A Microscopic Theory of a Single Hydrogen Centre in a Magnesium Crystal *

M. Gnirß † and F. Wahl
Institut für Theoretische Physik, Universität Tübingen

Z. Naturforsch. **47a,** 733–747 (1992); received February 17, 1992

A microscopic theory of a single hydrogen center embedded in a magnesium crystal is presented. Starting with a many-particle Schrödinger equation, an adiabatic decoupling yields in an electronic system a protonic system and a host lattice system. The storage energy is defined to consist of an electronic part and lattice contributions. The electronic problem is treated with the help of a special energy difference procedure developed by Wahl et al. This procedure is applied in a higher approximation to calculate the electronic energy difference eigenvalue between a metal crystal with and without a hydrogen impurity. The lattice problem is treated in the classical harmonic approximation.

1. Introduction

A world wide shortage of energy is leading to a growth of interest in a hydrogen energy economy. Hydrogen is available in practically unlimited quantities, and it is in many points of views an ideal source of energy. Besides the production of hydrogen one of the main problems is the storage of hydrogen. For stationary purposes or for energy storage in vehicles, metal hydrides become more and more interesting.

There is a lot of experimental and technical knowledge of hydrogen storage in metal hydrides [1]. But the theoretical understanding is not complete. The group of Wahl is interested in a better theoretical understanding of metal hydrides. A theory is proposed which is mostly based only on a few first principles [2]. Supposing a model of noninteracting hydrogen interstitials at low concentration, we treat a single hydrogen impurity stored on a tetrahedral interstitial in an infinite magnesium crystal [3].

Starting with a many-particle Schrödinger equation for a host crystal with stored hydrogen, a twofold adiabatic approximation separates the problem of calculating the heat of solution into three problems, containing the energy change in the electronic, in the protonic and in the ionic subsystem. The hierarchy of the coupling of these three subsystems determines the order of solving these problems.

The treatment of the electronic problem is done with a special field theoretical energy difference procedure developed by Wahl based on the New-Tamm-Dancoff Method. A detailed description of the formalism is given in [2]. A higher order approximation of this procedure is applied for this problem.

Proton and ions are treated as classical particles, and thermally induced movements are neglected. The total heat of solution is calculated dependent on the equilibrium positions of the relaxed host ions. An equilibrium investigation between the perturbation forces and the lattice forces results in the actually realized displacements of the host ions in the neighbourhood of the hydrogen impurity.

2. Model

To calculate the storage energy of a metal hydride, we introduce the following systems, which are shown schematically in Figure 1.

Initial System: A pure unperturbated host system and outside of the crystal a single hydrogen atom.

Reference System: A host system deformed by virtual Kanzaki forces and outside of the crystal a single hydrogen atom.

Hydride System: A host system with a single hydrogen atom inside the crystal.

Let E_I, E_R, and E_H be the total energy of the corresponding systems.

---

* Supported by the Friedrich Flick Förderungsstiftung.

† Present address: IBM Deutschland GmbH, Entwicklung und Forschung, Schönaicher Str. 220, W-7030 Böblingen, Germany

Reprint requests to Prof. Dr. F. Wahl, Institut für Theoretische Physik, Universität Tübingen, Auf der Morgenstelle, W-7400 Tübingen.

0932-0784 / 92 / 0600-0733 $ 01.30/0. – Please order a reprint rather than making your own copy.

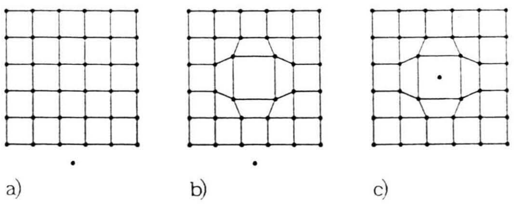

Figure 1. a) Schematic illustration of the Initial System, b) the Reference System and c) the Hydride System.

2.1 *Hydride System*

The time independent many-particle Schrödinger equation for a crystal with an interstitial hydrogen centre is

$$H_{\mathrm{H}}\,\Psi_{\mathrm{H}}(\boldsymbol{x}, \boldsymbol{Y}, \tilde{\boldsymbol{X}}) = E_{\mathrm{H}}\,\Psi_{\mathrm{H}}(\boldsymbol{x}, \boldsymbol{Y}, \tilde{\boldsymbol{X}}), \tag{2.1}$$

where $\boldsymbol{x}$ represents the electronic coordinates, $\boldsymbol{Y}$ the coordinates of the diluted proton and $\tilde{\boldsymbol{X}}$ the coordinates of the metal ions. The hamiltonian H_{H} is divided in a part including all electronical interactions ($H^{\mathrm{e}}_{\mathrm{H}}$), a protonical part ($H^{\mathrm{p}}_{\mathrm{H}}$) and a lattice part ($H^{\mathrm{w}}_{\mathrm{H}}$)

$$H_{\mathrm{H}} = H^{\mathrm{e}}_{\mathrm{H}} + H^{\mathrm{p}}_{\mathrm{H}} + H^{\mathrm{w}}_{\mathrm{H}} \tag{2.2}$$

with

$$H^{\mathrm{e}}_{\mathrm{H}} = -\sum_{\mu} \frac{\hbar^2}{2m_{\mathrm{e}}} \Delta_x + \frac{1}{2} \sum_{\mu,\mu'} \frac{e^2}{|\boldsymbol{x}_\mu - \boldsymbol{x}_{\mu'}|} - \sum_{\mu} \frac{e^2}{|\boldsymbol{x}_\mu - \boldsymbol{Y}|} - \sum_{\mu,n} V_n(\boldsymbol{x}_\mu - \tilde{\boldsymbol{X}}^n), \tag{2.3}$$

$$H^{\mathrm{p}}_{\mathrm{H}} = -\frac{\hbar^2}{2m_{\mathrm{p}}} \Delta_{\boldsymbol{Y}} + \sum_{n} U_n(\boldsymbol{Y} - \tilde{\boldsymbol{X}}^n), \tag{2.4}$$

$$H^{\mathrm{w}}_{\mathrm{H}} = -\sum_{n} \frac{\hbar^2}{2m_n} \Delta_{\tilde{X}^n} + \sum_{n,n'}{}' W_{n,n'}(\tilde{\boldsymbol{X}}^n - \tilde{\boldsymbol{X}}^{n'}). \tag{2.5}$$

The potentials $\sum_{n,\mu} V_n(\boldsymbol{x}_\mu - \tilde{\boldsymbol{X}}^n)$, $\sum_{n} U_n(\boldsymbol{Y} - \tilde{\boldsymbol{X}}^n)$ and $\sum_{n,n'} W_{n,n'}(\tilde{\boldsymbol{X}}^n - \tilde{\boldsymbol{X}}^{n'})$ in (2.3), (2.4), and (2.5) describe the interactions of the μ-th electron, the additional proton in the lattice, and the n'-th lattice ion with the crystal lattice. m_{e}, m_{p}, m_n are the masses of the electron, the proton and the n-th lattice ion.

For Ψ_{H} we make a product ansatz

$$\Psi(\boldsymbol{x}, \boldsymbol{Y}, \tilde{\boldsymbol{X}}) = \varphi(\boldsymbol{x}, \boldsymbol{Y}, \tilde{\boldsymbol{X}})\,\chi(\boldsymbol{Y}, \tilde{\boldsymbol{X}})\,\phi(\tilde{\boldsymbol{X}}), \tag{2.6}$$

and with (2.2) we get

$$\chi\,\phi\,H^{\mathrm{e}}_{\mathrm{H}}\,\varphi(\boldsymbol{x}, \boldsymbol{Y}, \tilde{\boldsymbol{X}}) + \varphi\,\phi\,H^{\mathrm{p}}_{\mathrm{H}}\,\chi(\boldsymbol{Y}, \tilde{\boldsymbol{X}}) + \varphi\,\chi\,H^{\mathrm{w}}_{\mathrm{H}}\,\phi(\tilde{\boldsymbol{X}}) = E_{\mathrm{H}}\,\varphi\,\chi\,\phi + F_{\boldsymbol{Y}} + F_{\tilde{\boldsymbol{X}}}. \tag{2.7}$$

$F_{\tilde{\boldsymbol{X}}}$ and $F_{\boldsymbol{Y}}$ are coupling terms describing the interactions of the subsystems. They represent the feedback of the electron movement to the proton and of the proton movement to the lattice.

2.2 *Reference System*

For calculating reasons we introduce a reference system with a hydrogen atom outside of the crystal but with the same positions of the lattice ions as in the hydride system. For this system the Schrödinger equation is

$$H_{\mathrm{R}}\,\Psi_{\mathrm{R}}(\boldsymbol{x}, \tilde{\boldsymbol{X}}) = E_{\mathrm{R}}\,\Psi_{\mathrm{R}}(\boldsymbol{x}, \tilde{\boldsymbol{X}}) \tag{2.8}$$

with

$$H_{\mathrm{R}} = H^{\mathrm{e}}_{\mathrm{R}} + H^{\mathrm{w}}_{\mathrm{R}} \tag{2.9}$$

and

$$H^{\mathrm{e}}_{\mathrm{R}} = -\sum_{\mu} \frac{\hbar^2}{2m_{\mathrm{e}}} \Delta_{\boldsymbol{x}} + \frac{1}{2} \sum_{\mu,\mu'}{}' \frac{e^2}{|\boldsymbol{x}_\mu - \boldsymbol{x}_{\mu'}|} - \sum_{n} V_n(\boldsymbol{x}_\mu - \tilde{\boldsymbol{X}}^n), \tag{2.10}$$

$$H^{\mathrm{w}}_{\mathrm{R}} = -\sum_{n} \frac{\hbar^2}{2m_n} \Delta_{\tilde{X}^n} + \frac{1}{2} \sum_{n,n'}{}' W_{n,n'}(\tilde{\boldsymbol{X}}^n - \tilde{\boldsymbol{X}}^{n'}). \tag{2.11}$$

With the help of a product ansatz for Ψ_{R},

$$\Psi_{\mathrm{R}}(\boldsymbol{x}, \tilde{\boldsymbol{X}}) = \varphi(\boldsymbol{x}, \tilde{\boldsymbol{X}})\,\phi(\tilde{\boldsymbol{X}}), \tag{2.12}$$

and (2.9) we get

$$\phi\,H^{\mathrm{e}}_{\mathrm{R}}\,\varphi(\boldsymbol{x}, \tilde{\boldsymbol{X}}) + \varphi\,H^{\mathrm{w}}_{\mathrm{R}}\,\phi(\tilde{\boldsymbol{X}}) = E_{\mathrm{R}}\,\varphi\,\phi + F^{\mathrm{R}}_{\tilde{X}}. \tag{2.13}$$

2.3 *Adiabatic Decoupling*

The mobility of the electrons compared with that of the proton and the nuclei is very high. Furthermore, interstitial protons are very mobile compared with the nuclei. This is the motivation for us to apply an adiabatic approximation (Born-Oppenheimer approximation) in two steps. Neglecting the coupling terms $F_{\boldsymbol{Y}}$ and $F_{\tilde{\boldsymbol{X}}}$ for the hydride system the following three subsystems result:

Electronic Subsystem:

$$H^{\mathrm{e}}_{\mathrm{H}}\,\varphi(\boldsymbol{x}, \boldsymbol{Y}, \tilde{\boldsymbol{X}}) = \varepsilon^{\mathrm{e}}_{\mathrm{H}}(\boldsymbol{Y}, \tilde{\boldsymbol{X}})\,\varphi(\boldsymbol{x}, \boldsymbol{Y}, \tilde{\boldsymbol{X}}). \tag{2.14}$$

Protonic System:

$$[\varepsilon^{\mathrm{e}}_{\mathrm{H}}(\boldsymbol{Y}, \tilde{\boldsymbol{X}}) + H^{\mathrm{p}}_{\mathrm{H}}(\tilde{\boldsymbol{X}})]\,\chi(\boldsymbol{Y}, \tilde{\boldsymbol{X}}) = E^{\mathrm{p}}_{\mathrm{H}}(\tilde{\boldsymbol{X}})\,\chi(\boldsymbol{Y}, \tilde{\boldsymbol{X}}). \tag{2.15}$$

Equation for the Lattice Subsystem:

$$[E^{\mathrm{p}}_{\mathrm{H}}(\tilde{\boldsymbol{X}}) + H^{\mathrm{w}}_{\mathrm{H}}]\,\phi(\tilde{\boldsymbol{X}}) = E^{\mathrm{w}}_{\mathrm{H}}\,\phi(\tilde{\boldsymbol{X}}). \tag{2.16}$$

In the electronic equation (2.14) the position of the proton $\boldsymbol{Y}$ and the positions of the lattice ions $\tilde{\boldsymbol{X}}$ are treated as parameters, i.e. the electronic state has to be calculated as a function of the instantaneous positions of the proton and the lattice ions. The electronic eigenvalue ε_H^e of (2.14) plays the role of an additional potential in the protonic system (2.15), where the lattice positions $\tilde{X}$ are treated as parameters. The protonic eigenvalue is an additional potential in the lattice equation (2.16). Treating the reference system in the same manner and neglecting $F_{\tilde{X}}^R$ we get the subsystems:

Electronic Subsystem:

$$H_R^e(\tilde{X})\,\varphi(x,\tilde{X}) = \varepsilon_R^e(\tilde{X})\,\varphi(x,\tilde{X}). \tag{2.17}$$

Equation for the Lattice Subsystem:

$$[\varepsilon_R^e(\tilde{X}) + H_R^w(\tilde{X})]\,\phi(\tilde{X}) = E_R^w\,\phi(\tilde{X}). \tag{2.18}$$

These systems can be solved successively. In the following we neglect proton movement and lattice vibrations. The proton is considered to be in the centre of an ideal tetrahedron built by the next neighbours of the diluted hydrogen proton. The unperturbed host lattice is considered as an ideal *hcp – lattice* of an infinite magnesium crystal.

2.4 *Definition of the Storage Energy*

The storage energy of a metal hydrogen system is defined as the difference between the energy of an unperturbed host crystal plus the ground state energy of one hydrogen atom ($E_0 = -13.6$ eV) outside of the crystal and the ground state energy of a crystal storing a hydrogen centre. Let U_0 be the energy of the ideal crystal. Then the energy of the initial system is

$$E_I = U_0 + E_0, \tag{2.19}$$

and the energy of the reference system is

$$E_R = E_I + \Delta U_W. \tag{2.20}$$

ΔU_W is the contribution of the distortion energy. The ground state energy of the crystal with diluted hydrogen is therefore

$$E_H = E_R + Q - E_0. \tag{2.21}$$

Q is the energy of the interactions of the additional electron, the proton and the lattice ions and can be split up into the interaction V_P between the proton and the lattice ions and in a term

$$\omega := \varepsilon_H^e - \varepsilon_R^e, \tag{2.22}$$

describing the total electronic energy difference between the reference and the hydride system:

$$Q = V_P + \omega = \sum_n \frac{Z e^2}{|\tilde{X}^n - Y|} + \omega. \tag{2.23}$$

Now the storage energy can be written as

$$\begin{aligned} \Delta E_{\text{stor}} &= E_H - E_I \\ &= Q + \Delta U_W - E_0 \\ &= \omega + V_P + \Delta U_W - E_0. \end{aligned} \tag{2.24}$$

Note that the storage energy ΔE_{stor} is depending on the ionic displacement field $s = (\ldots, s^n, \ldots)$, the coordinates X of the unperturbed lattice and the relaxed lattice positions $\tilde{X} = (\ldots, (X^n + s^n), \ldots)$. The calculation of the actually realized lattice positions $\tilde{X}$, respectively the displacement s is done in Chapter 4. So long the lattice displacements are taken as parameters.

3. The Electronic Problem

To get the storage energy, the electronic problem has to be treated first. The electronic contribution of the storage energy will be determined dependent on the lattice displacements in this chapter. The calculation of the electronic energy difference ω is done with a method introduced by Tamm [4] and Dancoff [5], which was later modified by Dyson [6]. This method was also applied in elementary particle physics [7]. Wahl et al. modified and adapted the method according the quantum field theory of Haken [8] to get a model for the description of metal hydrides [2].

To use this field quantum theoretical formalism we define creation operators ψ_s^+ and destruction operators ψ_s in a Fock space $\mathcal{H}_\psi$ with the anticommutation relations

$$\begin{aligned} \{\psi_s(x), \psi_{s'}(x')\}_+ &= \{\psi_s^+(x), \psi_{s'}^+(x')\}_+ = 0, \\ \{\psi_s(x), \psi_{s'}^+(x')\}_+ &= \delta(x - x') \cdot \delta_{ss'}. \end{aligned} \tag{3.1}$$

Let $|O_\psi\rangle$ be the bare vacuum. An arbitrary state in Fock space may be written as

$$\begin{aligned} |\phi\rangle = \sum_{j=1}^{\infty} \frac{1}{j!} \int \mathrm{d}x_1 \ldots \mathrm{d}x_j\, \varphi(x_1 \ldots x_N) \\ \cdot \psi^+(x_1) \ldots \psi^+(x_j) |O_\psi\rangle. \end{aligned} \tag{3.2}$$

We rewrite now the Hamiltonians of the hydride and the reference systems for the Schrödinger equations in the field theoretical formulation

$$\mathbb{H}_{\mathrm{R}}(\psi^+,\psi) := \sum_s \int \psi_s^+(\boldsymbol{x})\, H(\boldsymbol{x},\tilde{\boldsymbol{X}})\, \psi_s(\boldsymbol{x})\, \mathrm{d}\boldsymbol{x} + \sum_{s,s'} \int \psi_s^+(\boldsymbol{x})\, \psi_{s'}^+(\boldsymbol{x}')\, W(\boldsymbol{x},\boldsymbol{x}')\, \psi_{s'}(\boldsymbol{x}')\, \psi_s(\boldsymbol{x})\, \mathrm{d}\boldsymbol{x}\, \mathrm{d}\boldsymbol{x}', \tag{3.3}$$

$$\mathbb{H}_{\mathrm{H}}(\psi^+,\psi) := \mathbb{H}_{\mathrm{R}}(\psi^+,\psi) + \sum_s \int \psi_s^+(\boldsymbol{x})\, V_{\mathrm{p}}(\boldsymbol{x},\boldsymbol{Y})\, \psi_s(\boldsymbol{x})\, \mathrm{d}\boldsymbol{x}. \tag{3.4}$$

$H(\boldsymbol{x},\tilde{\boldsymbol{X}})$ is the one particle interaction

$$H(\boldsymbol{x},\tilde{\boldsymbol{X}}) := -\frac{\hbar^2}{2m_{\mathrm{e}}}\Delta + \sum_{\boldsymbol{m},i} V_i(\boldsymbol{x}-\tilde{\boldsymbol{X}}_{\boldsymbol{m},i})$$

containing the kinetic energy and the electron-ion interaction. The two particle interaction

$$W(\boldsymbol{x},\boldsymbol{x}') := \frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}$$

is describing the Coulomb potential of the electron-electron interaction, and the potential

$$V_{\mathrm{p}}(\boldsymbol{x},\boldsymbol{Y}) := -\frac{e^2}{|\boldsymbol{x}-\boldsymbol{Y}|}$$

is the interaction between the additional electron charge and the embedded proton of the additional hydrogen.

According to Haken [8] the bare vacuum is not used but the ground state of an ideal crystal with a filled valence band is used as a vacuum $|\Omega_\psi\rangle$. With the help of orthogonal projection operators $S_0(\boldsymbol{x},\boldsymbol{x}')$ and $S_1(\boldsymbol{x},\boldsymbol{x}')$ obeying the relations

$$\begin{aligned} S_i(\boldsymbol{x},\boldsymbol{x}')\cdot S_j(\boldsymbol{x}',\boldsymbol{x}'') &= S_i(\boldsymbol{x},\boldsymbol{x}'')\,\delta_{ij}, \quad i,j\in\{0,1\},\\ S_0(\boldsymbol{x},\boldsymbol{x}')+S_1(\boldsymbol{x},\boldsymbol{x}') &= \delta(\boldsymbol{x}-\boldsymbol{x}'),\\ S_i^+(\boldsymbol{x},\boldsymbol{x}') = S_i^*(\boldsymbol{x}',\boldsymbol{x}) &= S_i(\boldsymbol{x},\boldsymbol{x}'), \quad i\in\{0,1\}, \end{aligned} \tag{3.5}$$

which split up the momentum space in occupied and unoccupied states, we get the following relations

$$\psi^+(\boldsymbol{x}')\, S_0(\boldsymbol{x}',\boldsymbol{x})\,|\Omega_\psi\rangle = 0, \tag{3.6}$$

$$S_1(\boldsymbol{x},\boldsymbol{x}')\, \psi(\boldsymbol{x}')\,|\Omega_\psi\rangle = 0. \tag{3.7}$$

Analogues v^+, v and w^+, w in Fock spaces $\mathscr{H}_v$ and $\mathscr{H}_w$ are defined.

Wahl and Feist [9], proved that the simultaneous solving of the two Schrödinger equations

$$\mathbb{H}_{\mathrm{H}}|H\rangle = \varepsilon_{\mathrm{H}}^{\mathrm{e}}|H\rangle, \tag{3.8}$$

$$\mathbb{H}_{\mathrm{R}}|R\rangle = \varepsilon_{\mathrm{R}}^{\mathrm{e}}|R\rangle \tag{3.9}$$

is equivalent to the solution of the following equation in the form of a linear eigenvalue problem

$$\mathbb{B}|\boldsymbol{\Phi}_{\mathrm{HR}}\rangle = \omega|\boldsymbol{\Phi}_{\mathrm{HR}}\rangle \tag{3.10}$$

for the difference ω of the eigenvalues of (3.8) and (3.9) (see also (2.22)) and a functional Hamiltonian $\mathbb{B}$ depending only on elements of $\mathbb{1}\,\hat{\otimes}\,\mathscr{A}_v\,\hat{\otimes}\,\mathscr{A}_w$

$$\mathbb{B} = \mathbb{H}_{\mathrm{H}}(i\,w^+S_1 - i\,v\,S_0,\, i\,S_0\,v^+ - i\,S_1\,w) - \mathbb{H}_{\mathrm{R}}(i\,S_0\,w + i\,S_1\,v^+,\, -i\,v\,S_1 - i\,w^+S_0). \tag{3.11}$$

and the anti-linear functional

$$|\boldsymbol{\Phi}_{\mathrm{HR}}\rangle = [\chi_{\mathrm{R}}(i\,v\,S_1, i\,S_0\,w)]^+\,\chi_{\mathrm{H}}(i\,w^+S_1, i\,S_0\,v^+)|O_{vw}\rangle. \tag{3.12}$$

The following terms show the detailed structure of $\mathbb{H}_{\mathrm{H}}$ and $\mathbb{H}_{\mathrm{R}}$:

$$\mathbb{H}_{\mathrm{H}}(i\,w^+S_1 - i\,v\,S_0,\, i\,S_0\,v^+ - i\,S_1\,w) = \mathbb{H}_{\mathrm{H}}^{(0)} + \mathbb{H}_{\mathrm{H}}^{(1)} + \mathbb{H}_{\mathrm{H}}^{(1)+} + \mathbb{H}_{\mathrm{H}}^{(2)} + \mathbb{H}_{\mathrm{H}}^{(2)+}, \tag{3.13}$$

$$\mathbb{H}_{\mathrm{R}}(i\,S_0\,w + i\,S_1\,v^+,\, -i\,v\,S_1 - i\,w^+S_0) = \mathbb{H}_{\mathrm{R}}^{(0)} + \mathbb{H}_{\mathrm{R}}^{(1)} + \mathbb{H}_{\mathrm{R}}^{(1)+} + \mathbb{H}_{\mathrm{R}}^{(2)} + \mathbb{H}_{\mathrm{R}}^{(2)+} \tag{3.14}$$

with

$$\mathbb{H}_{\mathrm{H}}^{(0)} = C + H_1 + H_2 + H_3 + H_4 + H_5 + H_6, \tag{3.15}$$

$$\mathbb{H}_{\mathrm{H}}^{(1)} = H_7 + H_8 + H_9, \tag{3.16}$$

$$\mathbb{H}_{\mathrm{H}}^{(2)} = H_{10}, \tag{3.17}$$

$$\mathbb{H}_{\mathrm{R}}^{(0)} = R_1 + R_2 + R_3 + R_4 + R_5 + R_6, \tag{3.18}$$

$$\mathbb{H}_{\mathrm{R}}^{(1)} = R_7 + R_8 + R_9, \tag{3.19}$$

$$\mathbb{H}_{\mathrm{R}}^{(2)} = R_{10}, \tag{3.20}$$

and

$$H_1 = w_s^+(\boldsymbol{y})\, S_1(\boldsymbol{y},\boldsymbol{x})\, [D(\boldsymbol{x},\boldsymbol{x}') + V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})]\, \delta(\boldsymbol{x}-\boldsymbol{x}')\, S_1(\boldsymbol{x}',\boldsymbol{y}')\, w_s(\boldsymbol{y}'), \tag{3.21}$$

$$H_2 = v_s^+(\boldsymbol{y})\, S_0^*(\boldsymbol{y},\boldsymbol{x})\, [D^*(\boldsymbol{x},\boldsymbol{x}') + V_{\mathrm{H}}^*(\boldsymbol{x},\boldsymbol{Y})]\, \delta(\boldsymbol{x}-\boldsymbol{x}')\, S_0^*(\boldsymbol{x}',\boldsymbol{y}')\, v_s(\boldsymbol{y}'), \tag{3.22}$$

$$H_3 = \frac{1}{2}\, w_s^+(\boldsymbol{y})\, S_1(\boldsymbol{y},\boldsymbol{x})\, w_{s'}^+(\boldsymbol{y}')\, S_1(\boldsymbol{y}',\boldsymbol{x}')\, \frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\, S_1(\boldsymbol{x}',\boldsymbol{y}'')\, w_{s'}(\boldsymbol{y}'')\, S_1(\boldsymbol{x}',\boldsymbol{y}''')\, w_s(\boldsymbol{y}'''), \tag{3.23}$$

$$H_4 = \frac{1}{2}\, v_s^+(\boldsymbol{y})\, S_0^*(\boldsymbol{y},\boldsymbol{x})\, w_{s'}^+(\boldsymbol{y}')\, S_0^*(\boldsymbol{y}',\boldsymbol{x}')\, \frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\, S_0^*(\boldsymbol{x}',\boldsymbol{y}'')\, v_{s'}(\boldsymbol{y}'')\, S_0^*(\boldsymbol{x},\boldsymbol{y}''')\, v_s(\boldsymbol{y}'''), \tag{3.24}$$

$$H_5 = w_s^+(y)\, S_1(y,x)\, S_0(x,y')\, v_s^+(y') \frac{e^2}{|x-x'|} v_{s'}(y'')\, S_0(y'',x')\, S_1(x',y''')\, w_{s'}(y'''), \tag{3.25}$$

$$H_6 = -w_s^+(y)\, S_1(y,x)\, v_{s'}^+(y')\, S_0^*(y',x') \frac{e^2}{|x-x'|} S_0^*(x',y'')\, v_{s'}(y'')\, S_1(x,y''')\, w_s(y'''), \tag{3.26}$$

$$H_7 = -w_s^+(y)\, S_1(y,x)\, [D(x,x') + V_{\mathrm{H}}(x,Y)]\, \delta(x-x')\, S_0(x',y')\, v_s^+(y'), \tag{3.27}$$

$$H_8 = -w_s^+(y)\, S_1(y,x)\, w_{s'}^+(y')\, S_1(y',x') \frac{e^2}{|x-x'|} S_0(x',y'')\, v_{s'}^+(y'')\, S_1(x,y''')\, w_s(y''''), \tag{3.28}$$

$$H_9 = v_s^+(y)\, S_0^*(y,x)\, w_{s'}^+(y')\, S_1(y',x') \frac{e^2}{|x-x'|} S_0(x',y'')\, v_{s'}^+(y'')\, S_0^*(x,y''')\, v_s(y'''), \tag{3.29}$$

$$H_{10} = \frac{1}{2} w_s^+(y)\, S_1(y,x)\, w_{s'}^+(y')\, S_1(y',x') \frac{e^2}{|x-x'|} S_0(x',y'')\, v_{s'}^+(y'')\, S_0(x,y''')\, v_s^+(y'''), \tag{3.30}$$

$$R_1 = v_s^+(y)\, S_1^*(y,x)\, D^*(x,x')\, S_1^*(x',y')\, v_s(y'), \tag{3.31}$$

$$R_2 = -w_s^+(y)\, S_0(y,x)\, D(x,x')\, S_0(x',y')\, w_s(y'), \tag{3.32}$$

$$R_3 = \frac{1}{2} v_s^+(y)\, S_1^*(y,x)\, v_{s'}^+(y')\, S_1^*(y',x') \frac{e^2}{|x-x'|} S_1^*(x',y'')\, v_{s'}(y'')\, S_1^*(x,y''')\, v_s(y'''), \tag{3.33}$$

$$R_4 = \frac{1}{2} w_s^+(y)\, S_0(y,x)\, w_{s'}^+(y')\, S_0(y',x') \frac{e^2}{|x-x'|} S_0(x',y'')\, w_{s'}(y'')\, S_0(x,y''')\, w_s(y'''), \tag{3.34}$$

$$R_5 = w_s^+(y)\, S_0(y,x)\, S_1(x,y')\, v_s^+(y') \frac{e^2}{|x-x'|} v_{s'}(y'')\, S_1(y'',x')\, S_0(x',y''')\, w_{s'}(y'''), \tag{3.35}$$

$$R_6 = -w_s^+(y)\, S_0(y,x)\, v_{s'}^+(y')\, S_1^*(y',x') \frac{e^2}{|x-x'|} S_1^*(x',y'')\, v_{s'}(y'')\, S_0(x,y''')\, w_s(y'''), \tag{3.36}$$

$$R_7 = -w_s^+(y)\, S_0(y,x)\, D(x,x')\, S_1(x',y')\, v_s^+(y'), \tag{3.37}$$

$$R_8 = w_s^+(y)\, S_0(y,x)\, w_{s'}^+(y')\, S_0(y',x') \frac{e^2}{|x-x'|} S_1(x',y'')\, v_{s'}^+(y'')\, S_0(x,y''')\, w_s(y'''), \tag{3.38}$$

$$R_9 = -v_s^+(y)\, S_1^*(y,x)\, w_{s'}^+(y)\, S_0(y',x') \frac{e^2}{|x-x'|} S_1(x',y'')\, v_{s'}^+(y'')\, S_1^*(x,y''')\, v_s(y'''), \tag{3.39}$$

$$R_{10} = \frac{1}{2} w_s^+(y)\, S_0(y,x)\, w_{s'}^+(y')\, S_0(y',x') \frac{e^2}{|x-x'|} S_1(x',y'')\, v_{s'}^+(y'')\, S_1(x,y''')\, v_s^+(y'''). \tag{3.40}$$

In these terms $D(x,x')$ is the Hartree-Fock operator

$$D(x,x') = \left[-\frac{\hbar^2}{2m_e} \Delta + V_{\mathrm{W}}(x,X) + 2e^2 \int \mathrm{d}y \frac{S_0(y,y)}{|x-y|} \right] \delta(x-x') - e^2 \frac{S_0(x,x')}{|x-x'|}, \tag{3.41}$$

and in $\mathbb{H}_{\mathrm{H}}^{(0)}$

$$C := \operatorname{Spur}[V_{\mathrm{H}}(x,Y)\, S_0(x,x)] = -2e^2 \int \mathrm{d}x \frac{S_0(x,x)}{|x-Y|} \tag{3.42}$$

is the energy of the screened proton in the field of the metal electrons.

Instead of solving (3.10) we get the same result by solving

$$\langle \Phi' | \mathbb{B}\, \Phi_{\mathrm{HR}} \rangle = \omega \langle \Phi' | \Phi_{\mathrm{HR}} \rangle \tag{3.43}$$

for all base states $|\Phi'\rangle = \Phi' |O_{vw}\rangle \in \mathscr{H}_{vw}$,

$$\begin{aligned} |\Phi'\rangle := \left| \Phi^{m+J,\, m'+J'} \begin{pmatrix} x \\ s \end{pmatrix} \right\rangle &= \prod_{i=0}^{m+J} w_{s_i}^+(y_i)\, S_1(y_i,x_i) \\ &\cdot \prod_{j=0}^{m} v_{s_j'}^+(y_j')\, S_0^*(y_j',x_j') \prod_{i'=0}^{m'+J'} v_{s_{i'}''}^+(y_{i'}'')\, S_1^*(y_{i'}'',x_{i'}'') \\ &\cdot \prod_{j'=0}^{m'} w_{s_{j'}'''}^+(y_{j'}''')\, S_0(y_{j'}''',x_{j'}''')\, |O_{vw}\rangle \end{aligned} \tag{3.44}$$

for fixed J, J' and m, m'. With the interpretation of [2] J denotes the number of excess electrons outside the Fermi sphere and m the number of electron-hole pairs in the hydride system. J' and m' are the corresponding numbers for the reference system. In this work, treating the one center problem, we have to set $J=1$ and $J'=0$.

For an approximate solving of (3.43) we use projection operators $\mathbb{P}$ built up with the base vectors (3.44)

$$\mathbb{P}^{M+J,M'+J'} := \sum_{m=0}^{M}\sum_{m'=0}^{M'} \mathbb{P}^{m+J,m'+J'} \tag{3.45}$$

with

$$\mathbb{P}^{m+J,m'+J'} := \left|\boldsymbol{\Phi}^{m+J,m'+J'}\begin{pmatrix}\boldsymbol{x}\\ s\end{pmatrix}\right\rangle \cdot \frac{1}{(m+J)!\,m!\,(m'+J')!\,m'!}\left\langle \boldsymbol{\Phi}^{m+J,m'+J'}\begin{pmatrix}\boldsymbol{x}\\ s\end{pmatrix}\right| . \tag{3.46}$$

Symmetric insertion of the projectors for fixed J, J' and for suitable M, M' in (3.43) produces a finite system of coupled equations for an approximate solution $\omega^{M,M'}$ and $|\boldsymbol{\Phi}_{\mathrm{HR}}^{M,M'}\rangle$

$$\begin{aligned}&\langle \boldsymbol{\Phi}^{m+J,m'+J'}|\,\mathbb{B}\mathbb{P}^{M+J,M'+J'}\,|\boldsymbol{\Phi}_{\mathrm{HR}}^{M,M'}\rangle\\ &\quad=\omega^{M,M'}\langle \boldsymbol{\Phi}^{m+J,m'+J'}|\boldsymbol{\Phi}_{\mathrm{HR}}^{M,M'}\rangle.\end{aligned} \tag{3.47}$$

The convergence

$$\lim_{M,M'\to\infty} \omega^{M,M'}=\omega,$$

$$\lim_{M,M'\to\infty} |\boldsymbol{\Phi}_{\mathrm{HR}}^{M,M'}\rangle = |\boldsymbol{\Phi}_{\mathrm{HR}}\rangle$$

is assumed. To simplify the notation we define for each $m \leqq M$ and $m' \leqq M'$

$$h^{m,m'}\begin{pmatrix}\boldsymbol{x}\\ s\end{pmatrix} := \left\langle \boldsymbol{\Phi}^{m+J,m'+J'}\begin{pmatrix}\boldsymbol{x}\\ s\end{pmatrix}\middle|\,|\boldsymbol{\Phi}_{\mathrm{HR}}^{M,M'}\right\rangle, \tag{3.48}$$

$$\begin{aligned}B_{n,n'}^{m,m'}\begin{pmatrix}\boldsymbol{x}\,\boldsymbol{y}\\ s\,\sigma\end{pmatrix} &:= \frac{1}{(n+J)!\,n!\,(n'+J')!\,n'!}\\ &\quad\cdot\left\langle \boldsymbol{\Phi}^{m+J,m'+J'}\begin{pmatrix}\boldsymbol{x}\\ s\end{pmatrix}\middle|\,\mathbb{B}\,\middle|\boldsymbol{\Phi}^{n+J,n'+J'}\begin{pmatrix}\boldsymbol{y}\\ \sigma\end{pmatrix}\right\rangle.\end{aligned} \tag{3.49}$$

With these definitions (3.47) is rewritten (J, J' fixed)

$$\begin{aligned}&B_{n,n'}^{m,m'}\begin{pmatrix}\boldsymbol{x}\,\boldsymbol{y}\\ s\,\sigma\end{pmatrix} h^{n,n'}\begin{pmatrix}\boldsymbol{y}\\ s\end{pmatrix} = \omega^{M,M'}\,h^{m,m'}\begin{pmatrix}\boldsymbol{x}\\ s\end{pmatrix},\\ &\qquad n, m \in \{0,\dots,M\},\\ &\qquad n', m' \in \{0,\dots,M'\}.\end{aligned} \tag{3.50}$$

In principle it is possible to compute from the coupled equations (3.50) approximate J, J' states in the hydride and in the reference system. For this purpose we start with the equation with the highest indices of n, i.e. $n=M$, $n'=M'$. The wave function $h^{n,n'}$ is inverted with respect to lower order wave functions. The result is inserted in the next lower order wave function and the method is repeated until a one particle equation for $h^{0,0}$ is achieved. In a first step we treat the system in the lowest possible approximation. For the zeroth order approximation the cut off conditions to (3.47) are $M=0$ and $M'=0$. In a second step a higher order approximation calculation is done with $M=1$ and $M'=1$.

3.1 *Zeroth Order Approximation*

In a zeroth order approximation with the conditions $M=0$ and $M'=0$ one single eigenvalue equation is to be solved,

$$\mathbb{B}_{00}^{00}\begin{pmatrix}\boldsymbol{z}\,\boldsymbol{y}\\ s\,\sigma\end{pmatrix} h^{00}\begin{pmatrix}\boldsymbol{z}\\ s\end{pmatrix} = \omega^{00}\,h^{00}\begin{pmatrix}\boldsymbol{x}\\ s\end{pmatrix}. \tag{3.51}$$

With (3.49) and (3.11) we get

$$\begin{aligned}&S_1(\boldsymbol{z},\boldsymbol{x})\,[D(\boldsymbol{x},\boldsymbol{x}',\tilde{\boldsymbol{X}})+V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})\,\delta(\boldsymbol{x}-\boldsymbol{x}')+C]\\ &\quad\cdot S_1(\boldsymbol{x}',\boldsymbol{y}')\,h^{00}\begin{pmatrix}\boldsymbol{y}'\\ s\end{pmatrix} = \omega\,h^{00}\begin{pmatrix}\boldsymbol{z}\\ s\end{pmatrix},\end{aligned} \tag{3.52}$$

where C is the trace term of (3.42) and $D(\boldsymbol{x},\boldsymbol{x}',\tilde{\boldsymbol{X}})$ is the Hartree-Fock operator (3.41). The last term in D represents the exchange energy.

(3.52) is a Hartree-Fock equation for an electron in a distorted lattice and an orthogonalized wave function h onto the valence band. C diverges, but in the total energy balance it will be exactly compensated by the interaction of the proton and the lattice ions. ω is also divergent in an infinite lattice. In the following we combine ω and C to the finite term

$$\lambda = \omega - C. \tag{3.53}$$

For the calculation it will be an advantage to split up the Hartree-Fock operator into two terms, the first describing the interaction of an electron with the lattice ions in the positions of an ideal lattice and the second term the difference potential $V_D(\boldsymbol{x},\boldsymbol{x}',\tilde{\boldsymbol{X}})$ which contains the influence of the lattice distortion

$$\begin{aligned}&D(\boldsymbol{x},\boldsymbol{x}',\tilde{\boldsymbol{X}})\\ &\quad= D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X}) + [V_{\mathrm{W}}(\boldsymbol{x},\tilde{\boldsymbol{X}})-V_{\mathrm{W}}(\boldsymbol{x},\boldsymbol{X})]\,\delta(\boldsymbol{x}-\boldsymbol{x}')\\ &\quad= D(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{X}) + V_D(\boldsymbol{x},\boldsymbol{X},\tilde{\boldsymbol{X}})\,\delta(\boldsymbol{x}-\boldsymbol{x}').\end{aligned} \tag{3.54}$$

Now the following equation has to be solved:

$$S_1(z, \boldsymbol{x})\,[D(\boldsymbol{x}, \boldsymbol{x}', X) + [V_D(\boldsymbol{x}, X, \tilde{X}) + V_{\mathrm{H}}(\boldsymbol{x}, Y)]\,\delta(\boldsymbol{x}-\boldsymbol{x}')] \cdot S_1(\boldsymbol{x}', \boldsymbol{y}')\,h^{00}\begin{pmatrix} \boldsymbol{y}' \\ s \end{pmatrix} = \lambda\,h^{00}\begin{pmatrix} z \\ s \end{pmatrix}. \tag{3.55}$$

The interaction of the electron and the crystal electrons

$$V_{\mathrm{e}}(\boldsymbol{x}) = e^2 \int\limits_{\Omega} \mathrm{d}\boldsymbol{y}\,\frac{2S_0(\boldsymbol{y}, \boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|} \tag{3.56}$$

and the interaction with the crystal ions

$$V_{\mathrm{W}}(\boldsymbol{x}, X) = -\sum_{j}^{M} \frac{e^2 Z}{|\boldsymbol{x} - X^j|} \tag{3.57}$$

lead separately to divergent energy terms. Therefore they are combined to a common potential

$$V_{\mathrm{G}}(\boldsymbol{x}) = V_{\mathrm{W}}(\mathbf{x}, X) + V_{\mathrm{e}}(\boldsymbol{x}) \tag{3.58}$$

without divergence. Using the density

$$\varrho_0 = 2S_0(\boldsymbol{x}, \boldsymbol{x}) = \frac{k_{\mathrm{F}}^3}{3\pi^2} \tag{3.59}$$

of the valence band [10, p. 36] and dividing the whole crystal into elementary cells and into a sub-lattices for each atom in an elementary cell, a Fourier development of the potential will result in a sum over the reciprocal lattice. Looking at (3.55) we see that the projectors S_0 and S_1 garantee the orthogonality of h onto the valence band. Moreover, the function of the additional electron has to be orthogonal on the core electrons of the lattice ions. To introduce screening effects of the physical extension of the core electrons in the lattice to h, a Krasko potential [11, 12] is used for V_{G} instead of the Coulomb potential. This results in

$$V_{\mathrm{G}}(\boldsymbol{x}) = -\frac{4\pi Z e^2}{\Omega_0} \cdot \sum_{\boldsymbol{k} \in \mathrm{RG}, \boldsymbol{k} \neq 0} \frac{1}{k^2} F^K(\boldsymbol{k})\,(\mathrm{e}^{-i\boldsymbol{k}\boldsymbol{R}_1} + \mathrm{e}^{-i\boldsymbol{k}\boldsymbol{R}_2})\,\mathrm{e}^{i\boldsymbol{k}\boldsymbol{x}} \tag{3.60}$$

with $Z=2$ for the valence of magnesium, with $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ as vectors from the interstitial proton lying in the middle of a tetrahedron, each to a corner of the tetrahedron, and with Ω_0 as the volume of an elementary cell. $\boldsymbol{k}$ are vectors from the reciprocal lattice and

$$F^K(\boldsymbol{q}) = \frac{1-(2A_0-1)(\boldsymbol{q}R_{\mathrm{c}})^2}{[(\boldsymbol{q}R_{\mathrm{c}})^2+1]^2}, \tag{3.61}$$

where $A_0 = 2.588$ and $R_{\mathrm{c}} = 0.427\,a_0$ are constants and a_0 is the Bohr radius.

The difference potential V_D is evaluated using the assumption that only the next four neighbours are radially displaced by the interstitial hydrogen atom. The amount of the displacements s will be the same for all four neighbours

$$\tilde{X}^j = X^j + s\frac{X^j}{|X^j|}, \quad j = 0, \ldots, 3. \tag{3.62}$$

With this assumption λ is parameterized by the displacement s,

$$\lambda = \lambda(s) \quad \text{resp.} \quad \omega = \omega(s).$$

3.2 A Higher Order Approximation

In this section a higher order approximation of the electronic problem is examined. The cut off conditions for (3.50) now are $M=1$ and $M'=1$. These conditions are interpreted as one particle-hole pair in the hydride and one in the reference system. When looking only at correlations produced by one additional particle-hole pair, treating only three-particle correlations (3.50) is reduced to the system of equations with the detailed form

$$B_{00}^{00}\,h^{00} + B_{01}^{00}\,h^{01} + B_{10}^{00}\,h^{10} = \omega\,h^{00}, \tag{3.63}$$

$$B_{00}^{01}\,h^{00} + B_{01}^{01}\,h^{01} = \omega\,h^{01}, \tag{3.64}$$

$$B_{00}^{10}\,h^{00} + B_{10}^{10}\,h^{10} = \omega\,h^{10}. \tag{3.65}$$

The equations are coupled with the eigenvalue ω and with the one-particle function h^{00} (3.51) and the three-particle functions h^{01} and h^{10}. It is interesting to see the structure of the coupled equations: The zeroth order problem (3.51) is included in the first of the equations of the higher order approximation problem. The three-particle wave functions h^{01} and h^{10} have different characteristics. In

$$h^{10}\begin{pmatrix} \boldsymbol{x}_1 & \boldsymbol{x}_2 & \boldsymbol{x}_1' \\ s_1 & s_2 & s_1' \end{pmatrix} = \left\langle \boldsymbol{\Phi}^{1+1,0+0}\begin{pmatrix} \boldsymbol{x}_1 & \boldsymbol{x}_2 & \boldsymbol{x}_1' \\ s_1 & s_2 & s_1' \end{pmatrix} \middle| \boldsymbol{\Phi}_{\mathrm{HR}} \right\rangle$$
$$= \langle O_{vw}|\,[w_{s_1}^+(\boldsymbol{y}_1)\,S_1(\boldsymbol{y}_1, \boldsymbol{x}_1) \cdot w_{s_2}^+(\boldsymbol{y}_2)\,S_1(\boldsymbol{y}_2, \boldsymbol{x}_2)) \cdot v_{s_1}^+(\boldsymbol{y}_1')\,S_0^*(\boldsymbol{y}_1', \boldsymbol{x}_1')]^+ \cdot |\boldsymbol{\Phi}_{\mathrm{HR}}\rangle \tag{3.66}$$

with the interpretation of [2] we have a wave function of a state with the charge of the additional hydrogen electron in the hydride system and an electron-hole pair, whereas the function

$$h^{01}\begin{pmatrix} x_1 & x_1'' & x_1''' \\ s_1 & s_1'' & s_1''' \end{pmatrix} = \left\langle \Phi^{0+1,1+0}\begin{pmatrix} x_1 & x_1'' & x_1''' \\ s_1 & s_1'' & s_1''' \end{pmatrix} \middle| \Phi_{\mathrm{HR}} \right\rangle$$

$$= \langle O_{vw} | \, [w^+_{s_1}(y_1)\, S_1(y_1, x_1) \cdot v^+_{s_1''}(y_1'')\, S_1^*(y_1'', x_1'') \cdot w^+_{s_1'''}(y_1''')\, S_0(y_1''', x_1''')]^+ \cdot | \Phi_{\mathrm{HR}} \rangle \tag{3.67}$$

belongs to a state of the charge of the additional electron in the hydride system and an electron-hole pair in the reference system. In nature there will be naturally no interaction between the additional hydrogen electron in the hydride system and the electron-hole pair in the reference system, as these two systems are totally separated. This effect we see also in the possibility to anticommutate the creation operator $w^+ S_1$ of the hydrogen electron in the hydride system and the particle-hole pair $v^+ S_1^* \cdot w^+ S_0$ of the reference system. As a consequence of this, the three-particle wave function could be written as the product of the additional hydrogen electron in the hydride system and the electron-hole pair of the reference system.

3.2.1. Reduction to One Equation

The matrix elements are again calculated via (3.49). The form is taken from (3.13)–(3.20). Besides B^{00}_{00} of (3.51), B^{01}_{01} (see (3.77)) and B^{10}_{10} (see (3.83)) the remaining matrix elements take the form

$$B^{00}_{01}\begin{pmatrix} z & x_1 & x_1'' & x_1''' \\ \sigma & s_1 & s_1'' & s_1''' \end{pmatrix} = -S_1(z, x_1)\, S_1(x'', x)\, D(x, x')\, S_0(x', x''')\, \delta_{\sigma s_1}\, \delta_{s_1'' s_1'''}, \tag{3.68}$$

$$B^{01}_{00}\begin{pmatrix} z_1 & z_1'' & z_1''' & y_1 \\ s_1 & s_1'' & s_1''' & \varrho_1 \end{pmatrix} = -S_0(z_1''', x)\, D(x, x')\, S_1(x', z_1'')\, S_1(z_1, y_1)\, \delta_{s_1 \varrho_1}\, \delta_{s_1'' s_1'''}, \tag{3.69}$$

$$\begin{aligned} B^{00}_{10}\begin{pmatrix} z & x_1 & x_2 & x_1' \\ \sigma & s_1 & s_2 & s_1' \end{pmatrix} = & \frac{1}{2} S_1(z, x_2)\, S_0(x_1', x)\, [D(x, x') + V_{\mathrm{H}}(x, Y)\, \delta(x - x')]\, S_1(x', x_1)\, \delta_{s_1 s_1'}\, \delta_{\sigma s_2} \\ & - \frac{1}{2} S_1(z, x_1)\, S_0(x_1', x)\, [D(x, x') + V_{\mathrm{H}}(x, Y)\, \delta(x - x')]\, S_1(x', x_2)\, \delta_{s_2 s_1'}\, \delta_{\sigma s_1} \\ & - \frac{1}{2} S_1(z, x)\, S_1^*(x_2, x')\, \frac{e^2}{|x - x'|}\, S_0^*(x', x_1')\, S_1(x, x_1)\, \delta_{s_2 s_1'}\, \delta_{\sigma s_1} \\ & + \frac{1}{2} S_1(z, x)\, S_1^*(x_1, x')\, \frac{e^2}{|x - x'|}\, S_0^*(x', x_1')\, S_1(x, x_2)\, \delta_{s_1 s_1'}\, \delta_{\sigma s_2}, \end{aligned} \tag{3.70}$$

$$\begin{aligned} B^{10}_{00}\begin{pmatrix} z_1 & z_2 & z_1' & y_1 \\ s_1 & s_2 & s_1' & \varrho_1 \end{pmatrix} = & \frac{1}{2} S_1(z_1, x)\, [D(x, x') + V_{\mathrm{H}}(x, Y)\, \delta(x - x')]\, S_0(x', z_1')\, S_1(z_2, y_1)\, \delta_{s_2 \varrho_1}\, \delta_{s_1 s_1'} \\ & - \frac{1}{2} S_1(z_2, x)\, [D(x, x') + V_{\mathrm{H}}(x, Y)\, \delta(x - x')]\, S_0(x', z_1')\, S_1(z_1, y_1)\, \delta_{s_1 \varrho_1}\, \delta_{s_2 s_1'} \\ & - S_1(z_1, x)\, S_1(z_2, x')\, \frac{e^2}{|x - x'|}\, S_0(x', z_1')\, S_1(x, y_1)\, \delta_{s_1 \varrho_1}\, \delta_{s_2 s_1'} \\ & + S_1(z_2, x)\, S_1(z_1, x')\, \frac{e^2}{|x - x'|}\, S_0(x', z_1')\, S_1(x, y_1)\, \delta_{s_2 \varrho_1}\, \delta_{s_1 s_1'}. \end{aligned} \tag{3.71}$$

The Eqs. (3.64) and (3.65) were slightly transformed to

$$(B^{01}_{01} - \omega \mathbb{1})\, h^{01} = -B^{01}_{00}\, h^{00}, \tag{3.72}$$

$$(B^{10}_{10} - \omega \mathbb{1})\, h^{10} = -B^{10}_{00}\, h^{00}. \tag{3.73}$$

We intend to invert these two equations with the help of a Green's function G^{01} and G^{10} to insert the functions

$$h^{01} = -G^{01}\, B^{01}_{00}\, h^{00}, \tag{3.74}$$

$$h^{10} = -G^{10}\, B^{10}_{00}\, h^{00} \tag{3.75}$$

in (3.63). The result is a one-particle equation to be solved

$$B^{00}_{00}\, h^{00} - B^{00}_{01}\, G^{01}\, B^{01}_{00}\, h^{00} - B^{00}_{10}\, G^{10}\, B^{10}_{00}\, h^{00} = \omega\, h^{00}. \tag{3.76}$$

3.2.2. Green's Function G^{01}

To calculate h^{01} from (3.72), B^{01}_{01} is split into two terms

$$\begin{aligned} B^{01}_{01} &= B_0 + R \\ &= \langle \boldsymbol{\Phi}^{0+1,1+0} | C + H_1 - R_1 - R_2 | \boldsymbol{\Phi}^{0+1,1+0} \rangle \\ &\quad + \langle \boldsymbol{\Phi}^{0+1,1+0} | -R_5 | \boldsymbol{\Phi}^{0+1,1+0} \rangle . \end{aligned} \tag{3.77}$$

With this splitting-up, (3.72) is rewritten as

$$(B_0 - \omega \mathbb{1})\, h^{01} + R\, h^{01} = -B^{01}_{00}\, h^{00} . \tag{3.78}$$

With the inversion operator G^{01}_0 of $(B^{01}_{01} - \omega \mathbb{1})$, (3.78) can be solved:

$$h^{01} = -(\mathbb{1} + G^{01}_0 R)^{-1}\, G^{01}_0\, B^{01}_{00}\, h^{00} . \tag{3.79}$$

The Green's function $G^{01} = (\mathbb{1} + G^{01}_0 R)^{-1}\, \mathrm{G}^{01}_0$ is expanded in a power series

$$G^{01} = G^{01}_0 - G^{01}_0 R G^{01}_0 + G^{01}_0 R G^{01}_0 R G^{01}_0 - + \ldots , \tag{3.80}$$

and for R of (3.77) we get, using some anti-commutation relations,

$$R = -S_0(z''', y)\, S^*_1(z'', y)\, S_1(z_1, \boldsymbol{x}) \frac{e^2}{|\boldsymbol{x} - \boldsymbol{y}'|} S^*_1(y', x'')\, S_0(y', x''')\, \delta_{\sigma'' \sigma'''}\, \delta_{\sigma s}\, \delta_{s'' s'''} . \tag{3.81}$$

With the identity

$$S_1(\boldsymbol{x}, \boldsymbol{y})\, S^*_1(\boldsymbol{x}'', \boldsymbol{y}'')\, S_0(\boldsymbol{x}''', \boldsymbol{y}''')\, G^{01}_0(\boldsymbol{y}, \boldsymbol{y}'', \boldsymbol{y}''', z, z'', z''') = G^{01}_0(\boldsymbol{x}, \boldsymbol{x}'', \boldsymbol{x}''', z, z'', z''')$$

the terms of the series (3.80) are obtained:

$$\begin{aligned} G^{01}(\boldsymbol{x}, \boldsymbol{x}'', \boldsymbol{x}''', z, z'', z''') &= G^{01}_0(\boldsymbol{x}, \boldsymbol{x}'', \boldsymbol{x}''', z, z'', z''')\, \delta_{s_1 \sigma_1}\, \delta_{s''_1 s'''_1}\, \delta_{\sigma''_1 \sigma'''_1} \\ &+ G^{01}_0(\boldsymbol{x}, \boldsymbol{x}'', \boldsymbol{x}''', \boldsymbol{u}, \boldsymbol{v}, \boldsymbol{v}) \frac{e^2}{|\boldsymbol{v} - \boldsymbol{v}'|} G^{01}_0(\boldsymbol{u}, \boldsymbol{v}', \boldsymbol{v}', z, z'', z''')\, \delta_{s_1 \sigma_1}\, \delta_{s''_1 s'''_1}\, \delta_{\sigma''_1 \sigma'''_1} \\ &+ 2\, G^{01}_0(\boldsymbol{x}, \boldsymbol{x}'', \boldsymbol{x}''', \boldsymbol{u}, \boldsymbol{v}, \boldsymbol{v}) \frac{e^2}{|\boldsymbol{v} - \boldsymbol{v}'|} G^{01}_0(\boldsymbol{u}, \boldsymbol{v}', \boldsymbol{v}', \boldsymbol{u}_1, \boldsymbol{v}_1, \boldsymbol{v}_1) \\ &\cdot \frac{e^2}{|\boldsymbol{v}_1 - \boldsymbol{v}'_1|} G^{01}_0(\boldsymbol{u}_1, \boldsymbol{v}'_1, \boldsymbol{v}'_1, z, z'', z''')\, \delta_{s_1 \sigma_1}\, \delta_{s''_1 s'''_1}\, \delta_{\sigma''_1 \sigma'''_1} \\ &+ 4\, G^{01}_0(\boldsymbol{x}, \boldsymbol{x}'', \boldsymbol{x}''', \boldsymbol{u}, \boldsymbol{v}, \boldsymbol{v}) \frac{e^2}{|\boldsymbol{v} - \boldsymbol{v}'|} G^{01}_0(\boldsymbol{u}, \boldsymbol{v}', \boldsymbol{v}', \boldsymbol{u}_1, \boldsymbol{v}_1, \boldsymbol{v}_1) \\ &\cdot \frac{e^2}{|\boldsymbol{v}_1 - \boldsymbol{v}'_1|} G^{01}_0(\boldsymbol{u}_1, \boldsymbol{v}'_1, \boldsymbol{v}'_1, \boldsymbol{u}_2, \boldsymbol{v}_2, \boldsymbol{v}_2) \frac{e^2}{|\boldsymbol{v}_2 - \boldsymbol{v}'_2|} G^{01}_0(\boldsymbol{u}_2, \boldsymbol{v}'_2, \boldsymbol{v}'_2, z, z'', z''')\, \delta_{s_1 \sigma_1}\, \delta_{s''_1 s'''_1}\, \delta_{\sigma''_1 \sigma'''_1} + 8 \ldots + \ldots . \end{aligned} \tag{3.82}$$

3.2.3 Green's Function G^{10}

In a similar way the Green's function G^{10} is developed, splitting up B^{10}_{10} into two terms and neglecting the many-body correlations in H_3 and H_0 as well as the Coulomb potentials in H_1 and H_2,

$$B^{10}_{10} = B_0 + H\, \langle \boldsymbol{\Phi}^{1+1,0+0} | C + H_1 + H_2 | \boldsymbol{\Phi}^{1+1,0+0} \rangle + \langle \boldsymbol{\Phi}^{1+1,0+0} | H_5 | \boldsymbol{\Phi}^{1+1,0+0} \rangle . \tag{3.83}$$

For H we get with anticommutator relations

$$\begin{aligned} H = &\frac{1}{2} S_1(z_2, \boldsymbol{x}_2)\, S_1(z_1, \boldsymbol{x})\, S^*_0(z'_1, \boldsymbol{x}) \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} S_1(\boldsymbol{x}', \boldsymbol{x}_1)\, S^*_0(\boldsymbol{x}', \boldsymbol{x}'_1)\, \delta_{\sigma_2 s_2}\, \delta_{\sigma_1 \sigma'_1}\, \delta_{s_1 s'_1} \\ &- \frac{1}{2} S_1(z_1, \boldsymbol{x}_2)\, S_1(z_2, \boldsymbol{x})\, S^*_0(z'_1, \boldsymbol{x}) \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} S_1(\boldsymbol{x}', \boldsymbol{x}_1)\, S^*_0(\boldsymbol{x}', \boldsymbol{x}'_1)\, \delta_{\sigma_1 s_2}\, \delta_{\sigma_2 \sigma'_1}\, \delta_{s_1 s'_1} \\ &- \frac{1}{2} S_1(z_2, \boldsymbol{x}_1)\, S_1(z_1, \boldsymbol{x})\, S^*_0(z'_1, \boldsymbol{x}) \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} S_1(\boldsymbol{x}', \boldsymbol{x}_2)\, S^*_0(\boldsymbol{x}', \boldsymbol{x}'_1)\, \delta_{\sigma_2 s_1}\, \delta_{\sigma_1 \sigma'_1}\, \delta_{s_2 s'_1} \\ &+ \frac{1}{2} S_1(z_1, \boldsymbol{x}_1)\, S_1(z_2, \boldsymbol{x})\, S^*_0(z'_1, \boldsymbol{x}) \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} S_1(\boldsymbol{x}', \boldsymbol{x}_2)\, S^*_0(\boldsymbol{x}', \boldsymbol{x}'_1)\, \delta_{\sigma_1 s_1}\, \delta_{\sigma_2 \sigma'_1}\, \delta_{s_2 s'_1} . \end{aligned}$$

Using the inversion operator G^{10} of $(B^{10}_{10}-\omega\mathbb{1})$ we get in a similar way with neglecting some terms belonging to an exchange interaction [3]

$$\begin{aligned}G^{10}(z_1,z_2,z_1',y_1,y_2,y_1') &= G_0^{10}(z_1,z_2,z_1',y_1,y_2,y_1')\,\delta_{s_1\sigma_1}\delta_{s_2\sigma_2}\delta_{s_1\sigma_1'}\\ &\quad -2\,G_0^{10}(z_1,z_2,z_1',x,x_2,x)\frac{e^2}{|x-x'|}G_0^{10}(x',x_2,x',y_1,y_2,y_1')\,\delta_{s_2\sigma_2}\delta_{s_1s_1'}\delta_{\sigma_1\sigma_1'}\\ &\quad +4\,G_0^{10}(z_1,z_2,z_1',x,x_2,x)\frac{e^2}{|x-x'|}G_0^{10}(x',x_2,x',y,\hat{x}_2,y)\\ &\quad \cdot\frac{e^2}{|y-y'|}G_0^{10}(y',\hat{x}_2,y',y_1,y_2,y_1')\,\delta_{s_2\sigma_2}\delta_{s_1s_1'}\delta_{\sigma_1\sigma_1'}-8\ldots+\ldots.\end{aligned}\tag{3.84}$$

3.2.4 Contribution of the Reference System

The term $-BG^{01}B^{01}h^{00}$ in (3.76) represents the contribution of the reference system in our higher order approximation. The Hartree-Fock operator D is split up again into a Hartree-Fock operator D_0 of the ideal crystal and in the difference potential as we did earlier (3.54),

$$D(x,x')=D_0(x,x')+V_D(x,s)\,\delta(x-x'). \tag{3.85}$$

Now the spectral representation for the Hartree-Fock operator D_0

$$D_0(x,x')=\sum_k \varepsilon_k b_k^{0*}(x)\,b_k^0(x') \tag{3.86}$$

is used. b_k^0 are the Bloch functions of an ideal lattice. The eigenvalues ε_k are the band energies belonging to wave vectors k resulting from the electron gas approximation. With the screening functions

$$A_p(x,z)=b_p^0(x)\,g_p\,b_p^{0*}(z), \tag{3.87}$$

$$B_p(x,z)=b_p^0(x)\,f_p\,b_p^{0*}(z), \tag{3.88}$$

where f_p is the Fermi function and where $g_p=1-f_p$ is the complementary function,

$$f_k=\begin{cases}1, & \varepsilon(k)<\varepsilon_{\text{Fermi}},\\ 0, & \varepsilon(k)>\varepsilon_{\text{Fermi}},\end{cases} \tag{3.89}$$

we get the inversion operator of (3.78) in the following form [3]

$$G_0^{01}(x_1,x_1'',x_1''',z_1,z_1'',z_1''')=\sum_{p\,p''\,p'''}\frac{A_p(x_1,z_1)\,A^*_{p''}(x_1'',z_1'')\,B_{p'''}(x_1''',z''')}{\varepsilon_p-\varepsilon_{p''}+\varepsilon_{p'''}+C-\omega}. \tag{3.90}$$

With the orthogonality of the Bloch functions and using

$$A_p(z,x)\,D_0(x,x')\,B_p(x',z')=0, \tag{3.91}$$

$$B_p(z,x)\,D_0(x,x')\,A_p(x',z')=0, \tag{3.92}$$

after summing up over all spins we get

$$\begin{aligned}&-B^{00}_{01}\begin{pmatrix} z & x_1 & x_1'' & x_1'''\\ \sigma & s_1 & s_1'' & s_1'''\end{pmatrix}G^{01}(x_1,x_1'',x_1''',z_1,z_1'',z_1''')\,B^{01}_{00}\begin{pmatrix} z_1 & z_1'' & z_1''' & y_1\\ s_1 & s_1'' & s_1''' & \varrho_1\end{pmatrix}h^{00}\begin{pmatrix} y_1\\ \varrho_1\end{pmatrix}\\ &=-V_D(x,s)\,\delta(x-x')\left\{2\sum_{p\,p''\,p'''}\frac{A_p(z,y_1)\,A^*_{p''}(x,y')\,B_{p'''}(x',y)}{\varepsilon_p-\varepsilon_{p''}+\varepsilon_{p'''}+C-\omega}\right.\\ &\quad+4\sum_{p\,p''\,p'''}\frac{A_p(z,u)\,A^*_{p''}(x,v)\,B_{p'''}(x',v)}{\varepsilon_p-\varepsilon_{p''}+\varepsilon_{p'''}+C-\omega}\cdot\frac{e^2}{|v-v'|}\\ &\quad\left.\cdot\sum_{p_1\,p_1''\,p_1''}\frac{A_{p_1}(u,y_1)\,A^*_{p_1''}(v',y')\,B_{p_1'''}(v',y)}{\varepsilon_{p_1}-\varepsilon_{p_1''}+\varepsilon_{p_1'''}+C-\omega}+8\ldots\right\}\cdot V_D(y,s)\,\delta(y-y')\,h^{00}\begin{pmatrix} y_1\\ \sigma\end{pmatrix}.\end{aligned}\tag{3.93}$$

For the electron gas approximation we approximate the Bloch functions of the ideal lattice with plan waves

$$b_k^0(x)=\frac{1}{\Omega}e^{ikx}, \tag{3.94}$$

and instead of summation we use integration

$$\sum_{p_1p_2p_3}\to\frac{\Omega^3}{(2\pi)^9}\int \mathrm{d}p_1\int \mathrm{d}p_2\int \mathrm{d}p_3. \tag{3.95}$$

For $A_{\boldsymbol{p}}$ and $B_{\boldsymbol{p}}$ the representations

$$A_{\boldsymbol{p}}(\boldsymbol{x}, \boldsymbol{z}) = \frac{1}{\Omega}\, g_{\boldsymbol{p}}\, e^{i\boldsymbol{p}(\boldsymbol{x}-\boldsymbol{z})}, \tag{3.96}$$

$$B_{\boldsymbol{p}}(\boldsymbol{x}, \boldsymbol{z}) = \frac{1}{\Omega}\, f_{\boldsymbol{p}}\, e^{i\boldsymbol{p}(\boldsymbol{x}-\boldsymbol{z})}, \tag{3.97}$$

and for projectors S_0 and S_1

$$S_0(\boldsymbol{x}, \boldsymbol{z}) = \frac{1}{(2\pi)^3} \int \mathrm{d}\boldsymbol{k}\, f_{\boldsymbol{k}}\, e^{i\boldsymbol{k}(\boldsymbol{x}-\boldsymbol{z})}, \tag{3.98}$$

$$S_1(\boldsymbol{x}, \boldsymbol{z}) = \frac{1}{(2\pi)^3} \int \mathrm{d}\boldsymbol{k}\, g_{\boldsymbol{k}}\, e^{i\boldsymbol{k}(\boldsymbol{x}-\boldsymbol{z})}, \tag{3.99}$$

are used. The one particle energies $\varepsilon_{\boldsymbol{k}}$ of (3.86) in (3.76) are approximated via pseudopotential theory using only the first term of perturbation development of the valence

$$\varepsilon_{\boldsymbol{k}} = \frac{\hbar^2}{2m_e} \boldsymbol{k}^2. \tag{3.100}$$

The Green's function denominator yields

$$\frac{1}{\varepsilon_{\boldsymbol{p}_1} - \varepsilon_{\boldsymbol{p}_2} + \varepsilon_{\boldsymbol{p}_3} + C - \omega} = \frac{2m_{\mathrm{e}}}{\hbar^2} \frac{1}{\boldsymbol{p}_1^2 - \boldsymbol{p}_2^2 + \boldsymbol{p}_3^2 - \mu} \tag{3.101}$$

with

$$\mu := \frac{2m_{\mathrm{e}}}{\hbar^2}(C-\omega) = \frac{2m_{\mathrm{e}}}{\hbar^2}\lambda. \tag{3.102}$$

The Fourier representation is used for all Coulomb potentials,

$$\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|} = \frac{e^2}{2\pi^2} \int \mathrm{d}\boldsymbol{q}\, \frac{1}{\boldsymbol{q}^2}\, e^{i\boldsymbol{q}(\boldsymbol{x}-\boldsymbol{x}')}. \tag{3.103}$$

Using the abbreviation

$$P^0(\boldsymbol{k}) = Z F^K(\boldsymbol{k}) \sum_{j=0}^{3} \left(e^{i\boldsymbol{k}\boldsymbol{X}^j} - e^{i\boldsymbol{k}\boldsymbol{X}^j(1+s/|\boldsymbol{X}^j|)}\right) \tag{3.104}$$

with F^K from (3.61) the difference potential V_D is

$$V_D(\boldsymbol{x}, s) = \frac{e^2}{2\pi^2} \int \mathrm{d}\boldsymbol{k}\, \frac{e^{i\boldsymbol{k}\boldsymbol{x}}}{\boldsymbol{k}^2}\, P^0(\boldsymbol{k}). \tag{3.105}$$

Therefore the contribution of the reference system is

$$\begin{aligned}
-B^{00}_{01}\, G^{01}\, B^{01}_{00}\, h^{00} = &-2 \frac{1}{(2\pi)^3} \frac{2m_{\mathrm{e}}}{\hbar^2} \frac{e^4}{(2\pi^2)^2} \int \mathrm{d}z' \int \mathrm{d}\boldsymbol{p} \int \mathrm{d}\boldsymbol{p}'' \int \mathrm{d}\boldsymbol{p}''' \frac{g_{\boldsymbol{p}}\, g_{\boldsymbol{p}''}\, f_{\boldsymbol{p}'''}}{\boldsymbol{p}^2 - \boldsymbol{p}''^2 + \boldsymbol{p}'''^2 - \mu} \\
&\cdot e^{i\boldsymbol{p}\boldsymbol{z}} \frac{P^0(\boldsymbol{p}''-\boldsymbol{p}''')}{|\boldsymbol{p}''-\boldsymbol{p}'''|^2} \frac{P^0(\boldsymbol{p}'''-\boldsymbol{p}'')}{|\boldsymbol{p}'''-\boldsymbol{p}''|^2}\, e^{-i\boldsymbol{p}\boldsymbol{z}'} \\
&\cdot \sum_{v=0}^{\infty} \left[2 \frac{e2}{2\pi^2} \frac{2m_{\mathrm{e}}}{\hbar^2} \frac{1}{|\boldsymbol{p}''-\boldsymbol{p}'''|^2} \int \mathrm{d}\boldsymbol{q}\, \frac{g_{\boldsymbol{q}}\, f_{\boldsymbol{q}+\boldsymbol{p}'''-\boldsymbol{p}''}}{\boldsymbol{p}^2 - \boldsymbol{q}^2 + (\boldsymbol{q}+\boldsymbol{p}'''-\boldsymbol{p}'')^2 - \mu} \right]^v \cdot h^{00}\!\left(\frac{z'}{\sigma}\right).
\end{aligned} \tag{3.106}$$

3.2.5 Contribution of the Hydride System

With an analogues treatment and with combining the proton potential V_{H} and the difference potential $V_D(\boldsymbol{x}, \boldsymbol{x}')$, using the abbreviation P

$$P(\boldsymbol{k}) = P^0(\boldsymbol{k}) - 1, \tag{3.107}$$

the contribution of the hydride system leads to

$$\begin{aligned}
-B^{00}_{10}\, G^{10}\, B^{10}_{00}\, h^{00} = &\frac{1}{(2\pi)^3} \frac{2m_{\mathrm{e}}}{\hbar^2} \frac{e^4}{(2\pi^2)^2} \int \mathrm{d}z' \int \mathrm{d}\boldsymbol{p}_1 \int \mathrm{d}\boldsymbol{p}_2 \int \mathrm{d}\boldsymbol{p}_3 \frac{g_{\boldsymbol{p}_1}\, f_{\boldsymbol{p}_2}\, g_{\boldsymbol{p}_3}}{\boldsymbol{p}_1^2 - \boldsymbol{p}_2^2 + \boldsymbol{p}_3^2 - \mu} \\
&\Big\{ -2\, e^{i\boldsymbol{p}_3\boldsymbol{z}} \frac{P(\boldsymbol{p}_1-\boldsymbol{p}_2)}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \frac{P(\boldsymbol{p}_2-\boldsymbol{p}_1)}{|\boldsymbol{p}_2-\boldsymbol{p}_1|^2}\, e^{i\boldsymbol{p}_3\boldsymbol{z}'} + e^{i\boldsymbol{p}_3\boldsymbol{z}} \frac{P(\boldsymbol{p}_1-\boldsymbol{p}_2)}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \frac{P(\boldsymbol{p}_2-\boldsymbol{p}_3)}{|\boldsymbol{p}_2-\boldsymbol{p}_3|^2}\, e^{-i\boldsymbol{p}_1\boldsymbol{z}'} \\
&-2\, e^{i\boldsymbol{p}_3\boldsymbol{z}} \frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \frac{P(\boldsymbol{p}_2-\boldsymbol{p}_1)}{|\boldsymbol{p}_2-\boldsymbol{p}_1|^2}\, e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\boldsymbol{z}'} + e^{i\boldsymbol{p}_3\boldsymbol{z}} \frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \frac{P(\boldsymbol{p}_2-\boldsymbol{p}_3)}{|\boldsymbol{p}_2-\boldsymbol{p}_3|^2}\, e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\boldsymbol{z}'} \\
&-2\, e^{i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\boldsymbol{z}} \frac{P(\boldsymbol{p}_1-\boldsymbol{p}_2)}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \frac{g_{\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3}}{|\boldsymbol{p}_2-\boldsymbol{p}_1|^2}\, e^{-i\boldsymbol{p}_3\boldsymbol{z}'} + e^{i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\boldsymbol{z}} \frac{P(\boldsymbol{p}_1-\boldsymbol{p}_2)}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \frac{g_{\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3}}{|\boldsymbol{p}_3-\boldsymbol{p}_2|^2}\, e^{-i\boldsymbol{p}_1\boldsymbol{z}'}
\end{aligned}$$

$$-2\, e^{i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\boldsymbol{z}} \frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \frac{g_{\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3}}{|\boldsymbol{p}_2-\boldsymbol{p}_1|^2} e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\boldsymbol{z}'}$$

$$+ e^{i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\boldsymbol{z}} \frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \frac{g_{\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3}}{|\boldsymbol{p}_3-\boldsymbol{p}_2|^2} e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\boldsymbol{z}'} \Bigg\}$$

$$\cdot \sum_{\nu=0}^{\infty} \left[-1 \frac{e^2}{2\pi^2} \frac{2m_e}{\hbar^2} \frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \int \mathrm{d}\boldsymbol{q} \frac{g_{\boldsymbol{q}} f_{\boldsymbol{q}-\boldsymbol{p}_1+\boldsymbol{p}_2}}{\boldsymbol{p}_3^2+\boldsymbol{q}^2-(\boldsymbol{q}-\boldsymbol{p}_1+\boldsymbol{p}_2)^2-\mu} \right]^{\nu} \cdot h^{00}\begin{pmatrix} z' \\ \sigma \end{pmatrix}. \tag{3.108}$$

3.2.6 Influence of Green's Function

The inversion of (3.72) and (3.73) with h^{01} and h^{10} leads to the appearance of infinite series in (3.106) and (3.108). We abbreviate them with

$$D_R(\boldsymbol{p}''-\boldsymbol{p}''') = \sum_{\nu=0}^{\infty} [d_R(\boldsymbol{p}''-\boldsymbol{p}''')]^{\nu}, \tag{3.109}$$

$$D_H(\boldsymbol{p}_1-\boldsymbol{p}_2) = \sum_{\nu=0}^{\infty} [d_H(\boldsymbol{p}_1-\boldsymbol{p}_2)]^{\nu}. \tag{3.110}$$

Using the limits of the series

$$D_R(\boldsymbol{p}''-\boldsymbol{p}''') = \frac{1}{1-d_R(\boldsymbol{p}''-\boldsymbol{p}''')}, \tag{3.111}$$

$$D_H(\boldsymbol{p}_1-\boldsymbol{p}_2) = \frac{1}{1+d_H(\boldsymbol{p}_1-\boldsymbol{p}_2)} \tag{3.112}$$

and setting

$$\varkappa_R(\boldsymbol{p}''-\boldsymbol{p}''') := 1-d_R(\boldsymbol{p}''-\boldsymbol{p}''') \tag{3.113}$$

$$\varkappa_H(\boldsymbol{p}_1-\boldsymbol{p}_2) := 1+d_R(\boldsymbol{p}_1-\boldsymbol{p}_2) \tag{3.114}$$

we see that in reference system contribution th electron-electron potential and in the contribution of the hydrid system the electron-electron potential as well as the potential of the diluted hydrogen are not the pure Coulomb potential with the Fourier representations

$$V_R(\boldsymbol{p}''-\boldsymbol{p}''') = \frac{4\pi e^2}{|\boldsymbol{p}''-\boldsymbol{p}'''|}$$

and

$$V_H(\boldsymbol{p}_1-\boldsymbol{p}_2) = \frac{4\pi e^2}{|\boldsymbol{p}_1-\boldsymbol{p}_2|}$$

but effective potentials with the Fourier representation

$$V_R^{\text{eff}}(\boldsymbol{p}''-\boldsymbol{p}''') = \frac{1}{\varkappa_R(\boldsymbol{p}''-\boldsymbol{p}''')} V_R(\boldsymbol{p}''-\boldsymbol{p}'''), \tag{3.115}$$

$$V_H^{\text{eff}}(\boldsymbol{p}_1-\boldsymbol{p}_2) = \frac{1}{\varkappa_H(\boldsymbol{p}_1-\boldsymbol{p}_2)} V_H(\boldsymbol{p}_1-\boldsymbol{p}_2). \tag{3.116}$$

The effective potentials can be compared with the description of perturbation electron-electron interaction or with screening theory of impurities in solids. $\varkappa$ acts as a dielectric function screening long range interactions of the Coulomb potential. By the way, $\varkappa$ depends on the searched eigenvalue $\lambda(\omega)$, so hat the screening depends on the still to be determined electronical energy.

The main difference from the well known Lindhard theory of screening [10] is that our $\varkappa$ will not lead to Friedel oscillations of the effective potential $V^{\text{eff}}(r)$. One more difference from the Thomas Fermi theory is the behaviour of $\varkappa$ for small values of l_H or l_R. $\varkappa$ diverges as

$$\varkappa(\boldsymbol{l}) \to \frac{2m_e e^2 k_F^2}{\pi \hbar^2 c^2} \frac{1}{|\boldsymbol{l}|} \quad \text{for} \quad |\boldsymbol{l}| \to 0,$$

($\boldsymbol{l}_r = \boldsymbol{p}''-\boldsymbol{p}'''$, $c_r = \boldsymbol{p}^2-\mu$ resp. $\boldsymbol{l}_h = \boldsymbol{p}_1-\boldsymbol{p}_2$, $c_h = \boldsymbol{p}_3^2-\mu$) whereas in Thomas Fermi theory

$$\varepsilon(\boldsymbol{l}) \to \frac{4m_e e^2 k_F}{\pi \hbar^2} \frac{1}{|\boldsymbol{l}^2|} \quad \text{for} \quad |\boldsymbol{l}| \to 0.$$

In contrast to the Thomas Fermi theory it is not justified to approximate the screening effects in our theory with Yukawa potentials for V^{eff}.

3.2.7 Numerical Solution

In a first step the zeroth order problem is solved. For this purpose (3.55) is multiplied from the right and left side with development functions to transform the equation in a matrix eigenvalue problem. This problem is solved numerically. The calculated result is shown in Fig. 2 as a dotted line.

For the higher order approximation (3.76) is also transformed into a matrix eigenvalue problem. The integration are done as far as possible analytically. Altogether the integrals can be solved analytically

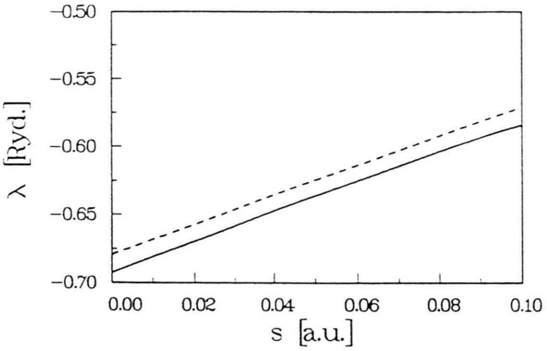

Fig. 2. Electronic energy eigenvalue of the higher order approximation (solid line) and the zeroth order approximation (dotted line) dependent on the lattice distortion *s*.

down to twofold and threefold integrations. The remaining integrations are solved numerically. As these matrix elements depend on the searched eigenvalue λ, the process to solve (3.76) is done iteratively: as an approximation for λ we use λ_0 of the zeroth order approximation in the matrixelements describing the influence of the higher order contributions. The resulting λ_1 after diagonalisation is used as a new approximation for the matrix elements, and so on. This procedure is continued until convergence for λ is reached. The results are shown as a solid line in Figure 2.

4. Lattice Static

The storage energy ΔE_{stor} (2.24) still depends on the proton position $\boldsymbol{Y}$ and the lattice coordinates $\tilde{\boldsymbol{X}}$. To calculate the storage energy the realized lattice distortion must first be determined. The equilibrium position

$$\tilde{\boldsymbol{X}} = \boldsymbol{X} + s \tag{4.1}$$

is got from minimizing the storage energy. Therefore the equilibrium conditions are

$$0 = \nabla_{\boldsymbol{Y}} \Delta E_{\mathrm{stor}}(\tilde{\boldsymbol{X}}, \boldsymbol{Y}) = \nabla_{\boldsymbol{Y}} Q(\tilde{\boldsymbol{X}}, \boldsymbol{Y}), \tag{4.2}$$

$$0 = \nabla_{\tilde{\boldsymbol{X}}} \Delta E_{\mathrm{stor}}(\tilde{\boldsymbol{X}}, \boldsymbol{Y}) = \nabla_{\tilde{\boldsymbol{X}}} [Q(\tilde{\boldsymbol{X}}, \boldsymbol{Y}) + \Delta U_{\mathrm{W}}(\tilde{\boldsymbol{X}})]. \tag{4.3}$$

Equation (4.2) permits in principle the determination of the proton position $\boldsymbol{Y}$ dependent on the lattice positions $\tilde{\boldsymbol{X}}$. With the interpretation of Q as the interaction between the additional electron, the proton and the lattice ions, and ΔU as distortion energy, the equilibrium

$$\boldsymbol{F}_{\mathrm{latt}}(\tilde{\boldsymbol{X}}) = -\boldsymbol{F}_{\mathrm{pert}}(\tilde{\boldsymbol{X}}) \tag{4.4}$$

between the perturbation force

$$\boldsymbol{F}_{\mathrm{pert}}(\tilde{\boldsymbol{X}}) = -\nabla_{\tilde{\boldsymbol{X}}} Q(\tilde{\boldsymbol{X}}, \boldsymbol{Y}) \tag{4.5}$$

and the lattice force

$$\boldsymbol{F}_{\mathrm{latt}}(\tilde{\boldsymbol{X}}) = -\nabla_{\tilde{\boldsymbol{X}}} \Delta U_{\mathrm{W}}(\tilde{\boldsymbol{X}}) \tag{4.6}$$

is contained in (4.3).

4.1 Lattice Forces

Since the lattice distortion (4.1) is small in general, the harmonic approximation can be applied for the lattice forces for the displaced ions. This leads to

$$\boldsymbol{F}_{\mathrm{latt}}(s) = -\mathscr{A}\, s \quad \text{resp.} \quad F_i^{\boldsymbol{m}} = -\sum_{\boldsymbol{n}, k} A_{ik}^{\boldsymbol{mn}} s_k^{\boldsymbol{n}} \tag{4.7}$$

with the tensor of the force constants

$$\mathscr{A} = (A_{ik}^{\boldsymbol{mn}}) := \left(\frac{\partial^2 \Delta U_{\mathrm{W}}}{\partial \tilde{X}_i^{\boldsymbol{m}}\, \partial \tilde{X}_k^{\boldsymbol{n}}} (\mathbf{X}) \right). \tag{4.8}$$

The force constants $A_{ik}^{\boldsymbol{mn}}$ describe the forces of an ion $\boldsymbol{m}$ in the direction i if the ion $\boldsymbol{n}$ is displaced in the direction k by one unit.

If ΔU is known, $\mathscr{A}$ can be determined. The calculation is done in [13].

4.2 Perturbation Forces

To calculate perturbation forces, the interaction Q (2.23)

$$Q(\tilde{\boldsymbol{X}}, \boldsymbol{Y}) = \sum_{\boldsymbol{n}} \frac{Z e^2}{|\tilde{\boldsymbol{X}}^{\boldsymbol{n}} - \boldsymbol{Y}|} + \omega(\tilde{\boldsymbol{X}}) \tag{4.9}$$

and renormalized eigenvalues λ (3.53)

$$\lambda(\tilde{\boldsymbol{X}}) = \omega(\tilde{\boldsymbol{X}}) + 2e^2 \int \mathrm{d}\boldsymbol{x}\, \frac{S_0(\boldsymbol{x}, \boldsymbol{x})}{|\boldsymbol{x} - \boldsymbol{Y}|}$$

are inserted in (4.5) assuming radial displacements of only the next four neighbours of the proton in the lattice. We get the perturbation force onto the m-th ion

$$F_{\mathrm{pert}}^{\boldsymbol{m}}(s) = \frac{Z e^2}{|d + s|^2} - \frac{\mathrm{d}}{\mathrm{d}s} \frac{1}{4} \lambda(s). \tag{4.10}$$

d is the distance of the proton to the ideal lattice position of one of the next neighbours (centre of the tetrahedron to one corner). The electronic value λ has to be multiplied with $\frac{1}{4}$, assuming equivalent displacements for all four next neighbours.

4.3 Equilibrium

The equilibrium position of the next neighbours is got from the force equilibrium

$$\mathscr{A}\, s = \boldsymbol{F}_{\text{latt}}(\boldsymbol{s}) = -\boldsymbol{F}_{\text{pert}}(\boldsymbol{s}). \qquad (4.11)$$

Equation (4.11) is inverted with the help of a Green's functions $\mathscr{G}$,

$$\boldsymbol{s} = -\mathscr{G}\, \boldsymbol{F}_{\text{pert}}(\boldsymbol{s}),$$

assuming again only displacements of the next neighbours. We get for the k-th Ion ($k=0, \ldots, 3$) the displacements $\boldsymbol{s}^k$

$$\boldsymbol{s}^k = F(s) \sum_i \mathscr{G}^{ki}\, \boldsymbol{n}^i =: F(s)\, \tilde{\boldsymbol{G}}^k. \qquad (4.12)$$

$\boldsymbol{n}^i$ are unit vectors parallel to the forces, e.g. from the centre to the corner of a tetrahedron. The vectors $\tilde{\boldsymbol{G}}^k$ were calculated in [13]. They are colinear, and this agrees with our approximation of radial displacements. To calculate the distortion we use the scalar form of (4.12)

$$s^i = |\tilde{\boldsymbol{G}}^i|\, F^i(s^i) = |\tilde{\boldsymbol{G}}^i| \left[\frac{2e^2}{(d^i + s^i)^2} - \frac{1}{4} \frac{\mathrm{d}}{\mathrm{d}s^i} \lambda(s^i) \right]. \qquad (4.13)$$

To solve this equation, the numerically calculated values of $\lambda(s)$ are used and interpolated with a spline function and differentiated. After transformation to a zero root problem it can be solved again numerically. We get the following results for the ions $i=0, \ldots, 2$:

$$s = 0.03789\ \text{Å},$$

$$F_{\text{pert}} = 4.156 \cdot 10^{-10}\ \text{N},$$

and for the ion 3:

$$s = 0.03739\ \text{Å},$$

$$F_{\text{pert}} = 3.98 \cdot 10^{-10}\ \text{N},$$

as $|\tilde{\boldsymbol{G}}^k|$ $k=0, 1, 2$ and $|\tilde{\boldsymbol{G}}^3|$ are slightly different. To get a feeling for the influence of the higher order approximation we have also calculated the displacements and forces with the results of the zeroth order approximation of the electronic problem:

$$s = 0.04097\ \text{Å},$$

$$F_{\text{pert}} = 4.49 \cdot 10^{-10}\ \text{N} \quad \text{for ion} \quad i = 0, \ldots, 2$$

and

$$s = 0.04254\ \text{Å},$$

$$F_{\text{pert}} = 4.53 \cdot 10^{-10}\ \text{N} \quad \text{for ion} \quad i = 3.$$

4.3.1 Volume Change

The interstitial hydrogen is a point defect in the metallic crystal. The resulting displacement field $\boldsymbol{s}$ alters the volume of the crystal by an amount ΔV. The calculated volume change is [3]

$$\Delta V = 3.09\ \text{Å}^3$$

(using only the results of the zeroth order approximation of the electronic problem, we get $\Delta V = 3.34\ \text{Å}^3$). Whereas the experimental value is $\Delta V = 2.93\ \text{Å}^3$ [14]. The difference between our theoretical result and the experimental value is not significant.

5. Storage Energy

All values needed to calculate the storage energy

$$\Delta E_{\text{stor}}(\tilde{\boldsymbol{X}}, \boldsymbol{Y}) = \sum_n \frac{Z e^2}{|\tilde{\boldsymbol{X}}^n - \boldsymbol{Y}|} - 2e^2 \int \mathrm{d}\boldsymbol{x}\, \frac{S_0(\boldsymbol{x}, \boldsymbol{x})}{|\boldsymbol{x} - \boldsymbol{Y}|} + \lambda(\tilde{\boldsymbol{X}}) + \Delta U_{\text{W}}(\tilde{\boldsymbol{X}}) - E_0 \qquad (5.1)$$

are known or can be gotten easily. To evaluate the proton ion potential, it is split up into a term only depending on the ideal lattice positions and in a term depending on the displacement of the next four neighbours

$$\sum_n \frac{Z e^2}{|\tilde{\boldsymbol{X}}^n - \boldsymbol{Y}|} = \sum_n \frac{Z e^2}{|\boldsymbol{X}^n - \boldsymbol{Y}|} + Z e^2 \sum_{n=0}^{3} \left(\frac{1}{d^n + s^n} - \frac{1}{d^n} \right). \qquad (5.2)$$

The term independent of the displacement is evaluated together with the second term of (5.1). We get the separate contributions to the storage energy

$\sum_n \frac{Z e^2}{\lvert\tilde{\boldsymbol{X}}^n - \boldsymbol{Y}\rvert} - 2e^2 \int \mathrm{d}\boldsymbol{x}\, \frac{S_0(\boldsymbol{x}, \boldsymbol{x})}{\lvert\boldsymbol{x} - \boldsymbol{Y}\rvert}$	−5.03 eV
$Z e^2 \sum_{n=0}^{3} \left(\frac{1}{d^n + s^n} - \frac{1}{d^n} \right)$	−1.11 eV
$\lambda(s)$	−8.33 eV
$\frac{1}{2} s \mathscr{A} s$	0.02 eV
$-e_0$	13.61 eV
ΔE_{stor}	−0.84 eV

To compare the calculated storage energy ΔE_{stor} with the experimental value of dilution heat ΔH, it has to be corrected by half the dissoziation energy:

$$\Delta E_{\mathrm{stor}}^{\mathrm{exp}} = \Delta H - \tfrac{1}{2} D_{\mathrm{H}},$$

so that we have experimental value [15, 16].

$$E_{\mathrm{stor}}^{\mathrm{exp}} = -2.6 \text{ eV}.$$

Our calculated amount of the storage energy is with respect to the experimental value too small.

Acknowledgement

M. Gnirß is highly indebted to the Friedrich Flick Förderungsstiftung for the financial support.

[1] G. Alefeld and J. Völkl (eds.), Hydrogen in Metals, Vol. I & II, Springer-Verlag, Berlin 1978.
[2] F. Wahl, R. Duscher, K. Göbel, and J. K. Maichle, Z. Naturforsch. **39a**, 524 (1984).
[3] M. Gnirß, Thesis. Tübingen 1989.
[4] J. Tamm, J. Phys. USSR **9**, 449 (1945).
[5] S. M. Dancoff, Phys. Rev. **78**, 382 (1950).
[6] F. J. Dyson, Phys. Rev. **91**, 421 (1953).
[7] H. Rampacher, H. Stumpf, and F. Wagner, Fortschr. Phys. **13**, 385 (1965).
[8] H. Haken, Quantenfeldtheorie des Festkörpers, Teubner-Verlag, Stuttgart 1973.
[9] F. Wahl and W. Feist, Z. Naturforsch. **36a**, 429 (1981).
[10] N. W. Ashcroft and N. D. Mermin, Solid State Physics, Holt-Saunders, International Edition, Philadelphia 1976.
[11] G. L. Krasko and Z. A. Gurskii, JETP Letters **9**, 363 (1969).
[12] G. L. Krasko, Electronic Properties and Equilibrium Lattice Parameters of Magnesium Hydride. Proceedings of the Miami International Symposium on Metal-Hydrogen Systems, 13.–15. April in Miami Beach, Florida (USA), editor T. Nejat-Vezirogh, Pergamon Press, Miami 1982.
[13] B. Bratscheck, B. Rager, and H. J. Volkert, Z. Naturforsch. **40a**, 439 (1985).
[14] H. Peisl, Lattice Strains Due to Hydrogen in Metals. In: [1, Vol I, S. 53].
[15] R. Griessen, and A. Driessen, Phys. Rev. B **30**, 4372 (1984).
[16] W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, Metal Hydrides, Academic Press, New York 1968.