

ON THE ION-ELECTRON INTERACTION ENERGY MODIFIED BY A CRYSTAL LATTICE OF POLARIZABLE ATOMS. V

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The classical ion-electron interaction energy, which is needed in the problem of the Wannier excitation in inorganic semiconductors, is calculated for cubic crystals in terms of a multipole expansion. It is also shown that the asymptotic form for large ion-electron distance gives the known formula charge-charge interaction modified by the dielectric constant.

The ion-electron interaction energy in crystal lattices is connected with the exciton problem, and with the problem of the existence of the ion-electron bound states in the crystal lattice. There are two limiting cases which can be solved in principle. The case of tight binding — the Frenkel exciton [1, 2, 3] occurs when the electron is localized about an ion in a definite unit cell; the case of the weak binding — Wannier exciton [4, 5] occurs when the ion-electron distances are large. Wannier suggested to ignore all the particles in the system except the ion and electron which interact according to the Coulomb law. The effect of the remaining electrons and cores is to provide a periodic potential which gives to these particles the effective masses m_i^* and m_e^* . Mott [6] was first to suggest a modification of the model of Wannier to account for the dielectric medium. In this paper we aim at finding the potential of the ion-electron interaction, which takes into account the structure of the crystal lattice. We assume that the lattice is rigid and thus the calculated potential is valid for the intermediate case of exciton, when the relative motion of the electron is fast enough so that the atoms cannot follow it, and slow enough so that we can account for the atomic or ionic electrons solely through the polarizabilities of atoms. Of course a full calculation, which is lacking so far, will take into account the interaction with lattice vibrations. We consider the simple cubic lattice of polarizable atoms, in which one atom is replaced by a positive ion. The electrostatic potential energy of such a system is given by the following form [1]:

$$V(\mathbf{R}_e) = \frac{q_1 e}{|\mathbf{R}_e|} - \frac{1}{2} \sum_i \sum_j S_i \underline{A}_{ij} S_j \quad (1.1)$$

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where: index "1" denotes that the ion is at the beginning of the coordinate system, q_1 is the charge of the ion, \mathbf{R}_e the position vector of the electron, and \mathbf{S}_i the electrical field intensity in lattice site i , defined in the following way:

$$\begin{aligned} \mathbf{S}_i &= q_1 \mathbf{S}'_i + e \mathbf{S}''_i \quad (i \neq 1) \\ \mathbf{S}'_i &\equiv \frac{(\mathbf{r}_{1i})}{|\mathbf{r}_{1i}|^3}; \quad \mathbf{S}''_i \equiv \frac{(\mathbf{r}_{ei})}{|\mathbf{r}_{ei}|^3}; \quad \mathbf{S}'_1 \equiv 0. \end{aligned}$$

Making use of the definition of the electrical field intensity, we express the polarizational energy of the lattice containing one ion and one electron in the following form:

$$V_{\text{pol}}(\mathbf{R}_e) = -\frac{1}{2} \sum_i \sum_j (q_1 \mathbf{S}'_i + e \mathbf{S}''_i) \underline{A}_{ij} (q_1 \mathbf{S}'_j + e \mathbf{S}''_j) = A + B + C \quad (1.2)$$

where

$$\begin{aligned} A &= -\frac{1}{2} q_1^2 \sum_{i \neq 1} \sum_{j \neq 1} \mathbf{S}'_i \underline{A}_{ij} \mathbf{S}'_j \\ B &= -\frac{1}{2} e^2 \sum_i \sum_j \mathbf{S}''_i \underline{A}_{ij} \mathbf{S}''_j \\ C &= -q_1 e \sum_{i \neq 1} \sum_j \mathbf{S}'_i \underline{A}_{ij} \mathbf{S}''_j. \end{aligned}$$

The term A in Eq. (1.2) is equal to the electrostatic energy of the Schottky defect [9] (except for the Madelung energy). The terms B corresponds to the energy of an additional electron in a lattice of polarizable atoms [10]. The periodicity of this energy is destroyed by the existence of a single ion with a different polarizability than the other atoms. Using a method similar to that given in [8] one can express the term B with the aid of the generalized polarizability function \underline{A}_{ij}^0 calculated for the perfect atomic lattice:

$$\begin{aligned} V_B(\mathbf{R}_e) &= -\frac{1}{2} e^2 \sum_i \sum_j \mathbf{S}''_i \underline{A}_{ij}^0 \mathbf{S}''_j - \\ &- \frac{1}{2} e^2 \sum_i \sum_j \mathbf{S}''_i \underline{A}_{i1}^0 \alpha^{-1} \frac{b}{\underline{U} + (\underline{U} - \alpha^{-1} \underline{A}_{11}^0) b} \underline{A}_{1j}^0 \mathbf{S}''_j. \end{aligned}$$

The second term which destroys the periodicity of the energy contains the correction $b = \frac{\alpha^b - \alpha}{\alpha}$, where α^b is the polarizability of the ion, and α is the polarizability of the atoms.

The term C in Eq. (1.2) expresses the ion-electron interaction energy modified by existence of the lattice. In the following we consider only the term C and we express it in the following form:

$$\begin{aligned} V_C(\mathbf{R}_e) &= q_1 |e| \sum_{i \neq 1} \sum_j \mathbf{S}'_i \underline{A}_{ij}^0 \mathbf{S}''_j + \\ &+ q_1 |e| \sum_{i \neq 1} \sum_j \mathbf{S}'_i \underline{A}_{i1}^0 \alpha^{-1} \frac{b}{\underline{U} + (\underline{U} - \alpha^{-1} \underline{A}_{11}^0) b} \underline{A}_{1j}^0 \mathbf{S}''_j. \end{aligned} \quad (1.3)$$

We can see that, because of symmetry, the second term of Eq. (1.3) is equal to zero, and therefore we obtain the ion-electron interaction energy in the form:

$$V_C(\mathbf{R}_e) = q_1|e| \sum_{i \neq 1} \sum_j S'_i \underline{A}_{ij}^0 S''_j. \quad (1.4)$$

Using the integral representation of the Kronecker delta for a simple cubic lattice [8] we express Eq. (1.4) in terms of the Fourier transform [10]:

$$V_C(\mathbf{R}_e) = q_1|e| \int_{\square} d\mathbf{k} S(\mathbf{k}) \underline{a}^0(\mathbf{k}, \alpha) \sum_j S''_j e^{-2\pi i \mathbf{k} r_j^0}$$

or equivalently

$$V_C(\mathbf{R}_e) = q_1|e| \int_{\square} d\mathbf{k} S(\mathbf{k}) \underline{a}^0(\mathbf{k}, \alpha) e^{-2\pi i \mathbf{k} \mathbf{R}_e} S(-\mathbf{k}, \mathbf{R}_e) \quad (1.5)$$

where

$$S(-\mathbf{k}, \mathbf{R}_e) = \sum_j S''_j e^{-2i\mathbf{k}(r_j^0 - \mathbf{R}_e)} = \sum_j S(r_j^0 - \mathbf{R}_e) e^{-2i\mathbf{k}(r_j^0 - \mathbf{R}_e)}.$$

This is a periodic function

$$\begin{aligned} S(-\mathbf{k}, \mathbf{R}_e + \mathbf{r}_n^0) &= \sum_j S(r_j^0 - \mathbf{r}_n^0 - \mathbf{R}_e) e^{-2\pi i \mathbf{k}(r_j^0 - \mathbf{r}_n^0 - \mathbf{R}_e)} = \\ &= \sum_{j'} S(r_{j'}^0 - \mathbf{R}_e) e^{-2\pi i \mathbf{k}(r_{j'}^0 - \mathbf{R}_e)} = S(-\mathbf{k}, \mathbf{R}_e) \end{aligned}$$

where \mathbf{r}_n^0 is an arbitrary lattice vector and $j' = j - n$. Expanding in a Fourier series the function $S(-\mathbf{k}, \mathbf{R}_e)$ [10], we obtain Eq. (1.5) in the following form:

$$V_C(\mathbf{R}_e) = q_1|e| \frac{1}{a^4} \sum_{\mathbf{v}} \int_{\square} d\mathbf{k} S(\mathbf{k}) \underline{a}^0(\mathbf{k}, \alpha) S^{\text{con}}(\mathbf{K}_v - \mathbf{k}) e^{2\pi i(\mathbf{K}_v - \mathbf{k}) \mathbf{R}'_e}. \quad (1.6)$$

The vectors $S(\mathbf{k})$, $S^{\text{con}}(\mathbf{K}_v - \mathbf{k})$, \mathbf{k} , \mathbf{K}_v , \mathbf{R}'_e in r. h. s. of the Eq. (1.6) are in this representation non-dimensional vectors. Putting into Eq. (1.6) $\mathbf{k} \rightarrow -\mathbf{k}$ and using the relations $S(-\mathbf{k}) = -S(\mathbf{k})$, $\underline{a}^0(-\mathbf{k}, \alpha) = \underline{a}^0(\mathbf{k}, \alpha)$ we obtain:

$$V_C(\mathbf{R}_e) = -q_1|e| \frac{1}{a^4} \sum_{\mathbf{v}} \int_{\square} d\mathbf{k} S(\mathbf{k}) \underline{a}^0(\mathbf{k}, \alpha) S^{\text{con}}(\mathbf{K}_v + \mathbf{k}) e^{2\pi i(\mathbf{K}_v + \mathbf{k}) \mathbf{R}'_e}. \quad (1.7)$$

The functions $S(\mathbf{k})$ and $\underline{a}^0(\mathbf{k}, \alpha)$ are periodic functions with the inverse lattice period:

$$S(\mathbf{k} + \mathbf{K}_v) = S(\mathbf{k}); \quad \underline{a}^0(\mathbf{k} + \mathbf{K}_v, \alpha) = \underline{a}^0(\mathbf{k}, \alpha).$$

Therefore we can express the equation (1.7) in an equivalent form:

$$\begin{aligned} V_C(\mathbf{R}_e) &= -q_1|e| \frac{1}{a^4} \sum_{\mathbf{v}} \int_{\square} d\mathbf{k} S(\mathbf{k} + \mathbf{K}_v) \underline{a}^0(\mathbf{k} + \mathbf{K}_v, \alpha) S^{\text{con}}(\mathbf{k} + \mathbf{K}_v) e^{2\pi i(\mathbf{k} + \mathbf{K}_v) \mathbf{R}'_e} = \\ &= -q_1|e| \frac{1}{a^4} \int_{V^{-1}} d\boldsymbol{\kappa} S(\boldsymbol{\kappa}) \underline{a}^0(\boldsymbol{\kappa}, \alpha) S^{\text{con}}(\boldsymbol{\kappa}) e^{2\pi i \boldsymbol{\kappa} \mathbf{R}'_e} \end{aligned} \quad (1.8)$$

where: $\boldsymbol{\kappa} = \mathbf{K} + \mathbf{k}$, V^{-1} — denotes that the integration area is the whole inverse lattice volume.

Therefore the ion-electron interaction energy in the crystal lattice of polarizable atoms is given for an arbitrary ion-electron distance in the following form:

$$V_{\text{ion-electron}}(\mathbf{R}_e) = -\frac{q_1|e|}{|\mathbf{R}_e|} - q_1|e| \int_{V^{-1}} d\kappa \mathcal{S}(\kappa) \underline{a}^0(\kappa, \alpha) \mathcal{S}^{\text{con}}(\kappa) e^{2\pi i \kappa \mathbf{R}'_e}. \quad (1.9)$$

The asymptotic form of the ion-electron interaction, Eq. (1.9), which represents a good approximation for large distances between the ion and electron, can be obtained by using the continuum approximation for the functions $\mathcal{S}(\kappa)$ and $\underline{a}^0(\kappa, \alpha)$ [9]:

$$\begin{aligned} V_{\text{ion-electron}}^{\text{as}} &= -\frac{q_1|e|}{|\mathbf{R}_e|} - q_1|e| \frac{1}{a^4} \int_{V^{-1}} d\kappa \mathcal{S}^{\text{con}}(\kappa) \underline{a}^{\text{con}}(\kappa, \alpha) \mathcal{S}^{\text{con}}(\kappa) e^{2\pi i \kappa \mathbf{R}'_e} = \\ &= -\frac{q_1|e|}{|\mathbf{R}_e|} + \frac{q_1|e|}{a} \frac{4\alpha'}{(1+2B)} \int_{V^{-1}} d\kappa \frac{1}{\kappa^2} e^{2\pi i \kappa \mathbf{R}'_e} \end{aligned} \quad (1.10)$$

where:

$$\begin{aligned} B &= \frac{4\pi}{3} \alpha'; \quad \alpha' = \frac{\alpha}{a^3} \\ \int_{V^{-1}} d\kappa \frac{1}{\kappa^2} e^{2\pi i \kappa \mathbf{R}'_e} &= \frac{\pi}{\mathbf{R}'_e}. \end{aligned}$$

Therefore we obtain:

$$V_{\text{ion-electron}}^{\text{as}} = -\frac{q_1|e|}{|\mathbf{R}_e|} \left(1 - \frac{4\pi\alpha'}{\left(1 + \frac{8\pi}{3}\alpha'\right)} \right) = -\frac{q_1|e|}{|\mathbf{R}_e|} \left[\frac{1 - \frac{4\pi}{3}\alpha'}{1 + \frac{8\pi}{3}\alpha'} \right].$$

Making use of the equation for the macroscopic dielectric constant ε :

$$\varepsilon = \frac{1 + \frac{8\pi}{3}\alpha'}{1 - \frac{4\pi}{3}\alpha'}$$

we obtain the known asymptotic form of the ion-electron interaction energy in the crystal lattice of polarizable atoms:

$$V_{\text{ion-electron}}^{\text{as}}(\mathbf{R}_e) = -\frac{q_1|e|}{\varepsilon|\mathbf{R}_e|}. \quad (1.11)$$

To find the influence of the crystal structure of the ion-electron interaction energy we have calculated the Fourier transforms of the energy for the asymptotic solution

TABLE I

Values of the transforms of the ion-electron interaction energy in the lattice of polarizable atoms for the direction $[1, 1, 1]$ of the vector κ

$\alpha' = 0.04$		$\alpha' = 0.1$	
$n_x = n_y = n_z$	$V_{1-e}(\kappa, \alpha')$	$V_{1-e}(\kappa, \alpha')$	$V_{1-e}^{as}(\kappa, \alpha')$
0.05	-0.155760147 · 10 ²	0.284640518 · 10 ⁻²	0.290208679 · 10 ²
0.1	0.360199154 · 10 ¹	0.670492214 · 10 ¹	0.725521697 · 10 ¹
0.2	0.646229401	0.129252578 · 10 ¹	0.181380424 · 10 ¹
0.3	0.154974735	0.343351247	0.806135219
0.4	0.325285264 · 10 ⁻¹	0.787084876 · 10 ⁻¹	0.453451061
0.5	0	0	0.290208679
0.6	-0.216856843 · 10 ⁻¹	-0.524723250 · 10 ⁻¹	0.201533805
0.7	-0.664177437 · 10 ⁻¹	-0.147150534	0.148065653
0.8	0.161557350	-0.323131445	0.113362765
0.9	-0.400221282	-0.744991349	0.895705799 · 10 ⁻¹
0.95	-0.819790244	-0.149810798 · 10 ⁻¹	0.803902156 · 10 ⁻¹
1.05	0.741714984	0.135543104 · 10 ⁻¹	0.658069567 · 10 ⁻¹
1.1	0.327453777	0.609538377	0.599604709 · 10 ⁻¹
1.2	0.1077049	0.215420964	0.503834512 · 10 ⁻¹
1.3	0.357634004 · 10 ⁻¹	0.792349032 · 10 ⁻¹	0.429302780 · 10 ⁻¹
1.4	0.929386467 · 10 ⁻²	0.224881393 · 10 ⁻¹	0.370164131 · 10 ⁻¹
1.5	0	0	0.322454088 · 10 ⁻¹
1.6	-0.813213159 · 10 ⁻²	-0.196771219 · 10 ⁻¹	0.283406913 · 10 ⁻¹
1.7	-0.273484827 · 10 ⁻¹	-0.605913966 · 10 ⁻¹	0.251045570 · 10 ⁻¹
1.8	-0.718032668 · 10 ⁻¹	-0.143613975	0.223926449 · 10 ⁻¹
1.9	-0.189578502	-0.352890639	0.200975539 · 10 ⁻¹
1.95	-0.399384991	-0.729847481	0.190801235 · 10 ⁻¹

$V_{\text{ion-electron}}^{\text{as}}(\boldsymbol{\kappa}, \alpha)$ and for the exact solution $V_{\text{ion-electron}}(\boldsymbol{\kappa}, \alpha)$ (as restricted to the considered model). The forms of the energy transforms follow from Eqs (1.8) and (1.10).

$$V_{\text{ion-electron}}(\boldsymbol{\kappa}, \alpha) = \frac{1}{a^3} S(\boldsymbol{\kappa}) \underline{a}^0(\boldsymbol{\kappa}, \alpha) S^{\text{con}}(\boldsymbol{\kappa})$$

$$V_{\text{ion-electron}}^{\text{as}}(\boldsymbol{\kappa}, \alpha) = \frac{1}{a^3} S^{\text{con}}(\boldsymbol{\kappa}) \underline{a}^{\text{con}}(\boldsymbol{\kappa}, \alpha) S^{\text{con}}(\boldsymbol{\kappa}) = \frac{4\alpha'}{(1+2B)} \frac{1}{\kappa^2}. \quad (1.12)$$

In Table I and in Fig. 1 we present the numerical results of the energy transforms for the direction $[1, 1, 1]$ of the vector $\boldsymbol{\kappa}$ and for two values of the reduced polarizability $\alpha' = 0.04, 0.1$. The calculations were done with the aid of the computer EMC ODRA-1204.

From the comparison of the obtained results it follows that in the limit $\boldsymbol{\kappa} \rightarrow 0$, which is equivalent with large distances R_e , the values of both transforms agreed very well.

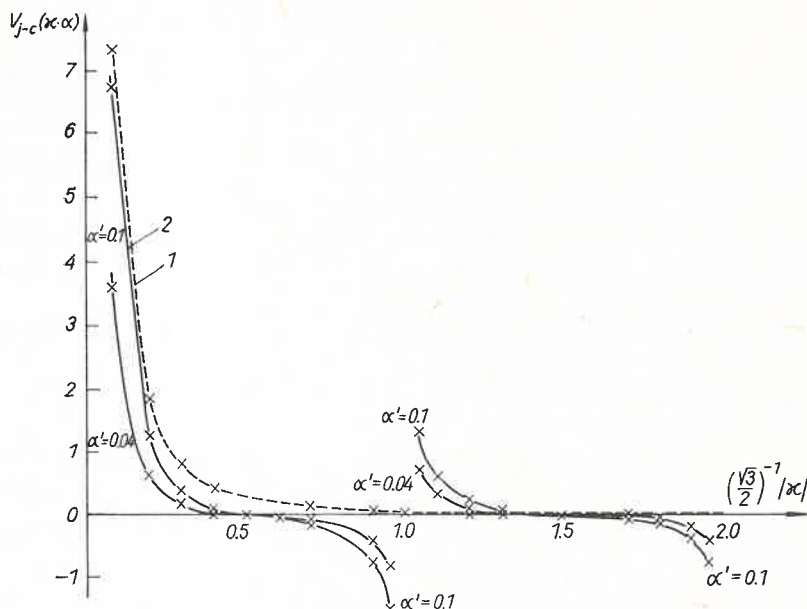


Fig. 1. Curves of the Fourier transform of the ion-electron interaction energy in the lattice of polarizable atoms for the direction $[1, 1, 1]$ of the vector $\boldsymbol{\kappa}$. 1 — $V_{\text{ion-electron}}^{\text{as}}(\boldsymbol{\kappa}, \alpha' = 0.1)$; 2 — $V_{\text{ion-electron}}(\boldsymbol{\kappa}, \alpha' = 0.1, 0.04)$

The differences which arise with larger values of the vector $\boldsymbol{\kappa}$ are the consequence of the fact that in the case of the asymptotic approximation the crystal lattice is treated as a continuous medium and the ion-electron interaction is modified by a constant quantity depending on the polarizability of the medium. In the case of an exact solution in the energy transform $V_{\text{ion-electron}}(\boldsymbol{\kappa}, \alpha)$ besides the ion-electron interaction there are interactions between the electron and induced dipole moments in the lattice sites. The points of the discontinuity on the curve $V_{\text{ion-electron}}(\boldsymbol{\kappa}, \alpha)$ in the inverse lattice sites represent these interactions. Besides, the difference follows from the symmetry of both transforms,

in the limit $\kappa \rightarrow 0$ both transforms having spherical symmetry. With larger values of the vector κ the symmetry of the transform $V_{\text{ion-electron}}^{\text{as}}(\kappa, \alpha)$ is also a spherical one, but the symmetry of the transform $V_{\text{ion-electron}}(\kappa, \alpha)$ is equivalent to the symmetry of the lattice. It will be interesting to investigate the solutions of the Schrodinger equation with the potential $V(r)$ replacing the asymptotic $V(r) = q, |e|/\epsilon R$ which was used so far in the discussion of the Wannier exciton.

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