Screening of Impurity Pseudopotentials in Polar Semiconductors

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Z. Naturforsch. **33a**, 1261–1267 (1978); received July 3, 1978

It is shown how the total pseudopotential of an impurity (and not its Coulomb potential only) is screened by the electronic and ionic polarization of the host crystal caused by the impurity itself. An atomic description of the host crystal and the static polarization is given by means of the dipolar model developed by Stumpf. The F-centre in alkali halides is treated as an example to test the method. For actual calculations, the BSG pseudopotential is used. Numerical results of the absorption and optical ionization energies are presented.

1. Introduction

A quantitative theory of impurities in polar semiconductors has to take into account, at least approximatively, the interactions between the impurity electron and the disturbed host crystal, which are

(I) the Coulomb and exchange interactions with the ions of the ideal host crystal,
(II) the interaction due to the Pauli principle, i.e. the wave function of the impurity electron has to be orthogonal to the wave functions of the core electrons,
(III) the interaction with the deviation of the disturbed host crystal from the ideal one, i.e. the electronic and ionic polarization of the crystal.

In the literature, the interactions I and II are extensively studied and usually approximated by a linear superposition of free ion pseudopotentials. The polarization effects III are then treated phenomenologically as corrections or are even neglected.

In this paper, we incorporate the polarization effects into the crystal potential from the very beginning and describe I together with III by the aid of the dipolar model developed by Stumpf [1, 2, 3] (Section 2). The interaction II is then taken into account (Sect. 3) using the pseudopotential method in the form proposed by Bartram et al. [4], referred to as BSG. This approach results in an effective pseudopotential of the impurity which is screened due to the electronic and ionic polarization of the crystal (Section 4).

Our method is applicable to any impurity in polar semiconductors. To have definite conditions, however, we treat the F-centre in alkali halides as an example. This defect is experimentally almost completely explored and therefore ideally suited to test theories before they are applied to more complicated impurities of practical interest.

For reviews of F-centre calculations the reader is referred to [5, 6, 7]. Theories being related to our approach will be discussed below.

2. The Nonlinear Equation for the Impurity Electron

The host crystal is described by means of the dipolar model developed by Stumpf [1]. In the present paper, the results of this approach are given only. For details, the reader is referred to [1, 2, 3].

Starting from first principles, the total energy of the crystal, containing one F-centre, is calculated using the Born-Oppenheimer and the Hartree-Fock approximation. After a multipole expansion up to second order with respect to the position vectors of the core electrons as well as the displacements of the ions from their ideal equilibrium position, the electronic and ionic polarization can be represented in terms of electronic dipoles $\mathfrak{m}_{l\mu}$ and ion displacements $\mathfrak{M}_{l\mu}$. These quantities are

$$\mathfrak{m}_{l\mu} = \sum_{n_{l\mu}} \int \Phi^*_{n_{l\mu}}(\mathfrak{r})\,(\mathfrak{r} - \mathring{\mathfrak{R}}_{l\mu})\,\Phi_{n_{l\mu}}(\mathfrak{r})\,d\mathfrak{r}\,, \quad (2.1\,a)$$

$$\mathfrak{M}_{l\mu} = \mathfrak{R}_{l\mu} - \mathring{\mathfrak{R}}_{l\mu}\,, \quad (2.1\,b)$$

where l labels the unit cells of the crystal, μ the ions in one cell and $n_{l\mu}$ the electrons of the $l\mu$-th ion. $\mathfrak{R}_{l\mu}$ and $\mathring{\mathfrak{R}}_{l\mu}$ are the ion positions in the distorted and ideal lattice respectively. $\Phi_{n_{l\mu}}$ are the polarized orbitals of the core electrons.

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The total adiabatic energy of the crystal, with the F-electron being in the state n, is then given by

$$\begin{aligned} U_n(\Psi_n, \mathfrak{m}, \mathfrak{M}) &= U_{\text{ideal}} + U_{\text{Pol}}(\mathfrak{m}, \mathfrak{M}) \\ &- \tfrac{1}{2} \int \Psi_n{}^*(\mathfrak{r})\, \Delta \Psi_n(\mathfrak{r})\, \mathrm{d}\mathfrak{r} \\ &+ \sum_{l\mu}{}' \{ \textstyle\int \xi_n(\mathfrak{r}) [a_\mu + (\mathfrak{m}_{l\mu} + a_\mu \mathfrak{M}_{l\mu}) \\ &\times \nabla_{l\mu} C(\mathfrak{r}, l\,\mu)]\, \mathrm{d}\mathfrak{r} \} \qquad (2.2) \\ &- \sum_{l\mu}{}' \{ \textstyle\int \Psi_n{}^*(\mathfrak{r})\, V_{l\mu}^{\text{ex}}(\mathfrak{r}, \mathfrak{r}')\, \Psi_n(\mathfrak{r}')\, \mathrm{d}\mathfrak{r}\, \mathrm{d}\mathfrak{r}' \\ &+ [1 + \mathfrak{M}_{l\mu} \nabla_{l\mu}]\, C^{\text{ex}}(l\,\mu, 0) \}\,, \end{aligned}$$

where $\sum_{l\mu}{}'$ means that the anion at the origin $\overset{\circ}{\mathfrak{R}}_{l\mu}=0$ is missing in the lattice summation.

The first two terms in (2.2) represent the energy of the polarized host crystal, which is separated into the energy of the ideal crystal U_{ideal} and the polarization energy given by

$$\begin{aligned} U_{\text{Pol}}(\mathfrak{m}, \mathfrak{M}) &= \tfrac{1}{2} \sum_{l\mu}{}' [\alpha_\mu^{-1}\, \mathfrak{m}_{l\mu}^2 + \tau^{-1} a_\mu{}^2\, \mathfrak{M}_{l\mu}^2] \\ &+ \tfrac{1}{2} \neq\!\!\sum_{l\mu,\, k\varrho} [(\mathfrak{m}_{l\mu} + a_\mu \nabla_{l\mu})\, V_{l\mu} \qquad (2.3) \\ &\otimes \nabla_{k\varrho} C(l\,\mu, k\,\varrho) (\mathfrak{m}_{k\varrho} + a_\varrho \mathfrak{M}_{k\varrho}) \\ &+ \mathfrak{M}_{l\mu} \nabla_{l\mu} \otimes \nabla_{k\varrho} C^{\text{ex}}(l\,\mu, k\,\varrho)\, \mathfrak{M}_{k\varrho}]\,, \end{aligned}$$

where $\neq\!\!\sum_{l\mu,\, k\varrho}$ means that the terms with $l\,\mu = k\,\varrho$ are omitted. a_μ and α_μ are the effective charges and the polarizabilities of the ions and τ is the lattice polarizability. $C(l\mu, k\varrho)$ and $C^{\text{ex}}(l\mu, k\varrho)$ are the Coulomb and repulsive interactions between the ions.

The third term in (2.2) is the kinetic energy of the F-electron and the remaining two terms are the Coulomb and the exchange interaction between the impurity, i.e. the anion vacancy together with the F-electron, and the perturbed host crystal. $V_{l\mu}^{\text{ex}}$ represents the exchange potential of the core electrons while the total charge density of the impurity is defined by

$$\xi_n(\mathfrak{r}) := - a_0\, \delta(\mathfrak{r}) - | \Psi_n(\mathfrak{r}) |^2\,. \qquad (2.4)$$

As indicated, U_n is a functional of the wave function Ψ_n, the electronic dipoles $\mathfrak{m}_{l\mu}$ and the ion displacements $\mathfrak{M}_{l\mu}$. In the static equilibrium, when the electron is in the relaxed state, the actual values of these quantities are fixed by the minimum conditions

$$\partial U_n / \partial \mathfrak{m}_{l\mu} = 0\,, \qquad (2.5\text{a})$$

$$\partial U_n / \partial \mathfrak{M}_{l\mu} = 0\,, \qquad (2.5\text{b})$$

$$\delta U_n / \delta \Psi_n = 0\,. \qquad (2.5\text{c})$$

The systems of Eqs. (2.5a, b) can be solved numerically by a transformation to the reciprocal space [8] or to symmetry vectors [9] respectively. In this paper, however, we avoid the enormous computational effort involved in these methods and use the integral approximation

$$\begin{aligned} &\sum_{l\mu} \nabla_{l\mu} C(l\,\mu, k\,\varrho)\, \nabla_{l\mu} f(\overset{\circ}{\mathfrak{R}}_{l\mu}) \\ &\quad \approx (4\pi/d^3) \int \nabla_{\mathfrak{R}} C(\mathfrak{R}, k\,\varrho)\, \nabla_{\mathfrak{R}} f(\mathfrak{R})\, \mathrm{d}\mathfrak{R} \qquad (2.6) \\ &\quad = (4\pi/d^3)\, f(\overset{\circ}{\mathfrak{R}}_{k\varrho})\,, \end{aligned}$$

where f is an arbitrary function and d is the nearest neighbour distance. This approximation is equivalent to replacing the k-summation in the reciprocal lattice by an integration over the whole k-space, an approximation often used in polaron theory [10].

Inserting (2.2) into (2.5a, b) yields equations for the electronic dipoles and the ion displacements, which can be solved analytically using (2.6). This results in

$$\begin{aligned} \mathfrak{m}_{l\mu}^n = &- \alpha^{\text{e}}\, \mathrm{d}^3 \nabla_{l\mu} [\textstyle\int \xi_n(\mathfrak{r})\, C(l\,\mu, \mathfrak{r})\, \mathrm{d}\mathfrak{r} \qquad (2.7\text{a}) \\ &+ \neq\!\!\sum_{k\varrho} a_\varrho\, \mathfrak{M}_{k\varrho}^n \nabla_{k\varrho} C(l\,\mu, k\,\varrho)] / (4\pi(1 + \alpha^{\text{e}}))\,, \end{aligned}$$

$$\begin{aligned} \mathfrak{M}_{l\mu}^n = &- \alpha^{\text{d}}\, \mathrm{d}^3 \nabla_{l\mu} [a_\mu \textstyle\int \xi_n(\mathfrak{r})\, C(l\,\mu, \mathfrak{r})\, \mathrm{d}\mathfrak{r} \qquad (2.7\text{b}) \\ &- (1 + \alpha^{\text{e}})\, C^{\text{ex}}(l\,\mu, 0)] / (4\pi\, a_\mu{}^2 (1 + \alpha^{\text{e}} + \alpha^{\text{d}})) \end{aligned}$$

with the definitions

$$\alpha^{\text{e}} := 4\pi \sum_\mu \alpha_\mu / 2 d^3\,, \qquad (2.8\text{a})$$

$$\alpha^{\text{d}} := 4\pi\, \tau / 2 d^3\,. \qquad (2.8\text{b})$$

Finally, the variation (2.5c) under the constraint of Ψ_n being normalized yields the "nonlinear Schrödinger equation", derived by Stumpf [1].

$$(- \tfrac{1}{2} \Delta + \sum_{l\mu}{}' V_{l\mu}(n))\, \Psi_n = E_n \Psi_n \qquad (2.9)$$

where the potentials due to the polarized and displaced ions of the crystal are

$$\begin{aligned} V_{l\mu}(n) = &- [a_\mu + (\mathfrak{m}_{l\mu} + a_\mu \mathfrak{M}_{l\mu})\, \nabla_{l\mu}] \\ &\cdot C(l\,\mu, \mathfrak{r}) + V_{l\mu}^{\text{ex}}(\mathfrak{r}, \mathfrak{r}')\,. \qquad (2.10) \end{aligned}$$

Our approach is advantagous in that it provides analytic expressions for the microscopic description of the polarization and distortion around the impurity and is not restricted to a few neighbours as in other theories [5, 8]. Therefore, we have been able to incorporate the polarization effects into the atomistic crystal potential.

3. The Pseudopotential

In this section, we will outline the pseudopotential method as far as is necessary for our purpose. We closely follow the modification proposed by BSG [4]. For details, we refer to the reviews given in [11, 12].

Equation (2.9) has to be solved under the constraint that the impurity electron orbital has to be orthogonal to the core electron orbitals. To eliminate this constraint, the pseudoequation is defined

$$\Big(-\tfrac{1}{2}\Delta + \sum_{l\mu}{}' V^{\mathrm{p}}_{l\mu}(n)\Big)\Phi_n = E_n{}^{\mathrm{p}}\,\Phi_n \tag{3.1}$$

where Φ_n is the pseudo wave function of the impurity electron and $V^{\mathrm{p}}_{l\mu}(n)$ is the pseudopotential.

This is chosen to be the optimum pseudopotential, which yields the smoothest pseudo wave function. According to [13], it is given by

$$\begin{aligned} V^{\mathrm{p}}_{l\mu}(n) = {} & V_{l\mu}(n) - \Big(P_{l\mu}\,V_{l\mu}(n) \\ & - \bar{V}^{\mathrm{p}}(n)\sum_{k\varrho}{}' P_{k\varrho} + \neq \sum_{k\varrho} P_{k\varrho}\,V_{l\mu}(n)\Big)\,, \end{aligned} \tag{3.2}$$

with the definition

$$P_{l\mu} := \sum_{n_{l\mu}} |\Phi_{n_{l\mu}}\rangle\langle\Phi_{n_{l\mu}}|\,, \tag{3.2a}$$

$$\bar{V}^{\mathrm{p}}(n) = \sum_{l\mu}{}' \langle\Phi_n\, V^{\mathrm{p}}_{l\mu}(n)\,\Phi_n\rangle\,. \tag{3.2b}$$

$P_{l\mu}$ is the projection operator for the core states of the $l\mu$-th ion and $\bar{V}^{\mathrm{p}}_{l\mu}(n)$ is the expectation value of the pseudopotential.

The connection between Eq. (2.9) and (3.1) is

$$E_n{}^{\mathrm{p}} \equiv E_n\,, \tag{3.3a}$$

$$\Psi_n = N_n\Big(1 - \sum_{k\varrho}{}' P_{k\varrho}\Big)\Phi_n\,, \tag{3.3b}$$

with the normalization factor

$$N_n := \Big(1 - \sum_{k\varrho}{}' \langle\Phi_n\, P_{k\varrho}\,\Phi_n\rangle\Big)^{-1/2}. \tag{3.3c}$$

Hence, it suffices to study the pseudo Schrödinger equation (3.1), because it provides the correct energy levels of the impurity electron. The true wave functions Ψ_n can be regained by an orthogonalization procedure.

The expression (3.2) is usually interpreted as the crystal potential $V_{l\mu}(n)$ and an additional "ion-size correction" (the terms in the bracket) which is caused by the electronic structure of the ions. It is the exact optimum crystal pseudopotential and was originally derived by BSG. Later on, it was used by other authors [14, 15].

In [16], the pseudopotential method was also applied to F-centre calculations but the last two terms on the right hand side of (3.2) were omitted as is often done in the literature [11, 12]. Neglecting $\bar{V}^{\mathrm{p}}(n)$ in (3.2) is equivalent to $N_n \approx 1$ in (3.3b). Omitting the term $P_{k\varrho}\,V_{l\mu}(n)$ means approximating the crystal pseudopotential by the sum of single ion pseudopotentials. From our numerical results we found, however, in accordance with BSG that these approximations are by no means justified, at least not for F-centre calculations.

The main difference between the BSG work and our approach is the incorporation of the polarization potential into the ion-size terms. This leads to the screening of the pseudopotential of the impurity as shown in the next section.

4. The Total Energy with Ion-Size Correction

The experimental absorption and emission energies are differences in the total energies of the crystal because both the electronic energy E_n and the polarization energy of the crystal (2.3) change during a transition of the impurity electron. Therefore, the differences in the electronic energies cannot be compared with experiment. This fact is often neglected in literature. Furthermore, the solution of (3.1) is very complicated as this is a nonlinear equation containing a nonlocal potential. Hence, we calculate the pseudo wave function and the corresponding energy levels of the crystal by means of a variational method minimizing the total adiabatic energy with respect to Φ_n.

To perform this program, (2.2) and (2.3) have to be reformulated in terms of the pseudo wave function Φ_n. This is achieved by replacing the electronic energies in (2.2) by the expectation value of the pseudo Hamiltonian of (3.1). In addition, one has to insert (3.3b) into (2.4) and the result into (2.7) to get the electronic dipoles and the ion displacements as functionals of Φ_n.

Before giving the explicit formulae, the approximations leading to the BSG pseudopotential are introduced:

(I) The core electron orbitals are approximated by free ion wave functions,

(II) the variation of Φ_n over each ion core is neglected in the integrals containing core electron orbitals.

Using these approximations, the expectation value of the pseudopotential (3.2) is given by

$$\bar{V}^{\mathrm{p}}(n) = -\sum_{l\mu}{}' \int |\Phi_n(\mathfrak{r})|^2 \{[a_\mu + (\mathfrak{m}_{l\mu} + a_\mu \mathfrak{M}_{l\mu}) \nabla_{l\mu}] \times C^{\mathrm{p}}(l\,\mu, \mathfrak{r}) + C^{\mathrm{p}}_{\mathrm{ex}}(l\,\mu, \mathfrak{r})\}\,\mathrm{d}\mathfrak{r} \tag{4.1}$$

where C^{p} and $C^{\mathrm{p}}_{\mathrm{ex}}$ are, respectively, the pseudo Coulomb and exchange potential of the $l\,\mu$-th ion, which are defined by

$$C^{\mathrm{p}}(l\,\mu, \mathfrak{r}) := N_n{}^2 \{C(l\,\mu, \mathfrak{r}) - A_\mu{}^{\mathrm{c}}\,\delta(\mathring{\mathfrak{R}}_{l\mu} - \mathfrak{r}) - \mp \sum_{k\varrho}{}' C(l\,\mu, k\,\varrho)\,B_\varrho\,\delta(\mathring{\mathfrak{R}}_{k\varrho} - \mathfrak{r})\}, \tag{4.2a}$$

$$C^{\mathrm{p}}_{\mathrm{ex}}(l\,\mu, \mathfrak{r}) := N_n{}^2 \{-A^{\mathrm{ex}}_\mu\,\delta(\mathring{\mathfrak{R}}_{l\mu} - \mathfrak{r})\} \tag{4.2b}$$

with the normalization factor (3.3c)

$$N_n = (1 - \sum_{l\mu}{}' B_\mu |\Phi_n(\mathring{\mathfrak{R}}_{l\mu})|^2)^{-1/2}\,. \tag{4.3}$$

In (4.2b) the term analogous to the last one in (4.2a) is missing as the overlap of core orbitals of different ions is neglected in our approach. The coefficients $A_\mu{}^{\mathrm{c}}$, A^{ex}_μ and B_μ are defined by

$$A_\mu{}^{\mathrm{c}} := \int \mathring{P}_{l\mu}\,C(l\,\mu, \mathfrak{r})\,\mathrm{d}\tau\,, \tag{4.4a}$$

$$A^{\mathrm{ex}}_\mu := \int (1 - \mathring{P}_{l\mu})\,V^{\mathrm{ex}}\,\mathrm{d}\tau\,, \tag{4.4b}$$

$$B_\mu := \int \mathring{P}_{l\mu}\,\mathrm{d}\tau \tag{4.4c}$$

where $\mathring{P}_{l\mu}$ is the projector (3.2a) approximated by the free ion orbitals. The coefficients (4.4) are characteristic of the ions only and were calculated from first principles by BSG. Their numerical values are given in Table 1.

Deriving (4.1), we have used the device proposed by Zwicker [15] to eliminate (3.2b) on the right hand side of (4.1). Therefore, the expectation value of the pseudopotential (4.1) does not depend on energy, in contrast to the BSG approach and the usual pseudopotential method [6]. Thus, the self-consistency problem is avoided and computational effort is reduced significantly.

Within the approximations I and II, the part of the dipoles (2.7a) and the displacements (2.7b) which is caused by the impurity electron becomes

$$\nabla_\mu \int |\Psi_n(\mathfrak{r})|^2\,C(l\,\mu, \mathfrak{r})\,\mathrm{d}\mathfrak{r} = \nabla_{l\mu} \int |\Phi_n(\mathfrak{r})|^2\,C^{\mathrm{p}}(l\,\mu, \mathfrak{r})\,\mathrm{d}\mathfrak{r}\,. \tag{4.5}$$

By the aid of (4.1) together with (3.1) and (2.7), we get the total adiabatic energy of the crystal as a functional of the pseudo wave function. After separating the energies due to the vacancy and the F-electron, the result is

$$U_t = U_{\mathrm{ideal}} + U_{\mathrm{Vac}} + U_n(\Phi_n)\,. \tag{4.6}$$

The energy of the vacancy is given by

$$\begin{aligned} U_{\mathrm{Vac}} = -\sum_{l\mu}{}' \{ & a_\mu\,a_0\,C(l\,\mu, 0) + C^{\mathrm{ex}}(l\,\mu, 0) \\ & + \alpha^{\mathrm{e}}\,d^3\,\mathring{\mathfrak{R}}_{l\mu}^{-4}/(8\,\pi(1 + \alpha^{\mathrm{e}} + \alpha^{\mathrm{d}})) \\ & + \alpha^{\mathrm{d}}\,d^3[\mathring{\mathfrak{R}}_{l\mu}^{-4} - 2\,\nabla_{l\mu}\,\mathring{\mathfrak{R}}_{l\mu}^{-1}\,\nabla_{l\mu}\,C^{\mathrm{ex}}(l\,\mu, 0) \\ & + (1 + \alpha^{\mathrm{e}})(\nabla_{l\mu}\,C^{\mathrm{ex}}(l\,\mu, 0))^2]/ \\ & (8\,\pi(1 + \alpha^{\mathrm{e}} + \alpha^{\mathrm{d}}))\}\,. \end{aligned} \tag{4.7}$$

The first two terms are the Coulomb and the exchange interactions of the missing anion and the remaining two terms are the energies of the electronic and ionic polarization of the host crystal caused by the vacancy. The part of the total energy U_t which actually depends on the pseudo wave function of the F-electron is

$$\begin{aligned} U_n(\Phi_n) = & -\tfrac{1}{2} \int \Phi_n{}^*(\mathfrak{r})\,\Delta\Phi_n(\mathfrak{r})\,\mathrm{d}\mathfrak{r} \\ & - \sum_{l\mu} \int |\Phi_n(\mathfrak{r})|^2 [a_\mu\,C^{\mathrm{p}}(l\,\mu, \mathfrak{r}) + C^{\mathrm{p}}_{\mathrm{ex}}(l\,\mu, \mathfrak{r})]\,\mathrm{d}r \\ & + \int |\Phi_n(\mathfrak{r})|^2 [a_0\,C^{\mathrm{p}}(0, \mathfrak{r}) + C^{\mathrm{p}}_{\mathrm{ex}}(0, \mathfrak{r})]\,\mathrm{d}\mathfrak{r} \\ & - \int |\Phi_n(\mathfrak{r})|^2 \{\sum_{\mu l}{}' \nabla_{l\mu}\,C^{\mathrm{p}}(l\,\mu, \mathfrak{r}) \\ & \times \nabla_{l\mu}[(\alpha^{\mathrm{e}} + \alpha^{\mathrm{d}})\,a_0\,C(l\,\mu, 0) \\ & + \alpha^{\mathrm{d}}\,C^{\mathrm{ex}}(l\,\mu, 0)]\,d^3/(4\,\pi(1 + \alpha^{\mathrm{e}} + \alpha^{\mathrm{d}}))\}\,\mathrm{d}\mathfrak{r} \\ & - \iint |\Phi_n(\mathfrak{r})|^2 [\sum_{l\mu}{}' (\alpha^{\mathrm{e}} + \alpha^{\mathrm{d}})\,\nabla_{l\mu}\,C^{\mathrm{p}}(l\,\mu, \mathfrak{r}) \\ & \times \nabla_{l\mu}\,C^{\mathrm{p}}(l\,\mu, \mathfrak{r})\,d^3/(8\,\pi(1 + \alpha^{\mathrm{e}} + \alpha^{\mathrm{d}}))] \\ & \times |\Phi_n(\mathfrak{r}')|^2\,\mathrm{d}\mathfrak{r}\,\mathrm{d}\mathfrak{r}'\,. \end{aligned} \tag{4.8}$$

The first two terms in (4.8) are the kinetic energy of the F-electron and its interaction with the pseudopotential of all the crystal ions. The third term is the interaction of the F-electron with the pseudopotential of the missing anion which is screened by the fourth term representing the interaction of the F-electron with the electronic and the ionic polarization caused by the vacancy. The last term is the energy of the crystal polarization caused by the F-electron itself.

5. The Total Energy of the Nonrelaxed State

If there is a radiative electronic transition, the maximum of the corresponding band is given by the difference between the total energies of the nonrelaxed final state n and the relaxed initial state n'. This is the well-known Franck-Condon principle.

Until now, we have treated the relaxed state only. The extension of our approach to the nonrelaxed state is straightforward. The minimum condition (2.5b) does no longer hold but the ion displacements are the same as in the initial state n'. In contrast, the electronic polarization follows the impurity electron instantanously and can therefore be calculated by means of (2.5a). This yields

$$\mathfrak{M}_{l\mu}^{n'} = -\alpha^{\mathrm{d}}\,\mathrm{d}^3\,\nabla_{l\mu}\Big[a_\mu \int \xi_{n'}(\mathfrak{r})\,C(l\,\mu,\mathfrak{r})\,\mathrm{d}\mathfrak{r} - (1+\alpha^{\mathrm{e}})\,C^{\mathrm{ex}}(l\,\mu,0)\Big]\Big/\big(4\pi\,a_\mu{}^2(1+\alpha^{\mathrm{e}}+\alpha^{\mathrm{d}})\big), \tag{5.1a}$$

$$\mathfrak{m}_{l\mu}^{n\,(n')} = -\alpha^{\mathrm{e}}\,\mathrm{d}^3\,\nabla_{l\mu}\Big[\int \xi_n(\mathfrak{r})\,C(l\,\mu,\mathfrak{r})\,\mathrm{d}\mathfrak{r} + \mp\sum_{k\varrho} a_\varrho\,\mathfrak{M}_{k\varrho}^{n'}\,\nabla_{k\varrho}\,C(l\,\mu,k\,\varrho)\Big]\Big/\big(4\pi(1+\alpha^{\mathrm{e}})\big) \tag{5.1b}$$

where ξ_n and $\xi_{n'}$ is the total impurity charge density (2.4) with the F-electron in the nonrelaxed state n and the relaxed state n' respectively.

We insert (5.1) into (2.2) and perform the transition from the true wave function $\Psi_n{}^{\mathrm{NR}}$ to the pseudo wave function $\Phi_n{}^{\mathrm{NR}}$ of the nonrelaxed state in exactly the same manner as in the preceeding section. The state dependent part of the total adiabatic energy is then given by

$$U_n{}^{\mathrm{NR}}(\Phi_n{}^{\mathrm{NR}}) = U_n(\Phi_n{}^{\mathrm{NR}}) + \tfrac{1}{2}\,U_{ST}(\Phi_n{}^{\mathrm{NR}},\Phi_{n'}) . \tag{5.2}$$

The first term on the right hand side of this equation has the same functional form as (4.8), i.e. the energy of the relaxed state. The second term is defined by

$$U_{ST}(\Phi_n{}^{\mathrm{NR}},\Phi_{n'}) = \alpha^{\mathrm{d}}\sum_{l\mu}{}'\Big\{\nabla_{l\mu}\int\big[|\Phi_n{}^{\mathrm{NR}}(\mathfrak{r})|^2 - |\Phi_{n'}(\mathfrak{r})|^2\big] \times C^{\mathrm{p}}(l\,\mu,\mathfrak{r})\,\mathrm{d}\mathfrak{r}\Big\}^2\,\mathrm{d}^3\big/\big(4\pi(1+\alpha^{\mathrm{e}})(1+\alpha^{\mathrm{e}}+\alpha^{\mathrm{d}})\big) . \tag{5.3}$$

$\Phi_{n'}$ being the pseudo wave function of the initial state. This energy is due to the deviation of the ionic polarization in the nonrelaxed state from its equilibrium value. It is identical with the so-called Stoke shift between the absorption and emission energies of the F-centre.

6. Numerical Methods and Results

The input data for our model are chosen as follows: To get the expected macroscopic behaviour of the dielectric screening, one has to relate the dimensionless electronic and ionic polarizabilities (2.8) with the dielectric constants by means of the Drude formula, as discussed in [2]. This yields

$$\alpha^{\mathrm{e}} = \varepsilon_\infty - 1 , \quad \alpha^{\mathrm{d}} = \varepsilon - \varepsilon_\infty . \tag{6.1a, b}$$

The low temperature values of the dielectric constants and the nearest neighbour distance d are taken from reference [17] and [18].

The first derivative of the repulsive potential C^{ex}, arising from the exchange interactions between the ion cores, can be calculated from the equilibrium condition for the ideal crystal. Taking into account nearest neighbour interactions only gives

$$\nabla_{l\mu}\,C^{\mathrm{ex}}(l\,\mu,0) = \left\{\begin{matrix} -\,\mathfrak{R}^{\circ}_{l\mu}\,\alpha_M/6\,R^{\circ\,3}_{l\mu} & \text{for} & R^{\circ}_{l\mu} = d \\ 0 & \text{for} & R^{\circ}_{l\mu} > d \end{matrix}\right\} \tag{6.2}$$

where α_M is the Madelung constant.

As mentioned above, the parameters $A_\mu{}^{\mathrm{c}}$, $A_\mu{}^{\mathrm{ex}}$ and B_μ of the BSG pseudopotential were calculated in [4]. There, the authors found it necessary to multiply their first principle values of $A_\mu{}^{\mathrm{c}}$ and $A_\mu{}^{\mathrm{ex}}$ by an adjusted parameter $\alpha = 0.53$ to get agreement with experiment. In our approach, we have used the same parameter which is already included in the numerical values listed in Table 1.

As trial functions for the ground state and the nonrelaxed excited state, we use the familiar functions

$$\Phi_{1s}(\mathfrak{r}) = \alpha^{3/2}(7\pi)^{-1/2}(1+\alpha\,r)\exp(-\alpha\,r) , \tag{6.3a}$$

$$\Phi_{2p}^{\mathrm{NR}}(\mathfrak{r}) = \beta^{5/2}\,\pi^{-1/2}\,r\cos\vartheta\exp(-\beta\,r) . \tag{6.3b}$$

These functions are inserted into (4.8) and (5.2) respectively, which yields the total energies as functionals of the variational parameters α and β. The resulting expressions contain multiple lattice

Table 1. The pseudopotential parameters A_μ^{c}, A_μ^{ex} and B_μ as calculated in [4]. A_μ^{c}, A_μ^{ex} are in units of eV.Å^3 and B$_\mu$ in Å^3. Note that the factor $\alpha = 0.53$ is included in A_μ^{c} and A_μ^{ex}.

Cation	A_μ^{c}	A_μ^{ex}	B_μ	Anion	A_μ^{c}	A_μ^{ex}	B_μ
Li$^+$	42.80	6.90	1.88	F$^-$	51.22	− 10.66	7.24
Na$^+$	53.04	6.37	2.80	Cl$^-$	102.77	− 27.85	18.97
K$^+$	104.73	3.54	8.88	Br$^-$	124.82	− 40.41	22.85
Rb$^+$	126.28	0.16	12.53	I$^-$	160.00	− 39.96	35.78

Table 2. The wave function parameters and the energy levels of the F-centre in the ground state ($n = 1$ s) and the non-relaxed excited state ($n = 2$ p). E_n is the electronic energy and U_n is the part of the total adiabatic energy which depends on the state of the F-electron.

Crystal	α	E_{1s}	U_{1s}	β	E_{2p}^{NR}	U_{2p}^{NR}	$(U_{2p}^{NR} - U_{1s})$	U_{abs}^{F} [a]
LiF	1.42	− 7.29	− 3.63	1.25	− 2.14	1.43	5.06	5.13
LiCl	1.15	− 6.53	− 3.48	1.00	− 3.36	− 0.25	3.23	3.30
LiBr	1.06	− 6.36	− 3.49	0.90	− 3.78	− 0.83	2.66	2.71
LiI	1.01	− 6.03	− 3.27	0.87	− 3.87	− 0.83	2.44	3.26
NaF	1.26	− 6.74	− 3.97	1.08	− 2.59	− 0.12	3.85	3.73
NaCl	1.06	− 6.04	− 3.60	0.92	− 3.16	− 0.86	2.74	2.77
NaBr	0.99	− 5.87	− 3.54	0.85	− 3.38	− 1.19	2.35	2.36
NaI	0.95	− 5.56	− 3.29	0.83	− 3.37	− 1.11	2.18	2.08
KF	1.03	− 6.98	− 4.45	0.95	− 4.32	− 1.83	2.62	2.83
KCl	0.94	− 5.80	− 3.75	0.83	− 3.54	− 1.59	2.15	2.31
KBr	0.90	− 5.59	− 3.63	0.78	− 3.54	− 1.70	1.93	2.06
KI	0.87	− 5.25	− 3.36	0.77	− 3.35	− 1.52	1.83	1.88
RbF	0.93	− 7.40	− 4.81	0.89	− 5.50	− 2.77	2.04	2.43
RbCl	0.88	− 5.82	− 3.84	0.79	− 3.88	− 1.98	1.87	2.05
RbBr	0.84	− 5.56	− 3.69	0.75	− 3.76	− 1.99	1.70	1.85
RbI	0.83	− 5.20	− 3.40	0.74	− 3.50	− 1.76	1.64	1.75

[a] maximum of the F-band taken from Ref. [4] energies are in units of eV and wave function parameters in Å^{-1}.

summations arising from the last term in (4.2a). To reduce the computational effort, we use approximation (2.6) again. The remaining single and double summations are carried out directly over symmetry shells of ions until convergence is reached.

Minimizing with respect to α and β gives the state dependent parts of the total energies of the ground state U_{1s} and the nonrelaxed excited state U_{2p}^{NR} together with the parameters of the wave functions. The values obtained are listed in Table 2. For ease of comparison, the electronic energies E_{1s} and E_{2p}^{NR}, calculated from (3.1), are also listed.

Taking the difference between U_{1s} and U_{p2}^{NR} gives the maximum of the absorption band which is compared with the experimental value in Table 2. The agreement is satisfactory.

As pointed out in [10], however, this agreement might be fortuitous because errors of the method could be cancelled by taking the difference between the ground and excited state energy. A better test of the method is the comparison of the calculated optical ionization energy with the energy of the transition to the highest optical bound state, i.e. the maximum of the K-band.

The optical ionization energy of the ground state is given by

$$W_0 = - |\chi| - U_{1s} \tag{6.4}$$

where χ is the electron affinity. The values obtained are listed in Table 3.

Table 3. Comparison of the calculated optical ionization energy of the ground state W_0 with the maximum of the K-band U^K. $|\chi|$ is the electron affinity. All energies are in units of eV.

Crystal	$\lvert\chi\rvert$ [a]	W_0	U^K [b]
NaCl	0.8 ± 0.2	2.80 ± 0.2	unresolved
KCl	0.6 ± 0.2	3.15 ± 0.2	2.71
KBr	0.9 ± 0.2	2.73 ± 0.2	2.36
KI	1.6 ± 0.2	1.76 ± 0.2	2.12

[a] taken from Ref. [19]. [b] taken from Ref. [20].

The comparison presented in Table 3 indicates that our approach yields correct absolute values for the F-centre energies. In addition, the calculated optical ionization energy for NaCl of 2.80 eV, which nearly coincides with the maximum of the F-band of 2.77 eV, explains the fact that the K-band cannot be resolved for this crystal.

7. Discussion

Starting with the nonlinear equation for the impurity electron (2.9), we have used the pseudopotential method to treat the orthogonality of the wave function to the core electron orbitals. The resulting expectation value of the total energy (4.8) shows that both the pseudo Coulomb and exchange potential of the vacancy is screened by the potential arising from the polarization of the host crystal caused by the vacancy.

In the literature, the electronic and ionic polarization of polar semiconductors is usually treated by means of the methods developed by Toyozawa [21] and Haken [22] respectively. This yields the screening of the Coulomb potential of the impurity. However, the exchange potential and the ion-size corrections remain unscreened.

In [23] a model was presented which is similar to our approach in emphasis. Unfortunately, different pseudopotentials for the crystal and the electronic polarization were chosen in this model. Besides, the nonlinearity of the polarization effects were suppressed. Therefore, we cannot agree with the conclusion of [23] that the polarization effects are of minor importance than the ion-size corrections.

In the theory of impurities in covalent semiconductors, the screening of the complete pseudopotential of the impurity by the electronic polarization is well established [24]. In our approach, we have shown that the screening of the impurity pseudopotential in polar semiconductors by the electronic and ionic polarization can also be treated.

It is a pleasure to thank Prof. H. Stumpf for his steady interest and many stimulating discussions. The author is indepted to the Deutsche Forschungsgemeinschaft for financial support.

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