Electronic Structure of a Single Hydrogen Centre in Magnesium Crystals

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In the present work, the problem "hydrogen storage in metals" is treated with the aid of the so-called New Tamm-Dancoff (NTD) procedure. We employ this method in lowest approximation for the evaluation of the electronic energy difference eigenvalue between a metal crystal with and without hydrogen centre. As an example we use Magnesium with hexagonal structure. For this system we calculate the difference eigenvalue with dependence on the displacement of the nearest neighbours and next nearest neighbours of the hydrogen centre, respectively. Finally we calculate the radial electron density distribution in the environment of the proton.

1. Introduction

For the microscopic description of hydrogen storage in metals a method based on "first principles" was introduced in [1]. The possibility of dividing up the storage into an electronic part and an elastic part is shown there. This paper deals with the electronic part exclusively. The elastic part is the topic of another examination [2].

The starting point for the evaluation of the electronic part of the storage energy is the many-body Schrödinger equation of the metal crystal disturbed by hydrogen atoms and the corresponding equation of the crystal without hydrogen centres, called reference system. An adiabatic decomposition of these Schrödinger problems yields an electronic system and a host lattice system. For the crystal with hydrogen atoms one obtains an additional protonic system. Our aim is to evaluate the electronic energy difference of the metal crystal with stored hydrogen atoms on the one hand, and the metal crystal without hydrogen atoms on the other hand.

The topic of the paper of Wahl et al. [1] is a procedure (called New Tamm-Dancoff (NTD) procedure) to determine such energy differences directly; that means, both electronic Schrödinger problems are united with the aid of an energy difference procedure and a following transformation yields a "functional equation". This functional equation has the form of a linear eigenvalue problem with the above mentioned energy difference as eigenvalue. In the present paper this difference problem is solved for a single hydrogen centre in the lowest approximation which is proposed in [1].

2. The General Conception

The starting point of our investigation is the nonlocal Schrödinger equation derived in [1] for the one centre problem in the lowest approximation. For this relation it is necessary to introduce some notations.

The coordinates are described in the following way:

$\boldsymbol{x}, \boldsymbol{z}$ electron coordinates,
$\boldsymbol{Y}$ proton coordinates,
$\boldsymbol{X} = \boldsymbol{X}_{\boldsymbol{m},i}$ coordinates of the host lattice disturbed by stored hydrogen atoms.

Then

$$V_{\mathrm{W}}(\boldsymbol{x}, \boldsymbol{X}) = \sum_{\boldsymbol{m},i} V(\boldsymbol{x} - \boldsymbol{X}_{\boldsymbol{m},i}) \tag{2.1}$$

is the crystal potential, and

$$V_{\mathrm{H}}(\boldsymbol{x}, \boldsymbol{Y}) = -\frac{e^2}{|\boldsymbol{x} - \boldsymbol{Y}|} \tag{2.2}$$

represents the potential of the hydrogen proton. In the following, the deformed metal crystal without hydrogen centres is denoted as reference system. The Hartree-Fock (HF) wavefunctions $\varphi_j(\boldsymbol{x})$ $(j = 1, \ldots, N)$ of the N metal electrons of this reference system suggest the definitions:

$$S_0(\boldsymbol{x}, \boldsymbol{x}') := \sum_{j=1}^{N} \varphi_j(\boldsymbol{x}) \cdot \varphi_j^*(\boldsymbol{x}')\,, \tag{2.3}$$

$$S_1(\boldsymbol{x}, \boldsymbol{x}') := \delta(\boldsymbol{x} - \boldsymbol{x}') - S_0(\boldsymbol{x}, \boldsymbol{x}')\,. \tag{2.4}$$

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$S_0(\boldsymbol{x},\boldsymbol{x}')$ and $S_1(\boldsymbol{x},\boldsymbol{x}')$ are orthogonal projection operators

$$\int S_i(\boldsymbol{x},\boldsymbol{z})\, S_j(\boldsymbol{z},\boldsymbol{x}')\, \mathrm{d}^3 z = S_i(\boldsymbol{x},\boldsymbol{x}')\, \delta_{ij}\,, \tag{2.5}$$

$$S_i(\boldsymbol{x},\boldsymbol{x}') = S_i^+(\boldsymbol{x},\boldsymbol{x}') = S_i^*(\boldsymbol{x}',\boldsymbol{x})\,, \quad i,j \in \{0, 1\}\,, \tag{2.6}$$

which split up the momentum space in occupied states (S_0) and unoccupied states (S_1):

$$S_0(\boldsymbol{x},\boldsymbol{x}') + S_1(\boldsymbol{x},\boldsymbol{x}') = \delta(\boldsymbol{x}-\boldsymbol{x}')\,. \tag{2.7}$$

By means of $S_0(\boldsymbol{x},\boldsymbol{x}')$ the HF-operator $D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X})$ of the metal electrons of the reference system may be described in the following way:

$$D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X}) = \Bigg[-\frac{\hbar^2}{2m}\Delta + V_{\mathrm{W}}(\boldsymbol{x},\boldsymbol{X}) + 2e^2 \int \mathrm{d}^3 x'' \frac{S_0(\boldsymbol{x}'',\boldsymbol{x}'')}{|\boldsymbol{x}-\boldsymbol{x}''|}\Bigg]\, \delta(\boldsymbol{x}-\boldsymbol{x}') - e^2 \frac{S_0(\boldsymbol{x},\boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|}\,. \tag{2.8}$$

$h(\boldsymbol{z})$ denotes the wavefunction of the additional hydrogen electron, while $w(\boldsymbol{X},\boldsymbol{Y})$ denotes the electronic energy difference eigenvalue between the host crystal with stored hydrogen centres and the reference system. As shown in [1], $h(\boldsymbol{z})$ satisfies the non-local Schrödinger equation

$$\begin{aligned} &S_1(\boldsymbol{z},\boldsymbol{x})\,[D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X}) + V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})\,\delta(\boldsymbol{x}-\boldsymbol{x}')] \\ &\quad \cdot S_1(\boldsymbol{x}',\boldsymbol{z}')\, h(\boldsymbol{z}') \\ &\quad = [\omega(\boldsymbol{X},\boldsymbol{Y}) - \mathrm{Tr}\,(V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})\, S_0(\boldsymbol{x},\boldsymbol{x})]\, h(\boldsymbol{z})\,. \end{aligned} \tag{2.9}$$

In the sense of an extended Einstein convention multiple arguments must be integrated.

The term

$$\mathrm{Tr}\,(V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})\, S_0(\boldsymbol{x},\boldsymbol{x})) = -e^2 \int \frac{2\,S_0(\boldsymbol{x},\boldsymbol{x})}{|\boldsymbol{x}-\boldsymbol{Y}|}\, \mathrm{d}^3 x \tag{2.10}$$

is constant with respect to the electron and host lattice coordinates.

The energy difference of the additional electron in the field of the screened proton and the screened host lattice on the one hand and the reference system on the other is

$$\lambda(\boldsymbol{X},\boldsymbol{Y}) := \omega(\boldsymbol{X},\boldsymbol{Y}) - \mathrm{Tr}\,(V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})\, S_0(\boldsymbol{x},\boldsymbol{x}'))\,. \tag{2.11}$$

Because the HF-solutions $\varphi_j(\boldsymbol{x})$ (2.3) of a distorted lattice are not known, the Bloch functions $b_{\boldsymbol{k},n}(\boldsymbol{x})$ of the ideal lattice are used as an approximation:

$$S_0(\boldsymbol{x},\boldsymbol{x}') \approx \sum_{\substack{\boldsymbol{k},n \\ \text{occ.}}} b_{\boldsymbol{k},n}(\boldsymbol{x})\, b^*_{\boldsymbol{k},n}(\boldsymbol{x}')\,. \tag{2.12}$$

Starting with this approximation it is advantageous to incorporate the crystal potential of the ideal host lattice

$$V^0_{\mathrm{W}}(\boldsymbol{x},\boldsymbol{X}) = \sum_{\boldsymbol{m},i} V(\boldsymbol{x} - \boldsymbol{X}^0_{\boldsymbol{m},i}) \tag{2.13}$$

in the HF-operator (2.8) formally:

$$D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X}) = D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X}^0) + V_{\mathrm{W}}(\boldsymbol{x},\boldsymbol{X}) - V^0_{\mathrm{W}}(\boldsymbol{x},\boldsymbol{X}^0)\,. \tag{2.14}$$

This results in the HF-operator $D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X}^0)$ of the ideal crystal and a difference potential

$$V_{\mathrm{D}}(\boldsymbol{x}) = V_{\mathrm{W}}(\boldsymbol{x},\boldsymbol{X}) - V^0_{\mathrm{W}}(\boldsymbol{x},\boldsymbol{X}^0)\,. \tag{2.15}$$

Multiplication of (2.9) from the left with S_1 and use of the relation

$$S_1(\boldsymbol{z},\boldsymbol{x}')\, D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X}^0) = D(\boldsymbol{z},\boldsymbol{x}',\boldsymbol{X}^0)\, S_1(\boldsymbol{x}',\boldsymbol{x})\,, \tag{2.16}$$

which is easily verified, yields the effective one-particle equation for the hydrogen electron

$$\begin{aligned} &D(\boldsymbol{z},\boldsymbol{x},\boldsymbol{X}^0)\, \varphi(\boldsymbol{x}) + S_1(\boldsymbol{z},\boldsymbol{x})\, V_{\mathrm{D}}(\boldsymbol{x})\, \varphi(\boldsymbol{x}) \\ &\quad + S_1(\boldsymbol{z},\boldsymbol{x})\, V_{\mathrm{H}}(\boldsymbol{x})\, \varphi(\boldsymbol{x}) = \lambda(\boldsymbol{X},\boldsymbol{Y})\, \varphi(\boldsymbol{z})\,. \end{aligned} \tag{2.17}$$

In (2.17) we have introduced the abbreviation

$$\varphi(\boldsymbol{z}) = S_1(\boldsymbol{z},\boldsymbol{z}')\, h(\boldsymbol{z}')\,. \tag{2.18}$$

Ignoring the exchange interaction yields an additional simplification of (2.17). $D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X}^0)$ is therefore reduced to a Hartree operator

$$D^{\mathrm{H}}(\boldsymbol{z},\boldsymbol{x},\boldsymbol{X}^0) = \Bigg[-\frac{\hbar^2}{2m}\Delta + V^0_{\mathrm{W}}(\boldsymbol{x},\boldsymbol{X}^0) + 2e^2 \int \frac{S_0(\boldsymbol{x}'',\boldsymbol{x}'')}{|\boldsymbol{x}-\boldsymbol{x}''|}\, \mathrm{d}^3 x''\Bigg]\, \delta(\boldsymbol{z}-\boldsymbol{x})\,. \tag{2.19}$$

Finally, the one-particle equation must be solved:

$$\begin{aligned} &D^{\mathrm{H}}(\boldsymbol{z},\boldsymbol{x},\boldsymbol{X}^0)\, \varphi(\boldsymbol{x}) + S_1(\boldsymbol{z},\boldsymbol{x})\, V_{\mathrm{D}}(\boldsymbol{x})\, \varphi(\boldsymbol{x}) \\ &\quad + S_1(\boldsymbol{z},\boldsymbol{x})\, V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})\, \varphi(\boldsymbol{x}) = \lambda(\boldsymbol{X},\boldsymbol{Y})\, \varphi(\boldsymbol{z})\,. \end{aligned} \tag{2.20}$$

Besides the term D^{H}, the screened difference potential $S_1 V_{\mathrm{D}}$ as well as the screened proton potential are important.

3. The Algebraic Problem and its Solution

In the following discussion we refer to the hexagonal lattice-structure. The Magnesium crystal is close to this lattice type ($c/a = \sqrt{8/3} = 1.633$, $c/a_{\mathrm{Mg}} = 1.623$). The interstitial lattice positions are of tetrahedron and octahedron structure, respectively. For energetical reasons the tetrahedron structure is preferred. Therefore, we assume tetrahedron positions for the protons in our model.

Furthermore we are treating a metal crystal with a very low hydrogen concentration (α-phase) so that we may ignore any interaction between the hydrogen centres, i.e. for our model it is sufficient to study one single hydrogen atom. As the origin of the coordinate system we take the centre of the tetrahedron.

Assuming the localization of the electron at the centre, the function φ may be expanded with respect to hydrogen wave functions

$$\varphi(z) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=l+1}^{\infty} b_{nlm}\, Y_l^m(\Omega_z)\, \chi_{nl}(z)\,. \tag{3.1}$$

We may ignore the spin coordinates, because in (2.20) no spin-spin interaction is included.

An approximation of the Bloch functions by means of plane waves and a transition from the k-summation to a k-integration, (2.12), yields

$$\begin{aligned} S_0(\boldsymbol{z},\boldsymbol{x}) &= \frac{1}{(2\pi)^3} \int \Theta(k_{\mathrm{F}} - |\boldsymbol{k}|)\, e^{i\boldsymbol{k}(\boldsymbol{z}-\boldsymbol{x})}\, \mathrm{d}^3k\,, \\ S_1(\boldsymbol{z},\boldsymbol{x}) &= \frac{1}{(2\pi)^3} \int \Theta(|\boldsymbol{k}| - k_{\mathrm{F}})\, e^{i\boldsymbol{k}(\boldsymbol{z}-\boldsymbol{x})}\, \mathrm{d}^3k\,. \end{aligned} \tag{3.2}$$

The addition and subtraction of a Coulomb term $V_{\mathrm{H}}(z) = -e^2/z$ for the additional electron and application of relation (2.7) leads to

$$\begin{aligned} &\left\{\frac{-\hbar^2}{2m}\Delta + V_{\mathrm{H}}(\boldsymbol{z})\right\} \varphi(\boldsymbol{z}) + \{V_{\mathrm{H}}(\boldsymbol{z},\boldsymbol{Y}) - V_{\mathrm{H}}(\boldsymbol{z})\}\, \varphi(\boldsymbol{z}) \\ &\quad + S_0(\boldsymbol{z},\boldsymbol{x})\, V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})\, \varphi(\boldsymbol{x}) \\ &\quad + \left\{V_{\mathrm{W}}^0(\boldsymbol{z},\boldsymbol{X}) + 2e^2 \int \frac{S_0(\boldsymbol{x}',\boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|}\, \mathrm{d}^3x'\right\} \varphi(\boldsymbol{z}) \\ &\quad + V_{\mathrm{D}}(\boldsymbol{z})\, \varphi(\boldsymbol{z}) - S_0(\boldsymbol{z},\boldsymbol{x})\, V_{\mathrm{D}}(\boldsymbol{x})\, \varphi(\boldsymbol{x}) \\ &= \lambda(\boldsymbol{X},\boldsymbol{Y})\, \varphi(\boldsymbol{z})\,. \end{aligned} \tag{3.3}$$

The first term describes a pure hydrogen problem.

Inserting (3.1) and (3.2) in (3.3), a following multiplication with hydrogen wavefunctions from the left results in the algebraic system of equations (in atomic units, Einstein convention)

$$\begin{aligned} &-\frac{1}{n^2} b_{l_2n_2m_2} + C\,U(\boldsymbol{Y})_{l_2n_2m_2}^{l_1n_1m_1} b_{l_1n_1m_1} \\ &\quad + C\,A_{l_2n_2m_2}^{l_1n_1m_1}(\boldsymbol{Y})\, b_{l_1n_1m_1} + G_{l_2n_2m_2}^{l_1n_1m_1} b_{l_1n_1m_1} \\ &\quad + D\,U_{l_2n_2m_2}^{l_1n_1m_1}(\boldsymbol{X})\, b_{l_1n_1m_1} + D\,A_{l_2n_2m_2}^{l_1n_1m_1} b_{l_1n_1m_1} \\ &= \Lambda(\boldsymbol{X},\boldsymbol{Y})\, b_{l_2n_2m_2}\,. \end{aligned} \tag{3.4}$$

The abbreviations and their meanings are in detail:

$$\Lambda(\boldsymbol{X},\boldsymbol{Y}) = \frac{\lambda(\boldsymbol{X},\boldsymbol{Y})}{E_0} \tag{3.5}$$

with the Rydberg energy $E_0 = 13.6$ eV,

$$\begin{aligned} &C\,U(\boldsymbol{Y})_{l_2n_2m_2}^{l_1n_1m_1} \\ &\quad = -2 \int \mathrm{d}^3z\, \chi_{n_2l_2}(z)\, z^2 \left(\frac{1}{|\boldsymbol{z}-\boldsymbol{Y}|} - \frac{1}{|\boldsymbol{z}|}\right) \chi_{n_1l_1}(z) \\ &\qquad \cdot Y_{l_2}^{m_2^*}(\Omega_z)\, Y_{l_1}^{m_1}(\Omega_z)\,, \end{aligned} \tag{3.6}$$

In case the proton is situated in the centre of the tetrahedron ($\boldsymbol{Y} = 0$), this term is reduced to zero. The influence of the shifting of the proton is described by this term.

$$\begin{aligned} &C\,A(\boldsymbol{Y})_{l_2n_2m_2}^{l_1n_1m_1} \\ &\quad = \frac{2}{(2\pi)^3} \int \mathrm{d}^3z \int \mathrm{d}^3x \int \mathrm{d}^3k\, \Theta(k_{\mathrm{F}} - |\boldsymbol{k}|)\, e^{i\boldsymbol{k}(\boldsymbol{z}-\boldsymbol{x})} \\ &\qquad \cdot e^{i\boldsymbol{k}(\boldsymbol{z}-\boldsymbol{x})} \frac{1}{|\boldsymbol{x}-\boldsymbol{Y}|}\, \chi_{n_2l_2}(z)\, z^2\, \chi_{n_1l_1}(x) \\ &\qquad \cdot Y_{l_2}^{m_2^*}(\Omega_z)\, Y_{l_1}^{m_1}(\Omega_x)\,. \end{aligned} \tag{3.7}$$

This equation represents the effect of the screening of the electron-proton interaction.

$$\begin{aligned} G_{l_2n_2m_2}^{l_1n_1m_1} &= \int \mathrm{d}^3z\, \mathring{A}(\boldsymbol{z})\, \chi_{n_2l_2}(z)\, z^2\, \chi_{n_1l_1}(z) \\ &\quad \cdot Y_{l_2}^{m_2^*}(\Omega_z)\, Y_{l_1}^{m_1}(\Omega_x) \end{aligned} \tag{3.8}$$

with $\mathring{A}(\boldsymbol{z}) = \dfrac{1}{E_0} A(\boldsymbol{z})$ and

$$A(\boldsymbol{z}) = V_{\mathrm{W}}^0(\boldsymbol{z},\boldsymbol{X}) + 2e^2 \int \frac{S_0(\boldsymbol{x}',\boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|}\, \mathrm{d}^3x'\,. \tag{3.9}$$

$A(\boldsymbol{z})$ and the corresponding matrix element $G_{l_2n_2m_2}^{l_1n_1m_1}$ describe the interaction of the additional electron with the ideal lattice and the valence electrons respectively.

Inserting $S_0(\boldsymbol{y},\boldsymbol{y})$ (3.2) we get

$$A(\boldsymbol{z}) = -e\left(\sum_{\boldsymbol{m},i} \frac{e_i}{|\boldsymbol{z}-\boldsymbol{X}_{\boldsymbol{m},i}^0|} + \int_{\Omega} \frac{\varrho^e}{|\boldsymbol{z}-\boldsymbol{y}|}\, \mathrm{d}^3y\right) \tag{3.10}$$

with

$$\varrho^e = -\frac{e_i k_{\mathrm{F}}^3}{3\pi^2}\,. \tag{3.11}$$

ϱ^e is the electronic charge density and e_i the valence charge of the host lattice atoms. The following discussion is analogous to Haug [3]. For one unit cell in the i-th sublattice the electronic charge density ϱ^e is defined

$$\varrho^e_{\boldsymbol{m},i} = \begin{cases} \varrho^e_i & \boldsymbol{x} \in \text{of the unit cell indexed with } \boldsymbol{m} \text{ and } i \\ 0 & \text{otherwise}. \end{cases}$$

If the positive charge of the ions is taken into account, this leads to a zero net charge. With the substitutions

$$\boldsymbol{X}^0_{\boldsymbol{m},i} = \boldsymbol{m} + \boldsymbol{z}_i \tag{3.12}$$

and

$$\boldsymbol{y} = \boldsymbol{m} + \boldsymbol{z}_i + \boldsymbol{s} \tag{3.13}$$

we get

$$A(\boldsymbol{z}) = -e \sum_{\boldsymbol{m},i} \left(\frac{e_i}{|\boldsymbol{z} - \boldsymbol{m} - \boldsymbol{z}_i|} + \int_{\Omega_0} \frac{\varrho^e}{|\boldsymbol{z} - \boldsymbol{m} - \boldsymbol{z}_i - \boldsymbol{s}|} \, \mathrm{d}^3 s \right). \tag{3.14}$$

Because there is no net charge in the unit cell a Fourier-transformation leads to

$$A(\boldsymbol{z}) = -e \sum_i \frac{4\pi}{\Omega_0} \sum_{\boldsymbol{g} \neq 0} \frac{e_i \, e^{i \boldsymbol{g}(\boldsymbol{z} - \boldsymbol{z}_i)}}{|\boldsymbol{g}^2|}. \tag{3.15}$$

The convergence behaviour of this term is very bad. This causes no difficulties, because we are interested only in the term (3.8) which contains $A(\boldsymbol{z})$ in an implicit manner. Based on the product of radial hydrogen wavefunctions, the convergence behaviour is better.

$$D\,U^{l_1 n_1 m_1}_{l_2 n_2 m_2}(\boldsymbol{X}) = -4 \int \mathrm{d}^3 z \, \chi_{n_2 l_2}(z) \, z^2 \, V_{\mathrm{D}}(\boldsymbol{z}) \, \chi_{n_1 l_1}(z) \cdot Y^{m_2^*}_{l_2}(\Omega_z) \, Y^{m_1}_{l_1}(\Omega_z), \tag{3.16}$$

$$D\,A^{l_1 n_1 m_1}_{l_2 n_2 m_2}(\boldsymbol{X}) = \frac{4}{(2\pi)^3} \int \mathrm{d}^3 z \int \mathrm{d}^3 x \int \mathrm{d}^3 k \, \Theta(k_{\mathrm{F}} - |\boldsymbol{k}|) \, \chi_{n_2 l_2}(z) \, z^2 \cdot e^{i \boldsymbol{k}(\boldsymbol{z} - \boldsymbol{x})} \, V_{\mathrm{D}}(\boldsymbol{z}) \, \chi_{n_1 l_1}(x) \, Y^{m_2^*}_{l_2}(\Omega_z) \, Y^{m_1}_{l_1}(\Omega_x). \tag{3.17}$$

$D\,U^{l_1 n_1 m_1}_{l_2 n_2 m_2}$ is the matrix element of the pure difference potential and $D\,A^{l_1 n_1 m_1}_{l_2 n_2 m_2}$ is the matrix element of the screening of the difference potential.

In the following, only the nearest neighbours and next nearest neighbours are considered. That leads to

$$V_{\mathrm{D}}(\boldsymbol{x}) = \sum_{\boldsymbol{m},i} \left(V(\boldsymbol{x} - \boldsymbol{X}_{\boldsymbol{m},i}) - V(\boldsymbol{x} - \boldsymbol{X}^0_{\boldsymbol{m},i}) \right) \approx \sum_{j=0}^{13} \left(V(\boldsymbol{x} - \boldsymbol{X}_j) - V(\boldsymbol{x} - \boldsymbol{X}^0_j) \right). \tag{3.18}$$

Assuming a radial displacement, the coordinates of the host lattice atoms are

$$\boldsymbol{X}^k_j = \boldsymbol{X}^{0k}_j + s_k \, \boldsymbol{e}_j, \quad \begin{array}{l} k \in [0, 1]; \\ j \in [0, 3], \; k = 0; \\ j \in [4, 13], \; k = 1. \end{array} \tag{3.19}$$

The displacements s_k are considerably smaller than the distance hydrogen centre – host lattice atom. Therefore, a Taylor expansion is feasible which is broken off after the first term.

$$V_{\mathrm{D}}(x) \approx -\sum_{j=0}^{3} s_0 \left. \frac{\partial V(\boldsymbol{x} - \boldsymbol{X}^0_j - s_0 \boldsymbol{e}_j)}{\partial s_0} \right|_{s_0 = 0} - \sum_{j=4}^{13} s_1 \left. \frac{\partial V(\boldsymbol{x} - \boldsymbol{X}^0_j - s_1 \boldsymbol{e}_j)}{\partial s_1} \right|_{s_1 = 0}. \tag{3.20}$$

The following abbreviations are introduced for the terms of the difference potential describing the next neighbours:

$$\mathrm{d}u\,1^{l_1 n_1 m_1}_{l_2 n_2 m_2}(s_0) = -4 \sum_{j=0}^{3} \int \mathrm{d}^3 z \, \chi_{n_2 l_2}(z) \, z^2 \left. \frac{\partial V(\boldsymbol{x} - \boldsymbol{X}^0_j - s_0 \boldsymbol{e}_j)}{\partial s_0} \right|_{s_0 = 0} \cdot \chi_{n_1 l_1}(z) \, Y^{m_2^*}_{l_2}(\Omega_z) \, Y^{m_1}_{l_1}(\Omega_z); \tag{3.21}$$

$$\mathrm{d}a\,1^{l_1 n_1 m_1}_{l_2 n_2 m_2}(s_0) = \frac{4}{(2\pi)^3} \sum_{j=0}^{3} \int \mathrm{d}^3 z \int \mathrm{d}^3 x \int \mathrm{d}^3 k \, \Theta(k_{\mathrm{F}} - |\boldsymbol{k}|) \, \chi_{n_2 l_2}(z) \, z^2 \cdot e^{i \boldsymbol{k}(\boldsymbol{z} - \boldsymbol{x})} \left. \frac{\partial V(\boldsymbol{x} - \boldsymbol{X}^0_j - s_0 \boldsymbol{e}_j)}{\partial s_0} \right|_{s_0 = 0} \chi_{n_1 l_1}(x) \cdot Y^{m_2^*}_{l_2}(\Omega_z) \, Y^{m_1}_{l_1}(\Omega_x). \tag{3.22}$$

$\mathrm{d}u\,1^{l_1 n_1 m_1}_{l_2 n_2 m_2}$ is the matrix element of the difference potential involving next neighbours. The dependence on the equilibrium positions $\boldsymbol{x}$ can be transformed into a dependence on the displacement s_0 with respect to the ideal lattice.

Then $\mathrm{d}a\,1^{l_1 n_1 m_1}_{l_2 n_2 m_2}(s_0)$ describes the influence of the screening on the difference potential.

For the next nearest neighbours, the summation j runs from 4 to 13. The corresponding terms are abbreviated with $\mathrm{d}u\,2^{l_1 n_1 m_1}_{l_2 n_2 m_2}(s_1)$ and $\mathrm{d}a\,2^{l_1 n_1 m_1}_{l_2 n_2 m_2}(s_1)$, respectively. s_1 is the displacement of the next nearest neighbours from their ideal lattice points.

With these abbreviations we obtain the algebraic equation

$$\begin{aligned} -\frac{1}{n^2} b_{l_2 n_2 m_2} &+ C\,U(\boldsymbol{Y})^{l_1 n_1 m_1}_{l_2 n_2 m_2} \, b_{l_1 n_1 m_1} \\ &+ C\,A^{l_1 n_1 m_1}_{l_2 n_2 m_2}(\boldsymbol{Y}) \, b_{l_1 n_1 m_1} + G^{l_1 n_1 m_1}_{l_2 n_2 m_2} \, b_{l_1 n_1 m_1} \\ &+ s_0 \, \mathrm{d}u\,1^{l_1 n_1 m_1}_{l_2 n_2 m_2}(s_0) \, b_{l_1 n_1 m_1} + s_0 \, \mathrm{d}a\,1^{l_1 n_1 m_1}_{l_2 n_2 m_2}(s_0) \, b_{l_1 n_1 m_1} \\ &+ s_1 \, \mathrm{d}u\,2^{l_1 n_1 m_1}_{l_2 n_2 m_2}(s_1) \, b_{l_1 n_1 m_1} + s_1 \, \mathrm{d}a\,2^{l_1 n_1 m_1}_{l_2 n_2 m_2}(s_1) \, b_{l_1 n_1 m_1} \\ = \Lambda(\boldsymbol{Y}, s_0, s_1) \, b_{l_2 n_2 m_2}. \end{aligned} \tag{3.23}$$

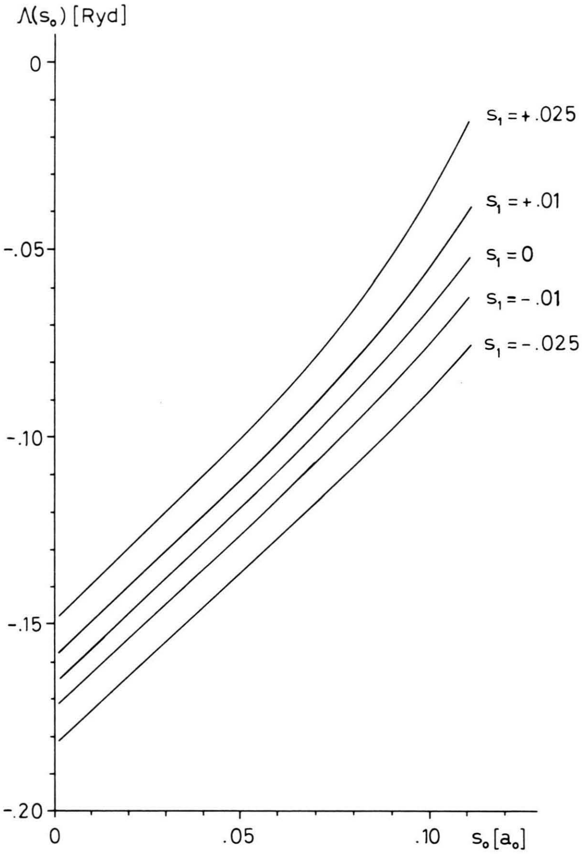

Fig. 1. The dependence of the energy difference eigenvalue Λ from the displacements s_0 of the next neighbours, for various values of the displacements s_1 of the next nearest neighbours.

The dependence of the energy difference eigenvalue Λ on the host lattice coordinates is transformed into a dependence on the displacements s_0 and s_1.

The solution of the difference problem (3.23) is illustrated in the Figs. 1 to 3*. All figures are based on the assumption that the proton is located in the centre of the tetrahedron ($\boldsymbol{Y} = 0$). In the diagrams 1 and 2 a plot of the electronic energy difference eigenvalue $\Lambda(\boldsymbol{Y}, s_0, s_1)$ is given. In the evaluation we have as parameters the radial displacement of the next neighbours and next nearest neighbours, respectively. Positive values of s_0 and s_1 belong to displacements which point away from the hydrogen centre. Analogously, the negative displacements point from the ideal lattice site to the hydrogen centre.

Figure 1 shows the dependence of $\Lambda(\boldsymbol{Y}, s_0, s_1)$ on s_0. The displacements s_1 of the next nearest neighbours are fixed.

In Fig. 2 the roles of s_0 and s_1 are exchanged. Now $\Lambda(\boldsymbol{Y}, s_0, s_1)$ is dependent on s_1 while s_0 is fixed. From these figures one can infer that, as the displacements s_0 and s_1 grow larger, the electronic bonding becomes weaker. Conversely, as s_0 and s_1 grow in the opposite direction, the bonding becomes stronger.

In Fig. 3 we can see a typical behaviour of the radial electron density distribution in the surroundings of the hydrogen centre.

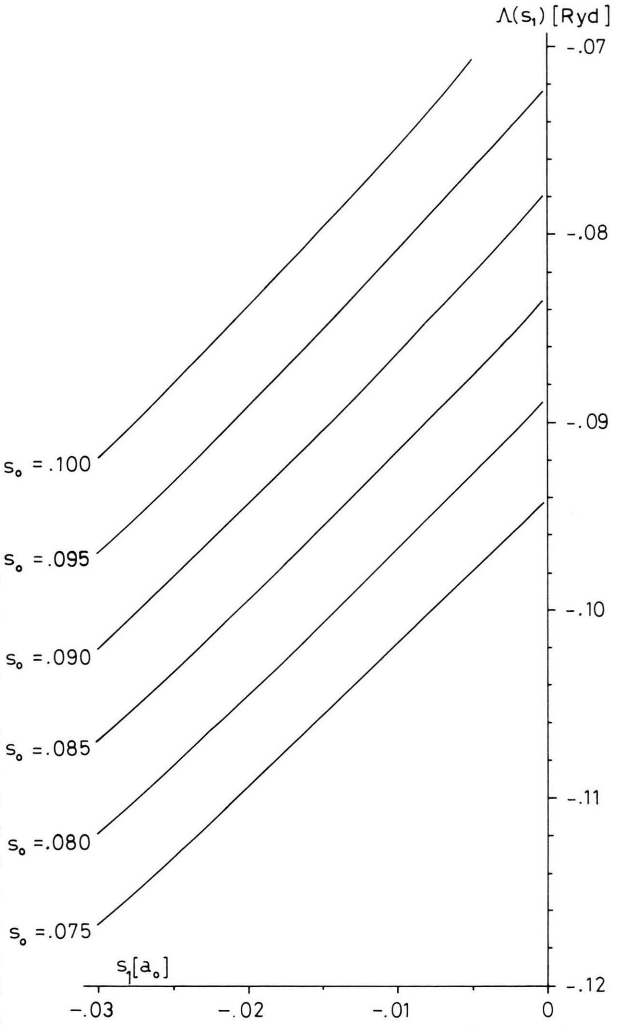

Fig. 2. The dependence of the energy difference eigenvalue Λ from the displacements s_1 of the next nearest neighbours, for various values of the displacements s_0 of the next neighbours.

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* For details concerning the calculations see [4].

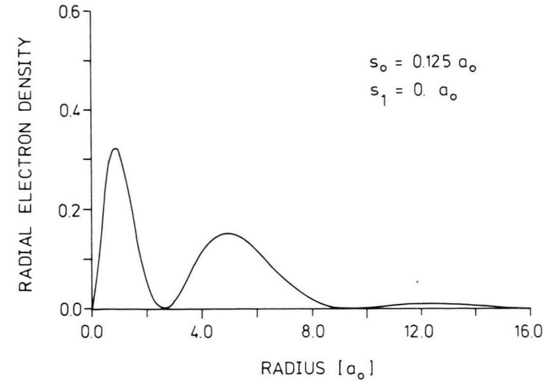

Fig. 3. The typical behaviour of the radial electron density distribution in the surroundings of the hydrogen center for two special values of the displacements of the next and next nearest neighbours.

The new equilibrium positions of the lattice ions can be calculated with the aid of a force equation. In this equation, the electronic influence (included in $\Lambda(\boldsymbol{Y}, s_0, s_1)$ and the elastic influence are of significance. The evaluation of these equilibrium positions and the corresponding volume extension are carried through by Bratschek et al. [2]. Thereby our results of $\Lambda(\boldsymbol{Y}, s_0, s_1)$ are employed. The new equilibrium positions are gained through a displacement of the next neighbours in a direction away from the hydrogen proton ($s_0 > 0$). The next nearest neighbours are shifted to the hydrogen centre ($s_1 < 0$). In this way, only the relevant regions of s_0 and s_1 are considered in Figs. 1 and 2.

The influence of a higher approximation in this formalism will be dealt with in a subsequent paper.

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