A Higher Order Approximation for the Electronic Structure of Hydrogen in Metals

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A functional energy difference method based on first principles is used to calculate the electronic contribution to the storage energy of hydrogen impurities in metals. That electronic problem is treated in a higher order approximation which means considering the coupling between one-electron wavefunctions and three-particle amplitudes. A formalism is presented to eliminate all higher order correlations and to reduce the whole system to a one-particle Schrödinger equation with the help of a suitable Green's function. The resulting one-electron eigenvalue problem contains some logarithmic singularities due to the fact that there is no gap between occupied and unoccupied electron states in the band structure of a metal. In an electron gas model a convergent theory is reached by an improvement of the Green's function leading to a screening of the long-range Coulomb potentials. The result is a complicated non-linear algebraic eigenvalue equation which is solved numerically for the special case of a single hydrogen perturbation in a magnesium crystal. The solution shows the influence of higher order electron correlations on the electronic energy eigenvalue of an interstitial hydrogen centre plot as a function of host lattice distortions.

Introduction

The present work contains a higher order approximation of a field theoretical method developed in an earlier paper in application on the electronic problem of hydrogen impurities implemented in a metal crystal [1]. The mathematical theory is based on a follow-on procedure of the so-called New Tamm-Dancoff (NTD) formalism [2]. In its original formulation the NTD-procedure consists of a field equation for the connection of τ-functions [3]. However, it is well-known that τ-functions are not suitable enough to represent physical reality [4]. But a convergent theory can be established by an appropriate transformation on φ-functions which means a normal ordering of field operators [5]. In application to solid state models it is possible to interpret the physical contents of the NTD-procedure [6] such that transparency of the formalism is now available [7]. Accordingly, treating a many-body problem in band theory, the transformation on φ-functions is reached by the transition from a kind of bare vacuum into a realistic ground state allowing energy and state computations with the help of particle-hole pairs in analogy to the semiconductor model theory of Haken [8].

Meanwhile, we are successful in establishing a transformation on a self-adjoint theory [1] with orthogonal state vectors as base system in contrast to the nonorthogonal φ-functions. In this formalism the corresponding functional operator is a difference of two essentially distinct many-particle Hamiltonians. As a direct consequence, in case of hydrogen impurities in a metal, we are able to construct the electronic states of the total system by a tensor product consisting of two different state vectors. The first of them describes additional hydrogen electrons inserted into the sea of remaining metal valence electrons while the second one can be interpreted as a kind of undisturbed many-particle state of the host lattice. The formalism presented in [1] enables us to compute the energy difference between these two states which means the electronic contribution of storage energy of hydrogen centres in metals.

The purpose of our follow-on NTD-method in application to solid state models is therefore assumed to represent the calculation of energy differences of quantum mechanical systems. Although the formulation of the shown procedure is based on functionals in form of generating operators such

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that a nomenclatur as e.g. "functional energy difference method" would be more suitable, we will use the notation "New Tamm-Dancoff procedure" for historical reasons.

1. Functional Formulation of the Electronic Problem

In a preceding paper [1] we discussed a formalism for calculating energy differences of quantum mechanical systems. In application to metal hydrides we will now briefly repeat the fundamental ideas, notations, and formulae.

The electronic subsystem of our many-particle problem is characterized by two Schrödinger equations [1]:

$$\mathbb{H}_{\mathrm{H}}(\psi^+, \psi)\, \chi_{\mathrm{H}}(\psi^+ S_1, S_0 \psi)\, |\Omega_\psi\rangle = \varepsilon^{N+n}\, \chi_{\mathrm{H}}(\psi^+ S_1, S_0 \psi)\, |\Omega_\psi\rangle , \tag{1.1}$$

$$\mathbb{H}_{\mathrm{R}}(\psi^+, \psi)\, \chi_{\mathrm{R}}(\psi^+ S_1, S_0 \psi)\, |\Omega_\psi\rangle = \varepsilon^{N}\, \chi_{\mathrm{R}}(\psi^+ S_1, S_0 \psi)\, |\Omega_\psi\rangle . \tag{1.2}$$

The first equation describes the behaviour of electrons in a metal disturbed by stored hydrogen atoms. We will call it "H-system". The second one represents a reference system (called "R-system") which consists of a host crystal indeed without hydrogen centres. ψ^+ and ψ are Fermi field operators obeying the canonical anticommutation relations (CAR). $\mathbb{H}_{\mathrm{H}}$ and $\mathbb{H}_{\mathrm{R}}$ denote the Hamiltonians belonging to H- and R-systems, respectively ([1], (5.1) – (5.6)). They both include a kinetic energy operator, a Coulomb potential $e^2/|\boldsymbol{x}-\boldsymbol{x}'|$ representing the electron-electron interaction, and an interaction $V_w(\boldsymbol{x}, \boldsymbol{X})$ between a definite number N of valence electrons and host lattice ions localized at equilibrium positions $\boldsymbol{X}$. In addition $\mathbb{H}_{\mathrm{H}}$ contains the potential $V_{\mathrm{H}}(\boldsymbol{x}, \boldsymbol{Y})$ of n stored hydrogen protons with coordinates $\boldsymbol{Y}$. $\chi_{\mathrm{H}}|\Omega_\psi\rangle$, $\chi_{\mathrm{R}}|\Omega_\psi\rangle$ and ε^{N+n}, ε^{N} are eigenvectors and electronic eigenvalues of $\mathbb{H}_{\mathrm{H}}$ and $\mathbb{H}_{\mathrm{R}}$, respectively. We choose a reference system which is deformed in the same way as the lattice of our H-system. This implies that we can split off elastic or vibrational contributions and treat them in a separate manner [9]. So we are sure that the eigenvalues ε^{N+n} and ε^{N} really contain only electronic portions.

According to the particle-hole formulation of Haken [8] we are working in a sort of valence band representation, i.e. we construct projection operators S_0, S_1 with the properties ([1], (5.7) – (5.9))

i) disjunction and idempotence

$$S_i(\boldsymbol{x}, \boldsymbol{y})\, S_j(\boldsymbol{y}, \boldsymbol{x}') = S_i(\boldsymbol{x}, \boldsymbol{x}')\, \delta_{ij}, \quad i, j \in \{0, 1\} , \tag{1.3}$$

ii) completeness

$$S_0(\boldsymbol{x}, \boldsymbol{x}') + S_1(\boldsymbol{x}, \boldsymbol{x}') = \delta(\boldsymbol{x}-\boldsymbol{x}') , \tag{1.4}$$

iii) self-adjointness

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

and interpret the state vector $|\Omega_\psi\rangle$ as a kind of quasi-particle vacuum defined by ([1], (5.10 a, b)):

$$\psi_s^+(\boldsymbol{y})\, S_0(\boldsymbol{y}, \boldsymbol{x})\, |\Omega_\psi\rangle = 0 , \tag{1.6}$$

$$S_1(\boldsymbol{x}, \boldsymbol{y})\, \psi_s(\boldsymbol{y})\, |\Omega_\psi\rangle = 0 . \tag{1.7}$$

In analogy to [1] we use an "extended Einstein convention" which we will keep through the rest of this paper and which means that one has to integrate or sum up all multiple appearing arguments and indices.

Physical significance as well as technical interests are not connected with absolute and infinite energy eigenvalues ε^{N+n}, ε^{N} but much more with energy differences like

$$\omega \equiv \omega^{(n)}(\boldsymbol{Y}, \boldsymbol{X}) = \varepsilon^{N+n}(\boldsymbol{Y}, \boldsymbol{X}) - \varepsilon^{N}(\boldsymbol{X}) . \tag{1.8}$$

In [1] we presented a functional method for the computation of eigenvalue differences, a follow-on procedure to the so-called New Tamm-Dancoff (NTD) formalism. With the aid of a generating operator

$$\boldsymbol{\Gamma} \equiv e^{i w^+ S_0 \psi}\, e^{-i \psi^+ S_1 v^+}\, e^{i \psi^+ S_1 w}\, e^{-i v S_0 \psi} \cdot e^{i w^+ S_1 \psi}\, e^{-i \psi^+ S_0 v^+}\, e^{i v S_1 \psi}\, e^{-i \psi^+ S_0 w} \tag{1.9}$$

we transformed the two Schrödinger problems (1.1), (1.2) into a functional equation determining the electronic energy difference ω:

$$\mathbb{B}\, |\Phi_{\mathrm{HR}}\rangle = \omega\, |\Phi_{\mathrm{HR}}\rangle . \tag{1.10}$$

Equation (1.10) acts in a suitably chosen CAR-tensor product space built by Fermi field operators v^+, v and w^+, w which anticommute among one another and among the ψ-field. The eigenstate $|\Phi_{\mathrm{HR}}\rangle$ results in an antilinear functional

$$|\Phi_{\mathrm{HR}}\rangle = [\chi_{\mathrm{R}}(-i v S_1, i S_0 w)]^+ \cdot \chi_{\mathrm{H}}(i w^+ S_1, i S_0 v^+)\, |O_{vw}\rangle , \tag{1.11}$$

where $|O_{vw}\rangle$ denotes the vacuum state in vw-space. Due to the dexterous transformation via (1.9) $\mathbb{B}$ is obtained as a self-adjoint functional difference Hamilton operator:

$$\begin{aligned}\mathbb{B} = {} & \mathbb{H}_{\mathrm{H}}(i\,w^{+} S_1 - i\,v\,S_0,\; i\,S_0\,v^{+} - i\,S_1\,w) \\ & - \mathbb{H}_{\mathrm{R}}(i\,S_0\,w + i\,S_1\,v^{+},\, -i\,v\,S_1 - i\,w^{+} S_0)\,.\end{aligned} \tag{1.12}$$

The detailed structure of $\mathbb{B}$ after normal-ordering with respect to creation and destruction operators is presented in [1], (6.11)–(6.19). A graphical interpretation of each constituent of $\mathbb{B}$ is given in [10]. It is shown that $\mathbb{B}$ contains all so-called "fundamental diagrams" [11] to compose higher order processes e.g. in perturbation theory.

For the computation of approximate solutions of (1.10) a cut-off procedure has to be applied. In accordance to [1] we define base states

$$\begin{aligned}|\Phi^{m+J,\,m'+J'}\big(\begin{smallmatrix}x\\ s\end{smallmatrix}\big)\rangle := {} & \prod_{i=0}^{m+J} w^{+}_{s_i}(\boldsymbol{y}_i)\, S_1(\boldsymbol{y}_i, \boldsymbol{x}_i) \\ & \cdot \prod_{j=0}^{m} v^{+}_{s'_j}(\boldsymbol{y}'_j)\, S_0^{*}(\boldsymbol{y}'_j, \boldsymbol{x}'_j) \\ & \cdot \prod_{i'=0}^{m'+J'} v^{+}_{s''_{i'}}(\boldsymbol{y}''_{i'})\, S_1^{*}(\boldsymbol{y}''_{i'}, x''_{i'}) \\ & \cdot \prod_{j'=0}^{m'} w^{+}_{s'''_{j'}}(\boldsymbol{y}'''_{j'})\, S_0(\boldsymbol{y}'''_{j'}, \boldsymbol{x}'''_{j'})\, |O_{vw}\rangle,\end{aligned} \tag{1.13}$$

where all factors corresponding to multiplication indices of zero are defined as unity operators in vw-space. Using the electron-hole description of [1], $|\phi^{m+J,\,m'+J'}\rangle$ can be interpreted to describe $(m+J)$ electrons outside the Fermi sphere and m defect electrons (holes) below the Fermi edge in our H-system. So J is identified with the number of excess electrons belonging to the additional hydrogen atoms in the H-system, and m is the number of particle-hole pairs added to the H-system to describe some elementary excitations, such as e.g. excitons. A quite analogous interpretation is possible for the R-system with the numbers J' and m', respectively.

The variable x on the left-hand side of (1.13) represents the whole set of space coordinates of $(m+J)$ electrons and m defect electrons of the H-system as well as $(m'+J')$ particles and m' antiparticles of the R-system:

$$\begin{aligned}x & \equiv (\boldsymbol{x}, \boldsymbol{x}', \boldsymbol{x}'', \boldsymbol{x}''') \\ & \equiv (\boldsymbol{x}_1 \ldots \boldsymbol{x}_{m+J}, \boldsymbol{x}'_1 \ldots \boldsymbol{x}'_m, \boldsymbol{x}''_1 \ldots \boldsymbol{x}''_{m'+J'}, \boldsymbol{x}'''_1 \ldots \boldsymbol{x}'''_{m'})\,.\end{aligned} \tag{1.14}$$

s means the corresponding set of spin coordinates.

Starting with the basic states of (1.13) we build projection operators in the usual manner ([1], (6.27)):

$$\mathbb{P}^{M+J,\,M'+J'} := \sum_{m=0}^{M} \sum_{m'=0}^{M'} \mathbb{P}^{m+J,\,m'+J'} \tag{1.15}$$

with ([1], (6.28))

$$\mathbb{P}^{m+J,\,m'+J'} := \frac{1}{(m+J)!\,m!\,(m'+J')!\,m'!} \cdot |\phi^{m+J,\,m'+J'}\rangle\langle\phi^{m+J,\,m'+J'}|\,. \tag{1.16}$$

M and M' denote the approximation's grade.

The cut of (1.10) is then achieved by inserting the projectors $\mathbb{P}^{M+J,\,M'+J'}$ symmetrically into (1.10) to preserve the equation's hermiticity, and multiplying the resulting equation by $\langle\phi^{m+J,\,m'+J'}|$ from the left side:

$$\begin{aligned}& \langle\phi^{m+J,\,m'+J'}|\,\mathbb{P}^{M+J,\,M'+J'}\,\mathbb{B}\,\mathbb{P}^{M+J,\,M'+J'}\,|\phi^{(M,\,M')}_{\mathrm{HR}}\rangle \\ & \quad = \omega^{(M,\,M')}\langle\phi^{m+J,\,m'+J'}|\,\mathbb{P}^{M+J,\,M'+J'}\,\phi^{(M,\,M')}_{\mathrm{HR}}\rangle.\end{aligned} \tag{1.17}$$

The lowest order approximation

$$M = 0 \quad \text{and} \quad M' = 0 \tag{1.18}$$

has been treated in the past very detailed [1, 9, 12] for the special case of one single hydrogen excess electron, which means

$$J = 1 \quad \text{and} \quad J' = 0\,. \tag{1.19}$$

The intention of the present work is the analysis of a higher order approximation of (1.17) defined by

$$J = 1\,, \quad J' = 0\,, \quad M = 1\,, \quad M' = 1\,. \tag{1.20}$$

2. Elimination Procedure

For our further investigations we want to fix the numbers J, J' of hydrogen excess electrons in both systems and likewise the numbers M, M' of particle-hole pairs. Defining for all $m \leqq M$ and $m' \leqq M'$ the wavefunction

$$h^{m,\,m'}\big(J, J' \,\big|\, \begin{smallmatrix}x\\ s\end{smallmatrix}\big) := \langle\phi^{m+J,\,m'+J'}\big(\begin{smallmatrix}x\\ s\end{smallmatrix}\big)\,|\,\Phi^{(M,\,M')}_{\mathrm{HR}}\rangle \tag{2.1}$$

and the matrix elements

$$B^{m,\,m'}_{v,\,v'}\big(J, J' \,\big|\, \begin{smallmatrix}z & x\\ \sigma & s\end{smallmatrix}\big) := \frac{1}{(v+J)!\,v!\,(v'+J')!\,v'!} \cdot \langle\phi^{m+J,\,m'+J'}\big(\begin{smallmatrix}z\\ \sigma\end{smallmatrix}\big)\,|\,\mathbb{B}\,|\,\phi^{v+J,\,v'+J'}\big(\begin{smallmatrix}x\\ s\end{smallmatrix}\big)\rangle \tag{2.2}$$

we get from (1.17) a finite system of matrix equations determining the approximate electronic energy difference eigenvalue $\omega^{(M,M')}$:

$$B^{m,m'}_{\nu,\nu'}\left(J,J'\,\middle|\,\begin{smallmatrix} z & x \\ \sigma & s \end{smallmatrix}\right) h^{\nu,\nu'}\left(J,J'\,\middle|\,\begin{smallmatrix} x \\ s \end{smallmatrix}\right) = \omega^{(M,M')}\, h^{m,m'}\left(J,J'\,\middle|\,\begin{smallmatrix} z \\ \sigma \end{smallmatrix}\right), \qquad m = 0, 1, \ldots, M; \quad m' = 0, 1, \ldots, M'. \tag{2.3}$$

Remember the extended Einstein convention, which means in this case a sum over the indices $\nu = 0, \ldots, M$ and $\nu' = 0, \ldots, M'$, and additionally an integration/sum over alle space/spin coordinates of electrons and holes in the H- and R-system.

Formally, the system (2.3) can be written quite analogous to an algebraic eigenvalue problem

$$\mathbf{B} \cdot H^{\downarrow} = \omega^{(M,M')} \cdot H^{\downarrow}. \tag{2.4}$$

In that notation the operator **B** represents a square matrix of rank $(M+1)$ where each matrix element itself represents once more a square matrix, now of rank $(M'+1)$. Likewise, the eigenvector $H^{\downarrow}$ can be interpreted as a column vector with $(M+1)$ components and each component is combined of $(M'+1)$ wavefunctions.

A lot of matrix elements $B^{m,m'}_{\nu,\nu'}$ are supposed to become zero which can be easily recognized if $\mathbb{B}$ is separated into its constituents ([1], (6.12) – (6.19)) and matrix elements are evaluated. An example is shown in [10]. There we proved the

Theorem: $B^{m,m'}_{\nu,\nu'}$ is not equal to zero if and only if one of the following two conditions is fullfilled:

i) $m = \nu$ and $|m' - \nu'| \leqq 2$, or (2.5 a)

ii) $m' = \nu'$ and $|m - \nu| \leqq 2$. (2.5 b)

As a direct consequence of that statement we get a kind of stripe structure of **B** consisting of a main diagonal block matrix followed by two diagonal block matrices on each side. A graphical illustration of that matrix is shown in [10].

For each $m \in \{0, 1, \ldots, M\}$ and $m' \in \{0, 1, \ldots, M'\}$ the wavefunctions $h^{m,m'}$ of the state vector $|\Phi^{(M,M')}_{\mathrm{HR}}\rangle$ are connected with all other components $h^{\nu,\nu'}$ via (2.3).

In principle it is possible to compute from that coupled equations (2.3) approximate J-particle states of the H-system and J'-particle states of the R-system, respectively. In practice, the many-particle wavefunctions $h^{\nu,\nu'}$ with large indices ν, ν' have to be eliminated and reduced step by step into one-electron wavefunctions. Therefore, we start with the eigenvalue equation of the highest grade (i.e. $\nu = M$ and $\nu' = M'$) and compute via inversion the wavefunction $h^{\nu,\nu'}$ in dependence of lower order amplitudes. The result is inserted into the remaining system such that an eigenvalue problem for the next lowest grade (i.e. $\nu = M$ and $\nu' = M' - 1$) is left. The successive application of this elimination procedure enables us to reduce our system into a one- or two-particle Schrödinger equation.

The main problem is a complete inversion of the individual eigenvalue equations which are represented by difficult integral equations. We will show how at least a partial inversion of the functional equation can be achieved.

For that purpose we split our functional operator $\mathbb{B}$ into two parts,

$$\mathbb{B} = \mathbb{B}_0 + \mathbb{B}_{\mathrm{Rest}}, \tag{2.6}$$

where $\mathbb{B}_0$ is an operator which can be easily inverted with the help of a Green's function $\mathbb{G}_0$ defined by

$$\mathbb{G}_0^{M+J,\,M'+J'}\, \mathbb{P}^{M+J,\,M'+J'} (\mathbb{B}_0 - \omega^{(M,M')} \cdot 1)\, \mathbb{P}^{M+J,\,M'+J'} \,|\,\Phi^{(M,M')}_{\mathrm{HR}}\rangle = \mathbb{P}^{M+J,\,M'+J'} \,|\,\Phi^{(M,M')}_{\mathrm{HR}}\rangle. \tag{2.7}$$

With (2.6) and (2.7) we rewrite (1.17) and conclude

$$h^{\nu,\nu'} = -\langle \Phi^{\nu+J,\,\nu'+J'} \,|\, \mathbb{G}_0^{M+J,\,M'+J'}\, \mathbb{P}^{M+J,\,M'+J'} (\mathbb{B} - \mathbb{B}_0)\, \mathbb{P}^{M+J,\,M'+J'} \,|\,\Phi^{(M,M')}_{\mathrm{HR}}\rangle. \tag{2.8}$$

In general, the right side of (2.8) does not contain only amplitudes $h^{\mu,\mu'}$ with $\mu < \nu$ and $\mu' < \nu'$ but also connections to $h^{\nu,\nu'}$ itself. Neglecting these knottings, the $h^{\nu,\nu'}$ of (2.8) can be used for elimination. But first of all we need a method to determine the Green's function $\mathbb{G}_0^{M+J,\,M'+J'}$.

3. Evaluation of the Green's Function

$\mathbb{G}_0^{M+J,\,M'+J'}$ is defined by

$$\mathbb{G}_0^{M+J,\,M'+J'}\, \mathbb{P}^{M+J,\,M'+J'} (\mathbb{B}_0 - \omega \cdot 1) \cdot \mathbb{P}^{M+J,\,M'+J'} \,|\,\Phi^{(M,M')}_{\mathrm{HR}}\rangle = \mathbb{P}^{M+J,\,M'+J'} \,|\,\Phi^{(M,M')}_{\mathrm{HR}}\rangle. \tag{3.1}$$

For $\mathbb{B}_0$ we take the essential one-particle contributions [1]

$$\begin{aligned}\mathbb{B}_0 = C &+ w_\varrho^+(\boldsymbol{y})\, S_1(\boldsymbol{y},\boldsymbol{x})\, D(\boldsymbol{x},\boldsymbol{x}')\, S_1(\boldsymbol{x}',\boldsymbol{y}')\, w_\varrho(\boldsymbol{y}') \\ &- v_\varrho^+(\boldsymbol{y})\, S_0^*(\boldsymbol{y},\boldsymbol{x})\, D^*(\boldsymbol{x},\boldsymbol{x}')\, S_0^*(\boldsymbol{x}',\boldsymbol{y}')\, v_\varrho(\boldsymbol{y}') \\ &- v_\varrho^+(\boldsymbol{y})\, S_1^*(\boldsymbol{y},\boldsymbol{x})\, D^*(\boldsymbol{x},\boldsymbol{x}')\, S_1^*(\boldsymbol{x}',\boldsymbol{y}')\, v_\varrho(\boldsymbol{y}') \\ &+ w_\varrho^+(\boldsymbol{y})\, S_0(\boldsymbol{y},\boldsymbol{x})\, D(\boldsymbol{x},\boldsymbol{x}')\, S_0(\boldsymbol{x}',\boldsymbol{y}')\, w_\varrho(\boldsymbol{y}')\,. \end{aligned} \tag{3.2}$$

The proton potential $V_\mathrm{H}(\boldsymbol{x},\boldsymbol{Y})$ is taken out of $\mathbb{B}_0$ and added to $\mathbb{B}_\mathrm{Rest}$. The term

$$\begin{aligned} C &:= \operatorname{Trace}\left[V_\mathrm{H}(\boldsymbol{x},\boldsymbol{Y})\, S_0(\boldsymbol{x},\boldsymbol{x})\right] \\ &= -2e^2 \sum_{\boldsymbol{n}} \int \mathrm{d}^3x\, \frac{S_0(\boldsymbol{x},\boldsymbol{x})}{|\boldsymbol{x}-\boldsymbol{Y}_{\boldsymbol{n}}|} \end{aligned} \tag{3.3}$$

is constant with respect to electron and host lattice coordinates. It represents a screened electrostatic interaction between stored interstitial hydrogen protons and a field built by the whole ensemble of metal electrons. Wahl showed that C is indeed divergent but is compensated in the total energy balance by a corresponding divergency, namely the interaction between hydrogen cores and host lattice ions [13]. Therefore we treat C as an additive energy shift and collect it with ω. $D(\boldsymbol{x},\boldsymbol{x}')$ is a Hartree-Fock operator of the metal electrons of the R-system:

$$\begin{aligned} D(\boldsymbol{x},\boldsymbol{x}') := &\left\{-\frac{\hbar^2}{2m}\Delta + V_w(\boldsymbol{x},\boldsymbol{X}) + 2e^2\int \mathrm{d}^3y\, \frac{S_0(\boldsymbol{y},\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|}\right\} \\ &\cdot \delta(\boldsymbol{x}-\boldsymbol{x}') - e^2\,\frac{S_0(\boldsymbol{x},\boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|}\,. \end{aligned} \tag{3.4}$$

We suppose that the solutions of the Hartree-Fock equations

$$D(\boldsymbol{x},\boldsymbol{x}')\, b_{\boldsymbol{k}}(\boldsymbol{x}') = \varepsilon_{\boldsymbol{k}}\, b_{\boldsymbol{k}}(\boldsymbol{x}) \tag{3.5}$$

are known. In case of an ideal lattice, $b_{\boldsymbol{k}}$ are Bloch functions and $\varepsilon_{\boldsymbol{k}}$ are the usual band energies belonging to wavenumbers $\boldsymbol{k}$ [14].

Let us mention that the Green's function belonging to $\mathbb{B}_0$ is logarithmically divergent when applying it to the right side of (2.8). This can easily be shown in an electron gas representation with the help of some analytical integrations (see Chapter 5). Nevertheless, that Green's function will be an essential part of an improvement which will be discussed in Chapter 6. Therefore it seems to be justified to spend some time in doing the computation of $\mathbb{G}_0^{M+J,\,M'+J'}$. First we make the ansatz

$$\begin{aligned}\mathbb{G}_0^{M+J,\,M'+J'} = &\sum_{m=0}^{M}\sum_{m'=0}^{M'} \frac{1}{(m+J)!\,m!\,(m'+J')!\,m'!} \\ &\cdot \left|\Phi^{m+J,\,m'+J'}\left(\begin{smallmatrix}y\\ \sigma\end{smallmatrix}\right)\right\rangle G_0^{m,m'}(J,J'\,|\,y,z)\left\langle \Phi^{m+J,\,m'+J'}\left(\begin{smallmatrix}z\\ \sigma\end{smallmatrix}\right)\right|. \end{aligned} \tag{3.6}$$

Inserting (3.6) into (3.1) and multiplying from the left with $\left\langle \phi^{\nu+J,\,\nu'+J'}\left(\begin{smallmatrix}x\\ s\end{smallmatrix}\right)\right|$ we get a system of equations for the determination of Green's function's matrix elements:

$$\begin{aligned} &G_0^{\nu,\nu'}(J,J'\,|\,x,z)\cdot Q\left(\begin{smallmatrix}z\\ s\end{smallmatrix}\,\middle|\,h\right) = h^{\nu,\nu'}\left(\mathrm{j},j'\,\middle|\,\begin{smallmatrix}x\\ s\end{smallmatrix}\right), \\ &\nu = 0,1,\ldots,M;\quad \nu' = 0,1,\ldots,M', \end{aligned} \tag{3.7}$$

where

$$\begin{aligned} Q\left(\begin{smallmatrix}z\\ s\end{smallmatrix}\,\middle|\,h\right) := &\left\langle \Phi^{\nu+J,\,\nu'+J'}\left(\begin{smallmatrix}z\\ s\end{smallmatrix}\right)\right|(\mathbb{B}_0-\omega\cdot 1) \\ &\cdot \mathbb{P}^{M+J,\,M'+J'}\left|\Phi_\mathrm{HR}^{(M,M')}\right\rangle. \end{aligned} \tag{3.8}$$

Equation (3.7) is obtained using the invariance of $G_0^{\nu,\nu'}$ when applying a suitable combination of S_0 and S_1 to it:

$$\begin{aligned} &\hat S_1(\boldsymbol{x},\boldsymbol{y})\cdot \hat S_0^*(\boldsymbol{x}',\boldsymbol{y}')\cdot \hat S_1^*(\boldsymbol{x}'',\boldsymbol{y}'')\cdot \hat S_0(\boldsymbol{x}''',\boldsymbol{y}''') \\ &\quad\cdot G_0^{\nu,\nu'}(J,J'\,|\,\boldsymbol{y},\boldsymbol{y}',\boldsymbol{y}'',\boldsymbol{y}''';\, z,z',z'',z''') \\ &= G_0^{\nu,\nu'}(J,J'\,|\,\boldsymbol{x},\boldsymbol{x}',\boldsymbol{x}'',\boldsymbol{x}''';\, z,z',z'',z''')\,. \end{aligned} \tag{3.9}$$

Here and in the following relations the ^-sign on the top of the letter is defined by

$$\hat S_i(\boldsymbol{x},\boldsymbol{y}) := \prod_j S_i(\boldsymbol{x}_j,\boldsymbol{y}_j)\,,\quad i\in\{0,1\}\,. \tag{3.10}$$

The proof of (3.9) is given in the appendix.

For the computation of Q we now evaluate all contractions between creation and destruction operators appearing in (3.8). Afterwards we expand the projection operators S_0, S_1 with respect to the one-electron functions $b_{\boldsymbol{k}}$:

$$S_0(\boldsymbol{x},\boldsymbol{x}') = \sum_{\boldsymbol{k}} b_{\boldsymbol{k}}(\boldsymbol{x})\, f_{\boldsymbol{k}}\, b_{\boldsymbol{k}}^*(\boldsymbol{x}')\,, \tag{3.11 a}$$

$$S_1(\boldsymbol{x},\boldsymbol{x}') = \sum_{\boldsymbol{k}} b_{\boldsymbol{k}}(\boldsymbol{x})\, g_{\boldsymbol{k}}\, b_{\boldsymbol{k}}^*(\boldsymbol{x}')\,. \tag{3.11 b}$$

The symbol $f_{\boldsymbol{p}}$ denotes the Fermi distribution function represented for absolute temperature $T=0$ by

$$f_{\boldsymbol{p}} := \begin{cases} 1 & \text{if } \boldsymbol{p}\in\{\text{occupied states}\}\,, \\ 0 & \text{if } \boldsymbol{p}\in\{\text{unoccupied states}\}\,. \end{cases} \tag{3.12}$$

$g_{\boldsymbol{p}}$ is the complement function:

$$g_{\boldsymbol{p}} := 1 - f_{\boldsymbol{p}} \tag{3.13}$$

f_p and g_p are introduced with a view to further investigations to keep the option open for discussing temperature dependent phenomena such as e.g. phase transitions.

The Hartree-Fock operator $D(\boldsymbol{x},\boldsymbol{x}')$ is replaced by its spectral representation:

$$D(\boldsymbol{x},\boldsymbol{x}') = \sum_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}}\, b_{\boldsymbol{k}}(\boldsymbol{x})\, b^*_{\boldsymbol{k}}(\boldsymbol{x}')\,. \tag{3.14}$$

Using the invariance relation (the proof can be found in the appendix)

$$\begin{aligned}&\hat{S}_1(\boldsymbol{x},\boldsymbol{y}) \cdot \hat{S}^*_0(\boldsymbol{x}',\boldsymbol{y}') \cdot \hat{S}^*_1(\boldsymbol{x}'',\boldsymbol{y}'') \cdot \hat{S}_0(\boldsymbol{x}''',\boldsymbol{y}''')\\ &\quad\cdot h^{\nu,\nu'}\left(J,J'\,\middle|\,\begin{smallmatrix}\boldsymbol{y} & \boldsymbol{y}' & \boldsymbol{y}'' & \boldsymbol{y}'''\\ s & s' & s'' & s'''\end{smallmatrix}\right)\\ &= h^{\nu,\nu'}\left(J,J'\,\middle|\,\begin{smallmatrix}\boldsymbol{x} & \boldsymbol{x}' & \boldsymbol{x}'' & \boldsymbol{x}'''\\ s & s' & s'' & s'''\end{smallmatrix}\right)\end{aligned} \tag{3.15}$$

we are able to expand $h^{\nu,\nu'}$ with respect to $b_{\boldsymbol{k}}$ in the following way:

$$\begin{aligned}&h^{\nu,\nu'}\left(J,J'\,\middle|\,\begin{smallmatrix}\boldsymbol{y}\\ s\end{smallmatrix}\right)\\ &= \sum_{\boldsymbol{q},\boldsymbol{q}',\boldsymbol{q}'',\boldsymbol{q}'''} c\left(J,J'\,\middle|\,\begin{smallmatrix}\boldsymbol{q} & \boldsymbol{q}' & \boldsymbol{q}'' & \boldsymbol{q}'''\\ s & s' & s'' & s'''\end{smallmatrix}\right) \cdot \hat{g}_{\boldsymbol{q}}\, \hat{b}_{\boldsymbol{q}}(\boldsymbol{y}) \cdot \hat{f}_{\boldsymbol{q}'}\, \hat{b}^*_{\boldsymbol{q}'}(\boldsymbol{y}')\\ &\quad\cdot \hat{g}_{\boldsymbol{q}''}\, \hat{b}^*_{\boldsymbol{q}''}(\boldsymbol{y}'') \cdot \hat{f}_{\boldsymbol{q}'''}\, \hat{b}_{\boldsymbol{q}'''}(\boldsymbol{y}''')\,.\end{aligned} \tag{3.16}$$

Inserting all these expansions into (3.8), multiplying from the left side by $\hat{b}^*_{\boldsymbol{p}}(z)\, \hat{b}_{\boldsymbol{p}'}(z')\, \hat{b}_{\boldsymbol{p}''}(z'')\, \hat{b}^*_{\boldsymbol{p}'''}(z''')$ and integrating all z, z', z'', z''', we are left with

$$\begin{aligned}&\hat{b}^*_{\boldsymbol{p}}(z)\, \hat{b}_{\boldsymbol{p}'}(z')\, \hat{b}_{\boldsymbol{p}''}(z'')\, \hat{b}^*_{\boldsymbol{p}'''}(z''') \cdot Q\left(\begin{smallmatrix}z\\ s\end{smallmatrix}\,\middle|\,h\right)\\ &= \Big[\sum_{\boldsymbol{p}} \varepsilon_{\boldsymbol{p}} - \sum_{\boldsymbol{p}'} \varepsilon_{\boldsymbol{p}'} - \sum_{\boldsymbol{p}''} \varepsilon_{\boldsymbol{p}''} + \sum_{\boldsymbol{p}'''} \varepsilon_{\boldsymbol{p}'''} + C - \omega\Big]\\ &\quad\cdot \hat{g}_{\boldsymbol{p}}\, \hat{f}_{\boldsymbol{p}'}\, \hat{g}_{\boldsymbol{p}''}\, \hat{f}_{\boldsymbol{p}'''}\, c\left(J,J'\,\middle|\,\begin{smallmatrix}\boldsymbol{p} & \boldsymbol{p}' & \boldsymbol{p}'' & \boldsymbol{p}'''\\ s & s' & s'' & s'''\end{smallmatrix}\right).\end{aligned} \tag{3.17}$$

Dividing the whole equation by the energy term enclosed in brackets, multiplying by $\hat{g}_{\boldsymbol{p}}\, \hat{b}_{\boldsymbol{p}}(\boldsymbol{x}) \cdot \hat{f}_{\boldsymbol{p}'}\, \hat{b}^*_{\boldsymbol{p}'}(\boldsymbol{x}') \cdot \hat{g}_{\boldsymbol{p}''}\, \hat{b}^*_{\boldsymbol{p}''}(\boldsymbol{x}'') \cdot \hat{f}_{\boldsymbol{p}'''}\, \hat{b}_{\boldsymbol{p}'''}(\boldsymbol{x}''')$ and summing up all $\boldsymbol{p}, \boldsymbol{p}', \boldsymbol{p}'', \boldsymbol{p}'''$, we get

$$\sum_{\boldsymbol{p}\,\boldsymbol{p}'\,\boldsymbol{p}''\,\boldsymbol{p}'''} \frac{\hat{b}_{\boldsymbol{p}}(\boldsymbol{x})\, \hat{g}_{\boldsymbol{p}}\, \hat{b}^*_{\boldsymbol{p}}(z) \cdot \hat{b}^*_{\boldsymbol{p}'}(\boldsymbol{x}')\, \hat{f}_{\boldsymbol{p}'}\, \hat{b}_{\boldsymbol{p}'}(z') \cdot \hat{b}^*_{\boldsymbol{p}''}(\boldsymbol{x}'')\, \hat{g}_{\boldsymbol{p}''}\, \hat{b}_{\boldsymbol{p}''}(z'') \cdot \hat{b}_{\boldsymbol{p}'''}(\boldsymbol{x}''')\, \hat{f}_{\boldsymbol{p}'''}\, \hat{b}^*_{\boldsymbol{p}'''}(z''')}{\sum_{\boldsymbol{p}} \varepsilon_{\boldsymbol{p}} - \sum_{\boldsymbol{p}'} \varepsilon_{\boldsymbol{p}'} - \sum_{\boldsymbol{p}''} \varepsilon_{\boldsymbol{p}''} + \sum_{\boldsymbol{p}'''} \varepsilon_{\boldsymbol{p}'''} + C - \omega} \cdot Q\left(\begin{smallmatrix}z\\ s\end{smallmatrix}\,\middle|\,h\right) = h^{\nu,\nu'}\left(J,J'\,\middle|\,\begin{smallmatrix}x\\ s\end{smallmatrix}\right). \tag{3.18}$$

With the abbreviations

$$A_{\boldsymbol{p}}(\boldsymbol{x},z) := b_{\boldsymbol{p}}(\boldsymbol{x})\, g_{\boldsymbol{p}}\, \hat{b}^*_{\boldsymbol{p}}(z)\,, \qquad B_{\boldsymbol{p}}(\boldsymbol{x},z) := b_{\boldsymbol{p}}(\boldsymbol{x})\, f_{\boldsymbol{p}}\, \hat{b}^*_{\boldsymbol{p}}(z) \tag{3.19 a), (3.19 b}$$

and comparing (3.18) with (3.7), we conclude the following form of the Green's function:

$$\mathbb{G}_0^{M+J,\,M'+J'} = \sum_{m=0}^{M} \sum_{m'=0}^{M'} \frac{1}{(m+J)!\,m!\,(m'+J')!\,m'!} \cdot \left|\Phi^{m+J,\,m'+J'}\left(\begin{smallmatrix}y\\ \sigma\end{smallmatrix}\right)\right\rangle G_0^{m,m'}(J,J'\,|\,y,z) \left\langle\Phi^{m+J,\,m'+J'}\left(\begin{smallmatrix}z\\ \sigma\end{smallmatrix}\right)\right| \tag{3.20}$$

with matrix elements

$$G_0^{\nu,\nu'}(J,J'\,|\,x,z) = \sum_{\boldsymbol{p},\boldsymbol{p}',\boldsymbol{p}'',\boldsymbol{p}'''} \frac{\hat{A}_{\boldsymbol{p}}(\boldsymbol{x},z) \cdot \hat{B}^*_{\boldsymbol{p}'}(\boldsymbol{x}',z') \cdot \hat{A}^*_{\boldsymbol{p}''}(\boldsymbol{x}'',z'') \cdot \hat{B}_{\boldsymbol{p}'''}(\boldsymbol{x}''',z''')}{\sum_{\boldsymbol{p}} \varepsilon_{\boldsymbol{p}} - \sum_{\boldsymbol{p}'} \varepsilon_{\boldsymbol{p}'} - \sum_{\boldsymbol{p}''} \varepsilon_{\boldsymbol{p}''} + \sum_{\boldsymbol{p}'''} \varepsilon_{\boldsymbol{p}'''} + C - \omega}. \tag{3.21}$$

Here we want to point especially to the structure of our Green's function. Obviously, the numerator of (3.21) is completely separated into wavefunctions of particles and antiparticles of H- and R-system. Contrary to that a factorization of the denumerator is impossible: All one-particle energies of electrons and holes contained in the H-system as well as in the R-system are correlated to one another. So the Green's function implies an unavoidable coupling between both systems.

4. Higher Order Approximation for the One-Centre Problem

The following treatments will be restricted to the so-called α-phase of a metal hydride, i.e. the concentration of hydrogen in the host crystal is assumed to be so small that all interactions between different hydrogen centres can be ignored and each interstitial hydrogen atom can be treated as one single perturbation. Therefore we concentrate on

$$J = 1 \quad \text{and} \quad J' = 0\,, \tag{4.1}$$

which means the implementation of one additional hydrogen atom in the H-system and no excess electrons and no excess protons in the R-system. The lowest approximation we can do in our formalism is

$$M = 0 \quad \text{and} \quad M' = 0\,. \tag{4.2}$$

Applied to (2.3) we get the so-called zeroth order NTD-approximation:

$$\begin{aligned}&B^{0,\,0}_{\;\;0,\,0}\left(1,0\,\middle|\,\begin{smallmatrix}z & \boldsymbol{x}\\ \sigma & s\end{smallmatrix}\right) \cdot h^{0,0}\left(1,0\,\middle|\,\begin{smallmatrix}\boldsymbol{x}\\ s\end{smallmatrix}\right)\\ &= \omega^{(0,0)} \cdot h^{0,0}\left(1,0\,\middle|\,\begin{smallmatrix}z\\ \sigma\end{smallmatrix}\right).\end{aligned} \tag{4.3}$$

The calculation of $B^{0,\,0}_{0,\,0}$ is easy [10]. Equation (4.3) then leads to the following non-local one-particle Schrödinger equation:

$$\begin{aligned} &S_1(\boldsymbol{z},\boldsymbol{z}')\,[D(\boldsymbol{z}',\boldsymbol{x}') + V_{\mathrm{H}}(\boldsymbol{z}',\boldsymbol{Y})\,\delta(\boldsymbol{z}'-\boldsymbol{x}')]\,\varphi_0(\boldsymbol{x}') \\ &\quad = (\omega^{(0,\,0)} - C)\,\varphi_\sigma(\boldsymbol{z}) \end{aligned} \tag{4.4}$$

with

$$\begin{aligned} \varphi_\sigma(\boldsymbol{z}) &:= h^{0,\,0}\left(1,0\,\middle|\,{}^{\boldsymbol{z}}_{\sigma}\right) \\ &= S_1(\boldsymbol{z},\boldsymbol{x})\,h^{0,\,0}\left(1,0\,\middle|\,{}^{\boldsymbol{x}}_{\sigma}\right). \end{aligned} \tag{4.5}$$

Equation (4.4) has been treated in the past at great length [1, 12, 13]. A numerical solution has been obtained in case of a hexagonal crystal structure based on magnesium as example. We will show the results later in this paper in connection with the discussion of our higher order NTD-approximation.

This improvement leading to a higher order formalism is achieved by adding one single electron-hole pair to the underlying Hartree-Fock ground state, i.e.

$$M = 1\,. \tag{4.6}$$

Because we are still interested in the electronic energy difference between H- and R-system the reference system has to be corrected, too:

$$M' = 1\,. \tag{4.7}$$

The system (2.3) now leads to four eigenvalue equations coupling a one-particle wavefunction

$$\begin{aligned} h^{0,\,0} \equiv h^{0,\,0}\left(1,0\,\middle|\,{}^{\boldsymbol{z}}_{\sigma}\right) &= \left\langle \phi^{0+1,\,0+0}\left({}^{\boldsymbol{z}}_{\sigma}\right) \middle| \Phi_{\mathrm{HR}} \right\rangle \\ &= \left\langle O_{vw} \middle| [w^+_\sigma(\boldsymbol{x})\,S_1(\boldsymbol{x},\boldsymbol{z})]^+\,\Phi_{\mathrm{HR}} \right\rangle \end{aligned} \tag{4.8}$$

with two different three-particle wavefunctions

$$\begin{aligned} h^{1,\,0} &\equiv h^{1,\,0}\begin{pmatrix} \boldsymbol{x}_1 & \boldsymbol{x}_2 & \boldsymbol{x}'_1 \\ s_1 & s_2 & s'_1 \end{pmatrix} \\ &= \left\langle \Phi^{1+1,\,0+0}\begin{pmatrix} \boldsymbol{x}_1 & \boldsymbol{x}_2 & \boldsymbol{x}'_1 \\ s_1 & s_2 & s'_1 \end{pmatrix} \middle| \Phi_{\mathrm{HR}} \right\rangle \\ &= \left\langle O_{vw} \middle| [w^+_{s_1}(\boldsymbol{y}_1)\,S_1(\boldsymbol{y}_1,\boldsymbol{x}_1)\cdot w^+_{s_2}(\boldsymbol{y}_2)\,S_1(\boldsymbol{y}_2,\boldsymbol{x}_2) \right. \\ &\qquad \left. \cdot\, v^+_{s'_1}(\boldsymbol{y}'_1)\,S^*_0(\boldsymbol{y}'_1,\boldsymbol{x}'_1)]^+\,\Phi_{\mathrm{HR}} \right\rangle, \end{aligned} \tag{4.9}$$

$$\begin{aligned} h^{0,\,1} &\equiv h^{0,\,1}\begin{pmatrix} \boldsymbol{x}_1 & \boldsymbol{x}''_1 & \boldsymbol{x}'''_1 \\ s_1 & s''_1 & s'''_1 \end{pmatrix} \\ &= \left\langle \Phi^{0+1,\,1+0}\begin{pmatrix} \boldsymbol{x}_1 & \boldsymbol{x}''_1 & \boldsymbol{x}'''_1 \\ s_1 & s''_1 & s'''_1 \end{pmatrix} \middle| \Phi_{\mathrm{HR}} \right\rangle \\ &= \left\langle O_{vw} \middle| [w^+_{s_1}(\boldsymbol{y}_1)\,S_1(\boldsymbol{y}_1,\boldsymbol{x}_1)\cdot v^+_{s''_1}(\boldsymbol{y}''_1)\,S^*_1(\boldsymbol{y}''_1,\boldsymbol{x}''_1) \right. \\ &\qquad \left. \cdot\, w^+_{s'''_1}(\boldsymbol{y}'''_1)\,S_0(\boldsymbol{y}'''_1,\boldsymbol{x}'''_1)]^+\,\Phi_{\mathrm{HR}} \right\rangle \end{aligned} \tag{4.10}$$

and additionally with a five-particle wavefunction $h^{1,\,1}$. In a first order approximation, we neglect all influences concerning five-particle interactions or higher correlations and treat only the three-particle contributions contained in $h^{1,\,0}$ and $h^{0,\,1}$. The remaining equations can be rewritten in the form

$$B^{0,\,0}_{0,\,0}\,h^{0,\,0} + B^{0,\,0}_{0,\,1}\,h^{0,\,1} + B^{0,\,0}_{1,\,0}\,h^{1,\,0} = \omega^{(1,\,1)}\cdot h^{0,\,0}, \tag{4.11}$$

$$[B^{1,\,0}_{1,\,0} - \omega^{(1,\,1)}\cdot 1]\,h^{1,\,0} = -\,B^{1,\,0}_{0,\,0}\,h^{0,\,0}, \tag{4.12}$$

$$[B^{0,\,1}_{0,\,1} - \omega^{(1,\,1)}\cdot 1]\,h^{0,\,1} = -\,B^{0,\,1}_{0,\,0}\,h^{0,\,0}. \tag{4.13}$$

To solve this system, we try to eliminate the wavefunctions $h^{1,\,0}$ and $h^{0,\,1}$ in (4.11) via approximate inversion of (4.12), (4.13) with the help of the methods described in Chapter 2 and Chapter 3. First we state that the matrix elements on the left side of (4.12) and (4.13) are composed of the following parts of $\mathbb{B}$:

$$B^{1,\,0}_{1,\,0} = \frac{1}{2!}\left\langle \Phi^{1+1,\,0+0} \middle| C + H_1 + H_2 + H_3 + H_5 + H_6 \middle| \Phi^{1+1,\,0+0} \right\rangle, \tag{4.14}$$

$$B^{0,\,1}_{0,\,1} = \left\langle \Phi^{0+1,\,1+0} \middle| C + H_1 - R_1 - R_2 - R_5 \middle| \Phi^{0+1,\,1+0} \right\rangle, \tag{4.15}$$

where ([1], (6.12) – (6.19))

$$H_1 = w^+_s(\boldsymbol{y})\,S_1(\boldsymbol{y},\boldsymbol{x})\,\{D(\boldsymbol{x},\boldsymbol{x}') + V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})\,\delta(\boldsymbol{x}-\boldsymbol{x}')\}\,S_1(\boldsymbol{x}',\boldsymbol{y}')\,w_s(\boldsymbol{y}') \tag{4.16}$$

$$H_2 = -\,v^+_s(\boldsymbol{y})\,S^*_0(\boldsymbol{y},\boldsymbol{x})\,\{D^*(\boldsymbol{x},\boldsymbol{x}') + V^*_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})\,\delta(\boldsymbol{x}-\boldsymbol{x}')\}\,S^*_0(\boldsymbol{x}',\boldsymbol{y}')\,v_s(\boldsymbol{y}'), \tag{4.17}$$

$$H_3 = \tfrac{1}{2}\,w^+_s(\boldsymbol{y})\,S_1(\boldsymbol{y},\boldsymbol{x})\,w^+_{s'}(\boldsymbol{y}')\,S_1(\boldsymbol{y}',\boldsymbol{x}')\,\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,S_1(\boldsymbol{x}',\boldsymbol{y}'')\,w_{s'}(\boldsymbol{y}'')\,S_1(\boldsymbol{x},\boldsymbol{y}''')\,w_s(\boldsymbol{y}'''), \tag{4.18}$$

$$H_5 = w^+_s(\boldsymbol{y})\,S_1(\boldsymbol{y},\boldsymbol{x})\,S_0(\boldsymbol{x},\boldsymbol{y}')\,v^+_s(\boldsymbol{y}')\,\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,v_{s'}(\boldsymbol{y}'')\,S_0(\boldsymbol{y}'',\boldsymbol{x}')\,S_1(\boldsymbol{x}',\boldsymbol{y}''')\,w_{s'}(\boldsymbol{y}'''), \tag{4.19}$$

$$H_6 = -\,w^+_s(\boldsymbol{y})\,S_1(\boldsymbol{y},\boldsymbol{x})\,v^+_{s'}(\boldsymbol{y}')\,S^*_0(\boldsymbol{y}',\boldsymbol{x}')\,\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,S^*_0(\boldsymbol{x}',\boldsymbol{y}'')\,v_{s'}(\boldsymbol{y}'')\,S_1(\boldsymbol{x},\boldsymbol{y}''')\,w_s(\boldsymbol{y}'''), \tag{4.20}$$

and

$$R_1 = v_s^+(\boldsymbol{y})\, S_1^*(\boldsymbol{y},\boldsymbol{x})\, D^*(\boldsymbol{x},\boldsymbol{x}')\, S_1^*(\boldsymbol{x}',\boldsymbol{y}')\, v_s(\boldsymbol{y}')\,, \tag{4.21}$$

$$R_2 = -\, w_s^+(\boldsymbol{y})\, S_0(\boldsymbol{y},\boldsymbol{x})\, D(\boldsymbol{x},\boldsymbol{x}')\, S_0(\boldsymbol{x}',\boldsymbol{y}')\, w_s(\boldsymbol{y}')\,, \tag{4.22}$$

$$R_5 = w_s^+(\boldsymbol{y})\, S_0(\boldsymbol{y},\boldsymbol{x})\, S_1(\boldsymbol{x},\boldsymbol{y}')\, v_s^+(\boldsymbol{y}')\, \frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\, v_{s'}(\boldsymbol{y}'')\, S_1(\boldsymbol{y}'',\boldsymbol{x}')\, S_0(\boldsymbol{x}',\boldsymbol{y}''')\, w_{s'}(\boldsymbol{y}''')\,. \tag{4.23}$$

Neglecting all two-particle interactions H_3, H_5, H_6, and R_5 as well as the proton potential $V_{\mathrm{H}}(\boldsymbol{x},\boldsymbol{Y})$ in H_1 and H_2 we only have to consider contributions contained in $\mathbb{B}_0$ such that the Green's function $\mathbb{G}_0$ of Chapt. 3 is applicable. Two-particle expressions are to be treated at a later time and the Green's function is to be expanded by such contributions (see Chapter 6).

With the replacements

$$h^{1,0} \approx -\, G_0^{1,0}\, B^{1,0}_{0,0}\, h^{0,0}\,, \qquad h^{0,1} \approx -\, G_0^{0,1}\, B^{0,1}_{0,0}\, h^{0,0} \tag{4.24), (4.25}$$

obtained from (4.12) and (4.13) we are left with the following eigenvalue equation determining energy and wavefunction of a single hydrogen excess electron in a metal crystal:

$$\begin{aligned} &B^{0,0}_{0,0}\left({z \atop \sigma};{y_1 \atop \varrho_1}\right) h^{0,0}\left({y_1 \atop \varrho_1}\right) - B^{0,0}_{1,0}\left({z \atop \sigma};{\boldsymbol{x}_1 \atop s_1}\,{\boldsymbol{x}_2 \atop s_2}\,{\boldsymbol{x}_1' \atop s_1'}\right) G_0^{1,0}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_1';z_1,z_2,z_1')\, B^{1,0}_{0,0}\left({z_1 \atop s_1}\,{z_2 \atop s_2}\,{z_1' \atop s_1'};{y_1 \atop \varrho_1}\right) h^{0,0}\left({y_1 \atop \varrho_1}\right) \\ &\quad - B^{0,0}_{0,1}\left({z \atop \sigma};{\boldsymbol{x}_1 \atop s_1}\,{\boldsymbol{x}_1'' \atop s_1''}\,{\boldsymbol{x}_1''' \atop s_1'''}\right) G_0^{0,1}(\boldsymbol{x}_1,\boldsymbol{x}_1'',\boldsymbol{x}_1''';z_1,z_1'',z_1''')\, B^{0,1}_{0,0}\left({z_1 \atop s_1}\,{z_1'' \atop s_1''}\,{z_1''' \atop s_1'''};{y_1 \atop \varrho_1}\right) h^{0,0}\left({y_1 \atop \varrho_1}\right) = \omega^{(1,1)} \cdot h^{0,0}\left({z \atop \sigma}\right). \end{aligned} \tag{4.26}$$

The first term in (4.26) represents the zeroth order NTD-approximation shown in (4.4) which has now to be corrected by two additional summands. Both of these summands contain a Green's function with an energy denominator which is responsible for an extreme non-linearity of that equation. Therefore, as well as due to our extended Einstein convention and to the Laplace operator as part of $B^{0,0}_{0,0}$, (4.26) is concerned as a non-local non-linear integral-differential equation which will cause some difficulties in its numerical solution.

The calculation of the matrix elements $B^{m,m'}_{\nu,\nu'}$ included in (4.26) is straightforward [10]. An evaluation of the products $B^{0,0}_{1,0}\, G_0^{1,0}\, B^{1,0}_{0,0}\, h^{0,0}$ and $B^{0,0}_{0,1}\, G_0^{0,1}\, B^{0,1}_{0,0}\, h^{0,0}$ shows that the first correction term leads to eight supplemented expressions refering to the H-system, and the second one results in only one additional potential term belonging to the R-system. Nearly each of these additional correction terms contain the Hartree-Fock operator $D(\boldsymbol{x},\boldsymbol{x}')$. This is very strange to understand because we would like to interpret the whole expression (4.26) as a kind of one-particle Schrödinger equation which should not contain any different kinetic energy contributions. Indeed it is possible to prove that all Laplace operators disappear – except the one belonging to $B^{0,0}_{0,0}$ contained in our zeroth order approximation. In order to see that we split the Hartree-Fock operator $D(\boldsymbol{x},\boldsymbol{x}')$ in the following way:

$$D(\boldsymbol{x},\boldsymbol{x}') = D_0(\boldsymbol{x},\boldsymbol{x}') + V_D(\boldsymbol{x})\, \delta(\boldsymbol{x}-\boldsymbol{x}')\,. \tag{4.27}$$

$D_0(\boldsymbol{x},\boldsymbol{x}')$ represents a Hartree-Fock operator with respect to a host lattice where all lattice ions are localized at ideal equilibrium positions $\boldsymbol{X}^0$:

$$\begin{aligned} &D_0(\boldsymbol{x},\boldsymbol{x}') \\ &\quad := \left\{-\frac{\hbar^2}{2m}\Delta + V_W^0(\boldsymbol{x},\boldsymbol{X}^0) + 2e^2 \int \mathrm{d}^3y\, \frac{S_0(\boldsymbol{y},\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|}\right\} \\ &\qquad \cdot \delta(\boldsymbol{x}-\boldsymbol{x}') - e^2\, \frac{S_0(\boldsymbol{x},\boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|}\,. \end{aligned} \tag{4.28}$$

$V_D(\boldsymbol{x})$ describes the difference potential between a host lattice with distorted metal ion coordinates $\boldsymbol{X}$ and a host lattice with ideal nucleus positions $\boldsymbol{X}^0$:

$$\begin{aligned} V_D(\boldsymbol{x}) &:= V_W(\boldsymbol{x}) - V_W^0(\boldsymbol{x}) \\ &\equiv V_W(\boldsymbol{x},\boldsymbol{X}) - V_W^0(\boldsymbol{x},\boldsymbol{X}^0)\,. \end{aligned} \tag{4.29}$$

For all further one-particle expansions we now choose the Bloch functions $b_{\boldsymbol{k}}^0(\boldsymbol{x})$ of an ideal lattice as a base system, i.e. the solutions of the Hartree-Fock equations

$$D_0(\boldsymbol{x},\boldsymbol{x}')\, b_{\boldsymbol{k}}^0(\boldsymbol{x}') = \varepsilon_{\boldsymbol{k}}\, b_{\boldsymbol{k}}^0(\boldsymbol{x})\,. \tag{4.30}$$

With the definitions (3.19) and the spectral representation (3.14) of D_0 with respect to $b_{\boldsymbol{k}}^0$ instead of $b_{\boldsymbol{k}}$ it is easy to show [10, 13] that

$$\begin{aligned} A_p(z,\boldsymbol{x})\, D_0(\boldsymbol{x},\boldsymbol{x}')\, B_{p'}(\boldsymbol{x}',z') &= 0\,, \\ B_p(z,\boldsymbol{x})\, D_0(\boldsymbol{x},\boldsymbol{x}')\, A_{p'}(\boldsymbol{x}',z') &= 0 \end{aligned} \tag{4.31}$$

and

$$S_1(z,z')\, D_0(z',\boldsymbol{x}') = D_0(z,z')\, S_1(z',\boldsymbol{x}')\,. \tag{4.32}$$

The proof of (4.31) and (4.32) is mainly based on the completeness of the system $\{b_k^0(x)\}$ and on the disjunctness of f_p and g_p due to (3.12), (3.13).

Except the zeroth order term all further correction terms in (4.26) contain a constellation in the form of (4.31) which means, including (4.27), that we can replace all Hartree-Fock operators $D(x, x')$ in each additional approach through the difference potential $V_D(x)$. Especially no kind of kinetic energy is left in any of the additional expressions such that we are allowed to interpret these terms in our higher order NTD-approximation as "supplemented potentials". The whole equation (4.26) rewrites then with the definitions

$$W(x) := V_W(x) - V_W^0(x) + V_{\mathrm{H}}(x) \tag{4.33}$$

and

$$\lambda := \omega^{(1,1)} - C \tag{4.34}$$

in form of the following non-linear non-local Schrödinger equation:

$$\begin{aligned}
&\{D_0(z,z') + S_1(z,z')\,V_{\mathrm{H}}(z') + S_1(z,z')\,V_D(z')\}\,\varphi_\sigma(z')\\
&\quad+\sum_{p_1p_2p_3}\frac{1}{\varepsilon_{p_1}-\varepsilon_{p_2}+\varepsilon_{p_3}-\lambda}\cdot[-2\,B_{p_1}(y,x)\,V_D(x)\,A_{p_2}(x,y)\,V_D(y)]\,A_{p_3}(z,z')\,\varphi_\sigma(z')\\
&\quad+\sum_{p_1p_2p_3}\frac{1}{\varepsilon_{p_1}-\varepsilon_{p_2}+\varepsilon_{p_3}-\lambda}\cdot\{[-2A_{p_1}(y,x)\,W(x)\,B_{p_2}(x,y)\,W(y)]\,A_{p_3}(z,z')\,\varphi_\sigma(z')\\
&\qquad\qquad+A_{p_1}(z,x)\,W(x)\,B_{p_2}(x,y)\,W(y)\,A_{p_3}(y,z')\,\varphi_\sigma(z')\}\\
&\quad+\sum_{p_1p_2p_3}\frac{1}{\varepsilon_{p_1}-\varepsilon_{p_2}+\varepsilon_{p_3}-\lambda}\cdot\left\{\left[-2A_{p_1}(y,x)\frac{e^2}{|x-z'|}B_{p_2}(x,y)\,W(y)\right]A_{p_3}(z,z')\,\varphi_\sigma(z')\right.\\
&\qquad\qquad\left.+A_{p_1}(z,x)\frac{e^2}{|x-z'|}B_{p_2}(x,y)\,W(y)\,A_{p_3}(y,z')\,\varphi_\sigma(z')\right\}\\
&\quad+\sum_{p_1p_2p_3}\frac{1}{\varepsilon_{p_1}-\varepsilon_{p_2}+\varepsilon_{p_3}-\lambda}\cdot\left\{\left[-2A_{p_1}(x,y)\,W(y)\,B_{p_2}(y,x)\frac{e^2}{|x-x'|}\right]S_1(z,x')\,A_{p_3}(x',z')\,\varphi_\sigma(z')\right.\\
&\qquad\qquad\left.+S_1(z,x)\,A_{p_1}(x,y)\,W(y)\,B_{p_2}(y,x')\frac{e^2}{|x-x'|}A_{p_3}(x',z')\,\varphi_\sigma(z')\right\}\\
&\quad+\sum_{p_1p_2p_3}\frac{1}{\varepsilon_{p_1}-\varepsilon_{p_2}+\varepsilon_{p_3}-\lambda}\cdot\left\{\left[-2A_{p_1}(x,y)\frac{e^2}{|y-z'|}B_{p_2}(y,x)\frac{e^2}{|x-x'|}\right]S_1(z,x')\,A_{p_3}(x',z')\,\varphi_\sigma(z')\right.\\
&\qquad\qquad\left.+S_1(z,x)\,A_{p_1}(x,y)\frac{e^2}{|y-z'|}B_{p_2}(y,x')\frac{e^2}{|x-x'|}A_{p_3}(x',z')\,\varphi_\sigma(z')\right\}=\lambda\,\varphi_\sigma(z)\,.
\end{aligned}\tag{4.35}$$

The first term in (4.35) represents the contribution of the zeroth order NTD-approximation. The second term describes the influence of $B^{0,0}_{0,1}\,G^{0,1}_{0}\,B^{0,1}_{0,0}\,h^{0,0}$; it characterizes the energy of a hydrogen excess electron in the H-system due to the presence of a particle-antiparticle pair in the R-system. The remaining eight additional potentials represent different interaction possibilities between a hydrogen electron and an electron-hole pair in the H-system. All terms in brackets are based on a kind of direct interaction. We call them "trace terms". They can be recognized formally because the variable inside brackets [...] found at the beginning will also be found at the end. Due to the extended Einstein convention each bracket can therefore be conceived as a closed function. Furthermore we note that each trace term has a factor of 2 in front of it which originates from a sum over spin indices. In contrast all other potential terms are due to the corresponding exchange interactions.

Before solving (4.35) let us discuss some special cases and points:

i) Suppressing the screening, i.e. in our formalism

$$S_0(x,x') = 0 \quad \text{and} \quad S_1(x,x') = \delta(x-x') \tag{4.36}$$

leads to

$$\{D_0(z,z') + W(z')\}\,\varphi_\sigma(z') = \lambda\,\varphi_\sigma(z)\,. \tag{4.37}$$

This equation has been treated in detail by Duscher and Maichle [12, 13].

ii) A very interesting point of view arises if the stored hydrogen proton is taken out of the metal and the host lattice deformation becomes zero, i.e.

$$W(x) = 0\,. \tag{4.38}$$

Then the only remaining terms are $D_0(z, z')$ out of the zeroth order approximation and the last two lines in (4.35) describing trace term and exchange contribution of a four-fermion interaction. So we have achieved an improvement of Hartree-Fock in higher order.

iii) A further particularity should be mentioned: All Green's function's denominators contain the eigenvalue parameter λ. Therefore we are talking about so-called "dynamical potentials" which means that the intensity of our potentials is driven by λ dependent on the state in view. So we do not get a fixed screening but a dynamical correction of the zeroth order equation (4.4).

5. Electron Gas Approximation

To calculate an explicit solution of (4.35) we depend on simple physical models. One of the most customary approximations in solid state physics is the one treating valence electrons of a metal as a kind of free electron gas [15]. The Bloch functions of the ideal lattice are then approximated by plane waves:

$$b_k^0(\boldsymbol{x}) = \frac{1}{\sqrt{\Omega}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} . \tag{5.1}$$

Here we implied that b_k^0 is normalized on a box of volume Ω fullfilling periodical Born-von Karman relations. The one-particle energies ε_k are evaluated via pseudo-potential theory yielding

$$\varepsilon_{\boldsymbol{k}} = \frac{\hbar^2}{2m}\boldsymbol{k}^2 + \varepsilon_0 . \tag{5.2}$$

ε_0 is assumed to be constant and can be interpreted as a kind of ionization energy in band theory. With these approximations the Green's function's energy denominator rewrites in

$$\frac{1}{\varepsilon_{p_1} - \varepsilon_{p_2} + \varepsilon_{p_3} - \lambda} = \frac{2m}{\hbar^2}\frac{1}{\boldsymbol{p}_1^2 - \boldsymbol{p}_2^2 + \boldsymbol{p}_3^2 - \mu} \tag{5.3}$$

with

$$\mu := \frac{2m}{\hbar^2}(\lambda - \varepsilon_0) . \tag{5.4}$$

As we are only interested in bound states of the hydrogen excess electron we note that λ and μ both have to have negative signs:

$$\lambda, \mu < 0 . \tag{5.5}$$

In the limit of a macroscopically extended metal crystal, we are allowed to treat the reciprocal lattice as continuum, i.e. to change all summations into integrations:

$$\frac{1}{\Omega}\sum_{k} \rightarrow \frac{1}{(2\pi)^3}\int d^3k , \tag{5.6a}$$

$$\sum_{p_1 p_2 p_3} \rightarrow \frac{\Omega^3}{(2\pi)^9}\int d^3p_1 \int d^3p_2 \int d^3p_3 . \tag{5.6b}$$

Especially the projectors S_0, S_1 are represented by

$$S_0(\boldsymbol{x}, \boldsymbol{z}) = \frac{1}{(2\pi)^3}\int d^3k\, f_{\boldsymbol{k}}\, e^{i\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{z})} , \tag{5.7a}$$

$$S_1(\boldsymbol{x}, \boldsymbol{z}) = \frac{1}{(2\pi)^3}\int d^3k\, g_{\boldsymbol{k}}\, e^{i\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{z})} . \tag{5.7b}$$

A_p and B_p are simplified to

$$A_p(\boldsymbol{x}, \boldsymbol{z}) = \frac{1}{\Omega}\, g_p\, e^{i\boldsymbol{p}\cdot(\boldsymbol{x}-\boldsymbol{z})} , \tag{5.8a}$$

$$B_p(\boldsymbol{x}, \boldsymbol{z}) = \frac{1}{\Omega}\, f_p\, e^{i\boldsymbol{p}\cdot(\boldsymbol{x}-\boldsymbol{z})} . \tag{5.8b}$$

The Coulomb potentials belonging to the electron-electron interaction in (4.35) are replaced by their Fourier transforms [16]:

$$\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|} \rightarrow \frac{e^2}{2\pi^2}\int d^3q\, \frac{1}{\boldsymbol{q}^2}\, e^{i\boldsymbol{q}\cdot(\boldsymbol{x}-\boldsymbol{x}')} . \tag{5.9}$$

To get a suitable representation of the potentials $V_{\mathrm{H}}(\boldsymbol{x})$, $V_D(\boldsymbol{x})$, and $W(\boldsymbol{x})$ in (4.35) we need some information on the structure of the host lattice, especially on the exact coordinates of stored hydrogen centres and surrounding metal ions. Therefore we have to specialize on a definite model describing the details of interstitial hydrogen perturbations in a host crystal. Following the treatments of Duscher and Maichle [12, 13] we choose a simple metal with hexagonal lattice structure containing one single hydrogen proton located at the centre of a tetrahedron. Let us fix the origin of our coordinate system at just that particular centre point $\boldsymbol{Y} = 0$ such that the hydrogen potential will be written by

$$V_{\mathrm{H}}(\boldsymbol{x}) = -\frac{e^2}{|\boldsymbol{x}|} . \tag{5.10}$$

Furthermore let us assume that the difference potential V_D defined by (4.29) is only built by contributions due to the nearest neighbours of the proton, i.e. for a hydrogen centre in tetrahedral configuration:

$$V_D(\boldsymbol{x}) = \sum_{j=0}^{3} \left[\frac{-Z e^2}{|\boldsymbol{x} - \boldsymbol{X}_j|} + \frac{Z e^2}{|\boldsymbol{x} - \boldsymbol{X}_j^0|} \right]. \tag{5.11}$$

Z denotes the valence of metal ion cores, e.g. $Z = 2$ for magnesium. The summation index j is counting the four tetrahedron edges with lattice coordinates $\boldsymbol{X}_j$ and $\boldsymbol{X}_j^0$, respectively.

Returning to our Fourier representation, (5.11) becomes

$$V_D(\boldsymbol{x}) = \frac{e^2}{2\pi^2} \int \mathrm{d}^3 k \, \frac{e^{i \boldsymbol{k} \cdot \boldsymbol{x}}}{\boldsymbol{k}^2} \, F^0(\boldsymbol{k}) \tag{5.12}$$

with

$$F^0(\boldsymbol{k}) := \sum_{j=0}^{3} Z \cdot (e^{-i \boldsymbol{k} \cdot \boldsymbol{X}_j^0} - e^{-i \boldsymbol{k} \cdot \boldsymbol{X}_j}). \tag{5.13}$$

With (4.33), (5.10), and (5.12) we get

$$W(\boldsymbol{x}) = \frac{e^2}{2\pi^2} \int \mathrm{d}^3 k \, \frac{e^{i \boldsymbol{k} \cdot \boldsymbol{x}}}{\boldsymbol{k}^2} \, F(\boldsymbol{k}). \tag{5.14}$$

where

$$F(\boldsymbol{k}) := \sum_{j=0}^{3} Z \cdot (e^{-i \boldsymbol{k} \cdot \boldsymbol{X}_j^0} - e^{-i \boldsymbol{k} \cdot \boldsymbol{X}_j}) - 1. \tag{5.15}$$

Inserting all those expressions in (4.35) yields the following "electron gas representation" of our higher order one-centre problem:

$$\begin{aligned}
&\{D_0(z, z') + S_1(z, z')\, V_{\mathrm{H}}(z') + S_1(z, z')\, V_D(z')\}\, \varphi_\sigma(z') \\
&- \frac{1}{(2\pi)^3} \frac{e^4}{(2\pi^2)^2} \frac{2m}{\hbar^2} \int \mathrm{d}^3 p_1 \int \mathrm{d}^3 p_2 \int \mathrm{d}^3 p_3 \frac{f_{\boldsymbol{p}_1} g_{\boldsymbol{p}_2} g_{\boldsymbol{p}_3}}{\boldsymbol{p}_1^2 - \boldsymbol{p}_2^2 + \boldsymbol{p}_3^2 - \mu} \cdot 2\, e^{i \boldsymbol{p}_3 \cdot \boldsymbol{z}} \frac{F^0(\boldsymbol{p}_1 - \boldsymbol{p}_2)}{|\boldsymbol{p}_1 - \boldsymbol{p}_2|^2} \frac{F^0(\boldsymbol{p}_2 - \boldsymbol{p}_1)}{|\boldsymbol{p}_2 - \boldsymbol{p}_1|^2} e^{-i \boldsymbol{p}_3 \cdot \boldsymbol{z}'} \varphi_\sigma(\boldsymbol{z}') \\
&+ \frac{1}{(2\pi)^3} \frac{e^4}{(2\pi^2)^2} \frac{2m}{\hbar^2} \int \mathrm{d}^3 p_1 \int \mathrm{d}^3 p_2 \int \mathrm{d}^3 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} \cdot \Big\{ -2\, e^{i \boldsymbol{p}_3 \cdot \boldsymbol{z}} \frac{F(\boldsymbol{p}_1 - \boldsymbol{p}_2)}{|\boldsymbol{p}_1 - \boldsymbol{p}_2|^2} \frac{F(\boldsymbol{p}_2 - \boldsymbol{p}_1)}{|\boldsymbol{p}_2 - \boldsymbol{p}_1|^2} e^{-i \boldsymbol{p}_3 \cdot \boldsymbol{z}'} \varphi_\sigma(\boldsymbol{z}') \\
&\qquad + e^{i \boldsymbol{p}_3 \cdot \boldsymbol{z}} \frac{F(\boldsymbol{p}_1 - \boldsymbol{p}_2)}{|\boldsymbol{p}_1 - \boldsymbol{p}_2|^2} \frac{F(\boldsymbol{p}_2 - \boldsymbol{p}_3)}{|\boldsymbol{p}_2 - \boldsymbol{p}_3|^2} e^{-i \boldsymbol{p}_1 \cdot \boldsymbol{z}'} \varphi_\sigma(\boldsymbol{z}') \\
&\qquad - 2\, e^{i \boldsymbol{p}_3 \cdot \boldsymbol{z}} \frac{1}{|\boldsymbol{p}_1 - \boldsymbol{p}_2|^2} \frac{F(\boldsymbol{p}_2 - \boldsymbol{p}_1)}{|\boldsymbol{p}_2 - \boldsymbol{p}_1|^2} e^{-i (\boldsymbol{p}_1 - \boldsymbol{p}_2 + \boldsymbol{p}_3) \cdot \boldsymbol{z}'} \varphi_\sigma(\boldsymbol{z}') \\
&\qquad + e^{i \boldsymbol{p}_3 \cdot \boldsymbol{z}} \frac{1}{|\boldsymbol{p}_1 - \boldsymbol{p}_2|^2} \frac{F(\boldsymbol{p}_2 - \boldsymbol{p}_3)}{|\boldsymbol{p}_2 - \boldsymbol{p}_3|^2} e^{-i (\boldsymbol{p}_1 - \boldsymbol{p}_2 + \boldsymbol{p}_3) \cdot \boldsymbol{z}'} \varphi_\sigma(\boldsymbol{z}') \\
&\qquad - 2\, e^{i (\boldsymbol{p}_1 - \boldsymbol{p}_2 + \boldsymbol{p}_3) \cdot \boldsymbol{z}} \frac{F(\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 \cdot \boldsymbol{z}'} \varphi_\sigma(\boldsymbol{z}') \\
&\qquad + e^{i (\boldsymbol{p}_1 - \boldsymbol{p}_2 + \boldsymbol{p}_3) \cdot \boldsymbol{z}} \frac{F(\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 \cdot \boldsymbol{z}'} \varphi_\sigma(\boldsymbol{z}') \\
&\qquad - 2\, e^{i (\boldsymbol{p}_1 - \boldsymbol{p}_2 + \boldsymbol{p}_3) \cdot \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) \cdot \boldsymbol{z}'} \varphi_\sigma(\boldsymbol{z}') \\
&\qquad + e^{i (\boldsymbol{p}_1 - \boldsymbol{p}_2 + \boldsymbol{p}_3) \cdot \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) \cdot \boldsymbol{z}'} \varphi_\sigma(\boldsymbol{z}') \Big\} = \lambda\, \varphi_\sigma(\boldsymbol{z}).
\end{aligned} \tag{5.16}$$

In an electron gas model the Fermi distribution is approximated by a spherical symmetric step function:

$$f_{\boldsymbol{k}} = \theta(\xi - |\boldsymbol{k}|), \tag{5.17 a}$$

$$g_{\boldsymbol{k}} = \theta(|\boldsymbol{k}| - \xi). \tag{5.17 b}$$

ξ denotes the radius of the Fermi sphere [16].

For simplicity in treating (5.16) we shall neglect the difference potential V_D in each higher order term. This rather strong approximation implies

$$F^0(\boldsymbol{k}) = 0 \qquad \text{for all } k \tag{5.18}$$

and

$$F(\boldsymbol{k}) = -1 \qquad \text{for all } k, \tag{5.19}$$

which means a total elimination of the reference system in (5.16). Further it turns out that

$$D(\boldsymbol{x}, \boldsymbol{x}') = D_0(\boldsymbol{x}, \boldsymbol{x}') \tag{5.20}$$

and

$$b_{\boldsymbol{k}}(\boldsymbol{x}) \approx b_{\boldsymbol{k}}^0(\boldsymbol{x}) \approx \frac{1}{\sqrt{\Omega}}\, e^{i \boldsymbol{k} \cdot \boldsymbol{x}}, \tag{5.21}$$

leading therefore to complete consistency in our theory.

One of the simplest and most characteristic terms in (5.16) is

$$L_1 := \frac{-m e^4}{8\pi^7 \hbar^2} \int \mathrm{d}^3 p_3\, g_{\boldsymbol{p}_3} \int \mathrm{d}^3 p_1 \int \mathrm{d}^3 p_2 \frac{g_{\boldsymbol{p}_1} f_{\boldsymbol{p}_2}}{\boldsymbol{p}_1^2 - \boldsymbol{p}_2^2 + \boldsymbol{p}_3^2 - \mu} \cdot \frac{1}{|\boldsymbol{p}_1 - \boldsymbol{p}_2|^4} \cdot e^{i \boldsymbol{p}_3 \cdot (\boldsymbol{z} - \boldsymbol{z}')} \varphi_\sigma(\boldsymbol{z}') \,. \tag{5.22}$$

It is possible to evaluate the integrations over $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ using analytical methods [10]. The result shows a logarithmic singularity located on top of the Fermi surface. The origin of that singularity is due to the two Coulomb potentials contained in each term of (4.35) which collide exactly at the boundary of occupied and unoccupied electron states. The phenomenon is typical for metals and also obtained by earlier authors but in completely different ways [17, 18]. In our case a solution of this difficulty is reached by introducing a slightly modified Green's function.

6. Improvement of the Green's Function

In the past we used (4.24) and (4.25) to eliminate the three-particle amplitudes $h^{1,0}$ and $h^{0,1}$ in (4.11). Because of (5.18) the influence of the R-system and therefore the influence of $h^{0,1}$ is now neglected such that an improvement of the Green's function is only required for the inversion of (4.12). For that purpose we change the splitting of $\mathbb{B}$ via (2.6) into

$$\mathbb{B} = \mathbb{B}_0 + \mathbb{Z} + \mathbb{B}'_{\mathrm{Rest}} \,, \tag{6.1}$$

where $\mathbb{Z}$ denotes a suitably chosen two-particle interaction as part of $\mathbb{B}_{\mathrm{Rest}}$. The eigenvalue equation describing our one-centre problem becomes then

$$\begin{aligned} &\mathbb{P}^{1+1,\,1+0} (\mathbb{B}_0 - \omega \cdot 1)\, \mathbb{P}^{1+1,\,1+0} | \Phi_{\mathrm{HR}} \rangle \\ &\quad + \mathbb{P}^{1+1,\,1+0}\, \mathbb{Z}\, \mathbb{P}^{1+1,\,1+0} | \Phi_{\mathrm{HR}} \rangle \\ &= - \mathbb{P}^{1+1,\,1+0}\, \mathbb{B}'_{\mathrm{Rest}}\, \mathbb{P}^{1+1,\,1+0} | \Phi_{\mathrm{HR}} \rangle \,. \end{aligned} \tag{6.2}$$

The filtering of $h^{1,0}$ out of (6.2) can be achieved step by step. First we multiply $\langle \phi^{1+1,\,0+0} |\, \mathbb{G}_0^{1+1,\,1+0}$ from the left side and obtain

$$h^{1,0} + G_0^{1,0} Z^{1,\,0}_{\;\;1,\,0} h^{1,0} \approx - G_0^{1,0} B^{1,\,0}_{\;\;0,\,0} h^{0,0} \tag{6.3}$$

with

$$Z^{1,\,0}_{\;\;1,\,0} := \frac{1}{2!} \langle \Phi^{1+1,\,0+0} |\, \mathbb{Z}\, | \Phi^{1+1,\,0+0} \rangle \,. \tag{6.4}$$

Here we suppressed all higher order correlations contained in $\mathbb{B}'_{\mathrm{Rest}}$. Formally, the three-particle wavefunction $h^{1,0}$ now becomes

$$h^{1,0} \approx - [1 + G_0^{1,0} Z^{1,\,0}_{\;\;1,\,0}]^{-1} G_0^{1,0} B^{1,\,0}_{\;\;0,\,0} h^{0,0} \,. \tag{6.5}$$

Expanding the operator $(1 + G_0 Z)^{-1}$ in power series [19] we obtain

$$h^{1,0} \approx - G^{1,0} B^{1,\,0}_{\;\;0,\,0} h^{0,0} \tag{6.6}$$

with a new Green's function

$$G^{1,0} := G_0^{1,0} - G_0^{1,0} Z^{1,\,0}_{\;\;1,\,0} G_0^{1,0} + G_0^{1,0} Z^{1,\,0}_{\;\;1,\,0} G_0^{1,0} Z^{1,\,0}_{\;\;1,\,0} G_0^{1,0} - + \ldots \,. \tag{6.7}$$

To get explicit expressions, we select for $\mathbb{Z}$ the two-particle interaction H_5 defined in (4.19):

$$\mathbb{Z} \equiv w_s^+(\boldsymbol{y})\, S_1(\boldsymbol{y}, \boldsymbol{x})\, \underset{\uparrow}{S_0}(\boldsymbol{x}, \boldsymbol{y}')\, v_s^+(\boldsymbol{y}') \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} v_{s'}(\boldsymbol{y}'')\, S_0(\boldsymbol{y}'', \boldsymbol{x}' \underset{\uparrow}{)}\, S_1(\boldsymbol{x}', \boldsymbol{y}''')\, w_{s'}(\boldsymbol{y}''') \,. \tag{6.8}$$

In analogy to Gell-Mann and Brückner [20] who treated a Coulomb interaction to compute the correlation energy in an electron gas we only consider the most important parts of the series (6.7). In a random phase approximation [21], which means neglecting all contributions belonging to an exchange interaction, we are left with the following substitution of $h^{1,0}$ in (4.11):

$$\begin{aligned} &B^{0,\,0}_{\;\;1,\,0} \left(\begin{smallmatrix} \boldsymbol{z}; & \boldsymbol{z}_1 & \boldsymbol{z}_2 & \boldsymbol{z}_1' \\ \sigma; & s_1 & s_2 & s_1' \end{smallmatrix}\right) h^{1,0} \left(\begin{smallmatrix} \boldsymbol{z}_1 & \boldsymbol{z}_2 & \boldsymbol{z}_1' \\ s_1 & s_2 & s_1' \end{smallmatrix}\right) \\ &= - B^{0,\,0}_{\;\;1,\,0} \left(\begin{smallmatrix} \boldsymbol{z}; & \boldsymbol{z}_1 & \boldsymbol{z}_2 & \boldsymbol{z}_1' \\ \sigma; & s_1 & s_2 & s_1' \end{smallmatrix}\right) \cdot \Big\{ 2^0 \cdot G_0^{1,0} (\boldsymbol{z}_1, \boldsymbol{z}_2, \boldsymbol{z}_1'; \boldsymbol{y}_1, \boldsymbol{y}_2, \boldsymbol{y}_1')\, \delta_{s_1 \sigma_1} \delta_{s_2 \sigma_2} \delta_{s_1' \sigma_1'} \\ &\qquad - 2^1 \cdot G_0^{1,0} (\boldsymbol{z}_1, \boldsymbol{z}_2, \boldsymbol{z}_1'; \boldsymbol{x}, \boldsymbol{x}_2, \boldsymbol{x}) \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} G_0^{1,0} (\boldsymbol{x}', \boldsymbol{x}_2, \boldsymbol{x}'; \boldsymbol{y}_1, \boldsymbol{y}_2, \boldsymbol{y}_1')\, \delta_{s_2 \sigma_2} \delta_{s_1 s_1'} \delta_{\sigma_1 \sigma_1'} \\ &\qquad + 2^2 \cdot G_0^{1,0} (\boldsymbol{z}_1, \boldsymbol{z}_2, \boldsymbol{z}_1'; \boldsymbol{x}, \boldsymbol{x}_2, \boldsymbol{x}) \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} G_0^{1,0} (\boldsymbol{x}', \boldsymbol{x}_2, \boldsymbol{x}'; \boldsymbol{y}, \tilde{\boldsymbol{x}}_2, \boldsymbol{y}) \frac{e^2}{|\boldsymbol{y} - \boldsymbol{y}'|} \\ &\qquad \cdot G_0^{1,0} (\boldsymbol{y}', \tilde{\boldsymbol{x}}_2, \boldsymbol{y}'; \boldsymbol{y}_1, \boldsymbol{y}_2, \boldsymbol{y}_1')\, \delta_{s_2 \sigma_2} \delta_{s_1 s_1'} \delta_{\sigma_1 \sigma_1'} - + \ldots \Big\} \cdot B^{1,\,0}_{\;\;0,\,0} \left(\begin{smallmatrix} \boldsymbol{y}_1 & \boldsymbol{y}_2 & \boldsymbol{y}_1'; & \boldsymbol{z}' \\ \sigma_1 & \sigma_2 & \sigma_1'; & \varrho \end{smallmatrix}\right) h^{0,0} \left(\begin{smallmatrix} \boldsymbol{z}' \\ \varrho \end{smallmatrix}\right) . \end{aligned} \tag{6.9}$$

Transforming the Coulomb potentials via (5.9) and replacing all integral operators by their electron gas representation we obtain

$$B^{0,0}_{1,0}\left(\begin{smallmatrix} z \\ \sigma\end{smallmatrix};\begin{smallmatrix} z_1 & z_2 & z_1' \\ s_1 & s_2 & s_1'\end{smallmatrix}\right) h^{1,0}\left(\begin{smallmatrix} z_1 & z_2 & z_1' \\ s_1 & s_2 & s_1'\end{smallmatrix}\right)$$

$$= \frac{1}{(2\pi)^3}\frac{e^4}{(2\pi^2)^2}\int \mathrm{d}^3 p_1 \int \mathrm{d}^3 p_2 \int \mathrm{d}^3 p_3 \frac{g_{\boldsymbol{p}_1} f_{\boldsymbol{p}_2} g_{\boldsymbol{p}_3}}{\varepsilon_{\boldsymbol{p}_1}-\varepsilon_{\boldsymbol{p}_2}+\varepsilon_{\boldsymbol{p}_3}-\lambda}\,[e^{i\boldsymbol{p}_3\cdot\boldsymbol{z}} - g_{\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3} e^{i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot\boldsymbol{z}}]$$

$$\cdot \frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2}\,\{1-f(\boldsymbol{p}_1-\boldsymbol{p}_2)+f^2(\boldsymbol{p}_1-\boldsymbol{p}_2)-+\ldots\}\,\delta_{\sigma\sigma_2}\delta_{\sigma_1\sigma_1'}$$

$$\cdot\left[\frac{\{e^{-i\boldsymbol{p}_1\cdot\boldsymbol{z}'}-e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot\boldsymbol{z}'}\}\,\delta_{\sigma_1\varrho}\delta_{\sigma_2\sigma_1'}}{|\boldsymbol{p}_3-\boldsymbol{p}_2|^2} - \frac{\{e^{-i\boldsymbol{p}_3\cdot\boldsymbol{z}'}-e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot\boldsymbol{z}'}\}\,\delta_{\sigma_2\varrho}\delta_{\sigma_1\sigma_1'}}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2}\right]\cdot\varphi_\sigma(\boldsymbol{z}')\,, \tag{6.10}$$

where $$f(\boldsymbol{p}_1-\boldsymbol{p}_2) := 2\frac{e^2}{2\pi^2}\frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2}\int \mathrm{d}^3 q \frac{g_{\boldsymbol{q}} f_{\boldsymbol{q}-\boldsymbol{p}_1+\boldsymbol{p}_2}}{\varepsilon_{\boldsymbol{p}_3}+\varepsilon_{\boldsymbol{q}}-\varepsilon_{\boldsymbol{q}-\boldsymbol{p}_1+\boldsymbol{p}_2}-\lambda}\,. \tag{6.11}$$

Comparing (6.10) with the supplemented potentials in (5.16) we recognize a kind of screening of both the proton potential and the electron-electron interaction. In place of the Fourier representation of a pure Coulomb potential

$$V(\boldsymbol{p}_1-\boldsymbol{p}_2) = \frac{4\pi e^2}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2} \tag{6.12}$$

we now have to consider an effective potential in the form of

$$V_{\text{eff}}(\boldsymbol{p}_1-\boldsymbol{p}_2) \tag{6.13}$$
$$= \{1-f(\boldsymbol{p}_1-\boldsymbol{p}_2)+f^2(\boldsymbol{p}_1-\boldsymbol{p}_2)-+\ldots\}\cdot V(\boldsymbol{p}_1-\boldsymbol{p}_2)\,.$$

In case of convergence we would like to rewrite (6.13) in

$$V_{\text{eff}}(\boldsymbol{l}) = \frac{1}{1+f(\boldsymbol{l})}V(\boldsymbol{l}) = \frac{V(\boldsymbol{l})}{\varkappa(\boldsymbol{l})} \tag{6.14}$$

with the abbreviations

$$\boldsymbol{l} := \boldsymbol{p}_1-\boldsymbol{p}_2 \tag{6.15}$$

and

$$\varkappa(\boldsymbol{l}) := 1+f(\boldsymbol{l})\,. \tag{6.16}$$

As $\varkappa$ depends on the eigenvalue parameter λ, it could be interpreted as "dynamical dielectric function". Therefore it would be possible to compare $\varkappa$ with the dielectric functions for free electrons evaluated in the literature [15, 21, 22].

To answer the question whether we are really dealing in (6.13) with a convergent geometric series, we have to compute the function $f(\boldsymbol{l})$. In the electron gas approximation, (6.11) leads to

$$f(\boldsymbol{l}) = \frac{2me^2}{\hbar^2\pi^2}\frac{1}{l^2}\int \mathrm{d}^3 q\,\frac{g_{\boldsymbol{q}} f_{\boldsymbol{q}-\boldsymbol{l}}}{\boldsymbol{q}^2-(\boldsymbol{q}-\boldsymbol{l})^2+b^2}\,, \tag{6.17}$$

where

$$b^2 := \boldsymbol{p}_3^2-\mu\,. \tag{6.18}$$

Because of the factor $g_{\boldsymbol{q}} f_{\boldsymbol{q}-\boldsymbol{l}}$ in (6.17) we split the integration region into two parts (see Figure 1):

$$f(\boldsymbol{l}) = f_1(\boldsymbol{l})\,\theta(|\boldsymbol{l}|-2\xi) + f_2(\boldsymbol{l})\,\theta(2\xi-|\boldsymbol{l}|)\,. \tag{6.19}$$

Introducing spherical coordinates we obtain [10]

$$f_1(\boldsymbol{l}) = \frac{1}{a_0\pi}\frac{1}{l^3}\left\{\left(\frac{(b^2+l^2)^2}{4l^2}-\xi^2\right)\cdot\ln\left|\frac{b^2+l^2-2\xi l}{b^2+l^2+2\xi l}\right| + \frac{b^2\xi}{l}+\xi l\right\} \tag{6.20}$$

and

$$f_2(\boldsymbol{l}) = \frac{1}{a_0\pi}\frac{1}{l^3}\left\{\left(\frac{(b^2-l^2)^2}{4l^2}-\xi^2\right)\cdot\ln\left|\frac{b^2-l^2+2\xi l}{b^2+l^2+2\xi l}\right| + \frac{b^2}{2}+\xi l + b^2\cdot\ln\left|\frac{b^2}{b^2+l^2+2\xi l}\right|\right\}\,. \tag{6.21}$$

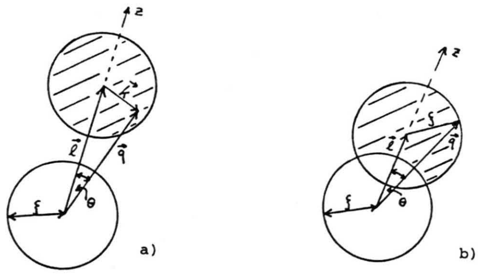

Fig. 1. Domain for integration to compute $f(\boldsymbol{l})$ a) in case of $|\boldsymbol{l}| \geqq 2\xi$; b) in case of $|\boldsymbol{l}| \leqq 2\xi$.

a_0 is the Bohr radius. Now it is easy to analyse the asymptotic behaviour: As l becomes infinite, $\varkappa(l)$ goes to 1 as

$$\varkappa(\boldsymbol{l}) \rightarrow 1+\frac{4\xi^3}{a_0\pi}\frac{1}{|\boldsymbol{l}|^4} \quad (|\boldsymbol{l}| \rightarrow \infty). \tag{6.22}$$

That is exactly what we were expecting because large distances l will cause very weak screening. Within this area the convergence in (6.13) will be ensured. As l becomes small, $\varkappa(l)$ goes to infinity as

$$\varkappa(\boldsymbol{l}) \rightarrow \frac{4\xi^2}{a_0\pi b^2}\frac{1}{|\boldsymbol{l}|} \quad (|\boldsymbol{l}| \rightarrow 0). \tag{6.23}$$

This singularity in the dielectric function for long-wavelength (small l) components of the potential is typical for metals due to their high conductivity. For a semi-conductor or an isolator the dielectric function remains finite over the whole range [22]. Although we are not sure that (6.13) leads to a convergent series for small l-values we feel free in summing up the series yielding

$$V_{\text{eff}}(\boldsymbol{l}) \approx \frac{1}{1+\dfrac{c}{l}}\frac{4\pi e^2}{l^2}=\frac{4\pi e^2}{l^2+c\,l}, \tag{6.24}$$

where

$$c := \frac{1}{a_0\pi}\frac{4\xi^2}{b^2}. \tag{6.25}$$

This action can be justified because an integration over $\boldsymbol{p}_3$ running from ξ to infinity is still standing out. Therefore an error in a small part of the integration range does not have large effects on the results.

To get an impression of the real appearance of V_{eff} we transform it back into $\boldsymbol{r}$-space representation. Although the integration over $\boldsymbol{l}$ cannot be achieved completely with analytical methods a good approximation is given by

$$\begin{aligned} V_{\text{eff}}(\boldsymbol{x}) &= 4\pi e^2 \int \mathrm{d}^3 l\, \frac{1}{l^2+c\,l}\, e^{-i\boldsymbol{l}\cdot\boldsymbol{x}} \qquad (6.26)\\ &\approx \frac{8\pi^2 e^2}{|\boldsymbol{x}|}\left[\sin(c\,x)\cdot c\,i(c\,x)-\cos(c\,x)\cdot s\,i(c\,x)\right]. \end{aligned}$$

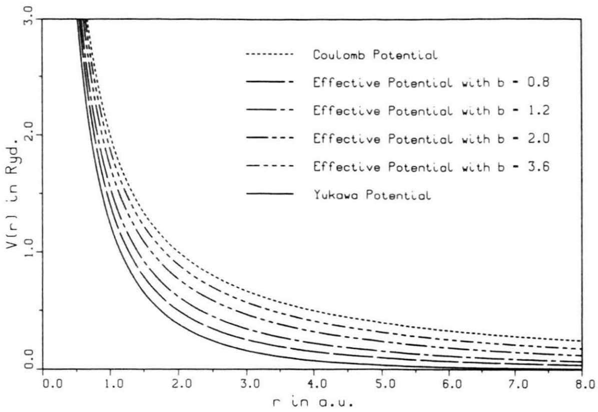

Fig. 2. The effective potential $V_{\text{eff}}(r)$ obtained by Gnirss for different values of b in comparison with Coulomb potential and Yukawa potential.

This means in particular that the long-range Coulomb potential is replaced by a more rapidly decreasing function. That result is confirmed by doing a numerical integration using (6.14) and the exact functions f_1, f_2 according to (6.20), (6.21)*. A plot is shown in Fig. 2 for different values of b. One can see that the graph belonging to the effective potential lies between the curves describing Coulomb potential and Yukawa potential. To avoid the logarithmic singularity which occurs exactly on top of the Fermi surface we are only interested in small values of b. But with decreasing b the slope gets stronger and stronger and the curves reach more similarity to a Yukawa potential than to the Coulomb potential. To simplify the numerical problems in the solution of our nonlinear eigenvalue equation we will therefore neglect the dependence between V_{eff} and μ in the following and approximate the effective potential (6.24) by a Yukawa potential

$$V'_{\text{eff}}(\boldsymbol{l}) = \frac{4\pi e^2}{\boldsymbol{l}^2+\alpha^2}, \tag{6.27}$$

where α is derived from the Thomas-Fermi theory [16] yielding

$$\alpha^2 := \xi/a_0\pi. \tag{6.28}$$

We conclude that the improvement of our Green's function leads to a replacement of one of the two Coulomb potentials colliding in each higher order term in (4.35) by an approximate Yukawa potential. Estimations done in [10] ensure that this is enough to guarantee convergence of the integrations in our higher order terms. Nevertheless, for symmetry in our further evaluations we also replace the second potential in each term by a Yukawa expression

$$V = 4\pi e^2/(\boldsymbol{l}^2+\beta^2) \tag{6.29}$$

setting β to zero after all integrations have been done.

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* Private communication with M. Gnirss.

7. The Nonlinear Eigenvalue Problem and its Numerical Solution

With the improvements and neglections discussed in Chapts. 5 and 6 we rewrite now the electron-gas representation of our higher order NTD-approximation (4.35) in the following way:

$$
\begin{aligned}
&\{D_0(z,z') + S_1(z,z')\,V_{\mathrm{H}}(z') + S_1(z,z')\,V_D(z')\}\,\varphi_\sigma(z')\\
&\quad -\frac{1}{16\pi^7}\frac{m e^4}{\hbar^2}\int d^3p_1\int d^3p_2\int d^3p_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}\cdot 2\,e^{i\boldsymbol{p}_3\cdot z}\,\frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\alpha^2}\,\frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\beta^2}\,e^{-i\boldsymbol{p}_3\cdot z'}\,\varphi_\sigma(z')\\
&\quad +\frac{1}{16\pi^7}\frac{m e^4}{\hbar^2}\int d^3p_1\int d^3p_2\int d^3p_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}\cdot e^{i\boldsymbol{p}_1\cdot z}\,\frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\beta^2}\,\frac{1}{|\boldsymbol{p}_3-\boldsymbol{p}_2|^2+\alpha^2}\,e^{-i\boldsymbol{p}_3\cdot z'}\,\varphi_\sigma(z')\\
&\quad +\frac{1}{16\pi^7}\frac{m e^4}{\hbar^2}\int d^3p_1\int d^3p_2\int d^3p_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}\cdot 2\,e^{i\boldsymbol{p}_3\cdot z}\,\frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\alpha^2}\,\frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\beta^2}\,e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot z'}\,\varphi_\sigma(z')\\
&\quad -\frac{1}{16\pi^7}\frac{m e^4}{\hbar^2}\int d^3p_1\int d^3p_2\int d^3p_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}\cdot e^{i\boldsymbol{p}_1\cdot z}\,\frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\beta^2}\,\frac{1}{|\boldsymbol{p}_3-\boldsymbol{p}_2|^2+\alpha^2}\,e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot z'}\,\varphi_\sigma(z') \qquad (7.1)\\
&\quad +\frac{1}{16\pi^7}\frac{m e^4}{\hbar^2}\int d^3p_1\int d^3p_2\int d^3p_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}\cdot 2\,e^{i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot z}\,\frac{g_{\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3}}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\alpha^2}\,\frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\beta^2}\,e^{-i\boldsymbol{p}_3\cdot z'}\,\varphi_\sigma(z')\\
&\quad -\frac{1}{16\pi^7}\frac{m e^4}{\hbar^2}\int d^3p_1\int d^3p_2\int d^3p_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}\cdot e^{i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot z}\,\frac{g_{\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3}}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\alpha^2}\,\frac{1}{|\boldsymbol{p}_3-\boldsymbol{p}_2|^2+\beta^2}\,e^{-i\boldsymbol{p}_3\cdot z'}\,\varphi_\sigma(z')\\
&\quad -\frac{1}{16\pi^7}\frac{m e^4}{\hbar^2}\int d^3p_1\int d^3p_2\int d^3p_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}\cdot 2\,e^{i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot z}\,\frac{g_{\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3}}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\alpha^2}\,\frac{1}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\beta^2}\,e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot z'}\,\varphi_\sigma(z')\\
&\quad +\frac{1}{16\pi^7}\frac{m e^4}{\hbar^2}\int d^3p_1\int d^3p_2\int d^3p_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}\cdot e^{i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot z}\,\frac{g_{\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3}}{|\boldsymbol{p}_1-\boldsymbol{p}_2|^2+\alpha^2}\,\frac{1}{|\boldsymbol{p}_3-\boldsymbol{p}_2|^2+\beta^2}\,e^{-i(\boldsymbol{p}_1-\boldsymbol{p}_2+\boldsymbol{p}_3)\cdot z'}\,\varphi_\sigma(z')\\
&\quad =\lambda\,\varphi_\sigma(z)\,.
\end{aligned}
$$

The solution of (7.1) is achieved by transforming it into an algebraic matrix equation

$$\sum_{l=0}^{\infty}\;\sum_{n=l+1}^{\infty}\;\sum_{m=-l}^{+l}\,[JO^{l\;n\;m}_{l_0\,n_0\,m_0}(s)+HN^{l\;n\;m}_{l_0\,n_0\,m_0}(\Lambda)]\cdot b_{l\,n\,m}=\Lambda\,(s)\,b_{l_0\,n_0\,m_0} \qquad (7.2)$$

and solving that nonlinear eigenvalue problem by successive iteration. Following is a brief description of the assumptions and notations leading to (7.2).

First we reformulate the equation of zeroth order represented by the first line in (7.1):

$$\{D_0(z,z')+S_1(z,z')\,V_{\mathrm{H}}(z')+S_1(z,z')\,V_D(z')\}\,\varphi_\sigma(z') =\lambda\,\varphi_\sigma(z)\,. \qquad (7.3)$$

Neglecting the exchange interaction contained in D_0, we obtain with the help of (1.4) and (4.28)

$$
\begin{aligned}
&\left[-\frac{\hbar^2}{2m}\Delta_z+V_{\mathrm{H}}(z)\right]\varphi_\sigma(z)\\
&\quad+[A(z)+V_D(z)]\,\varphi_\sigma(z)\\
&\quad-S_0(z,z')\,[V_{\mathrm{H}}(z')+V_D(z')]\,\varphi_\sigma(z')\\
&=\lambda\,\varphi_\sigma(z) \qquad (7.4)
\end{aligned}
$$

with

$$A(z):=V_W^0(z)+2e^2\int d^3y\,\frac{S_0(y,y)}{|z-y|}\,. \qquad (7.5)$$

The first bracket in (7.4) turns out to be a pure hydrogen problem and is immediately evaluated expanding φ with respect to hydrogen wavefunctions $\chi_{l\,n\,m}$ [23]:

$$\varphi_\sigma(z)=\sum_{l=0}^{\infty}\;\sum_{n=l+1}^{\infty}\;\sum_{m=-l}^{+l} b_{l\,n\,m}\,\chi_{l\,n\,m}(z,\sigma)\,, \qquad (7.6)$$

$$\left[-\frac{\hbar^2}{2m}\Delta_z-\frac{e^2}{|z|}\right]\chi_{l\,n\,m}(z)=-\frac{E_0}{n^2}\,\chi_{l\,n\,m}(z)\,, \qquad (7.7)$$

E_0 denotes the Rydberg energy:

$$E_0=\frac{m e^4}{2\hbar^2}=1\ \text{Ryd.}\approx 13.6\ \text{eV}\,. \qquad (7.8)$$

The transformation of (7.4) into an algebraic eigenvalue problem is achieved by multiplying from the left by $\chi^*_{l_0\,n_0\,m_0}(z,\sigma_0)$ and integrating or summing over z and σ. The result is a matrix equation

$$\sum_{l,n,m} JO^{l\;n\;m}_{l_0\,n_0\,m_0}\,b_{l\,n\,m}=\lambda\cdot b_{l_0\,n_0\,m_0}\,, \qquad (7.9)$$

which has been solved numerically by Duscher and Maichle [12] in case of magnesium as example. They treated the difference potential V_D by a Taylor

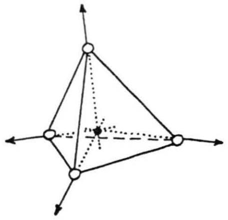

Fig. 3. A hydrogen proton in the centre of a tetrahedron with radial displacement.

expansion assuming first that the displacements s of host metal ions are only shifted in radial direction (see Fig. 3) and are absolutely equal for all nearest neighbours of the interstitial hydrogen proton:

$$|\boldsymbol{X}_j| = |\boldsymbol{X}_j^0| + s\,, \quad j \in \{0, 1, 2, 3\}\,. \tag{7.10}$$

The second assumption was that the shiftings are considerably smaller than the distance between the hydrogen centre and the host lattice ions

$$s \ll |\boldsymbol{X}_j|, |\boldsymbol{X}_j^0|\,, \quad j \in \{0, 1, 2, 3\}\,. \tag{7.11}$$

With these suppositions both the matrix $JO^{l\,n\,m}_{l_0 n_0 m_0}$ and the eigenvalue λ depend on the displacements s:

$$JO^{l\,n\,m}_{l_0 n_0 m_0} = JO^{l\,n\,m}_{l_0 n_0 m_0}(s)\,, \tag{7.12a}$$

$$\lambda = \lambda(s)\,. \tag{7.12b}$$

It is obvious that we now choose the same procedure as described above to treat (7.1), i.e. expanding φ with respect to hydrogen wave functions, multiplying by a complex conjugate function and integrating/summing all space/spin coordinates. Evidently the result is (7.2), a nonlinear algebraic eigenvalue equation to determine the coefficients $b_{l\,n\,m}$ as well as the difference energy

$$\Lambda := \lambda / E_0\,. \tag{7.13}$$

The detailed structures of $JO^{l\,n\,m}_{l_0 n_0 m_0}$ and $HN^{l\,n\,m}_{l_0 n_0 m_0}$ are shown in [10]. Note that only the angular integrations can be done with analytical methods expanding all plane waves with respect to spherical functions. The remaining integrations running over the radial parts of $\boldsymbol{p}_1$, $\boldsymbol{p}_2$, $\boldsymbol{p}_3$ have to be performed numerically mainly due to the non-factorizing Green's functions denominator and to the unusual integration boundaries described by g_p and f_p.

For a numerical solution of (7.2) the system has to be cut by choosing finite values for l, n and l_0, n_0, respectively. Duscher and Maichle showed that an upper boundary of $l_{\max} = 3$ and $n_{\max} = 7$ (which means a dimension of 78) is enough for $JO^{l\,n\,m}_{l_0 n_0 m_0}$. Contrary to that we cut the matrix $HN^{l\,n\,m}_{l_0 n_0 m_0}$ at $l_{\max} = 0$ and $n_{\max} = 4$ because some test calculations indicated that there is only a vanishingly small influence of non-spherical contributions to $HN^{l\,n\,m}_{l_0 n_0 m_0}$. For all that we needed a lot of CPU time to compute the whole matrix and to solve the nonlinear eigenvalue problem which we did in the following way:

We assumed a displacement s of the nearest neighbours of the hydrogen proton located in the centre of a tetrahedron, and calculated $JO(s)$. Then we solved the zeroth order approximation (7.9). Using the resulting eigenvalue λ_0 we calculated the matrix $HN(\lambda)$ and solved the eigenvalue problem (7.2). An improved eigenvalue λ_1 turned out. We recalculated $HN(\lambda)$ using λ_1 and obtained λ_2 by solving (7.2) once more. That procedure was repeated until the solution did not change its value. In our case convergence had established very fast, namely after the fourth iteration step. The plot in Fig. 4 shows the results obtained for λ_0 and λ_3 in case of magnesium with a Fermi wavelength $\xi = 1.36\,\text{Å}^{-1}$ [16].

It turns out that for all values of s the influence of the higher order approximation leads to a reduction of energy which means a stronger binding between hydrogen electron and hydrogen proton. That is exactly what we are expecting as a consequence of the contributions due to the three-particle interactions considered in the current report. To explain the scales in Fig. 4 we mention that a positive sign

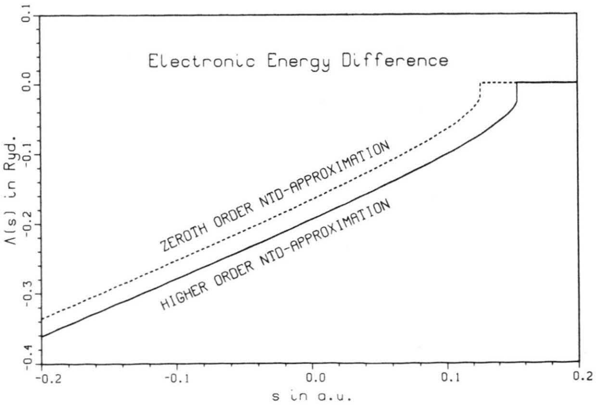

Fig. 4. The electronic energy difference eigenvalue λ as a function of host lattice displacements s for the case of zeroth order and higher order NTD-approximation evaluated for magnesium.

of the distortion s means a displacement of metal ion cores pointing away in radial direction from the centre of the tetrahedron (see Figure 3). By analogy negative values of s belong to shiftings towards the origin of coordinates. On the energy axis the zero point represents a kind of ionization of the excess electron with respect to the hydrogen proton, i.e. positive energy values describe non-localized electron states (scattering). Because our whole theory is only dealing with bound state energies and since the expansion (7.6) is only done with respect of localized functions, we do not have reliable values in the surrounding of that ionization point represented in Fig. 4 by the sudden crack of the curves.

We conclude that the stronger the host lattice distortion in direction to the centre point, the stronger the binding between excess electron and hydrogen proton. In addition the opposite proportionality is also valid. There is a wide range where the function $\lambda(s)$ shows a nearly linear behaviour, let us say in the interval

$$-0.2\,a_0 \leqq s \leqq 0.1\,a_0\,. \tag{7.14}$$

To emphasize the influence of the higher order NTD-approximation we mention that in this interval a nearly constant energy shift is coming out with an amount of about 0.03 Rydberg. This implies a relative change in energy with respect to the zeroth order solution of approximately 10% up to 20%:

$$0.1 \leqq \Delta\lambda/\lambda_0 \leqq 0.2\,. \tag{7.15}$$

Prior to that it has been obvious that the graph belonging to λ_3 looks like a parallel shifted line to the graph of the function $\lambda_0(s)$. The reason is of course that we neglected the difference potential V_D in each term of $HN^{l\;n\;m}_{l_0 n_0 m_0}$, i.e. we left the reference system totally out of consideration in our higher order approximation. Therefore most of the influence of the lattice distortion parameter s on the electronic energy difference eigenvalue λ is contained in $JO^{l\;n\;m}_{l_0 n_0 m_0}$. A rather small dependence between HN and s is implicitly at hand via $\lambda = \lambda(s)$ leading to the fact that the parallelism is not complete. It will be the purpose of a later work to analyse the influence of the R-system on $HN^{l\;n\;m}_{l_0 n_0 m_0}$ numerically [24].

With the results obtained above it is now possible to compute the probability amplitudes of the wavefunctions belonging to our higher order correlations. These amplitudes enable us to calculate the electron density distribution in the surrounding of a hydrogen centre stored in a metal crystal and to compare our density function with the evaluations done by Norskov [25]. Because we intend to do these density calculations not in the valence band representation obtained by the Γ-transformation (see (1.9)) but in the original Fock space representation we will postpone that formalism to a succeeding paper [26].

Appendix

We give a proof of the following statements:

i)
$$\hat{S}_1(\boldsymbol{x},\boldsymbol{y})\,\hat{S}_0^*(\boldsymbol{x}',\boldsymbol{y}')\,\hat{S}_1^*(\boldsymbol{x}'',\boldsymbol{y}'')\,\hat{S}_0(\boldsymbol{x}''',\boldsymbol{y}''')\;G_0^{\nu,\nu'}(J,J'\,|\,\boldsymbol{y},\boldsymbol{y}',\boldsymbol{y}'',\boldsymbol{y}''';\boldsymbol{z},\boldsymbol{z}',\boldsymbol{z}'',\boldsymbol{z}''')$$
$$= G_0^{\nu,\nu'}(J,J'\,|\,\boldsymbol{x},\boldsymbol{x}',\boldsymbol{x}'',\boldsymbol{x}''';\boldsymbol{z},\boldsymbol{z}',\boldsymbol{z}'',\boldsymbol{z}''')\,, \tag{A.1}$$

ii)
$$\hat{S}_1(\boldsymbol{x},\boldsymbol{y})\,\hat{S}_0^*(\boldsymbol{x}',\boldsymbol{y}')\,\hat{S}_1^*(\boldsymbol{x}'',\boldsymbol{y}'')\,\hat{S}_0(\boldsymbol{x}''',\boldsymbol{y}''')\;h^{\nu,\nu'}\!\left(J,J'\,\middle|\,\begin{smallmatrix}\boldsymbol{y} & \boldsymbol{y}' & \boldsymbol{y}'' & \boldsymbol{y}''' \\ s & s' & s'' & s'''\end{smallmatrix}\right)$$
$$= h^{\nu,\nu'}\!\left(J,J'\,\middle|\,\begin{smallmatrix}\boldsymbol{x} & \boldsymbol{x}' & \boldsymbol{x}'' & \boldsymbol{x}''' \\ s & s' & s'' & s'''\end{smallmatrix}\right). \tag{A.2}$$

Proof: The Green's function $\mathbb{G}_0^{M+J,\,M'+J'}$ is defined by (3.1). Inserting the ansatz (3.6) and multiplying from the left by $\langle\phi^{\nu+J,\,\nu'+J'}\binom{x}{s}|$ we obtain as a consequence of

$$\left\langle\Phi^{\nu+J,\,\nu'+J'}\tbinom{x}{s}\,\middle|\,\Phi^{m+J,\,m'+J'}\tbinom{y}{\sigma}\right\rangle = (m+J)!\,m!\,(m'+J')!\,m'!$$
$$\cdot\,\hat{S}_1(\boldsymbol{x},\boldsymbol{y})\cdot\hat{S}_0^*(\boldsymbol{x}',\boldsymbol{y}')\cdot\hat{S}_1^*(\boldsymbol{x}'',\boldsymbol{y}'')\cdot\hat{S}_0(\boldsymbol{x}''',\boldsymbol{y}''')\cdot\delta_{m,\nu}\,\delta_{m',\nu'}\,\delta_{\sigma,s} \tag{A.3}$$

the equation

$$\hat{S}_1(\boldsymbol{x},\boldsymbol{y})\cdot\hat{S}_0^*(\boldsymbol{x}',\boldsymbol{y}')\cdot\hat{S}_1^*(\boldsymbol{x}'',\boldsymbol{y}'')\cdot\hat{S}_0(\boldsymbol{x}''',\boldsymbol{y}''')\,G_0^{\nu,\nu'}(J,J'\,|\,y,z)\,Q\left(\tbinom{z}{s}\,\middle|\,h\right)$$
$$= h^{\nu,\nu'}\left(J,J'\,\middle|\,\tbinom{x}{s}\right), \tag{A.4}$$

Multiplying from the left by

$$\hat{S}_1(\boldsymbol{u},\boldsymbol{x}) \cdot \hat{S}_0^*(\boldsymbol{u}',\boldsymbol{x}') \cdot \hat{S}_1^*(\boldsymbol{u}'',\boldsymbol{x}'') \cdot \hat{S}_0(\boldsymbol{u}''',\boldsymbol{x}''') \tag{A.5}$$

and integrating over all x we are left with

$$\begin{aligned}&\hat{S}_1(\boldsymbol{u},\boldsymbol{x})\, \hat{S}_0^*(\boldsymbol{u}',\boldsymbol{x}')\, \hat{S}_1^*(\boldsymbol{u}'',\boldsymbol{x}'')\, \hat{S}_0(\boldsymbol{u}''',\boldsymbol{x}''')\, \hat{S}_1(\boldsymbol{x},\boldsymbol{y})\, \hat{S}_0^*(\boldsymbol{x}',\boldsymbol{y}')\, \hat{S}_1^*(\boldsymbol{x}'',\boldsymbol{y}'')\, \hat{S}_0(\boldsymbol{x}''',\boldsymbol{y}''') \cdot G_0^{\nu,\nu'}(J,J' \,|\, y,z)\, Q\left(\genfrac{}{}{0pt}{}{z}{s}\middle|\, h\right)\\ &= \hat{S}_1(\boldsymbol{u},\boldsymbol{x})\, \hat{S}_0^*(\boldsymbol{u}',\boldsymbol{x}')\, \hat{S}_1^*(\boldsymbol{u}'',\boldsymbol{x}'')\, \hat{S}_0(\boldsymbol{u}''',\boldsymbol{x}''')\, h^{\nu,\nu'}\left(J,J' \,\middle|\, \genfrac{}{}{0pt}{}{x}{s}\right).\end{aligned} \tag{A.6}$$

Because of the properties (1.3) we may rewrite (A.6) in the form

$$\begin{aligned}&\hat{S}_1(\boldsymbol{u},\boldsymbol{y})\, \hat{S}_0^*(\boldsymbol{u}',\boldsymbol{y}')\, \hat{S}_1^*(\boldsymbol{u}'',\boldsymbol{y}'')\, \hat{S}_0(\boldsymbol{u}''',\boldsymbol{y}''')\, G_0^{\nu,\nu'}(J,J' \,|\, y,z)\, Q\left(\genfrac{}{}{0pt}{}{z}{s}\middle|\, h\right)\\ &= \hat{S}_1(\boldsymbol{u},\boldsymbol{x})\, \hat{S}_0^*(\boldsymbol{u}',\boldsymbol{x}')\, \hat{S}_1^*(\boldsymbol{u}'',\boldsymbol{x}'')\, \hat{S}_0(\boldsymbol{u}''',\boldsymbol{x}''')\, h^{\nu,\nu'}\left(J,J' \,\middle|\, \genfrac{}{}{0pt}{}{x}{s}\right).\end{aligned} \tag{A.7}$$

Comparison of (A.7) with (A.4) proves (A.2).

The invariance relation (A.1) is obtained in a quite analogous way:

$$\begin{aligned}&\hat{S}_1(\boldsymbol{u},\boldsymbol{x})\, \hat{S}_0^*(\boldsymbol{u}',\boldsymbol{x}')\, \hat{S}_1^*(\boldsymbol{u}'',\boldsymbol{x}'')\, \hat{S}_0(\boldsymbol{u}''',\boldsymbol{x}''')\, G_0^{\nu,\nu'}(J,J' \,|\, y,z)\, Q\left(\genfrac{}{}{0pt}{}{z}{s}\middle|\, h\right)\\ &= h^{\nu,\nu'}\left(J,J' \,\middle|\, \genfrac{}{}{0pt}{}{u}{s}\right)\\ &= \hat{S}_1(\boldsymbol{u},\boldsymbol{x})\, \hat{S}_0^*(\boldsymbol{u}',\boldsymbol{x}')\, \hat{S}_1^*(\boldsymbol{u}'',\boldsymbol{x}'')\, \hat{S}_0(\boldsymbol{u}''',\boldsymbol{x}''')\\ &\cdot \hat{S}_1(\boldsymbol{x},\boldsymbol{y})\, \hat{S}_0^*(\boldsymbol{x}',\boldsymbol{y}')\, \hat{S}_1^*(\boldsymbol{x}'',\boldsymbol{y}'')\, \hat{S}_0(\boldsymbol{x}''',\boldsymbol{y}''') \cdot G_0^{\nu,\nu'}(J,J' \,|\, y,z)\, Q\left(\genfrac{}{}{0pt}{}{z}{s}\middle|\, h\right).\end{aligned} \tag{A.8}$$

Comparison of the coefficients in the first line of (A.8) with the one in the last line leads to (A.1). This finishes the proof.

As a special case we consider $J=1, J'=0$ and $\nu=\nu'=0$ resulting in

$$\hat{S}_1(\boldsymbol{x},\boldsymbol{y})\, h^{0,0}\left(1,0 \,\middle|\, \genfrac{}{}{0pt}{}{y}{\sigma}\right) = h^{0,0}\left(1,0 \,\middle|\, \genfrac{}{}{0pt}{}{x}{\sigma}\right). \tag{A.9}$$

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