $q=1$	$L_A^{(-)}(R/2,1) = M_A(R,\frac{1}{2}) - M_M(R,\frac{1}{2})$	$g(2x,2y,z) - g(2x,2y,z+\frac{1}{2})$
2	BaBiO$_3$ $q=2$	$L_A^{(-)}(\frac{1}{2}R,\sqrt{2}) + M_A(R,\frac{1}{2})$	$g'(x+y,y-x,z) - g'(x+y,y-x,z+\frac{1}{2}) + g(2x,2y,z)$
3	CsCl $q=1$	$L_F^{(+)}(\frac{1}{2}R,2) + M_A(R,1/\sqrt{2})$	$g'(x+y,y-x,z) + 2g(x-\frac{1}{2},y-\frac{1}{2},2z)$
4	CaF$_2$ $q=1$	$L_A(\text{NaCl},R) + L_A(\text{CsCl},\frac{1}{2}R)$	$g(2x,2y,z) - g(2x,2y,z+\frac{1}{2}) + 2g'(2x+2y,2y-2x,2z) + 4f(2x-\frac{1}{2},2y-\frac{1}{2},4z)$
5	ZnS $q=2$	$L_A(\text{CaF}_2) - L_s(\text{NaCl})$	$g(2x,2y,z) - g(2x,2y,z+\frac{1}{2}) - g(2x+\frac{1}{2},2y-\frac{1}{2},z-\frac{1}{4}) + g(2x+\frac{1}{2},2y$ $-\frac{1}{2},z+\frac{1}{4}) + 2g'(2x+2y,2y-2x,2z) + 4f(2x-\frac{1}{2},2y-\frac{1}{2},4z)$
6	Cu$_2$O $q=-1$	$L_A(\text{ZnS}) + L_N(\text{BaBiO}_3)$	$\frac{1}{2}[g(2x,2y,z) + g(2x,2y,z+\frac{1}{2}) - g(2x+\frac{1}{2},2y-\frac{1}{2},z-\frac{1}{4}) + g(2x+\frac{1}{2},2y$ $-\frac{1}{2},z+\frac{1}{4}) + 2g'(2x+2y,2y-2x,2z) + 4f(2x-\frac{1}{2},2y-\frac{1}{2},4z)] + 2g'(x+y,$ $y-x,z) - 2g'(x+y,y-x,z-\frac{1}{2})$
7	$C_{60}^{3-} A_3^+$ FCC $q=-1$	$L_A(\text{CaF}_2) + L_A(\text{NaCl})$	$2g(2x,2y,z+\frac{1}{2}) + 2g'(2x+2y,2y-2x,2z) + 4f(2x-\frac{1}{2},2y-\frac{1}{2},4z)$
8	$C_{60}^{3-} A_3^+$ BCC $q=-1$	$L_A(\text{BaBiO}_3) + L_N(\text{BaBiO}_3)$	$2[g'(x+y,y-x,z) - g'(x+y,y-x,z+\frac{1}{2})] + g(2x,2y,z) + g(2x,2y,z+\frac{1}{2})$
9	$C_{60}^{3-} A_3^+$ A15 $q=-1$	Three shifts in lattice 8	$2[g'(x+y,y-x,z) - g'(x+y,y-x,z+\frac{1}{2})] + g(2x,2y,z) + g(2x,2y,z+\frac{1}{2})$ $+4[f'(x-\frac{1}{2},y,4z) + f'(z,y-\frac{1}{2},4x)]$
10	$C_{60}^{4-} A_4^+$ Im,m,m $q=-1$	Five shifts in lattice 8	$3[g'(x+y,y-x,z) - g'(x+y,y-x,z+\frac{1}{2})] + g(2x,2y,z) + g(2x,2y,z+\frac{1}{2})$ $+4[f'(z-\frac{1}{2},y,4x) + f'(x-\frac{1}{2},z,4y) + f'(x,z-\frac{1}{2},4y)]$
11	$C_{60}^{6-} A_6^+$ BCC $q=-1$	Six shifts in lattice 8	$4[g'(x+y,y-x,z) - g'(x+y,y-x,z+\frac{1}{2})] + 2[g(2x,2y,z) + g(2x,2y,z+\frac{1}{2})]$ $+4[f'(x-\frac{1}{2},y,4z) + g'(x,z-\frac{1}{2},4y) + f'(x,z-\frac{1}{2},4y)$ $+f'(z,y-\frac{1}{2},4x) + f'(z-\frac{1}{2},y,4x)]$

^{a} $g(x,y,x) = g(x,y,z) = g(x,y,z,\frac{1}{2})$, $g'(x,y,z) = g(x,y,z,1/\sqrt{2})$, $f(x,y,z) = f(x,y,z,2)$, $f'(x,y,z) = f(x,y,z,4)$.

where $v(0, 0, 0)$ is the geometrical factor of the C_{60}^{x-} crystal site coinciding with the centre of the fullerene cage (A in figure 1). Let us calculate the potential which acts on an electron in the vicinity of this centre. Since the centre is empty, we must subtract the contribution of the charge eqk of the site A from the total crystal potential:

$$qe\left[v(x, y, z) - k\sqrt{x^2 + y^2 + z^2}\right] / R \qquad (16)$$

because, by definition, the geometrical factor (equations (1) and (5)) contains contributions from all point charges including that at the site A. In equation (16), x, y, z denote the electron coordinates in units of R with the origin at A.

A characteristic feature of our model is a detailed consideration of the ion whose wavefunction is to be calculated while all remaining crystal ions act on the chosen wavefunction as point charges. At the same time the initial approximation (15) means that the C_{60}^{x-} anion is considered in a crystal also as a point anion, i.e. the constant potential

$$eqv(0, 0, 0)/R \qquad (17)$$

acts on each particle within this ion. Thus, in order to obtain the polarization correction to the energy (15) directly from the calculation of a separate C_{60}^{x-} ion by means of some molecular program, the difference between equations (16) and (17) should be added to the electron energy operator in the Hartree–Fock molecular Hamiltonian:

$$V_A(x, y, z) = -qe^2\left[v(x, y, z) - k/\sqrt{x^2 + y^2 + z^2} - v(0, 0, 0)\right]/R. \qquad (18)$$

Naturally, equation (18) vanishes for $x^2 + y^2 + z^2$ approaching zero since by definition of $v(0, 0, 0)$ [6] the Coulomb singularity is excluded from $v(0, 0, 0)$. Finally, the total crystal energy in the proposed approximation is a sum of two parts: the standard Madelung energy of point charges at lattice sites and the internal energy of polarized molecular ions.

As an example, let us calculate the potentials of different fullerene atoms and the polarization energy of fullerene in a cubic lattice doped by an alkali metal. Three orientations of fullerene relative to cubic axes are discussed. Fullerene may be imagined as six mutually bonded naphthalene carbon cores which are slightly bent around the central bond. In the first orientation (a) these six 'butterflies' lie on the six coordinate half-axes passing through the middle of the central bond. There are only three unequal atomic potentials for three inequivalent 'naphthalene' atoms in this arrangement of fullerene. As a result the threefold degeneracy of representation t_{1u} of the icosahedral group is conserved. It is this level which is half filled in the C_{60}^{3-} anion (table 2).

In the second orientation (b) the fivefold rotation symmetry axis of fullerene coincides with the z axis, and the zy plane is the symmetry plane of the pentagons orthogonal to z. Here 16 different atomic potentials appear, 14 of which are repeated four times and two appear twice (only the two last and the largest in absolute value of the rest are presented in table 2). The remaining 13 are given in the footnotes to the table.

The third [7] orientation is suitable only for the FCC lattice where it means that the common bond of naphthalene hexagons is situated in front of the pentagon centre of the adjacent fullerene. According to [7] this position is favourable for intermolecular interaction in the neutral C_{60} crystal. However, as is seen from table 2, this is not the case for the ionic crystal.

It is worthwhile to mention that, in the second case (b), the degeneracy of the t_{1u} level is completely removed whereas, in the last orientation (c) with six different atomic potentials, the twofold degeneracy continues to exist.

Table 2. Polarization of ^4A_u-term of C_{60}^{3-} in cubic lattices.

Lattice	Orientation[a]	Energy of an electron near inequivalent atoms[b] (eV)			Shift of t_{1u} level (eV)			Polarization energy (eV)
FCC $R = 14.436$ Å	(a)	0.080 18	−0.020 61	0.029 44	0.019	0.020	0.020	0.053
	(b)	0.123 54	0.110 29	−0.419 39[c]	−0.051	−0.030	0.063	−0.126
	(c)	0.111 06	0.006 09	0.091 41[d]	−0.831	0.724	0.724	−0.056
BCC $R = 11.787$ Å	(a)	−0.893 55	0.111 78	0.330 73	−0.019	−0.019	−0.019	−0.650
	(b)	−0.456 65	0.259 39	−0.891 90[e]	−0.157	0.065	0.099	−0.608
$Pm3n$ A15 $R = 11.787$ Å	(a)	−0.276 71	−0.094 75	0.104 63	−0.016	−0.016	−0.016	−0.107
	(b)	−0.013 33	0.013 31	0.295 55[f]	−0.049	−0.019	0.075	−0.084

[a] See text.
[b] According to equation (18).
[c] The other fourfold degenerate potentials are 0.088 68, 0.015 50, 0.157 76, −0.101 97, 0.086 09, 0.148 32, 0.076 43, 0.087 98, −0.293 16, 0.065 95, 0.095 74, 0.056 39, and −0.258 07 eV.
[d] The remaining six values of potential are 0.126 26, −0.335 42 and −0.255 33 eV (the last two are sixfold degenerate).
[e] −0.450 85, −0.441 47, 0.315 94, −0.699 93, 0.339 30, 0.039 34, 0.065 92, 0.568 97, 0.478 07, 0.312 20, −0.146 54, 0.151 66 and 0.465 72 eV (see footnote c).
[f] −0.279 27, 0.041 66, 0.062 68, −0.172 68, 0.094 03, 0.241 87, 0.010 99, −0.169 73, −0.113 76, 0.236 06, −0.090 84, 0.039 88 and −0.162 77 eV (see footnote c).

Calculation of the ionic states has been performed by the same Roothaan open-shell version of the Hartree–Fock method as was used for free fullerene and described in detail in [2]. In the present work the crystal field (18) was included according to equation (18) in the diagonal of a molecular Hamiltonian.

4. Conclusion

A method for calculation of the lattice electric field at an arbitrary point of the ionic cubic crystal volume (an 'empty' as well as a node volume) with an accuracy of 10^{-5} is proposed and applied to fullerides. It is shown that local potentials at carbon atoms differ significantly owing to the high anisotropy of the crystal field at intermediate distances from the lattice sites. As a result, the degeneracy of one-electron levels of the fullerene ions and their polarization energy become dependent on the mutual orientations of the molecular and crystal symmetry axes. The polarization energy per cation is highly sensitive to the crystal symmetry and in the BCC system the polarization shift of the ^4A_u fullerene term becomes comparable with the total energy difference between different cubic phases obtained in the same approximation [2]. In contrast with ionic polarization in a homogeneous field, the polarization energy in the FCC phase with small distances between C_{60}^{3-} may achieve positive values for some orientations of the ions.

Acknowledgments

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