On the Calculation of F-center Wave Functions

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On the basis of a microscopic theory the ground state wave function of a F-center electron is calculated. In Sect. 1 we derive a HAMILTON operator regarding polarization effects and the distortion of the lattice. In Sect. 2 the wave function for the ground state is calculated assuming the lattice at absolute zero temperature. In Sect. 3 we describe the dependence of the wave function on the lattice oscillations. Numerical results are given in Sect. 4. We found for the ground state of the F-center a similarity law as supposed by experiments. In the appendices we give some details on regarding polarization effects.

We are interested in the wave functions of electrons trapped at point defects of alkali-halides of NaCl-structure. These electrons belonging to the impurity centers are coupled to all other electrons and nuclei of the crystal. We therefore in principle have to solve a many particle problem with a great number of degrees of freedom.

STUMPF and his coworkers established a model to treat this problem. In this paper we follow this treatment and improve its methods. In a first step we decompose the total crystal, which contains a great number of point-defects into smaller blocks (microblocks) containing only one defect [1]. Even if the concentration of the point defects is very large, one microblock contains not less then 10^3 ions on regular lattice sites. The processes at the point defects therefore can be assumed to be independent. The total crystal then can be treated as a statistical ensemble of independent microblocks and the calculation can be confined to that of the microblock wave functions.

As usually is done, we use the BORN–OPPENHEIMER approximation. In this approximation the wave function of the total crystal is factored into a nuclear part and an electronic part. The nuclear coordinates are contained in the latter only as parameters [1, 2]. This method leads to the classical FRANCK–CONDON principle, as every effect of velocity and acceleration on the electronic wave function is neglected. In a second step, we have to reduce the n-electron problem by the HARTREE–FOCK (HF) approximation. The assumption of the HARTREE method is that every electron moves in the average potential of all other electrons.

Since the closely bound core electrons can explicitly follow the motion of the trapped electrons, they cause correlation polarisation terms, which are explicitly considered by the quasi-adiabatic approximation. These terms are negligible only when fairely compact electronic states of impurity electrons are regarded. Since this is true for the problem to be treated, we use an HF product wave function.

LÖWDIN [3] solved the electron problem for perfect lattices with the HF procedure. In this paper his method is extended to distorted lattices. By means of a HF product wave function a HAMILTON operator for the trapped electron can be calculated. Additionally, electronic polarisations and the coupling of the trapped electron to the lattice is studied. We especially considered F-centers in alkali-halides, but the method can be easily extended to all other kinds of impurity centers.

The ground state wave function of the electron at absolute zero temperature of the lattice, is calculated for all crystals where the data needed have been available. For these lattices we found that the wave function does depend solely on the nearest neighbour distance of the ions d. SEIDEL [4] established this law by ENDOR-experiments. Our results are compared with this measurements in Fig. 1. Further diagrams are given for the variational parameter and the expectation value of the energy differences of the first excited state and the ground state, as given by measurements. The numerical results do

[1] H. STUMPF, Quantentheorie der Ionenkristalle, Springer-Verlag, Berlin 1961.
[2] M. BORN and K. HUANG, Dynamical Theory of Crystals Lattices, Oxford University Press, London 1954.
[3] P. O. LÖWDIN, Ph. D. Dissertation, Uppsala 1948.
[4] H. SEIDEL, Z. Phys. **165**, 237 [1961].

show that the aforementioned model for ionic crystals with the improvements achieved here gives the best agreement with experimental data. Further results on electronic transitions without radiation, will be given in a later paper.

Reduction of the *n*-electron Hamilton operator

Since we wish to describe one electron processes, we are looking for the one electron SCHRÖDINGER equation of the electron trapped at a point defect in an ionic crystal. To begin with, we shall give the general expressions calculated by the HF method, when used in ionic crystals. (Spin interactions have been omitted within this paper, since ions don't have unpaired spin. Relativistic effects, too, have been neglected.) To get simpler equations, we later specialize to F-centers in alkali-halides but this calculations can be easily extended to other defects in ionic crystals.

The *n*-electron HAMILTON operator in the BORN–OPPENHEIMER or adiabatic approximation [1, 2, 5] is given by

$$H^{\mathrm{e}} = \sum_i H_i + \tfrac{1}{2} \sum_{i,j} W_{i,j} \,. \tag{1.1}$$

(within this paper atomic units are used).

In (1.1) H_i is the HAMILTON operator of the ion i and W_{ik} the operator of the interaction energy of the ions i and k:

$$H_i = -\tfrac{1}{2} \sum_\alpha \Delta_{i\alpha} + \sum_\alpha \frac{e\, e_i}{|\, r_{i\alpha} - R_i \,|} + \tfrac{1}{2} \sum_{\alpha\beta}{}' \frac{e^2}{|\, r_{i\alpha} - r_{i\beta} \,|} \,, \tag{1.1a}$$

$$W_{ik} = \sum_{\alpha,\beta} \frac{e^2}{|\, r_{i\alpha} - r_{k\beta} \,|} - \sum_\alpha \frac{e\, e_k}{|\, r_{i\alpha} - R_k \,|} - \sum_\beta \frac{e\, e_i}{|\, r_{k\beta} - R_i \,|} + \frac{e_i\, e_k}{|\, R_i - R_k \,|} \,. \tag{1.1b}$$

We use the following notation:

Greek letters assigning electronic operators, $r_{i\alpha}$ electron coordinates, R_i nuclear coordinates, e_i charge of nucleus i, $a_i = \pm z\, e$ charge of ion i.

Applying the HF method the n-electron wave function is assumed to have the form:

$$\Psi_n(r_1, \ldots, r_N) = F \sum_{\lambda_1 \ldots \lambda_N} (-1)^P \psi_1^n(r_{\lambda_1}) \cdot \ldots \cdot \psi_N^n(r_{\lambda_N}) \,. \tag{1.2}$$

In (1.2) the sum is extended over all permutations P of the electronic coordinates and F is the normalization factor. If the $\psi_i{}^n$ are orthonormal, i. e.

$$(\psi_i^n, \psi_k^n) = \delta_{ik} \tag{1.3}$$

the expectation value of the energy U_n will be

$$U_n = \sum_i E_{ni} + \tfrac{1}{2} \sum_{i,j}{}' (\Psi_n, W_{ij}\, \Psi_n) \tag{1.4}$$

with

$$E_{ni} = (\Psi_n, H_i\, \Psi_n) \tag{1.4a}$$

and approximately [6]

$$\begin{aligned}(\Psi_n, W_{ik}\, \Psi_n) = {} & + \frac{e_i\, e_k}{|\, R_i - R_k \,|} \\ & - \sum_\alpha \left(\psi_{i\alpha}^n(r_{i\alpha}), \frac{e\, e_k}{|\, r_{i\alpha} - R_k \,|} \psi_{i\alpha}^n(r_{i\alpha}) \right) - \sum_\beta \left(\psi_{k\beta}^n(r_{k\beta}), \frac{e\, e_i}{|\, r_{k\beta} - R_i \,|} \psi_{k\beta}^n(r_{k\beta}) \right) \\ & + 2 \sum_{\alpha,\beta} \left\{ \left(\psi_{i\alpha}^n(r_{i\alpha})\, \psi_{k\beta}^n(r_{k\beta}), \frac{e^2}{|\, r_{i\alpha} - r_{k\beta} \,|} \psi_{i\alpha}^n(r_{i\alpha})\, \psi_{k\beta}^n(r_{k\beta}) \right) \right. \\ & \left. - \left(\psi_{i\alpha}^n(r_{i\alpha})\, \psi_{k\beta}^n(r_{k\beta}), \frac{e^2}{|\, r_{i\alpha} - r_{k\beta} \,|} \psi_{i\alpha}^n(r_{k\beta})\, \psi_{k\beta}^n(r_{i\alpha}) \right) \right\} .\end{aligned} \tag{1.4b}$$

If the electronic states of the core electrons are fairly compact (1.4a) is simply the energy expectation value of the ion i in the HF approximation.

For perfect lattices LÖWDIN solved the eigenvalue problem by insertion of the free ion orbitals in (1.4a) and approximating the interaction energy of ion i with all other ions by the MADELUNG energy $\pm\, \alpha_{\mathrm{M}}\, z/d$. Since he got good results, we assume this approximation as a zero order approximation. For non perfect lattices WAHL [7, 8] assumed the orbitals $\psi_{k\beta}^n$ to be linear combinations of the free ion ground state orbitals and some excited state wave functions:

$$\psi_{k\beta}^n = \tilde{\psi}_{k\beta}^0 + \sum_\nu f_{k\beta}^\nu\, \tilde{\psi}_{k\beta}^\nu \,. \tag{1.5}$$

WAHL then gets a system of nonlinear equations to determine the $f_{k\beta}^\nu$ and the eigenvalue U_n. Since we are not interested in the wave functions of the great

[5] B. S. GOURARY and F. J. ADRIAN, Solid State Phys. **10**, 148 [1960].

[6] For ionic crystal terms as

$$\left(\psi_{k\beta}^n(r_{i\alpha}), \frac{e\, e_k}{|\, r_{i\alpha} - R_k \,|} \psi_{k\beta}^n(r_{i\alpha}) \right)$$

are negligible, because the ionic orbitals are compact.

[7] F. WAHL, Z. Naturforschg. **19 a**, 620 [1964].

[8] F. WAHL, Ann. Phys. Leipzig **11**, 151 [1963].

number of core electrons, but only in their influence on the trapped electron's state, we ought not know the $f^{\nu}_{k\beta}$ explicitly. As shown in Appendix A $f^{\nu}_{k\beta} \neq 0$ does mean electronic polarization of the ion k, and we can express the correlation of the electronic states by dipole interactions.

To have a simpler notation, we now specialize to the problem of an electron trapped to an anion-vacancy. Let the vacancy be at $R_1 = 0$ and denote the coordinates of the trapped electron by r. We then have instead of the anion HAMILTON operator H_1 from (1.1a)

$$H_t = -\tfrac{1}{2}\Delta . \tag{1.6a}$$

By means of Appendix A (A.12) – (A.14) we express the interaction energy of the trapped electron and the ion k by the ionic charge a_k and the polarization dipole m_k.

$$(\Psi_n, W_{1k}\Psi_n) = \left(\psi^n_1(r), \frac{-e\,a_k}{|r-R_k|} - e\,\frac{m_k(r-R_k)}{|r-R_k|^3}\,\psi^n_1(r)\right). \tag{1.6b}$$

In (1.6b) exchange interactions have been neglected, because the ground state of the electron is assumed to be compact. By the numerical results this assumptions will be confirmed.

For $i>1$ $(\Psi_n, H_i\Psi_n)$ is approximated by the internal energy of ion i [see (1.4a)]. The ground state energy is a constant E_i^0. We write for $E_{ni}-E_i^0$ in (1.4a) the polarization energy of an ion with polarizability α_i in an external field $\boldsymbol{E}_{\text{ext}}$

$$E_{ni}-E_i^0 = \frac{m_i^2}{2\,\alpha_i} = \frac{1}{2}\,m_i\,\boldsymbol{E}_{\text{ext}}(R^\circ_i). \tag{1.7a}$$

In (A.15) we give an approximation for the interaction energy of two ions i and k by classical point charges, dipoles and a repulsive potential.

$$(\Psi_n, W_{ik}\Psi_n) = \frac{a_i a_k}{|R_i-R_k|} + a_k\frac{m_i(R_k-R_i)}{|R_k-R_i|^3} + a_i\frac{m_k(R_i-R_k)}{|R_i-R_k|^3} + m_i\nabla_i\frac{m_k(R_i-R_k)}{|R_i-R_k|^3} + \frac{b}{|R_i-R_k|^\eta}. \tag{1.7b}$$

In Eq. (1.7b) the exchange interactions due to PAULI's exclusion principle have been approximated by $b/|R_i-R_k|^\eta$.

Insertion of (1.6) and (1.7) into (1.4) gives

$$\begin{aligned} U_n = {} & \left(\psi^n_1, -\tfrac{1}{2}\Delta - e\left[\sum_{k>1}\left(\frac{a_k}{|r-R_k|} + \frac{m_k(r-R_k)}{|r-R_k|^3}\right)\right]\psi^n_1\right) + \tfrac{1}{2}\sum'_{i,k>1}\frac{a_i a_k}{|R_i-R_k|} \\ & + \tfrac{1}{2}\sum'_{i,k>1} m_i\nabla_i\frac{m_k(R_i-R_k)}{|R_i-R_k|^3} + \sum'_{i,k} a_k\frac{m_i(R_k-R_i)}{|R_i-R_k|^3} + \tfrac{1}{2}\sum'_{i,k}\frac{b}{|R_k-R_i|^\eta}. \end{aligned} \tag{1.8}$$

In Appendix A we show how the polarization dipoles depend on the electronic states of the core electrons. Since every electronic state depends on all other electronic states, the polarization dipoles are functionals of the trapped electrons state too. To calculate the polarization dipoles, we have to regard the symmetry of the regular lattice, because in a regular lattice the ions are not polarized. We therefore rewrite (1.8) splitting it into terms with the symmetry of the regular lattice and "defect terms". As can be seen from (1.9) the vacancy can be thought to be build by a point charge $-a_1$ that is put into the regular lattice at R°_1.

$$\begin{aligned} U_n = {} & \left(\psi^n_1, \left[-\tfrac{1}{2}\Delta + \frac{e\,a_1}{|r|} - \sum_{k=1}\frac{e\,a_k}{|r-R^\circ_k|} - \sum_{k=1}\left(\frac{e\,a_k}{|r-R_k|} - \frac{e\,a_k}{|r-R^\circ_k|}\right) + \sum_{k>1}\frac{m_k(r-R^\circ_k)}{|r-R^\circ_k|^3}\right]\psi^n_1\right) \\ & + \tfrac{1}{4}\sum'_{i,k=1}\frac{a_i a_k}{|R_i-R_k|} + \tfrac{1}{2}\sum'_{i,k=1}\left(\frac{a_i a_k}{|R_i-R_k|} - \frac{a_i a_k}{|R^\circ_i-R^\circ_k|}\right) + \tfrac{1}{2}\sum'_{i,j=1}\frac{b}{|R_i-R_j|^\eta} + \tfrac{1}{2}\sum'_{i,k>1} m_i\nabla_i\frac{m_k(R^\circ_i-R^\circ_k)}{|R^\circ_i-R^\circ_k|^3} \\ & + \tfrac{1}{2}\sum_{i>1}\frac{m_i^2}{\alpha_i} + \sum'_{i,k>1} a_k\frac{m_i(R_k-R^\circ_i)}{|R_k-R^\circ_i|^3} - a_1\sum_{k>1}\frac{a_k}{|R^\circ_k|} - \sum_{k>1}\left(\frac{a_1 a_k}{|R_k|} - \frac{a_1 a_k}{|R^\circ_k|}\right) - \sum_{k>1}\frac{b}{|R_k|^\eta}. \end{aligned} \tag{1.9}$$

To get a short notation we use the following abbreviations: The COULOMB potential of the regular lattice Φ_0

$$\Phi_0(r) := \sum_{k=1} a_k/|r-R^\circ_k| \tag{1.10a}$$

omitting the anion at $R^\circ_1 = \boldsymbol{O}$ or putting a point charge $-a_1$ at R°_1

$$\Phi_0'(r) := \sum_{k=1}\frac{a_k}{|r-R^\circ_k|} = \Phi_0(r) - \frac{a_1}{|r|}. \tag{1.10b}$$

When an anion is missing the mean equilibrium positions of the ions will not be longer at R°_k. We denote by $R_k{}^n$ the new positions. The distortion of

the lattice then can be expressed by "displacement"-dipoles $M_k = a_k(R_k - R^\circ_k)$. The potential of these dipoles is:

$$\Phi_d(r) := \sum_{k=1} \left(\frac{a_k}{|r-R_k|} - \frac{a_k}{|r-R^\circ_k|} \right) \quad (1.10c)$$
$$= \sum_{k=1} \frac{M_k(r-R^\circ_k)}{|r-R^\circ_k|^3}.$$

The potential of the anion vacancy at R°_1

$$\Phi_a(r) := -a_1/|r| \quad (1.10d)$$

the charge distribution of the trapped electron $\varrho^n(r) = -e\,\psi_1^n(r)^* \psi_1^n(r)$ gives rise to the potential $\Phi_e{}^n(r)$:

$$\Phi_e{}^n(r) := \int \frac{\varrho^n(r')}{|r-r'|}\,dr' \quad (1.10e)$$

finally the potential of the electronic polarization dipoles located approximately at R°_i is given by Φ_m:

$$\Phi_m(r) := \sum_i \frac{m_i(r-R^\circ_i)}{|r-R^\circ_i|^3}. \quad (1.10f)$$

Because of the symmetry of the regular lattice the total field vanishes at every regular lattice point

$$\sum_{k=1} \frac{a_k(R^\circ_k - R^\circ_i)}{|R^\circ_k - R^\circ_i|^3} = 0 \quad (1.11a)$$

and therefore

$$\sum_{i>1} m_i \sum_{k=1} a_k \frac{(R^\circ_k - R^\circ_i)}{|R^\circ_k - R^\circ_i|^3} = \sum_{k=1} a_k\,\Phi_m(R^\circ_k) = 0 \quad (1.11b)$$

We now rewrite (1.9)

$$U_n = \left(\psi_1^n(r), \left[-\tfrac{1}{2}\Delta - e\,(\Phi_0'(r) + \Phi_d(r) + \Phi_m(r))\right]\psi_1^n(r)\right)$$
$$+ \tfrac{1}{2}\sum_{i,k}{}' \frac{a_i a_k}{|R^\circ_i - R^\circ_k|} + \tfrac{1}{2}\sum_i M_i \nabla_i \Phi_d(R^\circ_i) + \tfrac{1}{2}\sum_{i,k}{}' \frac{b}{|R_i - R_k|^\eta} + \tfrac{1}{2}\sum_i m_i \nabla_i \Phi_m(R^\circ_i) \quad (1.12)$$
$$+ \tfrac{1}{2}\sum_i \frac{m_i^2}{\alpha_i} + \sum_{k=1} a_k(\Phi_m(R_k) - \Phi_m(R^\circ_k)) - a_1(\Phi_0'(R^\circ_1) + \Phi_d(R^\circ_1) + \Phi_m(R_1)) - \sum_{j>1} \frac{b}{|R_j|^\eta}.$$

The expectation value (1.12) depends on the state of the trapped electron explicitly and on the state of all other electrons too, because of the electronic polarization dipoles. As shown in Appendix B the potential $\Phi_m(r)$ of these dipoles can be expressed by means of the COULOMB potential $\Phi_s(r)$, that has not the symmetry of the regular crystal

$$\Phi_s(r) := \Phi_a(r) + \Phi_e{}^n(r) + \Phi_d(r) \quad (1.13)$$
$$\Phi_m(r) = [\gamma/(1-\gamma)]\;\Phi_s(r). \quad (1.14)$$

We now replace $\Phi_m(r)$ within (1.12) by means of (1.14) and use the identities in the order as given in the following equations:

(I) $$\tfrac{1}{2}\sum_i \frac{m_i^2}{\alpha_i} = -\tfrac{1}{2}\sum_i m_i \nabla_i(\Phi_a + \Phi_e{}^n + \Phi_d + \Phi_m)$$

(II) $$-\tfrac{1}{2}\sum_i m_i \nabla_i \Phi_a = \frac{a_1}{2}\Phi_m(R_1{}^0)\,;\quad -\tfrac{1}{2}\sum_i m_i \nabla_i \Phi_e{}^n = \tfrac{1}{2}(\psi_1^n, \Phi_m \psi_1^n)$$

(III) $$\tfrac{1}{2}\sum_i m_i \nabla_i \Phi_d = \tfrac{1}{2}\sum M_i \nabla_i \Phi_m = \tfrac{1}{2}\frac{\gamma}{1-\gamma}\sum_i M_i \nabla_i(\Phi_d + \Phi_e + \Phi_a),$$

(IV) $$\tfrac{1}{2}\sum_i M_i \nabla_i \Phi_a = -\frac{a_1}{2}\Phi_d(R_1{}^0)\,;\quad \tfrac{1}{2}\sum_i M_i \nabla_i \Phi_e = -\tfrac{1}{2}(\psi_1^n(r), \Phi_d(r)\,\psi_1^n(r)).$$

Eq. (1.14) should be used only if Φ_s is bounded and continuous at the point r. Since Φ_a and $\Phi_e{}^n$ have singularities at $R_1{}^0$, one tries to get a potential as good as possible by adding the two potentials. We then use approximately for (1.14) at $R_1{}^0$

$$\Phi_m(0) = [\gamma/(1-\gamma)]\,(\Phi_d(0) + \Phi_e{}^n(r_a) + \Phi_a(r_a))$$

where r_a is a radiusvector of the order of magnitude of one or two lattice constants. This approximation is easily understood by regarding appendix B.

After some manipulations we arrive at the following expression for the energy expectation value.

$$U_n = \left(\psi_1^n(r), \left[-\frac{1}{2}\Delta - \Phi_0'(r) - \frac{1}{1-\gamma}\Phi_d(r) - \frac{1}{2}\frac{\gamma}{1-\gamma}(\Phi_a(r) + \Phi_e{}^n(r))\right]\psi_1^n(r)\right)$$
$$+ \frac{1}{2}\sum_{i,k}{}'\left(\frac{a_i a_k}{|R^\circ_i - R^\circ_k|} + \frac{b}{|R_i - R_j|^\eta}\right) + \frac{1}{2}\frac{1}{1-\gamma}\sum_{i,k}{}'\left(\frac{a_i a_k}{|R_i - R_k|} - \frac{a_i a_k}{|R^\circ_i - R^\circ_k|}\right) \quad (1.15)$$
$$- a_1\left(\Phi_0'(R^\circ_1) + \frac{1}{1-\gamma}\Phi_d(R^\circ_1) + \frac{1}{2}\frac{\gamma}{1-\gamma}(\Phi_a(r_a) + \Phi_e{}^n(r_a)) - \sum_{j>1}\frac{b}{|R_j|^\eta}\right.$$

The expectation value (1.15) depends explicitly only on the wave function of the trapped electron. If we now wish to solve the eigenvalue problem, this can be done easily by the direct RITZ variational principle, as shown in the next paragraph.

An one electron SCHRÖDINGER equation can be found by variation of (1.15) with respect to $\psi_1{}^n(r)$ [9, 10].

The solution of the Schrödinger equation for the trapped electron [11]

The HAMILTON operator (1.1) as well as the energy expectation value (1.15) depends on the nuclear coordinates as parameters. For many electronic processes, it is necessary to know the dependence of the wave function on these parameters. But since it is senseless to solve the eigenvalue problem of H^e for all positions of the nuclei, STUMPF and his coworkers [1] gave a method with which to solve this problem and to have all information necessary. The first step is to solve the SCHRÖDINGER equation for those values of the parameters R_j which give the minimum of energy. These are denoted by R_j^s and can be calculated by the "Reziprokmatrix" techniques [12] which were worked out by this group. This wave function corresponds to a crystal at the temperature of absolute zero. In the next step which is worked out in the succeeding paragraph the dependence on temperature is treated.

The energy U_n from (1.15) depends on the charge distribution of the trapped electron

$$\varrho_n(x) = -e\,\psi_n{}^*(x)\,\psi_n(x)$$

and the positions of the ions. The ground state wave function and energy is calculated by minimizing (1.15). For the ground state we can simply use an hydrogen s-function as a trial function

$$\psi_s(x) = \pi^{-1/2}\beta^{3/2}\exp\{-\beta\,|\,x\,|\}\,. \tag{2.1}$$

Using (2.1) we get from (1.15) the energy of the ground state which depends on the variational parameter β and the mean positions of the ions R_j:

$$\begin{aligned} U_s(\beta, R_j) = {} & \frac{\beta^2}{2} - \sum_{j>1} a_j \left[\frac{1}{|\,R^\circ{}_j\,|} - \left(\beta + \frac{1}{|\,R^\circ{}_j\,|}\right)\exp(-2\beta\,|\,R^\circ{}_j\,|)\right] \\ & - \frac{1}{1-\gamma}\sum a_j \left[\frac{1}{|\,R_j\,|} - \left(\beta + \frac{1}{|\,R_j\,|}\right)\exp(-2\beta\,|\,R_j\,|) - \frac{1}{|\,R^\circ{}_j\,|} + \left(\beta + \frac{1}{|\,R^\circ{}_j\,|}\right)\exp(-2\beta\,|\,R^\circ{}_j\,|)\right] \\ & - \frac{1}{2}\frac{\gamma}{1-\gamma}\frac{3}{8}\beta - a_1\frac{1}{2}\frac{\gamma}{1-\gamma}\left(\beta + \frac{1}{|\,r_a\,|}\right)\exp(-2\beta\,|\,r_a\,|) + V(R_k)\,. \end{aligned} \tag{2.2}$$

In (2.2) $V(R_k)$ is given by:

$$\begin{aligned} V(R_k) = {} & \frac{1}{2}\sum_{i,j}{}' \left(\frac{a_i a_j}{|\,R^\circ{}_i - R^\circ{}_j\,|} + \frac{b}{|\,R_i - R_j\,|^\eta}\right) + \frac{1}{2}\frac{1}{1-\gamma}\sum_{i,j}{}' \left(\frac{a_i a_j}{|\,R_i - R_j\,|} - \frac{a_i a_j}{|\,R^\circ{}_i - R^\circ{}_j\,|}\right) \\ & - \sum_j \frac{b}{|\,R_j\,|^\eta} - a_1 \sum \frac{a_j}{|\,R^\circ{}_j\,|} - \frac{a_1}{1-\gamma}\sum_j \left(\frac{a_j}{|\,R_j\,|} - \frac{a_j}{|\,R^\circ{}_j\,|}\right). \end{aligned} \tag{2.3}$$

Now we must minimize (2.2) with respect to β and the zero temperature positions of the ions R_j^s. These positions depend on β^s and are given by the conditions

$$\frac{\partial U_s(\beta^s, R_k)}{\partial R_k}\bigg|_{R=R_k{}^s} \doteq 0\,. \tag{2.4a}$$

Because of the variational principle we have the condition

$$F_s(\beta) := \partial U_s/\partial\beta \doteq 0\,. \tag{2.4b}$$

[9] Standard Books of Quantum Mechanics e. g. A. MESSIAH, Quantum Mechanics, North-Holland Publishing Co., Amsterdam 1965, Volume II, Ch. XVIII.

[10] A. S. DAVYDOV, Quantum Mechanics, Pergamon Press, Oxford 1965.

[11] The calculations of GOURARY and ADRIAN (GA) [5] were made without observing the distortions of the perfect lattice. As our numerical calculation with the ground state shows, this does not lead to great errors, as the dislocations of the nearest neighbours are only about 1% of the lattice constant. For extended wave functions one finds a distortion of 10% to 15%. The numerical results of GA show that the part of the wave function which depends only on the radius fall off for the excited state more strongly than for the ground state in contradiction to the hydrogen electron wave function. Therefore their calculation seems to be selfcontradictory for excited states.

[12] L. KERN-BAUSCH, Z. Naturforschg. **21 a**, 798 [1966].

We divide U_s into two parts P and Q. P has the symmetry of the regular lattice and Q contains the interaction energy of the defect.

$$U_s = P + Q\,. \tag{2.4c}$$

With
$$Q = \frac{1}{1-\gamma} \sum_{j>1} a_j \left(\beta + \frac{1}{|R_j|}\right) \exp(-2\beta |R_j|) - \sum_{j>1} \frac{b}{|R_j|^\eta} + C(\beta) \tag{2.4d}$$

and
$$P = U_s - Q\,. \tag{2.4e}$$

β^s gives the value of the variational parameter β where U_s is at its minimum.

To begin with, we consider (2.4a) for arbitrary but fixed values of β. This set of equations gives an equilibrium condition between the forces produced by the color center and the equilibrium forces of the lattice.

The forces caused by the defect in the crystal are given by

$$-k_l = \frac{\partial Q}{\partial (R_1 - R_l)} = + \frac{-e\,a_l}{1-\gamma} \frac{(R_1 - R_l)}{|R_1 - R_l|^3} (1 + 2\beta |R_1 - R_l| + 2\beta^2 |R_1 - R_l|^2) \exp(-2\beta |R_1 - R_l|) + \frac{b\,\eta}{|R_1 - R_l|^{\eta+2}} (R_1 - R_l)\,. \tag{2.5}$$

From (2.5) one notices, that the forces fall off as $\exp(-a\,x)$ and $x^{-(\eta+1)}$. They are therefore regarded only in respect to neighbours of order 3.

The dilatation vectors y_{1k}

$$y_{1k} := R_1 - R_k - R^\circ{}_1 + R^\circ{}_k \tag{2.6}$$

can be represented due to the symmetry of the problem as

$$y_{1k} = \mu (R^\circ{}_1 - R^\circ{}_k)\,. \tag{2.7}$$

By means of the above mentioned "Reziprokmatrix" we find these dilatations of the ions of 1st, and 2nd, and 3rd order, centered about the point defect.

To do this we expand (2.4c) into a power series of the dislocations y_{1l} to first order.

$$0 = \frac{\partial P}{\partial y_{1l}} + \frac{\partial Q}{\partial y_{1l}} = \frac{\partial P}{\partial y_{1l}}\bigg|_{y_{1l}=0} + \sum_k \frac{\partial^2 P}{\partial y_{1l}\,\partial y_{1k}}\bigg|_{y_{1j}=0} y_{1k} + \cdots + \frac{\partial Q}{\partial y_{1l}}\bigg|_{y_{1l}=0} + \sum_k \frac{\partial^2 Q}{\partial y_{1l}\,\partial y_{1k}}\bigg|_{y_{1k}=0} y_{1k} + \cdots\,. \tag{2.8}$$

Since P is the energy of the ideal crystal, the first term on the right hand side of (2.8) does vanish. Using the defect forces (2.5) we rewrite (2.8)

$$\sum_k \frac{\partial^2 P}{\partial y_{1l}\,\partial y_{1k}} y_{1k} = k_l(y_{1j}), \quad l = 2, 3, 4, \ldots\,. \tag{2.9}$$

The "Reziprokmatrix" R is defined as the inverse of the matrix

$$\left(\frac{\partial^2 P}{\partial y_{1l}\,\partial y_{1k}}\right)_{l,k}, \qquad R\left(\frac{\partial^2 P}{\partial y_{1l}\,\partial y_{1k}}\right) = \mathbf{1}\,. \tag{2.10}$$

We write for (2.9)

$$y_{1i} = \sum_l R_{il}\, k_l(y_{1j}), \quad i = 2, 3, 4, \ldots\,. \tag{2.11}$$

This formulation of the equilibrium condition is very useful, because for point defects only in the surrounding of the defect the dislocations y_{1i} will be different from zero and therefore the great number of Eqs. (2.4) is reduced to a very small number that can be explicitly numerical treated. To solve (2.11) an iterative process is carried out. In the first step the defect forces are approximated by $k_l(0)$, then (2.11) gives first order $y_{1i}^{(1)}$ and this will be used to calculate first order forces $k_l(y_{1i}^{(1)})$. By means of (2.11) second order $y_{1i}^{(2)}$ are calculated. This process converges rapidly versus the equilibrium dislocations y_{1i}.

Since the whole problem is spherical symmetric with respect to the anion vacancy, the set of Eqs. (2.10) can be reduced another time. All dislocations are known, when the projections on one special axis and with respect to one special ion are known. In the notation of KERN-BAUSCH the projection of these dilatations on one special axis 1 with respect to the anion vacancy are given by

$$\begin{aligned} y_1{}^1 &= \sum_j P_{1j}\, k_j{}^1, \\ y_2{}^1 &= \sum_j P_{2j}\, k_j{}^1, \\ y_3{}^1 &= \sum_j P_{3j}\, k_j{}^1. \end{aligned} \tag{2.8}$$

Where the force component in this direction 1 will be used in (2.8) and the matrix P_{ij} is given by KERN-BAUSCH [14].

As was mentioned above the forces k_j and therefore the dilatations depend on the electronic state described by β.

A solution of the electronic problem can now be found in the following way:

1st step:

take any value $\beta^{(0)}$ for the parameter β and calculate $y_i^{(0)}$ by (2.8);

2nd step:

calculate a new $\beta^{(1)}$ from (2.4b) with $y_i^{(0)}$ and then new $y_i^{(1)}$ and continue until equilibrium is established.

This calculations have been done with the aid of a digital computer. Due to the symmetry of the problem all sums in (2.4b) can be computed easily. One observes that on every shell of radius $d\sqrt{n}$ around the point defect, there are either kations or anions, therefore the sums within the lattice can be computed very quickly and over a wide range of the lattice without any difficulty. When this is done there is no need for introducing an effective mass to regard the effect of the periodic lattice on the state of the electron. This seems to us important, for the considerations of McLeane [13] do show that an effective mass approximation for the ground state of an electron is very obvious.

The wave function of the trapped electron in dynamical lattice coupling

In the last chapter the static equilibrium positions and the variational parameter as a function of these positions have been calculated. However, in dynamic processes the coupling of the wave function to the oscillations of the lattice is rather important. To this aim an extension of β^n into a Taylor series is made:

$$\beta^n(R_k) = \beta^n(R_k{}^n) + \sum_i \frac{\partial \beta^n}{\partial R_i}(R_i - R_i{}^n) + \dots . \quad (3.1)$$

If there are only small oscillations about $R_i{}^n$ the effect of the oscillations should be expressable by the first order terms

$$\beta_i{}^n := \partial \beta^n / \partial R_i . \quad (3.2)$$

An expansion of the expression (2.4b) gives

$$F_n(\beta) = F_n(\beta^n)\Big|_{R_k{}^n} + \sum_k (R_k - R_k{}^n)\frac{\partial}{\partial R_k} F_n(\beta) + \dots . \quad (3.3)$$

[13] T. P. McLeane in "Semiconductors" (Proc. Intern. School of Phys. "Enrico Fermi", Varena, Course 22, 1961), Academic Press, New York 1963, p. 479.

The first term $F_n(\beta^n)$ vanishes in accordance with the static calculations of the preceeding paragraph. We now demand the second term of (3.3) to be zero

$$\sum_k (R_k - R_k{}^n)\frac{\partial}{\partial R_k} F_n(\beta) \doteq 0 . \quad (3.4a)$$

As this should be true for every choice of the R_k, this is equivalent to

$$\frac{\partial}{\partial R_k} F_n(\beta) = \frac{\partial^2 U_n}{\partial \beta\, \partial R_k} + \beta_k{}^n \frac{\partial^2 U_n}{(\partial \beta)^2} \doteq 0 . \quad (3.4b)$$

For the ground state of the F-center the sum

$$\begin{aligned} N_s := \frac{\partial^2 U_s}{(\partial \beta)^2} &= 1 + \sum_j 4\beta a_j |R^\circ{}_j|^2 \exp(-2\beta |R^\circ{}_j|) \\ &+ \frac{1}{1-\gamma}\sum_j 4\beta a_j \,[|R_j|^2 \exp(-2\beta|R_j|) \\ &- |R^\circ{}_j|^2 \exp(-2\beta|R^\circ{}_j|)] \end{aligned} \quad (3.5)$$

can be calculated directly by the same arguments as the lattice sums in the preceeding paragraphs. Only that part of (2.2) which depends on both R_k and β need be considered for further calculations.

$$V(\beta^s, R_k) := U_s(\beta^s, R_k) - V(R_k) . \quad (3.6)$$

For the following we consider a kation and an anion together as an elementary cell and after expanding (3.6) similary to (3.3), we transform to center of mass coordinates.

$$\begin{aligned} V(\beta^s, R_k) &= V(\beta^s, R_k{}^s) + \frac{1}{1-\gamma}\sum X_{aj}(A_{2j} - A_{2j-1}) \\ &- \frac{1}{1-\gamma}\sum X_{0j}\left(\frac{M_-}{M_a}A_{2j} + \frac{M_+}{M_a}A_{2j-1}\right) \end{aligned} \quad (3.7)$$

with
$$\begin{aligned} A_j = -\frac{R_j{}^s}{|R_j{}^s|^3}\,[(1 + 2\beta|R_j{}^s| + 2\beta^2|R_j{}^s|^2) \\ \cdot \exp(-2\beta|R_j{}^s|) - 1], \end{aligned} \quad (3.8a)$$

$$\begin{aligned} X_{aj} &= (R_{2j-1} - R^s_{j-1})\cdot\frac{M_+}{M_a} + (R_{2j} - R^s_{2j})\cdot\frac{M_-}{M_a}, \\ X_{0j} &= (R_{2j} - R^s_{2j}) - (R_{2j-1} - R^s_{2j-1}) \end{aligned} \quad (3.8b)$$

(+ or odd index denotes an anion, − or even index denotes a kation).

The first sum in (3.7) gives the interaction energy of the center of mass motion and the second, that of relative motion of the ions with the electron.

If the limit of the elastic sound waves is considered, the motion of the center of gravity tends to the acoustic branch of the phonon spectrum; the relative motion, which corresponds to dipol oscillations, to the optical branch. We neglect the coupling of the electron to the elastic sound waves and arrive at

$$\sum X_{aj}(A_{2j} - A_{2j-1}) = 0 . \quad (3.9)$$

Therefore β does not depend on X_{aj}.

A second coordinate transformation is now carried out. Let

$$\eta_1 = \frac{1}{\Gamma^s}\left(\frac{\partial}{\partial X_{01}}, \ldots, \frac{\partial}{\partial X_{0\,3N/2}}\right) V(\beta^s, R_k) \qquad (3.10)$$

be a normalized base vector of that part of center of gravity space corresponding to relative motion. Γ^s is the normalisation factor

$$(\Gamma^s)^2 = \sum_j \left(\frac{\partial V}{\partial X_{0j}}\right)\left(\frac{\partial V}{\partial X_{0j}}\right) \qquad (3.11)$$

and let $$\eta_1, \eta_2, \ldots, \eta_{3N/2} \qquad (3.12)$$

be a base of this space.

If R is an arbitrary vector of this space, its components q_j with respect to the base (3.12) are given by

$$q_j = \sum_\alpha \eta_\alpha^j X_{0\alpha} \qquad (3.13)$$

and (3.1) becomes in the new coordinate system

$$\beta(R_k) = \beta(R_k{}^s) + \sum_\mu B_\mu \cdot q_\mu \qquad (3.14)$$

with $$B_\mu := \partial\beta/\partial q_\mu .$$

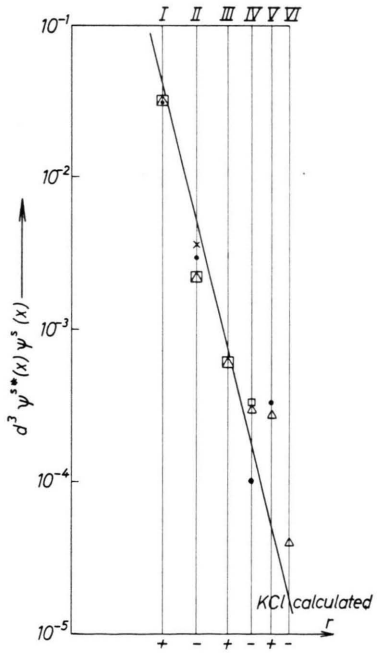

Fig. 1. Electronic density $d^3\Psi^{s*}(x)\,\Psi^s(x)$ of the ground state of KCl compared with the Endor-measurements of SEIDEL [4]. The measurements have been carried out to neighbours of order VI. □ KCl, ● NaCl, △ KBr.

Insertion of the transformation (3.13) in (3.4) gives for

$$\frac{\partial\beta}{\partial q_1} = B_1 = -\frac{1}{N_s}\frac{\partial\Gamma^s}{\partial\beta} \qquad (3.15)$$

as η_1 is normalized. If $\eta_2, \ldots, \eta_{3N/2}$ are independent from the electronic state, it follows that

$$B_\mu = 0, \quad \mu = 2, 3, \ldots \qquad (3.15a)$$

and therefore

$$\beta^s(R_k) = \beta^s(R_k{}^s) + B_1\, q_1 . \qquad (3.16)$$

$\partial\Gamma^s/\partial\beta$ was found too by straightforward addition of the terms as mentioned above.

WAGNER [14] did show that the normal coordinate q_1 does belong to the longitudinal optical branch of the phonon spectrum, which is assumed to be quasi-degenerated. This is important to know, when polarization energies shall be calculated.

Numerical results

Numerical calculations have been carried out for LiF, NaCl, NaBr, KCl, KBr, KJ. For consistency arguments we used the data as given by KERN-BAUSCH. They are listed in Table 1. The most interesting result of the static calculations can be seen in Table 2. For all alkali-halides which belong to the same kation, the product $\beta^s d$ is a constant. This does mean: There is a law of similarity among the alkali-halides for the ground state of an electron trapped at an anion vacancy.

This law was supposed by SEIDEL, who measured the electron density using ENDOR-methods. Fig. 1 gives the electron density as calculated from his measurements. It should be noted that polarization effects have not been taken into account by him. The measurements of SEIDEL are compared with our result, as given by the straight line.

MOLLWO [15] first stated that for the maximum of the F-center absorption band there holds $d^2 \cdot \nu = \text{const}$, this law was corrected by IVEY [16]. We suppose therefore that for the first excited state there should be also a similarity law. To demonstrate this we plotted in Fig. 2 the absorption energies and the variational parameter against the lattice constant. Calculations for the excited state have not been carried out by us,

[14] M. WAGNER, Z. Naturforschg. **15 a**, 889 [1960].
[15] E. MOLLWO, Nachr. Akad. Wiss. Göttingen, Math.-Phys. Kl. **1931**, p. 97.
[16] H. F. IVEY, Phys. Rev. **72**, 341 [1947].

	d [Å]	γ	η	P_{t1}	P_{t2}	P_{t3}
LiF	2.01	− 0.696	7	$\frac{d^3}{e^2}\begin{pmatrix}+0.17045\\+0.12659\\+0.01215\end{pmatrix}$	$\begin{pmatrix}+0.50277\\-0.17934\\-0.21010\end{pmatrix}$	$\begin{pmatrix}+0.04860\\-0.21010\\-0.65828\end{pmatrix}$
NaCl	2.81	− 0.902	8	$\frac{d^3}{e^2}\begin{pmatrix}-0.07874\\+0.02067\\-0.00175\end{pmatrix}$	$\begin{pmatrix}+0.08269\\-0.19551\\-0.04887\end{pmatrix}$	$\begin{pmatrix}-0.00701\\-0.04887\\-0.32120\end{pmatrix}$
NaBr	2.98	− 1.044	8	$\frac{d^3}{e^2}\begin{pmatrix}-0.09072\\+0.02122\\-0.00640\end{pmatrix}$	$\begin{pmatrix}+0.09490\\-0.21297\\-0.05456\end{pmatrix}$	$\begin{pmatrix}-0.02559\\-0.05456\\-0.32638\end{pmatrix}$
KCl	3.14	− 0.820	9	$\frac{d^3}{e^2}\begin{pmatrix}-0.17718\\+0.01266\\-0.00488\end{pmatrix}$	$\begin{pmatrix}+0.05064\\-0.20658\\+0.00289\end{pmatrix}$	$\begin{pmatrix}-0.01954\\+0.00289\\-0.21975\end{pmatrix}$
KBr	3.29	− 0.922	9	$\frac{d^3}{e^2}\begin{pmatrix}-0.17696\\+0.01488\\-0.00770\end{pmatrix}$	$\begin{pmatrix}+0.05954\\-0.21017\\+0.00769\end{pmatrix}$	$\begin{pmatrix}-0.03081\\+0.00769\\-0.21615\end{pmatrix}$
KJ	3.53	− 1.087	9	$\frac{d^3}{e^2}\begin{pmatrix}-0.16629\\+0.01526\\-0.01313\end{pmatrix}$	$\begin{pmatrix}+0.06104\\-0.21958\\+0.00119\end{pmatrix}$	$\begin{pmatrix}-0.05262\\+0.00119\\-0.22484\end{pmatrix}$

Table 1. Data as used for our calculations [12].

	$\beta^s \cdot 10^{-7}$ cm^{-1}	$\beta^s d$	$\beta^s d(\gamma=0)$	$\beta^s d$(GA)
LiF	7.24	1.47	1.63	1.71
NaCl	5.88	1.65	1.84	1.92
NaBr	5.58	1.66		
KCl	5.51	1.73	2.00	1.99
KBr	5.28	1.74	2.04	
KJ	4.95	1.75	2.08	

Table 2. The variational parameter for the ground state. The second column shows the similarity law. Column three gives the results when polarization is neglected. The last column gives the results of GA [5].

using the same methods as for the ground state, because only the ground state wave function was needed for our further calculations of non radiative electronic transitions. For comparison we therefore list

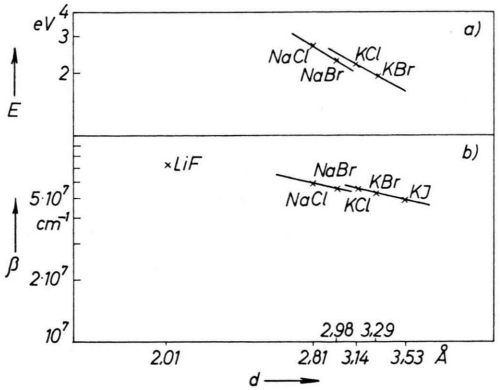

Fig. 2 a. IVEY's similarity law. F-center absorption energy plotted against nearest neighbour distance of the ions.

Fig. 2 b. Law of similarity for alkali halides. Variational parameter β_s for the ground state plotted against d.

in line 3 of Table 3 the values as calculated by GA. The footnote [11] should be noted. We also calculated for comparison the variational parameter β and the expectation values U_s assuming $\gamma=0$ (that is no polarization) and got for the ground state approximately the same results as GA (Table 2). But the similarity law could not be found again. At least we found that for the ground state the effect of the lattice distortions is negligible. The values of the

	LiF	NaCl	NaBr	KCl	KBr	KJ
$\gamma \neq 0$	5.06	4.18	3.93	3.98	3.80	3.52
$\gamma=0$	6.40	5.64	5.47	5.35	5.21	4.98
GA	7.25	5.82		5.38		

Table 3. Energy expectation values for the ground state $-U_s(R_k^s)+V(R_k^s)$ with respect to $V(R_k)$ from (2.2) in eV. The first line gives the results when polarization has been regarded, the second line the results when $\gamma=0$ and the third the results given by GA [5].

	Ground State			Vacancy		
	y_1	y_2	y_3	y_1	y_2	y_3
LiF	+3.7	+0.5	+0.0	+5.0	−3.9	+3.7
NaCl	−0.5	−0.3	+0.1	+3.0	−3.3	+2.6
NaBr	−0.7	−0.3	+0.0	+3.1	−3.2	+2.4
KCl	−1.2	−0.4	+0.1	+4.2	−4.0	+2.6
KBr	−1.4	−0.4	+0.1	+4.0	−3.9	+2.5
KJ	−1.5	−0.3	−0.0	+3.5	−3.6	+2.3

Table 4. The distortion of the lattice in percent of the lattice constant. The first three columns give the dislocations when the electron is trapped at the vacancy, the last for the vacancy without an electron. The radial displacement are given by $r_i=\sqrt{i}\cdot y_i$. + denotes an outgoing displacement.

	LiF	NaCl	NaVr	KCl	KBr	KJ	
N_c	3.48	4.36	4.56	4.34	4.82	5.08	10^{-27} erg · cm^{-2}
Γ^s	6.63	3.18	2.24	2.28	2.32	1.85	10^{-4} dyn
B_1	− 10.10	− 4.08	− 2.68	− 7.68	− 2.55	− 2.03	10^{14} cm^{-2}

Table 5. Results from chapter 3. First line N_s as defined in (3.5), second line gives Γ^s (3.11), the third shows the coupling constant as defined in (3.15).

lattice distortions are given in Table 4. All numerical calculations have been done by means of the same program for a digital computer, where only the data have been changed.

The errors that will be done neglecting polarisation effects and lattice distortion effects by setting $\gamma = 0$ can be seen from Table 2, column 4, and Table 3, line 3. Though the electron dipole interaction energy is only of order 10^{-2} eV the total energy varies on about 25%.

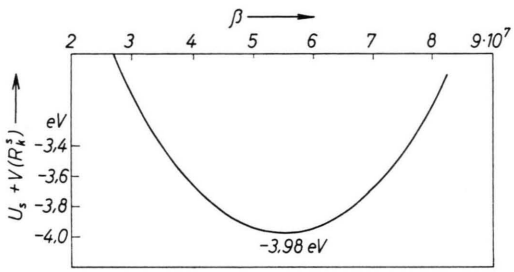

Fig. 3. Energy expectation value as a function of the variational parameter β (for KCl). Calculation for fixed lattice distortion
$y_1 = -3.98 \times 10^{-10}$ cm^{-1},
$y_2 = -1.34 \times 10^{-10}$ cm^{-1},
$y_3 = +0.36 \times 10^{-10}$ cm^{-1}.

Acknowledgments

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Appendix A

During the reduction of the n-electron problem, we have to express quantum mechanical energy expectation values by classical terms. All this terms lead to one type of integral, which is calculated within this paragraph for the example on a Li^+ ion.

The integral that should be evaluated is

$$\int \frac{\Psi^{n*}_{k\beta}(r_{k\beta})\,\Psi^{n}_{k\beta}(r_{k\beta})}{|r_{k\beta}-R|}\,\mathrm{d}r_{k\beta}\,. \tag{A.1}$$

The origin of the coordinate system is chosen to be at $R = \boldsymbol{O}$.

For convenience we then introduce the relative coordinates of the electron $X_{k\beta}$ with respect to the nucleus k.

$$r_{k\beta} = R_k + X_{k\beta}\,. \tag{A.2}$$

We now expand $1/|X_{k\beta} - (R - R_k)|$ into spherical harmonics

$$\frac{1}{|X_{k\beta}-(R-R_k)|} = \sum_{l=0}^{\infty} \frac{|X_{k\beta}|^l}{|R-R_k|^{l+1}} \cdot P_l(\cos\vartheta_\beta), \qquad |X_{k\beta}| \ll |R-R_k| \tag{A.3}$$

where $\cos\vartheta_\beta$ is given by

$$\cos\vartheta_\beta = \frac{(R-R_k)\,X_{k\beta}}{|R-R_k|\,|X_{k\beta}|}\,. \tag{A.4}$$

To second order in $|R-R_k|^{-1}$ we find for (A.3)

$$\frac{1}{|X_{k\beta}-(R-R_k)|} = \frac{1}{|R-R_k|} + \frac{X_{k\beta}(R-R_k)}{|R-R_k|^3}\,. \tag{A.5}$$

Now, we substitute (A.5) into (A.1)

$$\int \frac{\Psi^{n*}_{k\beta}(r_{k\beta})\,\Psi^{n}_{k\beta}(r_{k\beta})}{|r_{k\beta}-R|}\,\mathrm{d}r_{k\beta} = \frac{1}{|R-R_k|} + \int \Psi^{n*}_{k\beta}(r_{k\beta})\,\frac{X_{k\beta}(R-R_k)}{|R-R_k|^3}\,\Psi^{n}_{k\beta}(r_{k\beta})\,\mathrm{d}r_{k\beta}\,. \tag{A.6}$$

When we assume $\Psi^n_{k\beta}$ to be a linear combination of the free ion ground state orbital and the first excited state wave functions, we can evaluate the integral easily.

Since k shall denote a Li^+ ion we have

$$\Psi^n_{k\beta}(r_{k\beta}) \sim \tilde{\psi}^s(X_{k\beta}) + \sum_\nu f^\nu_{k\beta}\,\tilde{\psi}^\nu_{k\beta}(X_{k\beta}), \qquad \beta = 1, 2\,. \tag{A.7}$$

The polar axis of the $X_{k\beta}$ coordinate system is chosen to be inclined by an angle ϑ_0 with respect to the $(R-R_k)$ direction. In this coordinate system we find for the second term of (A.5)

$$\frac{X_{k\beta}(R-R_k)}{|R-R_k|^3} = \frac{|X_{k\beta}|\cdot\cos(\vartheta_0-\vartheta_\beta)}{|R-R_k|^2}\,. \tag{A.8}$$

We now assume the $\tilde{\psi}^{\nu}$ to be hydrogen like wave functions

$$\begin{aligned}
\tilde{\psi}^{1s}(X_{k\beta}) &= z_1^{3/2}\cdot 2\cdot\exp(-z_1\cdot|X_{k\beta}|)\times(1/4\pi)^{1/2},\\
\tilde{\psi}^{2s}(X_{k\beta}) &= (\tfrac{1}{2}z_2)^{3/2}(2-z_2|X_{k\beta}|)\exp(-\tfrac{1}{2}z_5|X_{k\beta}|)\times(1/4\pi)^{1/2},\\
\tilde{\psi}^{2p0}(X_{k\beta}) &= (\tfrac{1}{2}z_3)^{3/2}(z_3|X_{k\beta}|/\sqrt{3})\exp(-\tfrac{1}{2}z_2|X_{k\beta}|)\times(3/4\pi)^{1/2}\cdot\cos\vartheta_\beta,\\
\tilde{\psi}^{2p+1}(X_{k\beta}) &= (\tfrac{1}{2}z_4)^{3/2}(z_4|X_{k\beta}|/\sqrt{3})\exp(-\tfrac{1}{2}z_3|X_{k\beta}|)\times(3/8\pi)^{1/2}\cdot\sin\vartheta_\beta\cdot\exp(i\Phi_\beta),\\
\tilde{\psi}^{2p-1}(X_{k\beta}) &= (\tfrac{1}{2}z_5)^{3/2}(z_5|X_{k\beta}|/\sqrt{3})\exp(-\tfrac{1}{2}z_4|X_{k\beta}|)\times(3/8\pi)^{1/2}\cdot\sin\vartheta_\beta\cdot\exp(-i\Phi_\beta).
\end{aligned}\tag{A.9}$$

In the integral (A.6) every function (A.9) can combine with every other but by symmetry arguments most of them do vanish.

The only non vanishing terms combine a s-function and a p-function. We therefore first carry out the angular integration.

$$(\sqrt{3}/4\pi)\int(\cos\vartheta_0\cos\vartheta_\beta+\sin\vartheta_0\sin\vartheta_\beta)\cos\vartheta_\beta(\sin\vartheta_\beta\,\mathrm{d}\vartheta_\beta)\,\mathrm{d}\Phi_\beta=\sqrt{3}\cos\vartheta_0. \tag{A.10a}$$

The radial integration gives for an 1s and a 2p function

$$c_{12}\cdot f^{2p}_{k\beta} \tag{A.10b}$$

and for a 2s and 2p function

$$c_{22}\cdot f^{2s}_{k\beta}\cdot f^{2p}_{k\beta} \tag{A.10c}$$

where c_{12} and c_{22} are constants depending on the parameters z_1, z_2 and z_3. With

$$m_{k\beta}=f^{2p}_{k\beta}\sqrt{3}(c_{12}+c_{22}f^{2s}_{k\beta}) \tag{A.11}$$

we write for (A.1)

$$\int\frac{\Psi^{n*}_{k\beta}(r_{k\beta})\,\Psi^{n}_{k\beta}(r_{k\beta})}{|r_{k\beta}-R|}\,\mathrm{d}r_{k\beta}=\frac{1}{|R-R_k|}+\frac{m_{k\beta}\cdot\cos\vartheta_0}{|R-R_k|^2}. \tag{A.12}$$

We see by (A.10) – (A.12) that the excitation of higher electronic states is equivalent to polarization effects and we can express the influence of one electronic wave function on another wave function by a point charge with the potential

$$1/|R-R_k| \tag{A.13}$$

and a dipole with the potential

$$m_k\cdot(R-R_k)/|R-R_k|^3 \tag{A.14}$$

Collecting all interaction terms of two ions, we therefore approximate the interaction expectation value by

$$\frac{a_i\,a_k}{|R_i-R_k|}+\frac{m_i(R_k-R_i)}{|R_k-R_i|^3}+\frac{m_k(R_i-R_k)}{|R_i-R_k|^3}+m_i\bigtriangledown_i\frac{m_k(R_i-R_k)}{|R_i-R_k|^3}+\frac{b}{|R_i-R_k|^\eta}. \tag{A.15}$$

The first term gives the point charge interactions the second two terms give the point charge-dipole interaction, the next term denotes dipole-dipole interactions and the last term is taken to approximate the exchange interaction [4].

Appendix B [17]

In a free ion k of polarizability α_k a homogenous electric field induces an electric moment m_k

$$m_k=\alpha_k\cdot\boldsymbol{E}(R_k). \tag{B.1}$$

This linear polarization law, exactly valid for homogenous fields only, will also be used as an approximation in the neighbourhood of the ions even though the field varies strongly.

As we mentioned above, only the fields that do not have the symmetry of a periodic regular lattice give cause to polarization effects. We therefore devide the potential of the total field $\Phi(x)$ into one part having the symmetry of the perfect lattice

$$\Phi_0(x)=\sum_{j=1}\frac{a_j}{|x-R^\circ_j|} \tag{B.2}$$

and the perturbation potential $\Phi_s(x)$

$$\Phi_s(x):=\Phi(x)-\Phi_0(x). \tag{B.3}$$

The polarizing field is formed by the field $-\bigtriangledown\Phi_s$ and the dipoles m_k. With (B.1) we have

$$m_k=-\alpha_k\bigtriangledown_{x=R_k}\left(\Phi_s(x)+\sum_{l(\neq k)}\frac{m_l(x-R^\circ_l)}{|x-R^\circ_j|^3}\right). \tag{B.4}$$

The polarization dipoles are approximately localized at the regular lattice sites R°_k.

To solve the system of equations (B.4) an iteration process is carried out. The first order approximation is found by inserting free ion orbitals, that is, non polarized ions or $m_l^{(0)}=0$. Then from (B.4) it follows that

$$m^{(1)}{}_k=-\alpha_k\bigtriangledown\Phi_s(x) \tag{B.5}$$

[17] The following is a revised calculation of that given by H. Rampacher, Z. Naturforschg. **17 a**, 1057 [1962].

and the first order polarization potential is

$$\varphi^{(1)}(x) = \Phi_s(x) + \sum_{l(\neq k)} \frac{m^{(1)}{}_l (x - R^\circ{}_l)}{|x - R^\circ{}_l|^3} . \quad \text{(B.6)}$$

Now the sum in (B.6) is transformed into an integral which is extended over the entire crystal with exception of a sphere centered on $R^\circ{}_k$ with the radius r_a.

If we use an average polarizability

$$\alpha = \tfrac{1}{2} (\alpha_+ + \alpha_-)$$

we obtain

$$\varphi^{(1)}{}_m(x) = -\frac{\alpha}{d^3} \int dx' \left(\nabla_{x'} \Phi_s(x') \nabla_{x'} \frac{1}{|x - x'|} \right) \quad \text{(B.7)}$$

(d^3 is the volume element).

With the aid of GREEN's formula we find for (B.7) [18, 19]

$$\varphi^{(1)}{}_m(x) = -\frac{\alpha}{d^3} \int\limits_{|x' - R^\circ{}_k| = r_a} ds' \left(\Phi_s(x') \nabla \frac{1}{|x - x'|} \right) . \quad \text{(B.8)}$$

If Φ_s falls off to zero, the integral on the outer surface can be neglected. For $x = R^\circ{}_k$ we obtain

$$\varphi^{(1)}{}_m(R^\circ{}_k) = -\frac{\alpha}{d^3} \int d\Omega \, \Phi_s(x') \cong -\frac{4\pi\alpha}{d^3} \Phi_s(R^\circ{}_k) \quad \text{(B.9a)}$$

or

$$\varphi^{(1)}(R^\circ{}_k) = \Phi_s(R^\circ{}_k) [1 + \gamma] . \quad \text{(B.9b)}$$

With

$$\gamma = -4\pi\alpha/d^3 \quad \text{(B.10)}$$

we get for $m^{(2)}{}_k$

$$m^{(2)}{}_k = -\alpha_k \nabla \left(\Phi_s(x) + \gamma \Phi_s(x) \right)|_{x = R^\circ{}_k} \quad \text{(B.11)}$$

and therefore for $|\gamma| < 1$

$$\varphi(x) = \varphi^{(\infty)}(x) = (1/(1 - \gamma)) \Phi_s(x), \quad \text{(B.12a)}$$

$$m_k = -(\alpha_k/(1 - \gamma)) \nabla \Phi_s(x)|_{x = R^\circ{}_k} , \quad \text{(B.13)}$$

$$\varphi_m(x) = (\gamma/(1 - \gamma)) \Phi_s(x) . \quad \text{(B.12b)}$$

There are $N = 1/d^3$ particles in one macroscopic volume element and therefore, from (B.13) the polarization of this element is

$$\boldsymbol{P}(x) = \frac{\alpha}{d^3} \frac{1}{1 + (4\pi\alpha/d^3)} \boldsymbol{E}_s(x) \quad \text{(B.14)}$$

where $\boldsymbol{E}_s$ is the polarizing field

$$\boldsymbol{E}_s(x) = -\nabla \Phi_s(x) .$$

The Eqs. (B.8) to (B.14) hold only under the condition that Φ_s falls off to zero.

[18] That GREEN's formula can be used here was shown by H. KÖNIG, Jahresber. Dtsch. Math. Verein. **1964**, 66 („Ein einfacher Beweis für den GAUSSschen Integralsatz").

[19] Except for a set of LEBESGUES-measure zero the right hand side is assumed to be integrable.