On the Electronic Structure of Metal Hydrides
I. Exposition of a Many-Electron Theory

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We present the concept of a many-electron theory for the calculation of the energy difference between an undisturbed metallic host lattice and a crystal disturbed by stored hydrogen atoms. With the help of an elimination procedure a multidimensional system of equations is reduced to a one-particle Schrödinger equation for the electron of the hydrogen. The interaction with the electrons of the metal is then described by a dynamical potential depending on the state of the electron itself. A first order approximation with static screening is discussed and then generalized to a self-consistent calculation of one-electron functions which are used as a basis for expansions.

The well-known property of many metals and alloys to absorb hydrogen has attracted great interest in recent years as a possibility for hydrogen storage [1]. While it is almost impossible to review the experimental research in this field [2] the theoretical understanding of this complex phenomenon is still in the beginning [3]. An important reason for this is the fact that only the solution of a many-electron problem can give an adequate description of an electronic defect represented by a proton in a host metal lattice and an electron belonging to it. Perhaps a one-electron theory with static (rigid) screening [4] is insufficient to provide information for example about the forces between lattice atoms and protons. In order to calculate energies and lattice distortions for metal hydrides it is therefore reasonable to start with a many-electron theory and derive dynamical potentials from it, i.e. potentials depending on the electronic state. In this way we want to treat particularly the question of the localization of an additional electron. We regard this as a prerequisite for the discussion of phase transitions connected with the storage of hydrogen in metals.

§ 1. Adiabatic Decomposition of the Many-Particle Schrödinger Equation

The starting point of our investigation is the many-particle Schrödinger equation

$$i\hbar\dot{\Psi}(\boldsymbol{x},\boldsymbol{X},\boldsymbol{Y}) = \mathscr{H}\Psi(\boldsymbol{x},\boldsymbol{X},\boldsymbol{Y})\,, \tag{1.1}$$

The labels $\boldsymbol{x}$, $\boldsymbol{X}$ and $\boldsymbol{Y}$ refer to the set of electron coordinates $\boldsymbol{x}_\mu$, to the set of nuclear coordinates of the host lattice atoms $\boldsymbol{X}_{\boldsymbol{m},i}$ and to the coordinates of the absorbed protons $\boldsymbol{Y}_{\boldsymbol{n}}$, respectively. The Hamilton operator is *

$$\begin{aligned}\mathscr{H} = &-\sum_{\mu}\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\boldsymbol{x}_\mu^2} - \sum_{\boldsymbol{m},i}\frac{\hbar^2}{2M_i}\frac{\partial^2}{\partial\boldsymbol{X}_{\boldsymbol{m},i}^2}\\ &-\sum_{\boldsymbol{n}}\frac{\hbar^2}{2M}\frac{\partial^2}{\partial\boldsymbol{Y}_{\boldsymbol{n}}^2} + \frac{1}{2}\sum_{\mu,\mu'}\frac{e^2}{|\boldsymbol{x}_\mu-\boldsymbol{x}_{\mu'}|}\\ &+\frac{1}{2}\sum_{\substack{\boldsymbol{m},i\\ \boldsymbol{m}',i'}}\frac{e_{\boldsymbol{m},i}\,e_{\boldsymbol{m}',i'}}{|\boldsymbol{X}_{\boldsymbol{m},i}-\boldsymbol{X}_{\boldsymbol{m}',i'}|} + \frac{1}{2}\sum_{\boldsymbol{n},\boldsymbol{n}'}\frac{e^2}{|\boldsymbol{Y}_{\boldsymbol{n}}-\boldsymbol{Y}_{\boldsymbol{n}'}|}\\ &-\sum_{\substack{\boldsymbol{m},i\\ \mu}}\frac{e_{\boldsymbol{m},i}\,e}{|\boldsymbol{x}_\mu-\boldsymbol{X}_{\boldsymbol{m},i}|} - \sum_{\boldsymbol{n},\mu}\frac{e^2}{|\boldsymbol{x}_\mu-\boldsymbol{Y}_{\boldsymbol{n}}|}\\ &+\sum_{\substack{\boldsymbol{m},i\\ \boldsymbol{n}}}\frac{e_{\boldsymbol{m},i}\,e}{|\boldsymbol{X}_{\boldsymbol{m},i}-\boldsymbol{Y}_{\boldsymbol{n}}|}\end{aligned} \tag{1.2}$$

where $e_{\boldsymbol{m},i}$ denotes the charge of an atom of kind i in the basic cell with label $\boldsymbol{m}$. It may be suitable to consider atomic cores instead of the nuclei of the host lattice. The Coulomb interaction between nuclei and electrons will then be replaced by pseudopotentials

$$-\sum_{\boldsymbol{m},i}\frac{e\,e_{\boldsymbol{m},i}}{|\boldsymbol{x}_\mu-\boldsymbol{X}_{\boldsymbol{m},i}|} \to V_{\mathrm{W}}(\boldsymbol{x}_\mu)\,. \tag{1.3}$$

We assume that the extremely high mobility of the protons justifies an adiabatic approximation in two steps. For this purpose we make the following ansatz [5]:

$$\begin{aligned}&\Psi(\boldsymbol{x},\boldsymbol{X},\boldsymbol{Y};t)\\ &\quad=\psi(\boldsymbol{x},\boldsymbol{X},\boldsymbol{Y})\,\chi(\boldsymbol{Y},\boldsymbol{X})\,\Phi(\boldsymbol{X})\,e^{-i/\hbar Et}\end{aligned} \tag{1.4}$$

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* It is $\partial^2/\partial\boldsymbol{x}^2 := \Delta_x$ etc.

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resulting in a decomposition into three subsystems:

1. the electronic system:

$$\Big(-\sum_{\mu}\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{x}_\mu}-\sum_{\substack{m,i\\ \mu}}\frac{e\,e_{m,i}}{|\boldsymbol{x}_\mu-\boldsymbol{X}_{m,i}|} -\sum_{n,\mu}\frac{e^2}{|\boldsymbol{x}_\mu-\boldsymbol{Y}_n|}+\frac{1}{2}\sum_{\mu,\mu'}\frac{e^2}{|\boldsymbol{x}_\mu-\boldsymbol{x}_{\mu'}|}\Big) \cdot \psi_n(\boldsymbol{x},\boldsymbol{X},\boldsymbol{Y})=E_n(\boldsymbol{Y},\boldsymbol{X})\,\psi_n(\boldsymbol{x},\boldsymbol{X},\boldsymbol{Y})\,, \qquad (1.5)$$

2. the system of the protons:

$$\Big(-\sum_{n}\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \boldsymbol{Y}_n^2}+\sum_{\substack{m,i\\ n}}\frac{e_{m,i}\,e}{|\boldsymbol{X}_{m,i}-\boldsymbol{Y}_n|} +\frac{1}{2}\sum_{n,n'}\frac{e^2}{|\boldsymbol{Y}_n-\boldsymbol{Y}_{n'}|}+E_n(\boldsymbol{Y},\boldsymbol{X})\Big) \cdot \chi_{nk}(\boldsymbol{Y},\boldsymbol{X})=E_{nk}(\boldsymbol{X})\,\chi_{nk}(\boldsymbol{Y},\boldsymbol{X})\,, \qquad 1.6)$$

3. the system of the nuclei (or cores) of the host lattice:

$$\Big(-\sum_{m,i}\frac{\hbar^2}{2M_i}\frac{\partial^2}{\partial \boldsymbol{X}_{m,i}}+\frac{1}{2}\sum_{\substack{m,i\\ m',i'}}\frac{e_{m,i}\,e_{m',i'}}{|\boldsymbol{X}_{m,i}-\boldsymbol{X}_{m',i'}|} +E_{nk}(\boldsymbol{X})\Big)\,\Phi_{nkm}(\boldsymbol{X})=E\,\Phi_{nkm}(\boldsymbol{X})\,. \qquad (1.7)$$

If we neglect interference terms which in the adiabatic decomposition (1.4) are considered as perturbations responsible for the exchange of energy and momentum between the subsystems, only a one-directional coupling of the three subsystems is left: The energy eigenvalues $E_n(\boldsymbol{Y},\boldsymbol{X})$ of (1.5) represent a potential for the proton system, the eigenvalues $E_{n,k}(\boldsymbol{X})$ play the role of a potential for the nuclei of the host lattice. Equations (1.6) and (1.7) determine the dynamics of protons and the host lattice nuclei respectively, and both are responsible for the lattice structure and the deformations caused by the hydrogen. Before investigating the static stability of the lattice the electron equation must be solved because the substitution of the partial energies $E_n(\boldsymbol{Y},\boldsymbol{X})$ and $E_{n,k}(\boldsymbol{X})$ by some fitted potentials will not be possible for a metal lattice with interstitial protons.

We therefore start with the Schrödinger equation (1.5) and investigate the many-electron problem treating $\boldsymbol{X}$ and $\boldsymbol{Y}$ as parameters. As can be expected for a many-body problem the total energy, in this case the energy of a metallic crystal, is very large compared with the energy difference of elementary excitations. When treating a host lattice with a stored hydrogen one faces the problem of the "difference of large numbers" (eventually infinitely large in the thermodynamic limit). To avoid this difficulty we use the New Tamm-Dancoff procedure (NTD) which has been mathematically developed so far [6] that we can rely on it for the calculation of energy differences.

§ 2. The Hamilton Operator of the Many-Electron System Expressed by Hermitian Field Operators

Instead of Eq. (1.5) we write the Hamiltonian of the electron system in a more general form using field operators

$$\mathscr{H}^{\mathrm{e}}=\int \mathrm{d}^3x\,\psi^+(\boldsymbol{x})\Big(-\frac{\hbar^2}{2m}\Delta+V_{\mathrm{W}}(\boldsymbol{x})+V_{\mathrm{H}}(\boldsymbol{x})\Big)\psi(\boldsymbol{x}) +\frac{1}{2}\iint \mathrm{d}^3x\,\mathrm{d}^3x'\,\psi^+(\boldsymbol{x})\,\psi^+(\boldsymbol{x}')\,\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\psi(\boldsymbol{x}')\,\psi(\boldsymbol{x})\,. \qquad (2.1)$$

$V_{\mathrm{W}}(\boldsymbol{x})$ is the single particle potential of the host lattice atoms or ions (see (1.3)) and

$$V_{\mathrm{H}}(\boldsymbol{x})=-\sum_{n}\frac{e^2}{|\boldsymbol{x}-\boldsymbol{Y}_n|} \qquad (2.2)$$

is the potential of the stored protons. $\psi^+(\boldsymbol{x})$ and $\psi(\boldsymbol{x})$ are creation and annihilation operators for an electron field obeying the anticommutation relation

$$\{\psi(\boldsymbol{x}),\,\psi^+(\boldsymbol{x}')\}_+=\delta(\boldsymbol{x}-\boldsymbol{x}')\,. \qquad (2.3)$$

To achieve an efficient presentation of the following calculations we use the Hermitian field operators [7].

$$\hat{\Psi}=U^+\begin{pmatrix}\psi(\boldsymbol{x})\\ \psi^+(\boldsymbol{x})\end{pmatrix} \qquad (2.4)$$

with U denoting the unitary 2×2-matrix:

$$U=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & i\\ 1 & -i\end{pmatrix},\qquad UU^+=U^+U=I\,. \qquad (2.5)$$

The anticommutation relation of (2.4) is

$$\{\hat{\Psi}_\sigma(\boldsymbol{x}),\,\hat{\Psi}_\varrho(\boldsymbol{x}')\}_+=\delta_{\varrho,\sigma}\,\delta(\boldsymbol{x}-\boldsymbol{x}')\,. \qquad (2.6)$$

We have the relation

$$\hat{\Psi}^{\mathrm{T}}(\boldsymbol{x})=\hat{\Psi}^+(\boldsymbol{x}) \qquad (2.7)$$

with $\Psi(\boldsymbol{x})^{\mathrm{T}}$ being the transposed operator which can be represented by the row operator

$$\hat{\Psi}(\boldsymbol{x})^{\mathrm{T}} = {}^{(\psi(\boldsymbol{x}),\,\psi^{+}(\boldsymbol{x}))}U^{\#} = {}^{(\psi^{+}(\boldsymbol{x}),\,\psi(\boldsymbol{x}))}U \tag{2.8}$$

using the relation *

$$U^{+}U^{\#} = U^{\#}U^{+} = U U^{\mathrm{T}} = U^{\mathrm{T}} U = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{2.9}$$

Applying these Hermitian field operators the Hamiltonian takes the form [8]

$$\begin{aligned} \mathscr{H}^{\mathrm{e}} &\equiv \hat{\mathscr{H}}^{\mathrm{e}} \\ &= \frac{1}{2}\int \hat{\Psi}(\boldsymbol{x})^{\mathrm{T}}(\hat{D}(\varDelta) + \hat{V}_{\mathrm{W}}(\boldsymbol{x}) + \hat{V}_{\mathrm{H}}(\boldsymbol{x}))\,\hat{\Psi}(\boldsymbol{x})\,\mathrm{d}^3x + \frac{1}{4}\,\frac{e^2}{2}\iint \mathrm{d}^3x\,\mathrm{d}^3x'\,\hat{\Psi}(\boldsymbol{x})^{\mathrm{T}}\,\hat{\Psi}(\boldsymbol{x}')^{\mathrm{T}}\,\frac{\hat{E}\otimes\hat{E}}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\hat{\Psi}(\boldsymbol{x}')\,\hat{\Psi}(\boldsymbol{x}) \\ &\quad + \frac{1}{4}\iint \mathrm{d}^3x\,\mathrm{d}^3x'\left(\hat{\Psi}(\boldsymbol{x})^{\mathrm{T}}\,\hat{E}\,\hat{\Psi}(\boldsymbol{x})\,\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\delta(\boldsymbol{x}'-\boldsymbol{x}') - \hat{\Psi}(\boldsymbol{x})^{\mathrm{T}}\,\hat{E}\,\hat{\Psi}(\boldsymbol{x}')\,\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\delta(\boldsymbol{x}-\boldsymbol{x}')\right) \\ &\quad + \frac{1}{8}\iint \mathrm{d}^3x\,\mathrm{d}^3x'\,\delta(\boldsymbol{x}-\boldsymbol{x})\,\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\delta(\boldsymbol{x}'-\boldsymbol{x}') + \tfrac{1}{2}\int \mathrm{d}^3x\,\delta(\boldsymbol{x}-\boldsymbol{x})\,[D(\varDelta) + V_{\mathrm{W}}(\boldsymbol{x}) + V_{\mathrm{H}}(x)] \end{aligned} \tag{2.10}$$

where we write

$$\hat{E} = U^{+}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} U\,. \tag{2.11}$$

Expressions marked by ^ are skew-symmetric 2×2 matrices

$$\hat{D}(\varDelta) = -\frac{\hbar^2}{2m}\,\varDelta\cdot\hat{E}\,; \tag{2.12}$$

$$\hat{V}_{\mathrm{W}}(\boldsymbol{x}) = V_{\mathrm{W}}(\boldsymbol{x})\cdot\hat{E}\,; \quad \hat{V}_{\mathrm{H}}(\boldsymbol{x}) = V_{\mathrm{H}}(\boldsymbol{x})\cdot\hat{E}\,.$$

The components of a matrix expression like

$$\hat{\Psi}(\boldsymbol{x})^{\mathrm{T}}\,\hat{\Psi}(\boldsymbol{x}')^{\mathrm{T}}\,\frac{\hat{E}\otimes\hat{E}}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\hat{\Psi}(\boldsymbol{x}')\,\hat{\Psi}(\boldsymbol{x}) \tag{2.13a}$$

are

$$\sum_{\substack{\sigma\sigma' \\ \varrho\varrho'}} \hat{\Psi}_{\sigma}(\boldsymbol{x})\,\hat{\Psi}_{\varrho}(\boldsymbol{x}')\,\frac{\hat{E}_{\sigma\sigma'}\,\hat{E}_{\varrho\varrho'}}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\hat{\Psi}_{\varrho'}(\boldsymbol{x}')\,\hat{\Psi}_{\sigma'}(\boldsymbol{x}) \tag{2.13b}$$

where we agree that the first $\hat{E}$ in (2.13) refers to the outer $\hat{\Psi}(\boldsymbol{x})$, while the second $\hat{E}$ combines with the inner $\hat{\Psi}(\boldsymbol{x})$. This formalism will also be used in subsequent expressions of the same kind.

Notice the divergent, δ-functions like terms in the second and third line of equation (2.10). They will be formally kept and not be specified here as they are compensated for in a subsequent transformation.

§ 3. Mapping on a System of Functionals for the Energy Difference

An eigenvalue problem for the energy differences is obtained by a suitable mapping on the "u space" of source functions [9]. Therefore, we introduce the generating operator

$$\hat{V} := e^{ic} \tag{3.1}$$

which is to be understood as a formal power series. Let c be defined by

$$\begin{aligned} c &:= \int u^{+}(\boldsymbol{x})\,\hat{\Psi}(\boldsymbol{x})\,\mathrm{d}^3x \\ &= \int (v^{+}(\boldsymbol{x})\,\psi^{+}(\boldsymbol{x}) + w^{+}(\boldsymbol{x})\,\psi(\boldsymbol{x}))\,\mathrm{d}^3x\,. \end{aligned} \tag{3.2}$$

The source field

$$u(\boldsymbol{x}) := U^{+}\begin{pmatrix} w(\boldsymbol{x}) \\ v(\boldsymbol{x}) \end{pmatrix}; \quad u^{+}(\boldsymbol{x}) = {}^{(w^{+}(\boldsymbol{x}),\,v^{+}(\boldsymbol{x}))}U \tag{3.3}$$

is a Fermi field obeying

$$\{u_{\sigma}(\boldsymbol{x}), u_{\sigma'}^{+}(\boldsymbol{x}')\}_{+} = \delta_{\sigma\sigma'}\,\delta(\boldsymbol{x}-\boldsymbol{x}') \tag{3.4}$$

but it anticommutes with $\hat{\Psi}(\boldsymbol{x})$:

$$\begin{aligned} &\{u(\boldsymbol{x}), \hat{\Psi}(\boldsymbol{x}')\}_{+} = 0\,; \\ &\{u^{+}(\boldsymbol{x}), \hat{\Psi}(\boldsymbol{x}')\}_{+} = 0\,. \end{aligned} \tag{3.5}$$

Equations (3.4) and (3.5) are consistent with

$$\begin{aligned} &\{v(\boldsymbol{x}), v^{+}(\boldsymbol{x}')\}_{+} = \delta(\boldsymbol{x}-\boldsymbol{x}')\,; \\ &\{w(\boldsymbol{x}), w^{+}(\boldsymbol{x}')\}_{+} = \delta(\boldsymbol{x}-\boldsymbol{x}')\,; \end{aligned} \tag{3.6}$$

$$\begin{aligned} &\{v(\boldsymbol{x}), w^{+}(\boldsymbol{x}')\}_{+} = 0\,; \\ &\{v(\boldsymbol{x}), \psi^{+}(\boldsymbol{x}')\}_{+} = 0 \quad \text{etc.} \end{aligned} \tag{3.7}$$

which means that all remaining anti-commutators of $v(\boldsymbol{x})$, $w(\boldsymbol{x})$, $\psi(\boldsymbol{x})$ and of the adjoint operators vanish.

We want to calculate the energy difference of an undisturbed host lattice with separated hydrogen and a lattice with additional protons and electrons. Let $\mathscr{H}_0^e$ describe a state of the system where the

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* U^{T} is the transposed matrix and $U^{\#}$ is the adjoint and transposed, i.e. the complex conjugate matrix of U.

$\mathbf{X}^0$-coordinates in $V_{\mathrm{w}}(\boldsymbol{x}) \equiv V^0_{\mathrm{w}}(\boldsymbol{x})$ assume the values of the ideal lattice and the $\mathbf{Y}^0$-coordinates of the protons in $V_{\mathrm{H}}(\boldsymbol{x}) \equiv V^0_{\mathrm{H}}(\boldsymbol{x})$ represent positions outside the crystal. In $\mathscr{H}^e_{\mathrm{H}}$ the $\mathbf{X}$-coordinates include the distortion of the lattice and the $\mathbf{Y}$-coordinates are the positions of the protons inside the crystal.

The electron states $|a\rangle = |H\rangle$ and $|b\rangle = |0\rangle$ are defined by the eigenvalue problems

$$\mathscr{H}^e_{\mathrm{H}}\,|H\rangle = E_{\mathrm{H}}\,|H\rangle \quad \text{and}$$
$$\mathscr{H}^e_0\,|0\rangle = E_0\,|0\rangle\,. \tag{3.8}$$

By forming the expression

$$\langle b|\,(\hat{V}\hat{\mathscr{H}}^e_{\mathrm{H}} - \hat{\mathscr{H}}^e_0\hat{V})\,|a\rangle = \omega_{ab}\,\langle b|\,\hat{V}\,|a\rangle \tag{3.9}$$

we get an eigenvalue problem for the energy difference

$$\omega_{ab} = E_a - E_b\,. \tag{3.10}$$

Projecting equation (3.9) on the vacuum $|0)$ of u space

$$u(\boldsymbol{x})\,|0) = 0 \tag{3.11}$$

and denoting the functional $\langle b|\,\hat{V}\,|a\rangle$ by

$$T_{0\mathrm{H}}(u^+) = \langle 0|\,\hat{V}\,|H\rangle \tag{3.12}$$

results in a linear functional equation for the energy differences

$$\mathscr{A}(u^+, u)\,T_{0\mathrm{H}}(u^+)\,|0(= \omega_{\mathrm{H}0}\,T_{0\mathrm{H}}(u^+)\,|0(\,. \tag{3.13}$$

The determination of the functional operator $\mathscr{A}$ is then obtained with the functional relation [6]

$$e^{ic}\,\hat{\Psi}_\sigma(\boldsymbol{x})\,e^{-ic} = \hat{\Psi}_\sigma(\boldsymbol{x}) + i\,u_\sigma{}^+(\boldsymbol{x}) \tag{3.14}$$

and the replacement

$$i\,\hat{\Psi}_\sigma(\boldsymbol{x})\,\hat{V}\,|0) = (u_\sigma(\boldsymbol{x}) + \tfrac{1}{2}\,u_\sigma{}^+(\boldsymbol{x}))\,\hat{V}\,|0)\,. \tag{3.15}$$

The detailed calculation leads to

$$\begin{aligned}\mathscr{A} = \Bigg\{C &+ \frac{1}{2}\int \mathrm{d}^3x\Big[u^+(\boldsymbol{x})\,(\hat{H}^0_{\mathrm{H}}(\boldsymbol{x}) + \hat{H}^0_0(\boldsymbol{x}) + 2\,\hat{B}(\boldsymbol{x}))\,u(\boldsymbol{x}) - u^{\mathrm{T}}(\boldsymbol{x})\,(\hat{H}^0_{\mathrm{H}}(\boldsymbol{x}) - \hat{H}^0_0(\boldsymbol{x}))\,u(\boldsymbol{x})\\ &- \frac{1}{4}\,u^+(\boldsymbol{x})\,(\hat{H}^0_0\,(\boldsymbol{x}) - \;H^0_{\mathrm{H}}\,(\boldsymbol{x}))\,u^{\#}\;(\boldsymbol{x})\Big] - \frac{e^2}{2}\iint \mathrm{d}^3x\,\mathrm{d}^3x'\Big[u^+(\boldsymbol{x})\,u^{\mathrm{T}}(\boldsymbol{x}')\,\frac{\hat{E}\otimes\hat{E}}{|\boldsymbol{x}-\boldsymbol{x}'|}\,u(\boldsymbol{x}')\,u(\boldsymbol{x})\\ &+ \frac{1}{4}\,u^+(\boldsymbol{x})\,u^+(\boldsymbol{x}')\,\frac{\hat{E}\otimes\hat{E}}{|\boldsymbol{x}-\boldsymbol{x}'|}\,u^{\#}\;(\boldsymbol{x}')\;u(\boldsymbol{x})\Big]\Bigg\}\,.\end{aligned} \tag{3.16}$$

Here we have set

$$\hat{H}^0_{\mathrm{H}}(\boldsymbol{x}) = D(\Delta) + \hat{V}_{\mathrm{w}}(\boldsymbol{x}) + \hat{V}_{\mathrm{H}}(\boldsymbol{x})\,, \tag{3.17 a}$$

$$\hat{H}^0_0(\boldsymbol{x}) = \hat{D}(\Delta) + \hat{V}^0_{\mathrm{w}}(\boldsymbol{x}) + \hat{V}^0_{\mathrm{H}}(\boldsymbol{x})\,, \tag{3.17 b}$$

$$\hat{B}(\boldsymbol{x}) = \frac{1}{2}\left(\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\delta(\boldsymbol{x}'-\boldsymbol{x}') - \frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\delta(\boldsymbol{x}-\boldsymbol{x}')\right)\hat{E}\,, \tag{3.17 c}$$

$$C = \tfrac{1}{4}\int \mathrm{d}^3x\,\mathrm{Tr}[\hat{E}\,(\hat{V}_{\mathrm{w}}(\boldsymbol{x}) - \hat{V}^0_{\mathrm{w}}(\boldsymbol{x}) + \hat{V}_{\mathrm{H}}(\boldsymbol{x}) - \hat{V}^{\mathrm{H}}_0(\boldsymbol{x}))]\,. \tag{3.17 d}$$

For $B(\boldsymbol{x})$ in Eq. (3.17 c) we refer to the remark at the end of § 2.

§ 4. A Normal Ordering Transformation Based on a Physical Initial State

The functional equation (3.13) is not yet a meaningful description of a physical system in the sense that the relevant solutions of the problem could be derived from it by simple approximations. The reason for this is the use of the generating operator (3.1) which allows for a simple mapping on a functional system but does not guarantee the normal ordering of the field operators $\psi(\boldsymbol{x})$ and $\psi^+(\boldsymbol{x})$. This normal ordering can easily be recovered by a transformation (φ-transformation) which simultaneously considers the intended physical model.

In our case we transform to an initial situation corresponding to a good single-particle approximation for the unperturbed host crystal. So we are sure that later on the problem of one proton or a few protons in the lattice will be sufficiently well described by low order approximations.

Let $S_0(\boldsymbol{x}, \boldsymbol{x}')$ and $S_1(\boldsymbol{x}, \boldsymbol{x}')$ be two projection operators fulfilling the relations [8]

$$S_0(\boldsymbol{x}, \boldsymbol{x}') + S_1(\boldsymbol{x}, \boldsymbol{x}') = \delta(\boldsymbol{x}-\boldsymbol{x}')\,, \tag{4.1}$$

$$\int S_\alpha(\boldsymbol{x}, \boldsymbol{x}'')\,S_\alpha(\boldsymbol{x}'', \boldsymbol{x}')\,\mathrm{d}^3\boldsymbol{x}'' = \delta_{\alpha,a'}\,S_\alpha(\boldsymbol{x}, \boldsymbol{x}')\,, \quad \alpha, \alpha' = 0, 1. \tag{4.2}$$

If we introduce these operators into Eq. (3.2) we get the decomposition

$$c = a + b \tag{4.3}$$

with

$$a = \iint \mathrm{d}^3x\, \mathrm{d}^3x' \,(v^+(\boldsymbol{x})\, S_1(\boldsymbol{x}', \boldsymbol{x})\, \psi^+(\boldsymbol{x}') + w^+(\boldsymbol{x})\, S_0(\boldsymbol{x}, \boldsymbol{x}')\, \psi(\boldsymbol{x}'))\,, \tag{4.4}$$

and

$$b = \iint \mathrm{d}^3x\, \mathrm{d}^3x' \,(v^+(\boldsymbol{x})\, S_0(\boldsymbol{x}', \boldsymbol{x})\, \psi^+(\boldsymbol{x}') + w^+(\boldsymbol{x})\, S_1(\boldsymbol{x}, \boldsymbol{x}')\, \psi(\boldsymbol{x}'))\,. \tag{4.5}$$

For the normal ordering we use the formula

$$e^{i(a+b)} = e^{\frac{1}{2}[a,b]}\, e^{ia}\, e^{ib} \tag{4.6}$$

which is applicable in our case and we get

$$\tfrac{1}{2}[a,b] = \iint w^+(\boldsymbol{x})\, F(\boldsymbol{x}, \boldsymbol{x}')\, v^+(\boldsymbol{x}')\, \mathrm{d}^3x\, \mathrm{d}^3x' \tag{4.7}$$

with

$$F(\boldsymbol{x}, \boldsymbol{x}') = \tfrac{1}{2}\,(S_1(\boldsymbol{x}, \boldsymbol{x}') - S_0(\boldsymbol{x}, \boldsymbol{x}'))\,. \tag{4.8}$$

Applying Eq. (4.8) we can now convert the functional $T_{0\mathrm{H}}$ to a functional

$$\Phi_{0\mathrm{H}} = \langle 0 |\, e^{ia}\, e^{ib}\, | H \rangle \tag{4.9}$$

which belongs to a normally ordered generating operator with respect to a suitable initial state. To transform the functional equation (3.13) we return to the double component formulation and define

$$\hat{F}(\boldsymbol{x}, \boldsymbol{x}') := U^+ \begin{pmatrix} F(\boldsymbol{x}, \boldsymbol{x}') & 0 \\ 0 & -F(\boldsymbol{x}', \boldsymbol{x}) \end{pmatrix} U\,. \tag{4.10}$$

Then we have

$$\hat{F}(\boldsymbol{x}, \boldsymbol{x}')^{\mathrm{T}} = -\hat{F}(\boldsymbol{x}', \boldsymbol{x}) \tag{4.11}$$

and the relation between the T- and Φ-functional is

$$T_{0\mathrm{H}} = e^{\mathscr{F}}\, \Phi_{0\mathrm{H}} \tag{4.12}$$

with

$$\mathscr{F} = \tfrac{1}{2} \iint \mathrm{d}^3x\, \mathrm{d}^3x'\, u^+(\boldsymbol{x})\, \hat{F}(\boldsymbol{x}, \boldsymbol{x}')\, u^{\#}(\boldsymbol{x}')\,. \tag{4.12a}$$

For the following calculations we introduce the double component projection operators

$$\hat{S}_0(\boldsymbol{x}, \boldsymbol{x}') = U^+ \begin{pmatrix} S_0(\boldsymbol{x}, \boldsymbol{x}') & 0 \\ 0 & -S_0(\boldsymbol{x}', \boldsymbol{x}) \end{pmatrix} U\,, \tag{4.13a}$$

$$\hat{S}_1(\boldsymbol{x}, \boldsymbol{x}') = U^+ \begin{pmatrix} S_1(\boldsymbol{x}, \boldsymbol{x}') & 0 \\ 0 & -S_1(\boldsymbol{x}', \boldsymbol{x}) \end{pmatrix} U \tag{4.13b}$$

and

$$\hat{\Lambda}^{(+)}(\boldsymbol{x}, \boldsymbol{x}') = U^+ \begin{pmatrix} S_1(\boldsymbol{x}, \boldsymbol{x}') & 0 \\ 0 & S_0(\boldsymbol{x}', \boldsymbol{x}) \end{pmatrix} U\,, \tag{4.14a}$$

$$\hat{\Lambda}^{(-)}(\boldsymbol{x}, \boldsymbol{x}') = U^+ \begin{pmatrix} S_0(\boldsymbol{x}, \boldsymbol{x}') & 0 \\ 0 & S_1(\boldsymbol{x}', \boldsymbol{x}) \end{pmatrix} U\,. \tag{4.14b}$$

The following relations hold

$$\hat{S}_\alpha(\boldsymbol{x}, \boldsymbol{x}')^{\mathrm{T}} = -\hat{S}_\alpha(\boldsymbol{x}', \boldsymbol{x})\,, \quad \alpha = 0, 1, \tag{4.15}$$

$$\Lambda^{(\pm)}(\boldsymbol{x}, \boldsymbol{x}')^{\mathrm{T}} = \Lambda^{(\mp)}(\boldsymbol{x}', \boldsymbol{x}) \tag{4.16}$$

as well as

$$\hat{F}(\boldsymbol{x}, \boldsymbol{x}') = \tfrac{1}{2}\,(\hat{S}_1(\boldsymbol{x}, \boldsymbol{x}') - \hat{S}_0(\boldsymbol{x}, \boldsymbol{x}')) = \tfrac{1}{2}\,(\hat{\Lambda}^{(+)}(\boldsymbol{x}, \boldsymbol{x}') - \hat{\Lambda}^{(-)}(\boldsymbol{x}, \boldsymbol{x}')). \tag{4.17}$$

The so-called F-function $F(\boldsymbol{x}, \boldsymbol{x}')$ can be determined from a nonlinear eigenvalue problem. The variety of the solutions should then characterize such different types of solid states as insulators, semiconductors and metals. This ambitious program can be weackened if one incorporates into the F-function some information about an intended model. It is then possible to stay in the scope of a linear theory for the functional equation. In our description of metals the projection operators S_0 and S_1 can be build up with the aid of Bloch functions

$$S_0(\boldsymbol{x}, \boldsymbol{x}') = \sum_{\boldsymbol{k}m} b_{\boldsymbol{k},m}(\boldsymbol{x})\, f_{\boldsymbol{k}m}\, b^*_{\boldsymbol{k}m}(\boldsymbol{x}') = S_0{}^*(\boldsymbol{x}', \boldsymbol{x}), \tag{4.18}$$

$$S_1(\boldsymbol{x}, \boldsymbol{x}') = \sum_{\boldsymbol{k}m} b_{\boldsymbol{k},m}(\boldsymbol{x})\, g_{\boldsymbol{k}m}\, b^*_{\boldsymbol{k}m}(\boldsymbol{x}') = S_1{}^*(\boldsymbol{x}', \boldsymbol{x}). \tag{4.19}$$

The wave vector $\boldsymbol{k}$ and the band index m must eventually be extended by a spin index. $f_{\boldsymbol{k}m}$ is the Fermi distribution function and $g_{\boldsymbol{k}m} = 1 - f_{\boldsymbol{k}m}$.

With this choice of projection operators we take as initial state that one which has occupied single particle states up to the Fermi level. From this ground state we can create excitations like holes, additional electrons etc.

One is not bound to Bloch functions, of course. Other functions which are labeled by an energy parameter for instance can be used, as we will do in Section 10.

§ 5. The $\boldsymbol{\varphi}$-Functional System

We now multiply the functional equation (3.13) from the left by $e^{-\mathscr{F}}$ to get

$$e^{-\mathscr{F}} \mathscr{A} T\,|\,0) = \omega\, e^{-\mathscr{F}}\, T\,|\,0)$$
$$\Rightarrow \quad e^{-\mathscr{F}} \mathscr{A}\, e^{\mathscr{F}}\, \Phi\,|\,0) = \omega\, \Phi\,|\,0)\,. \tag{5.1}$$

The result is the functional equation of the φ-system

$$\mathscr{B}\, \Phi\,|\,0) = \omega\, \Phi\,|\,0) \tag{5.2}$$

from which the physically interesting solutions can be derived. The new functional operator is simply calculated with the aid of

$$e^{-\mathscr{F}}\, u(\boldsymbol{x})\, e^{\mathscr{F}} = u(\boldsymbol{x}) - [\mathscr{F}, u(\boldsymbol{x})]_- = u(\boldsymbol{x}) + \int \hat{F}(\boldsymbol{x}, \boldsymbol{x}')\, u^{\#}(\boldsymbol{x}')\, \mathrm{d}^3\boldsymbol{x}', \tag{5.3a}$$

$$e^{-\mathscr{F}}\, u^{+}(\boldsymbol{x})\, e^{\mathscr{F}} = u^{+}(\boldsymbol{x}) \tag{5.3b}$$

and is found to be

$$\mathscr{B} = \mathscr{A}(u^{+}, u + \hat{F}\, u^{\#}) = \mathscr{B}_0 + \mathscr{B}_{\mathrm{I}} + \mathscr{B}_{\mathrm{II}} + C' \tag{5.4}$$

with

$$\mathscr{B}_0 = \mathscr{D}_0\,, \tag{5.5a}$$

$$\mathscr{B}_{\mathrm{I}} = \mathscr{D}_0^{(\mathrm{a})} + \mathscr{D}_0^{(\mathrm{b})}\,, \tag{5.5b}$$

$$\mathscr{B}_{\mathrm{II}} = \mathscr{D}_1^{(\mathrm{a})} + \mathscr{D}_1^{(\mathrm{b})} + \mathscr{D}_{-1}^{(\mathrm{a})} + \mathscr{D}_{-1}^{(\mathrm{b})} + \mathscr{D}_{-2}\,. \tag{5.5c}$$

The terms

$$\mathscr{D}_0 = \iint u^{+}(\boldsymbol{x})\, \hat{D}_0(\boldsymbol{x}, \boldsymbol{x}')\, u(\boldsymbol{x}')\, \mathrm{d}^3x\, \mathrm{d}^3x'\,, \tag{5.6}$$

$$D_0(\boldsymbol{x}, \boldsymbol{x}') = \left(\hat{D}(\Delta) + \hat{V}^0_{\mathrm{w}}(\boldsymbol{x}) + \frac{e^2}{2}\int \mathrm{d}^3y\, \frac{\hat{E}}{|\boldsymbol{x}-\boldsymbol{y}|}\, \mathrm{Sp}[\hat{E}\, \hat{S}_0(\boldsymbol{y}, \boldsymbol{y})]\right) \cdot \delta(\boldsymbol{x}-\boldsymbol{x}') - e^2\, \frac{\hat{S}_0(\boldsymbol{x}, \boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|} \tag{5.6a}$$

are in the form of a Hartree-Fock-Hamiltonian with Coulomb interaction

$$\frac{e^2}{2}\, \frac{\hat{E}}{|\boldsymbol{x}-\boldsymbol{y}|}\, \mathrm{Sp}[\hat{E}\, \hat{S}_0(\boldsymbol{y}, \boldsymbol{y})]$$

and exchange interaction

$$-\, e^2\, \frac{\hat{S}_0(\boldsymbol{x}, \boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|}$$

which is easily recognized if an expansion of the type (4.18) is introduced for $S_0(\boldsymbol{x}, \boldsymbol{x}')$. A striking peculiarity is the compensation of the divergencies in Eq. (3.16) originating from (3.17c). More precisely, the φ-transformation replaces the divergencies by $S_0(\boldsymbol{x}, \boldsymbol{x}')$.

Further we have

$$\mathscr{D}_0^{(\mathrm{a})} = \iint \mathrm{d}^3x\, \mathrm{d}^3x'\, u^{+}(\boldsymbol{x}) \cdot (\Lambda^{(+)}(\boldsymbol{x}, \boldsymbol{x}')\, \hat{W}(\boldsymbol{x}') + \Lambda^{(-)}(\boldsymbol{x}, \boldsymbol{x}')\, \hat{V}^0_{\mathrm{H}}(\boldsymbol{x}'))\, u(\boldsymbol{x}')\,, \tag{5.7}$$

collecting terms of the disturbed crystal in

$$\hat{W}(\boldsymbol{x}) = \hat{V}_{\mathrm{w}}(\boldsymbol{x}) - \hat{V}^0_{\mathrm{w}}(\boldsymbol{x}) + \hat{V}_{\mathrm{H}}(\boldsymbol{x}) \tag{5.7a}$$

$$\mathscr{D}_0^{(\mathrm{b})} = \frac{e^2}{2} \iiiint \mathrm{d}^3x\, \mathrm{d}^3x'\, \mathrm{d}^3y\, \mathrm{d}^3y' \Bigg\{ u^{+}(\boldsymbol{y})\, u^{+}(\boldsymbol{y}') \left(\frac{\hat{\Lambda}^{(+)}(\boldsymbol{y}, \boldsymbol{x})\, \hat{E} \otimes \hat{\Lambda}^{(+)}(\boldsymbol{y}', \boldsymbol{x}')\, \hat{E}}{|\boldsymbol{x}-\boldsymbol{x}'|} - \frac{\hat{\Lambda}^{(-)}(\boldsymbol{y}, \boldsymbol{x})\, \hat{E} \otimes \hat{\Lambda}^{(-)}(\boldsymbol{y}', \boldsymbol{x}')\, \hat{E}}{|\boldsymbol{x}-\boldsymbol{x}'|} \right) u(\boldsymbol{x}')\, u(\boldsymbol{x}) + \frac{1}{2}\, u^{+}(\boldsymbol{y}) (\hat{\Lambda}^{(+)}(\boldsymbol{y}, \boldsymbol{x})\, \hat{E}\, \hat{\Lambda}^{(-)}(\boldsymbol{x}, \boldsymbol{y}') - \hat{\Lambda}^{(-)}(\boldsymbol{y}, \boldsymbol{x})\, \hat{E}\, \hat{\Lambda}^{(+)}(\boldsymbol{x}, \boldsymbol{y}'))\, u^{++}(\boldsymbol{y}')\, \frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\, u^{\mathrm{T}}(\boldsymbol{x}')\, \hat{E}\, u(\boldsymbol{x}') \Bigg\}\,, \tag{5.8}$$

$$\mathscr{D}_1^{(\mathrm{a})} = -\, \tfrac{1}{2} \int \mathrm{d}^3x\, u^{\mathrm{T}}(\boldsymbol{x})\, (\hat{W}(\boldsymbol{x}) - \hat{V}^0_{\mathrm{H}}(\boldsymbol{x}))\, u(\boldsymbol{x})\,, \tag{5.9}$$

$$\mathscr{D}_1^{(\mathrm{b})} = -\, \frac{e^2}{2}\, \mathrm{d}^3x\, \mathrm{d}^3x'\, u^{+}(\boldsymbol{x})\, u^{\mathrm{T}}(\boldsymbol{x}')\, \frac{\hat{E} \otimes \hat{E}}{|\boldsymbol{x}-\boldsymbol{x}'|}\, u(\boldsymbol{x}')\, u(\boldsymbol{x})\,, \tag{5.10}$$

$$\mathscr{D}_{-1}^{(\mathrm{a})} = -\, \tfrac{1}{2} \iiiint \mathrm{d}^3x\, \mathrm{d}^3x'\, \mathrm{d}^3y\, \mathrm{d}^3y'\, u^{+}(\boldsymbol{x}) \{ \hat{\Lambda}^{(+)}(\boldsymbol{x}, \boldsymbol{y})\, \hat{D}_0(\boldsymbol{y}, \boldsymbol{y}')\, \hat{\Lambda}^{(-)}(\boldsymbol{y}', \boldsymbol{x}') - \hat{\Lambda}^{(-)}(\boldsymbol{x}, \boldsymbol{y})\, \hat{D}_0(\boldsymbol{y}, \boldsymbol{y}')\, \hat{\Lambda}^{(+)}(\boldsymbol{y}', \boldsymbol{x}') + \delta(\boldsymbol{y}-\boldsymbol{y}')\, (\hat{\Lambda}^{(+)}(\boldsymbol{x}, \boldsymbol{y})\, \hat{W}(\boldsymbol{y})\, \hat{\Lambda}^{(-)}(\boldsymbol{y}, \boldsymbol{x}') + \hat{\Lambda}^{(-)}(\boldsymbol{x}, \boldsymbol{y})\, \hat{V}^0_{\mathrm{H}}(\boldsymbol{y})\, \hat{\Lambda}^{(+)}(\boldsymbol{y}, \boldsymbol{x}') \}\, u^{\#}(\boldsymbol{x}')\,, \tag{5.11}$$

$$\mathscr{D}_{-1}^{(\mathrm{b})} = -\, \frac{e^2}{2} \iiiiint \mathrm{d}^3x\, \mathrm{d}^3x'\, \mathrm{d}^3y\, \mathrm{d}^3y'\, \mathrm{d}^3y''\, u^{+}(y)\, u^{+}(y') \tag{5.12}$$

$$\cdot \left\{ \frac{\hat{\Lambda}^{(+)}(\boldsymbol{y}, \boldsymbol{x})\, \hat{E} \otimes \hat{\Lambda}^{(+)}(\boldsymbol{y}', \boldsymbol{x}')\, \hat{E}\, \hat{\Lambda}^{(-)}(\boldsymbol{x}, \boldsymbol{y}'')}{|\boldsymbol{x}-\boldsymbol{x}'|} + \frac{\hat{\Lambda}^{(-)}(\boldsymbol{y}, \boldsymbol{x})\, \hat{E} \otimes \hat{\Lambda}^{(-)}(\boldsymbol{y}', \boldsymbol{x}')\, \hat{E}\, \hat{\Lambda}^{(+)}(\boldsymbol{x}', \boldsymbol{y}'')}{|\boldsymbol{x}-\boldsymbol{x}'|} \right\} u^{\#}(\boldsymbol{y}'')\, u(\boldsymbol{x})\,,$$

$$\mathscr{D}_{-2} = \frac{e^2}{8} \iiiint\!\!\iint \mathrm{d}^3x\, \mathrm{d}^3x'\, \mathrm{d}^3y\, \mathrm{d}^3y'\, \mathrm{d}^3y''\, \mathrm{d}^3y'''\, u^+(y)\, u^+(\boldsymbol{y}') \cdot \left\{ \frac{\hat{\Lambda}^{(+)}(\boldsymbol{y},\boldsymbol{x})\, \hat{E}\, \hat{\Lambda}^{(-)}(\boldsymbol{x},\boldsymbol{y}''') \otimes \hat{\Lambda}^{(+)}(\boldsymbol{y}',\boldsymbol{x}')\, \hat{E}\, \hat{\Lambda}^{(-)}(\boldsymbol{x}',\boldsymbol{y}'')}{|\boldsymbol{x}-\boldsymbol{x}'|} - \frac{\hat{\Lambda}^{(-)}(\boldsymbol{y},\boldsymbol{x})\, \hat{E}\, \hat{\Lambda}^{(+)}(\boldsymbol{x},\boldsymbol{y}''') \otimes \hat{\Lambda}^{(-)}(\boldsymbol{y}',\boldsymbol{x}')\, \hat{E}\, \hat{\Lambda}^{(+)}(\boldsymbol{x}',\boldsymbol{y}'')}{|\boldsymbol{x}-\boldsymbol{x}`|} \right\} u^{\#}(\boldsymbol{y}'')\, u^{\#}(\boldsymbol{y}''') \,. \tag{5.13}$$

Finally, $C' = \frac{1}{2} \int \mathrm{d}^3x\, \mathrm{Tr}[\hat{S}_0(\boldsymbol{x},\boldsymbol{x})(\hat{W}(\boldsymbol{x}) - \hat{V}^0_{\mathrm{H}}(\boldsymbol{x}))]\,.$ (5.14)

The contribution $V^0_{\mathrm{H}}(x)$ in Eqs . (5.7), (5.9), (5.11) and (5.14) depend on coordinates of protons describing positions outside the crystal and can be neglected in the main problem.

§ 6. The Elimination Procedure

If we apply an expansion of the form

$$\Phi\,|0) = \sum_{m=0}^{\infty} \frac{1}{m!} \cdot \iint \cdots \int \mathrm{d}^3x_1 \ldots \mathrm{d}^3x_m\, u^+(\boldsymbol{x}_m) \cdots u^+(\boldsymbol{x}_1)\, \hat{\varphi}^{(m)}(\boldsymbol{x}_1 \ldots \boldsymbol{x}_m)\,|0) \tag{6.1}$$

for the functional (4.9) and multiply the functional equation (5.2) by the vectors of the base $(0|\prod_{i=1}^{n} u(\boldsymbol{z}_i)$ we obtain an infinite system of coupled equations for the so-called φ-functions $\varphi^{(m)}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_m)$:

$$\sum_m \hat{B}^k{}_m\, \hat{\varphi}^{(m)} = \omega\, \hat{\varphi}^{(k)}\,. \tag{6.2}$$

To calculate approximations a cut-off criterion must be given. The easiest way is to use projection operators

$$\mathscr{P}_N = \sum_{n=0}^{N} \iint \cdots \int \mathrm{d}^3x_1 \ldots \mathrm{d}^3x_n \cdot u^+(\boldsymbol{x}_1) \ldots u^+(\boldsymbol{x}_n)\,|0)\, \frac{1}{n!}\, (0|\,u(\boldsymbol{x}_n) \ldots u(\boldsymbol{x}_1) \tag{6.3}$$

which are inserted in the functional equation

$$\mathscr{P}_N\, \mathscr{B}\, \mathscr{P}_N\, \Phi\,|0) = \omega^{(N)}\, \mathscr{P}_N\, \Phi\,|0)\,. \tag{6.4}$$

Given a fixed integer N and projecting as in Eq. (6.2) we get a finite system of matrix equations. It decomposes into an even and an odd subsystem

$$\sum_{m=0}^{M} \hat{B}^{2k}{}_{2m}\, \hat{\varphi}^{(2m)} = \omega^{(N)}\, \varphi^{(2k)}\,, \quad k = 0, 1, \ldots, M = N/2 \tag{6.5}$$

and

$$\sum_{m=0}^{M} \hat{B}^{2k+1}{}_{2m+1}\, \hat{\varphi}^{(2m+1)} = \omega^{(N)}\, \varphi^{(2k+1)}\,, \quad k = 0, 1, \ldots, M = (N-1)/2 \tag{6.6}$$

respectively.

We abandon the specification of the complete system (6.2) and restrict to the odd system (6.6) in the simple approximation with $N = 3$. Then two equations remain, one for $\varphi^{(1)}(\boldsymbol{x})$ and another one for $\hat{\varphi}^{(3)}(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3)$. We can eliminate $\hat{\varphi}^{(3)}$ and are left with one equation for $\hat{\varphi}^{(1)}$. As will be seen later, it contains the wave equation of an additional electron in the framework of a many-electron problem for the disturbed metal lattice.

The first equation is

$$\begin{aligned}
&\langle 0|\,u(\boldsymbol{z})\, \mathscr{P}_3\, \mathscr{B}\, \mathscr{P}_3\, \Phi\,|0\rangle \\
&= \langle 0|\,u(\boldsymbol{z})\,(\mathscr{D}_0 + \mathscr{D}_0^{(\mathrm{a})} + \mathscr{D}_0^{(\mathrm{b})} + \mathscr{D}_1^{(\mathrm{a})} + \mathscr{D}_1^{(\mathrm{b})})\, \Phi\,|0\rangle \\
&= \int \mathrm{d}^3x\, (\hat{D}_0(\boldsymbol{z},\boldsymbol{x}) + \hat{\Lambda}^{(+)}(\boldsymbol{z},\boldsymbol{x})\, \hat{W}(\boldsymbol{x}) \\
&\quad + \hat{\Lambda}^{(-)}(\boldsymbol{z},\boldsymbol{x})\, V^0_{\mathrm{H}}(\boldsymbol{x}))\, \hat{\varphi}^{(1)}(\boldsymbol{x}) \\
&\quad + \sum_{\sigma,\sigma'} \tfrac{1}{2} [\hat{W}(\boldsymbol{x}) - \hat{V}^0_{\mathrm{H}}(\boldsymbol{x})]_{\sigma\sigma'}\, \hat{\varphi}^{(3)}(\boldsymbol{z}, \underset{\sigma'}{\boldsymbol{x}}, \underset{\sigma}{\boldsymbol{x}}) \\
&\quad + \frac{e^2}{2} \sum_{\sigma,\sigma'} \int \mathrm{d}^3x\, \frac{\hat{E} \otimes \hat{E}_{\sigma\sigma'}}{|\boldsymbol{z}-\boldsymbol{x}|}\, \hat{\varphi}^{(3)}(\boldsymbol{z}, \underset{\sigma'}{\boldsymbol{x}}, \underset{\sigma}{\boldsymbol{x}}) \\
&= (\omega - C')\, \hat{\varphi}^{(1)}(\boldsymbol{z})\,.
\end{aligned} \tag{6.7}$$

As $\hat{W}(\boldsymbol{x})$ and $\hat{E}$ are 2×2 matrices and $\hat{\varrho}^{(3)}(\boldsymbol{z}_1, \boldsymbol{z}_2, \boldsymbol{z}_3)$ is a tensorial product of two-component vectors, we have labeled the components by σ and σ' where necessary.

The second equation is

$$\begin{aligned}
&\langle 0|\,u(\boldsymbol{z}_1)\, u(\boldsymbol{z}_2)\, u(\boldsymbol{z}_3)\, \mathscr{P}_3\, \mathscr{B}\, \mathscr{P}_3\, \Phi\,|0) = (0|\prod_{i=1}^{3} u(\boldsymbol{z}_i)(\mathscr{D}_0 + \mathscr{D}_0^{(\mathrm{a})} + \mathscr{D}_0^{(\mathrm{b})} + \mathscr{D}_{-1}^{(\mathrm{a})} + \mathscr{D}_{-1}^{(\mathrm{b})})\, \Phi\,|0) \\
&= \int \mathrm{d}^3x\, \{\hat{D}_0(\boldsymbol{z}_1,\boldsymbol{x})\, \hat{\varphi}^{(3)}(\boldsymbol{x},\boldsymbol{z}_2,\boldsymbol{z}_3) + \hat{D}_0(\boldsymbol{z}_2,\boldsymbol{x})\, \hat{\varphi}^{(3)}(\boldsymbol{z},\boldsymbol{x},\boldsymbol{z}_3) + \hat{D}_0(\boldsymbol{z}_3,\boldsymbol{x})\, \hat{\varphi}^{(3)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{x})\} \\
&\quad + (0|\prod_{i=1}^{3} u(\boldsymbol{z}_i)(\mathscr{D}_0^{(\mathrm{a})} + \mathscr{D}_0^{(\mathrm{b})})\, \Phi\,|0) - \hat{R}^{(a)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3) - \hat{R}^{(b)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3) = (\omega - C')\, \hat{\varphi}^{(3)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3)\,.
\end{aligned} \tag{6.8}$$

The expressions

$$\begin{aligned} R^{(a)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3) = -\iint \mathrm{d}^3x\,\mathrm{d}^3x' \{ & (\hat{\Lambda}^{(+)}(\boldsymbol{z}_1,\boldsymbol{x})\,\hat{D}_0(\boldsymbol{x},\boldsymbol{x}')\,\hat{\Lambda}^{(-)}(\boldsymbol{x}',\boldsymbol{z}_2) - \hat{\Lambda}^{(-)}(\boldsymbol{z}_1\,\boldsymbol{x})\,\hat{D}_0(\boldsymbol{x},\boldsymbol{x}')\,\hat{\Lambda}^{(+)}(\boldsymbol{x}',\boldsymbol{z}_2))\,\hat{\varphi}^{(1)}(\boldsymbol{z}_3) \\ & + \delta(\boldsymbol{x}-\boldsymbol{x}')(\hat{\Lambda}^{(+)}(\boldsymbol{z}_1,\boldsymbol{x})\,\hat{W}(\boldsymbol{x})\,\hat{\Lambda}^{(-)}(\boldsymbol{x},\boldsymbol{z}_2) + \hat{\Lambda}^{(-)}(\boldsymbol{z}_1,\boldsymbol{x})\,V_{\mathrm{H}}^0(\boldsymbol{x})\,\hat{\Lambda}^{(+)}(\boldsymbol{x},\boldsymbol{z}_2))\,\hat{\varphi}^{(1)}(\boldsymbol{z}_3) \\ & + \text{permutations of } \boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3\}, \end{aligned} \tag{6.9}$$

and

$$\begin{aligned} \hat{R}^{(b)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3) = -\iint \mathrm{d}^3x\,\mathrm{d}^3x' \Big\{ & \hat{\Lambda}^{(+)}(\boldsymbol{z}_2,\boldsymbol{x}')\,\hat{E}\,\hat{\Lambda}^{(-)}(\boldsymbol{x}',\boldsymbol{z}_3)\,\frac{e^2}{|\boldsymbol{x}'-\boldsymbol{x}|}\,\hat{\Lambda}^{(+)}(\boldsymbol{z}_1,\boldsymbol{x})\,\hat{E}\,\hat{\varphi}^{(1)}(\boldsymbol{x}) \\ & + \hat{\Lambda}^{(-)}(\boldsymbol{z}_2,\boldsymbol{x}')\,\hat{E}\,\hat{\Lambda}^{(+)}(\boldsymbol{x}',\boldsymbol{z}_3)\,\frac{e^2}{|\boldsymbol{x}'-\boldsymbol{x}|}\,\hat{\Lambda}^{(-)}(\boldsymbol{z}_1,\boldsymbol{x})\,\hat{E}\,\hat{\varphi}^{(1)}(\boldsymbol{x}) \\ & + \text{permutations of } \boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3 \Big\} \end{aligned} \tag{6.10}$$

accomplish the coupling to $\varphi^{(1)}$.

If we neglect the term

$$(0|\prod_{i=1}^{3} u(\boldsymbol{z}_i)(\mathscr{D}_0^{(\mathrm{a})} + \mathscr{D}_0^{(\mathrm{b})})\,\Phi\,|0)$$

it means that we leave out of consideration three-particle bound states and scattering states as well as the influence of an external disturbance on three-particle states**. In such a case the solution of Eq. (6.8) is directly obtained by a Green function $\hat{G}$ which will be calculated in the next section:

$$\begin{aligned} \hat{\varphi}^{(3)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3) = & \iiint \mathrm{d}^3z_1'\,\mathrm{d}^3z_2'\,\mathrm{d}^3z_3' \\ & \cdot \hat{G}(\boldsymbol{z}_1,\boldsymbol{z}_1';\boldsymbol{z}_2,\boldsymbol{z}_2';\boldsymbol{z}_3,\boldsymbol{z}_3') \\ & \cdot (\hat{R}^{(a)}(\boldsymbol{z}_1',\boldsymbol{z}_2',\boldsymbol{z}_3') + \hat{R}^{(b)}(\boldsymbol{z}_1',\boldsymbol{z}_2',\boldsymbol{z}_3')). \end{aligned} \tag{6.11}$$

The function $\hat{\varphi}^{(3)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3)$ calculated in this way can be inserted in Eq. (6.7) to give a kind of Schrödinger equation for $\hat{\varphi}^{(1)}$

$$\begin{aligned} \int \mathrm{d}^3x (\hat{D}_0(\boldsymbol{z},\boldsymbol{x}) & + \hat{\Lambda}^{(+)}(\boldsymbol{z},\boldsymbol{x})\,\hat{W}(\boldsymbol{x}) \\ & + \hat{\Lambda}^{(-)}(\boldsymbol{z},\boldsymbol{x})\,V_{\mathrm{H}}^0(\boldsymbol{x}))\,\hat{\varphi}^{(1)}(\boldsymbol{x}) \\ & + \sum_{\varrho=1}^{2}(\hat{P}_{\varrho}^{(\mathrm{a})}(\boldsymbol{z}|\varphi^{(1)}) + \hat{P}_{\varrho}^{(\mathrm{b})}(\boldsymbol{z}|\varphi^{(1)})) \\ & = (\omega - C')\,\hat{\varphi}^{(1)}(\boldsymbol{z}). \end{aligned} \tag{6.12}$$

This equation will be treated and interpreted in the following

§ 7. The Green Function

To construct the Green function we need the auxiliary definitions:

1. We assume the Bloch functions $b_{\boldsymbol{k}m}(\boldsymbol{x})$ to be solutions of the Hartree-Fock problem of the ideal host crystal

$$\begin{aligned} \int D_0(\boldsymbol{x},\boldsymbol{x}')\,b_{\boldsymbol{k}m}(\boldsymbol{x}')\,\mathrm{d}^3x' = \int \mathrm{d}^3x' \Bigg\{ \Bigg(& D(\Delta) + V_{\mathrm{w}}^0(x) \\ & e^2 \sum_n \int \mathrm{d}^3y\,\frac{b_{\boldsymbol{l}n}(\boldsymbol{y})\,f_{\boldsymbol{l}n}\,b_{\boldsymbol{l}n}^*(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|}\,b_{\boldsymbol{k}m}(\boldsymbol{x})\Bigg)\,\delta(\boldsymbol{x}-\boldsymbol{x}') \\ & - e^2 \sum_{\boldsymbol{l}n} \frac{b_{\boldsymbol{l}n}(\boldsymbol{x})\,f_{\boldsymbol{l}n}\,b_{\boldsymbol{l}n}^*(\boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|}\,b_{\boldsymbol{k}m}^{(\boldsymbol{x}')}\Bigg\} = \varepsilon_{\boldsymbol{k}m}\,b_{\boldsymbol{k}m}(\boldsymbol{x}). \end{aligned} \tag{7.1}$$

with eigenvalues $\varepsilon_{\boldsymbol{k}m}$.

These functions will supply a base for the expansion of the projection operators (4.18) and (4.19).

2. Let another set of projection operators be defined by

$$\begin{aligned} \hat{I}_{\boldsymbol{k}m}^{(+)}(\boldsymbol{x}) &= b_{\boldsymbol{k}m}(\boldsymbol{x}) \cdot \hat{I}^{(+)}; \\ \hat{I}_{\boldsymbol{k}m}^{(-)}(\boldsymbol{x}) &= b_{\boldsymbol{k}m}^*(x) \cdot \hat{I}^{(-)} \end{aligned} \tag{7.2}$$

with

$$\hat{I}^{(+)} = U^+\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} U; \quad \hat{I}^{(-)} = U^+\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} U, \tag{7.3}$$

$$\hat{I}^{(+)} + \hat{I}^{(-)} = \hat{I} := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \tag{7.3a}$$

$$\hat{I}^{(+)}\,\hat{I}^{(+)} = \hat{I}^{(+)}; \quad \hat{I}^{(-)}\,\hat{I}^{(-)}\,\hat{I}^{(-)}; \quad \hat{I}^{(+)}\,\hat{I}^{(-)} = 0.$$

Further on we use

$$\begin{aligned} \hat{A}_{\boldsymbol{k}m}^{(+)}(\boldsymbol{x},\boldsymbol{x}') &= \hat{I}_{\boldsymbol{k}m}^{(+)}(\boldsymbol{x}) \cdot \hat{I}_{\boldsymbol{k}m}^{(+)}(\boldsymbol{x}')^+; \\ \hat{A}_{\boldsymbol{k}m}^{(-)}(\boldsymbol{x},\boldsymbol{x}') &= \hat{I}_{\boldsymbol{k}m}^{(-)}(\boldsymbol{x}) \cdot \hat{I}_{\boldsymbol{k}m}^{(-)}(\boldsymbol{x}')^+. \end{aligned} \tag{7.4}$$

The following relations hold

$$(\hat{I}_{\boldsymbol{k}m}^{(\pm)}(\boldsymbol{x}))^{\mathrm{T}} = \hat{I}_{\boldsymbol{k}m}^{(\mp)}(\boldsymbol{x})^+, \tag{7.5}$$

$$\begin{aligned} \int \hat{I}_{\boldsymbol{k}m}^{(\pm)}(\boldsymbol{x})^+ \cdot \hat{I}_{\boldsymbol{k}'m'}^{(\pm)}(\boldsymbol{x})\,\mathrm{d}^3x &= \delta_{\boldsymbol{k},\boldsymbol{k}'}\,\delta_{m,m'}\,\hat{I}^{(\pm)}; \\ \int \hat{I}_{\boldsymbol{k}m}^{(+)}(\boldsymbol{x})^+ \cdot \hat{I}_{\boldsymbol{k}',m'}^{(-)}(\boldsymbol{x})\,\mathrm{d}^3x &= 0, \end{aligned} \tag{7.6}$$

** As the functional operator $\mathscr{B}$ does not conserve the number of particles, the concept of three-particle states is only a certain approximation (see also [6]).

$$\int \hat{I}^{(\pm)}_{\boldsymbol{k}m}(\boldsymbol{x})^{+}\,\hat{A}^{(\pm)}_{\boldsymbol{k}'m'}(\boldsymbol{x},\boldsymbol{x}')\,\mathrm{d}^3x = \hat{I}^{(\pm)}_{\boldsymbol{k}m}(\boldsymbol{x}')^{+}\,\delta_{\boldsymbol{k},\boldsymbol{k}'}\,\delta_{m,m'}\,. \tag{7.7}$$

With the help of the above definitions we want to construct the Green function for a partial problem of (6.8) namely

$$\iiint \hat{G}(\boldsymbol{z}_1,\boldsymbol{z}_1';\boldsymbol{z}_2,\boldsymbol{z}_2';\boldsymbol{z}_3,\boldsymbol{z}_3') \cdot \hat{D}(\boldsymbol{z}_1',\boldsymbol{z}_2',\boldsymbol{z}_3'\,|\,\hat{\varphi}^{(3)})\,\mathrm{d}^3z_1'\,\mathrm{d}^3z_2'\,\mathrm{d}^3z_3' = \hat{\varphi}^{(3)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3) \tag{7.8}$$

with

$$\begin{aligned}\hat{D}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3\,|\,\hat{\varphi}^{(3)}) = \int \mathrm{d}^3x\,(&\hat{D}_0(\boldsymbol{z}_1,\boldsymbol{x})\,\hat{\varphi}^{(3)}(\boldsymbol{x},\boldsymbol{z}_2,\boldsymbol{z}_3)\\ &+\hat{D}_0(\boldsymbol{z}_2,\boldsymbol{x})\,\hat{\varphi}^{(3)}(\boldsymbol{z}_1,\boldsymbol{x}_1,\boldsymbol{z}_3)\\ &+\hat{D}_0(\boldsymbol{z}_3,\boldsymbol{x})\,\hat{\varphi}^{(3)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{x}))\\ &+(C'-\omega)\,\hat{\varphi}^{(3)}(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3)\;.\end{aligned} \tag{7.9}$$

For that purpose we write (5.6a) with (7.1) in the following way

$$\hat{D}_0(\boldsymbol{x},\boldsymbol{x}') = D_0(\boldsymbol{x},\boldsymbol{x}')\,\hat{E} = \sum_{\boldsymbol{k}m}\varepsilon_{\boldsymbol{k}m}(\hat{A}^{(+)}_{\boldsymbol{k}m}(\boldsymbol{x},\boldsymbol{x}')-\hat{A}^{(-)}_{\boldsymbol{k}m}(\boldsymbol{x},\boldsymbol{x}')) \tag{7.10}$$

and expand $\hat{\varphi}^{(3)}$ using (7.2)

$$\hat{\varphi}^{(3)}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_3) = \sum_{\pm\pm\pm}\ \sum_{\substack{\boldsymbol{q}_1\boldsymbol{q}_2\boldsymbol{q}_3\\ j_1\,j_2\,j_3}} \hat{I}^{(\pm)}_{\boldsymbol{q}_1 j_1}(\boldsymbol{x}_1)\otimes\hat{I}^{(\pm)}_{\boldsymbol{q}_2 j_2}(\boldsymbol{x}_2)\otimes\hat{I}^{(\pm)}_{\boldsymbol{q}_3 j_3}(\boldsymbol{x}_3)\,\varphi^{\pm\,\pm\,\pm}_{\substack{\boldsymbol{q}_1\boldsymbol{q}_2\boldsymbol{q}_3\\ j_1\,j_2\,j_3}}\,. \tag{7.11}$$

The $(\pm)$-summation is extended over $2^3=8$ terms.

Introducing expressions (7.10) and (7.11) into Eq. (7.9) and multiplying from the left by the eight possible combinations

$$\hat{I}^{(\pm)}_{\boldsymbol{p}_1 i_1}(\boldsymbol{z}_1')^{+}\otimes\hat{I}^{(\pm)}_{\boldsymbol{p}_2 i_2}(\boldsymbol{z}_2')^{+}\otimes\hat{I}^{(\pm)}_{\boldsymbol{p}_3 i_3}(\boldsymbol{z}_3')^{+}\,,$$

eight equations arise which take the form

$$\begin{aligned}\iiint \mathrm{d}^3z_1'\,\mathrm{d}^3z_2'\,\mathrm{d}^3z_3'\,&\hat{I}^{(\pm)}_{\boldsymbol{p}_1 i_1}(\boldsymbol{z}_1')^{+}\otimes\hat{I}^{(\pm)}_{\boldsymbol{p}_2 i_2}(\boldsymbol{z}_2')^{+}\\ &\otimes\hat{I}^{(\pm)}_{\boldsymbol{p}_3 i_3}(\boldsymbol{z}_3')^{+}\,\hat{D}(\boldsymbol{z}_1',\boldsymbol{z}_2',\boldsymbol{z}_3'\,|\,\varphi^{(3)})\\ =(\pm\,&\varepsilon_{\boldsymbol{p}_1 i_1}\pm\varepsilon_{\boldsymbol{p}_2 i_2}\pm\varepsilon_{\boldsymbol{p}_3 i_3}+C-\omega)\\ &\cdot\hat{I}^{(\pm)}\otimes\hat{I}^{(\pm)}\otimes\hat{I}^{(\pm)}\,\varphi^{\pm\,\pm\,\pm}_{\substack{\boldsymbol{p}_1\boldsymbol{p}_2\boldsymbol{p}_3\\ i_1\,i_2\,i_3}}\,.\end{aligned} \tag{7.12}$$

Now each of these equations is divided by the energy expression on the right-hand side and multiplied with the corresponding operator

$$\hat{I}^{(\pm)}_{\boldsymbol{p}_1 i_1}(\boldsymbol{z}_1)\otimes\hat{I}^{(\pm)}_{\boldsymbol{p}_2 i_2}(\boldsymbol{z}_2)\otimes\hat{I}^{(\pm)}_{\boldsymbol{p}_3 i_3}(\boldsymbol{z}_3)\,.$$

Then we sum over all $\boldsymbol{p}_1 i_1$, $\boldsymbol{p}_2 i_2$, $\boldsymbol{p}_3 i_3$ and finally add up the eight equations. On the right-hand side the function $\varphi^{(3)}$ appears while the left-hand side gives the structure of the Green function

$$\hat{G}(\boldsymbol{z}_1,\boldsymbol{z}_1';\boldsymbol{z}_2,\boldsymbol{z}_2';\boldsymbol{z}_3,\boldsymbol{z}_3') = \sum_{\pm\pm\pm}\ \sum_{\substack{\boldsymbol{p}_1\boldsymbol{p}_2\boldsymbol{p}_3\\ i_1\,i_2\,i_3}} \frac{\hat{A}^{(\pm)}_{\boldsymbol{p}_1 i_1}(\boldsymbol{z}_1,\boldsymbol{z}_1')\otimes\hat{A}^{(\pm)}_{\boldsymbol{p}_2 i_2}(\boldsymbol{z}_2,\boldsymbol{z}_2')\otimes\hat{A}^{(\pm)}_{\boldsymbol{p}_3 i_3}(\boldsymbol{z}_3,\boldsymbol{z}_3')}{\pm\varepsilon_{\boldsymbol{p}_1 i_1}\pm\varepsilon_{\boldsymbol{p}_2 i_2}\pm\varepsilon_{\boldsymbol{p}_3 i_3}+C'-\omega}\,.$$

§ 8. First Order Approximation for Electron Problem of Hydrogen

Bevore tackling the eigenvalue problem (6.12), especially the terms $\hat{P}^{(a,b)}_{\varrho}(\boldsymbol{z}\,|\,\hat{\varphi}^{(1)})$, we consider the simplest approximation by putting $N=1$ in Equation (6.4). The $\hat{P}^{(a,b)}_{\varrho}$ in Eq. (6.12) disappear and we are left with

$$\begin{aligned}\int \mathrm{d}^3x\,(&\hat{D}_0(\boldsymbol{z},\boldsymbol{x})+\hat{\Lambda}^{(+)}(\boldsymbol{z},\boldsymbol{x})\,\hat{W}(\boldsymbol{x})\\ &+\hat{\Lambda}^{(-)}(\boldsymbol{z},\boldsymbol{x})\,\hat{V}^0_{\mathrm{H}}(\boldsymbol{x}))\,\hat{\varphi}^{(1)}(\boldsymbol{x}) = (\omega-C')\,\hat{\varphi}^{(1)}(\boldsymbol{z}).\end{aligned} \tag{8.1}$$

Using the definition

$$\hat{\varphi}^{(1)}(\boldsymbol{z}) = U^{+}\begin{pmatrix}\varphi^{(e)}(\boldsymbol{z})\\ \varphi^{(\mathrm{L})}(\boldsymbol{z})\end{pmatrix} \tag{8.2}$$

and multiplying from the left by U, Eq. (8.1) can be separated into

$$\begin{aligned}\int \mathrm{d}^3x\,(&D_0(\boldsymbol{z},\boldsymbol{x})+S_1(\boldsymbol{z},\boldsymbol{x})\,W(\boldsymbol{x})\\ &+S_0(\boldsymbol{z},\boldsymbol{x})\,V^0_{\mathrm{H}}(\boldsymbol{x}))\,\varphi^{(e)}(\boldsymbol{x}) = (\omega-C')\,\varphi^{(e)}(\boldsymbol{z})\,,\end{aligned} \tag{8.3a}$$

$$\begin{aligned}-\int \mathrm{d}^3x\,(&D_0(\boldsymbol{z},\boldsymbol{x})+S_0{}^{*}(\boldsymbol{z},\boldsymbol{x})\,W(\boldsymbol{x})\\ &+S_1{}^{*}(\boldsymbol{z},\boldsymbol{x})\,V^0_{\mathrm{H}}(\boldsymbol{x}))\,\varphi^{(\mathrm{L})}(\boldsymbol{x}) = (\omega-C')\varphi^{(\mathrm{L})}(\boldsymbol{z})\,.\end{aligned} \tag{8.3b}$$

To interpret these equations we first consider the projection operators S_0 and S_1 for the two regions (A) outside and (K) inside the crystal. $V^{\mathrm{H}}_0(\boldsymbol{x})$ is the potential of free protons outside. The projection operators connected with it must be determined in this region by $S_0(\boldsymbol{z},\boldsymbol{x})=0$ and $S_1(\boldsymbol{z},\boldsymbol{x})=\delta(\boldsymbol{z}-\boldsymbol{x})$; $\boldsymbol{x}\in(\mathrm{A})$. For there are only protons and no background of many electrons, so that a normal ordering with respect to the pure vacuum is appropriate. This is accomplished by the above choice of S_0 and S_1. If we now choose the expansion (4.19) for S_1; $\boldsymbol{x}\in(\mathrm{K})$ we can show that (8.3a) contains the equation for an additional electron in the disturbed crystal. Beyond this we find equations for the electrons in the bands of the undisturbed crystal. To prove it we expand $\varphi^{(e)}(z)$ with respect to the Bloch functions

$$\varphi^{(e)}(\boldsymbol{z}) = \sum_{\boldsymbol{k}m} b_{\boldsymbol{k}m}(\boldsymbol{z})\,\varphi^{(\nu)}_{\boldsymbol{k}m} \tag{8.4}$$

and use (4.19). After multiplication by $b^{*}_{\boldsymbol{p}i}(\boldsymbol{z})$ and integrating Eq. (8.3a) decomposes into two systems namely

$$\varepsilon_{\boldsymbol{p}i}\,\varphi^{(e)}_{\boldsymbol{p}i} + \sum_{\boldsymbol{k},m} g_{\boldsymbol{p}i}\,W_{\boldsymbol{p}i,\boldsymbol{k}m}\,\varphi^{(e)}_{\boldsymbol{k}m} = (\omega - C')\,\varphi^{(e)}_{\boldsymbol{p}i} \tag{8.5a}$$

for $\boldsymbol{p}$, i outside the Fermi surface and

$$(\varepsilon_{\boldsymbol{p}i} + C' - \omega)\,\varphi^{(e)}_{\boldsymbol{p}i} = 0 \tag{8.5b}$$

for $\boldsymbol{p}$, i inside the Fermi surface. $W_{\boldsymbol{p}i,\boldsymbol{k}m}$ stands for

$$W_{\boldsymbol{p}i,\boldsymbol{k}m} = \int \mathrm{d}^3x\, b^*_{\boldsymbol{p},i}(\boldsymbol{x})\, W(\boldsymbol{x})\, b_{\boldsymbol{k},m}(\boldsymbol{x})\,. \tag{8.6}$$

Equation (8.3a) is therefore a Schrödinger equation for the energy difference ω of an additional electron in the disturbed crystal relative to the ideal crystal. The constant C' represents the potential energy of a defect screened by the Bloch functions:

$$\begin{aligned} C' &= \tfrac{1}{2}\int \mathrm{d}^3x\, \mathrm{Tr}\,[\hat{S}_0(\boldsymbol{x},\boldsymbol{x})(\hat{W}(\boldsymbol{x}) - V^0_{\mathrm{H}}(\boldsymbol{x}))] \\ &= \sum_{\boldsymbol{l}n} f_{\boldsymbol{l}n} \int b^*_{\boldsymbol{l}n}(\boldsymbol{x})(V_{\mathrm{w}}(\boldsymbol{x}) - V^0_{\mathrm{w}}(\boldsymbol{x}) + V_{\mathrm{H}}(\boldsymbol{x})) \\ &\quad \cdot b^{(x)}_{\boldsymbol{l}n}(\boldsymbol{x})\,\mathrm{d}^3x\,. \end{aligned} \tag{8.7}$$

It depends on the displacements of the lattice and the positions of the stored protons.

The second Eq. (8.3b) describes the energy difference of a defect electron in the disturbed lattice relative to the ideal crystal. For the expansion corresponding to (8.4)

$$\varphi^{(\mathrm{L})}(\boldsymbol{x}) = \sum_{\boldsymbol{k}m} b^*_{\boldsymbol{k}m}(\boldsymbol{x})\,\varphi^{(L)}_{\boldsymbol{k}m} \tag{8.8}$$

leads to

$$(\varepsilon_{\boldsymbol{p}i} + C' - \omega)\,\varphi^{(L)}_{\boldsymbol{p}i} = 0 \tag{8.9a}$$

for electrons outside the Fermi surface and to

$$\begin{aligned} -\Big(\varepsilon_{\boldsymbol{p}i}\,\varphi^{(L)}_{\boldsymbol{p}i} + \sum_{\boldsymbol{k}m} f_{\boldsymbol{p}i}\,W_{\boldsymbol{p}i,\boldsymbol{k}m}\,\varphi^{(L)}_{\boldsymbol{k}m}\Big) \\ = (\omega - C')\,\varphi^{(L)}_{\boldsymbol{p},i} \end{aligned} \tag{8.9b}$$

for an electron in the disturbed lattice. In fact, the energy difference $\mu = -(\omega - C')$ is negative relative to the ideal crystal indicating the energy of a defect electron. In equation (8.9a) we omitted a term which depends on the potential of the protons outside the crystal. For there, the energy of a hydrogen atom or molecule would be counted separately.

In the following we are, of course, only interested in Eq. (8.3a) which we want to take as a starting point for further investigations. It contains the disturbing potentials already including a screening, but a rigid one, not depending on the actual state of the electrons. Further it may happen that Bloch functions are inadequate as a base for the expansion of the projection operators S_0 and S_1. An alternative will be given in Section 10.

§ 9. Single Particle Equation with a Dynamically Screened Potential

We return to Eq. (6.12) and now calculate the additional terms $\hat{P}^{(a,b)}_{\varrho}$. As we are only interested in the first component part we eliminate this with the help of the projection operator $U\hat{I}^{(+)}$. Otherwise we use Bloch functions $b_{\boldsymbol{k}m}(\boldsymbol{x})$ for the expansion and omit the proton potentials $V^0_{\mathrm{H}}(\boldsymbol{x})$. We then get

$$\begin{aligned} \hat{P}^{(\mathrm{a})}_1(\boldsymbol{z}\,|\,\hat{\varphi}^{(1)}) &= \tfrac{1}{2}\iiiint \mathrm{d}^3z_1'\,\mathrm{d}^3z_2'\,\mathrm{d}^3z_3'\,\mathrm{d}^3x\,[\hat{W}(\boldsymbol{x})]_{\sigma\sigma'}\,\hat{G}(\boldsymbol{z},\boldsymbol{z}_1';\underset{\sigma'}{\boldsymbol{x}}\,\boldsymbol{z}_2';\underset{\sigma'}{\boldsymbol{x}},\boldsymbol{z}_3')\,\hat{R}^{(a)}(\boldsymbol{z}_1',\boldsymbol{z}_2',\boldsymbol{z}_3') \\ &= -\tfrac{1}{2}\iiiint \mathrm{d}^3z_1'\,\mathrm{d}^3z_2'\,\mathrm{d}^3z_3'\,\mathrm{d}x \sum_{\sigma\sigma'}[\hat{W}(\boldsymbol{x})]_{\sigma\sigma'} \sum_{\pm\pm\pm}\sum_{\substack{\boldsymbol{p}_1\boldsymbol{p}_2\boldsymbol{p}_3\\ i_1\,i_2\,i_3}} \frac{\hat{A}^{(\pm)}_{\boldsymbol{p}_1 i_1}(\boldsymbol{z},\boldsymbol{z}_1') \otimes \hat{A}^{(\pm)}_{\boldsymbol{p}_2 i_2}(\underset{\sigma'}{\boldsymbol{x}},\boldsymbol{z}_2') \otimes \hat{A}^{(\pm)}_{\boldsymbol{p}_3 i_3}(\underset{\sigma'}{\boldsymbol{x}},\boldsymbol{z}_3')}{\pm\varepsilon_{\boldsymbol{p}_1 i_1} \pm \varepsilon_{\boldsymbol{p}_2 i_2} \pm \varepsilon_{\boldsymbol{p}_3 i_3} + C' - \omega} \\ &\quad \cdot \iint \mathrm{d}^3y\,\mathrm{d}^3y'\,\{\hat{\Lambda}^{(+)}(\boldsymbol{z}_1',\boldsymbol{y})\,\hat{D}_0(\boldsymbol{y},\boldsymbol{y}')\,\hat{\Lambda}^{(-)}(\boldsymbol{y}',\boldsymbol{z}_2')\,\hat{\varphi}^{(1)}(\boldsymbol{z}_3') - \hat{\Lambda}^{(-)}(\boldsymbol{z}_1',\boldsymbol{y})\,\hat{D}_0(\boldsymbol{y},\boldsymbol{y}')\,\hat{\Lambda}^{(+)}(\boldsymbol{y}',\boldsymbol{z}_2')\hat{\varphi}^{(1)}(\boldsymbol{z}_3') \\ &\quad + \delta(\boldsymbol{y}-\boldsymbol{y}')\,\hat{\Lambda}^{(+)}(\boldsymbol{z}_1',\boldsymbol{y})\,\hat{W}(\boldsymbol{y})\,\hat{\Lambda}^{(-)}(\boldsymbol{y},\boldsymbol{z}_2')\,\hat{\varphi}^{(1)}(\boldsymbol{z}_3') + \text{Permu. in } \boldsymbol{z}_1',\boldsymbol{z}_2',\boldsymbol{z}_3'\}\,. \end{aligned} \tag{9.1}$$

Using the definitions (8.6) and also

$$D_{0;\boldsymbol{p}i,\boldsymbol{l}n} = \iint \mathrm{d}^3x\,\mathrm{d}^3x'\,b^*_{\boldsymbol{p}i}(\boldsymbol{x})\,D_0(\boldsymbol{x},\boldsymbol{x}')\,b_{\boldsymbol{l}n}(\boldsymbol{x}') \tag{9.2}$$

the evaluation gives the result

$$\begin{aligned} U\hat{I}^{(+)}\,\hat{P}^{(\mathrm{a})}_1 &= \sum_{\substack{\boldsymbol{p}i\\ \boldsymbol{l}n,\boldsymbol{l}'n'}} \int \mathrm{d}^3z'\,b_{\boldsymbol{p}i}(\boldsymbol{z})\,\{(D_{0;\boldsymbol{p}i,\boldsymbol{l}n}(f_{\boldsymbol{l}n} - f_{\boldsymbol{p}i}) + g_{\boldsymbol{p}i}\,W_{\boldsymbol{p}i,\boldsymbol{l}n}\,f_{\boldsymbol{l},n})\,W_{\boldsymbol{l}n,\boldsymbol{l}'n}\,b^*_{\boldsymbol{l}'n'}(\boldsymbol{z}') \\ &- W_{\boldsymbol{l}n,\boldsymbol{l}'n'}(D_{0,\boldsymbol{l}'n',\boldsymbol{l}n}(f_{\boldsymbol{l}n} - f_{\boldsymbol{l}'n'}) + g_{\boldsymbol{l}'n'}\,W_{\boldsymbol{l}'n',\boldsymbol{l}n}\,f_{\boldsymbol{l}n})\,b^*_{\boldsymbol{p}i}(\boldsymbol{z}')\}\,\varphi^{(e)}(\boldsymbol{z}') \cdot \frac{1}{\varepsilon_{\boldsymbol{p}i} - \varepsilon_{\boldsymbol{l}n} + \varepsilon_{\boldsymbol{l}'n'} + C' - \omega}\,. \end{aligned} \tag{9.3}$$

The other terms can be calculated in the same way:

$$U\hat{I}^{(+)}\,\hat{P}_1^{(\mathrm{b})} = \sum_{\substack{pi\\ ln,\,l'n'}} \iint \mathrm{d}^3x\,\mathrm{d}^3x'\, b_{pi}(\boldsymbol{z})\,\{b^*_{pi}(\boldsymbol{x}')\,b_{ln}(\boldsymbol{x}')\,W_{ln,\,l'n'}\,b^*_{l'n'}(\boldsymbol{x})\,\varphi^{(e)}(\boldsymbol{x}) - b_{pi}(\boldsymbol{x})\,\varphi^{(e)}(\boldsymbol{x})\cdot b_{ln}(\boldsymbol{x}')\,W_{ln,\,l'n'}\,b^*_{ln'}(\boldsymbol{x}')\}\,\frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|}\,\frac{g_{ip}\,\mathfrak{f}_{ln}\,g_{l'n'} + \mathfrak{f}_{pi}\,g_{ln}\,\mathfrak{f}_{l'n'}}{\varepsilon_{pi} - \varepsilon_{ln} + \varepsilon_{l'n'} + C' - \omega}, \tag{9.4}$$

$$U\hat{I}^{(+)}\,\hat{P}_2^{(\mathrm{a})} = \sum_{\substack{pi\\ ln,\,l'n'}} \iint \mathrm{d}^3x\,\mathrm{d}^3z'\, b_{pi}(\boldsymbol{z})\,\frac{e^2}{|\boldsymbol{z}-\boldsymbol{x}|}\,\frac{1}{\varepsilon_{pi} - \varepsilon_{ln} + \varepsilon_{l'n'} + C' - \omega} \cdot\{(D_{0;\,pi,\,ln}(\mathfrak{f}_{ln} - \mathfrak{f}_{pi}) + g_{pi}\,W_{pi,\,ln}\,\mathfrak{f}_{ln})\,b^*_{ln}(\boldsymbol{x})\,b_{l'n'}(\boldsymbol{x})b^*_{l'n'}(z')\,\varphi^{(e)}(z') - b^*_{pi}(\boldsymbol{z}')\,\varphi^{(e)}(\boldsymbol{z}')\,(D_{0;\,l'n',}(\mathfrak{f}_{ln} - \mathfrak{f}_{l'n'}) + g_{l'n'}\,W_{l'n',\,ln}\,\mathfrak{f}_{ln})\,b^*_{ln}(\boldsymbol{x})b_{l'n'}(\boldsymbol{x})\}\,, \tag{9.5}$$

and

$$U\hat{I}^{(+)}\,\hat{P}_2^{(\mathrm{b})} = \sum_{\substack{pi\\ ln,\,l'n'}} \iiint \mathrm{d}^3x\,\mathrm{d}^3x'\,\mathrm{d}^3z'\, b_{pi}(\boldsymbol{z})\cdot\frac{g_{pi}\,\mathfrak{f}_{ln}\,g_{l'n'} + \mathfrak{f}_{pi}\,g_{ln}\,\mathfrak{f}_{l'n'}}{\varepsilon_{pi} - \varepsilon_{ln} + \varepsilon_{l'n'} + C' - \omega}\,\frac{e^2}{|\boldsymbol{z}-\boldsymbol{x}|}\,\frac{e^2}{|\boldsymbol{x}'-\boldsymbol{z}'|} \cdot\{b^*_{pi}(\boldsymbol{x}')\,b_{ln}(\boldsymbol{x})\,b^*_{ln}(\boldsymbol{x})\,b_{l'n'}(\boldsymbol{x})\,b^*_{l'n'}(\boldsymbol{z}')\,\varphi^{(e)}(\boldsymbol{z}') - b^*_{pi}(\boldsymbol{z}')\,\varphi^{(e)}(\boldsymbol{z}')\cdot b_{l'n'}(\boldsymbol{x})\,b_{l'n'}(\boldsymbol{x}')\,b_{ln}(\boldsymbol{x}')\,b^*_{ln}(\boldsymbol{x})\}\,. \tag{9.6}$$

For the sake of completeness we everywhere kept the term $D_{0;\,pi,\,ln}(l_n - \mathfrak{f}_{pi})$ though it vanishes by considering relation (7.1):

$$D_{0;\,pi,\,ln}(\mathfrak{f}_{ln} - \mathfrak{f}_{pi}) = \varepsilon_{pi}\,\delta_{p,\,l}\,\delta_{i,n}(\mathfrak{f}_{ln} - \mathfrak{f}_{pi}) = 0\,. \tag{9.7}$$

Equations (9.3) and (9.5) can be simplified in this way. Further simplifications result from approximations. But the corresponding calculations are postponed and will be done in connection with applications.

§ 10. Self-Consistent Calculation of a Basic Set of Functions

Up to now we supposed the solutions of the translation-invariant problem (7.1) to be the base for the expansions. However, one can go a step further and use the solutions of the disturbed problem (8.1) and (8.3a) as a base for the expansion of the operators S_0, S_1 and $\Lambda^{(+)}$, $\Lambda^{(-)}$, respectively. In this way one has to treat a self-consistent problem of the kind

$$\int \mathrm{d}^3x\,[D_0(\boldsymbol{z},\boldsymbol{x}) + \sum_{\mu}(\chi_\mu(\boldsymbol{z})\,g_\mu\,\chi^*_\mu(\boldsymbol{x})\,W(\boldsymbol{x}) + \chi_\mu(\boldsymbol{z})\,\mathfrak{f}_\mu\,\chi^*_\mu(\boldsymbol{x})\,V^0_{\mathrm{H}}(\boldsymbol{x})]\,\chi_\varkappa(\boldsymbol{z}) = \varepsilon_\varkappa\,\chi_\varkappa(\boldsymbol{z}), \tag{10.1}$$

where $\chi_\varkappa(\boldsymbol{x})$ denotes the more general functions and $\varepsilon_\varkappa$ the corresponding energies*. We want to substitute these functions into the higher NTD-approximation of Section 6. To that purpose it is necessary to keep the neglected term of Eq. (6.8), namely,

$$\langle 0|\prod_{i=1}^{3} u(\boldsymbol{z}_i)\,\mathscr{D}_0^{(\mathrm{a})}\,\boldsymbol{\Phi}\,|0\rangle = \int[\hat{\Lambda}^{(+)}(\boldsymbol{z}_1,\boldsymbol{x})\,\hat{W}(\boldsymbol{x}) + \hat{\Lambda}^{(-)}(\boldsymbol{z}_1,\boldsymbol{x})\,\hat{V}^0_{\mathrm{H}}(\boldsymbol{x}) \cdot\varphi^{(3)}(\boldsymbol{x},\boldsymbol{z}_2,\boldsymbol{z}_3) + \text{Permut. in } \boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{z}_3]\,\mathrm{d}^3x \tag{10.2}$$

and use the more general problem (10.1) instead of (7.1). All the other evaluations, e.g. the construction of the Green function, are quite analogous if $b_{km}(\boldsymbol{x})$ is replaced by $\chi_\varkappa(\boldsymbol{x})$ and ε_{km} by $\varepsilon_\varkappa$. However, there is an important change in the results of Sect. 9 because the terms (9.3) and (9.5) disappear. This can easily be recognized by the vanishing of $\mathscr{D}^{(\mathrm{a})}_{-1}$. To prove it we insert the underlined expressions in Eq. (5.11) and notice that they vanish because of their projection property:

$$\mathscr{D}^{(\mathrm{a})}_{-1} = -\tfrac{1}{2}\iiiint \mathrm{d}^3x\,\mathrm{d}^3x'\,\mathrm{d}^3y\,\mathrm{d}^3y'\,u^+(\boldsymbol{x}) \cdot\{\hat{\Lambda}^{(+)}(\boldsymbol{x},\boldsymbol{y})[D_0(\boldsymbol{y},\boldsymbol{y}') + \underline{\hat{\Lambda}^{(+)}(\boldsymbol{y},\boldsymbol{y}')\,\hat{W}(\boldsymbol{y}')} + \underline{\hat{\Lambda}^{(-)}(\boldsymbol{y},\boldsymbol{y}')\,\hat{V}^0_{\mathrm{H}}(\boldsymbol{y}')]}\,\hat{\Lambda}^{(-)}(\boldsymbol{y}',\boldsymbol{x}') - \hat{\Lambda}^{(-)}(\boldsymbol{x},\boldsymbol{y})[\hat{D}_0(\boldsymbol{y},\boldsymbol{y}') + \underline{\hat{\Lambda}^{+}(\boldsymbol{y},\boldsymbol{y}')\,\hat{W}(\boldsymbol{y}')} + \hat{\Lambda}^{(-)}(\boldsymbol{y},\boldsymbol{y}')\,\hat{V}^0_{\mathrm{H}}(\boldsymbol{y}')]\,\hat{\Lambda}^{(+)}(\boldsymbol{y}',\boldsymbol{x}')\}\,u^{\#}(\boldsymbol{x}')\,. \tag{10.3}$$

In Eq. (10.3) the parts in rectangular brackets are diagonal so that we have

$$\mathscr{D}^{(\mathrm{a})}_{-1} = -\tfrac{1}{2}\iiint \mathrm{d}^3x\,\mathrm{d}^3x'\,\mathrm{d}^3y\;\,u^+(\boldsymbol{x}) \cdot\{\hat{\Lambda}^{(+)}(\boldsymbol{x},\boldsymbol{y})\,\hat{\varepsilon}_\varkappa\,\hat{\Lambda}^{(-)}(\boldsymbol{y},\boldsymbol{x}') - \hat{\Lambda}^{(-)}(\boldsymbol{x},\boldsymbol{y})\,\hat{\varepsilon}_\varkappa\,\hat{\Lambda}^{(+)}(\boldsymbol{y},\boldsymbol{x}')\}\,u^{\#}(\boldsymbol{x}') = 0\,. \tag{10.4}$$

where we used the abbreviation $\hat{\varepsilon}_\varkappa = \varepsilon_\varkappa\,\hat{E}$.

---

* Let $\varkappa$ denote a complete set of quantum numvers.

The remaining terms (9.4) and (9.6) are now

$$
\begin{aligned}
U\hat{I}^{(+)}\,P_1^{(\mathrm{b})} &= \sum_{\varkappa,\mu,\mu'} \iint \mathrm{d}^3x\,\mathrm{d}^3x' \cdot \frac{e^2}{|\boldsymbol{x}-\boldsymbol{x}'|} \\
&\cdot \frac{g_x f_u g_{u'} + f_x g_u f_{u'}}{\varepsilon_\varkappa - \varepsilon_\mu + \varepsilon_{\mu'} + C' - \omega} \\
&\cdot \chi_\varkappa(\boldsymbol{z}) \{\chi_\varkappa{}^*(\boldsymbol{x}')\,\chi_\mu(\boldsymbol{x}')\,W_{\mu,\mu'}\,\chi^*_{\mu'}(\boldsymbol{x})\,\varphi^{(e)}(\boldsymbol{x}) \\
&- \chi^*(\boldsymbol{x})\,\varphi^{(e)}(\boldsymbol{x}) \cdot \chi_\mu(\boldsymbol{x}')\,W_{\mu,\mu'}\,\chi^*_{\mu'}(\boldsymbol{x})\} \qquad (10.5)
\end{aligned}
$$

and

$$
\begin{aligned}
U\hat{I}^{(+)}\,P_2^{(\mathrm{b})} &= \sum_{\varkappa,\mu,\mu'} \iiint \mathrm{d}^3x\,\mathrm{d}^3x'\,\mathrm{d}^3z'\,\chi_\varkappa(\boldsymbol{z}) \qquad (10.6) \\
&\cdot \frac{g_\varkappa f_\mu g_{\mu'} + f_\varkappa g_\mu f_{\mu'}}{\varepsilon_\varkappa - \varepsilon_\mu + \varepsilon_\mu + C' - \omega}\,\frac{e^2}{|\boldsymbol{z}-\boldsymbol{x}|}\,\frac{e^2}{|\boldsymbol{x}'-\boldsymbol{z}'|} \\
&\cdot \{\chi_\varkappa{}^*(\boldsymbol{x}')\,\chi_\mu(\boldsymbol{x}')\,\chi_\mu{}^*(\boldsymbol{x})\,\chi_{\mu'}(\boldsymbol{x})\,\chi^*_{\mu'}(\boldsymbol{z}')\,\varphi^{(e)}(\boldsymbol{z}') \\
&- \chi_\varkappa{}^*(\boldsymbol{z}')\,\varphi^{(e)}(\boldsymbol{z}') \cdot (\chi_\mu{}^*(\boldsymbol{x})\,\chi_{\mu'}(\boldsymbol{x})\,\chi^*_{\mu'}(\boldsymbol{x}')\,\chi_\mu(\boldsymbol{x}'))\}\,.
\end{aligned}
$$

Formaly the self-consistent determination of the functions has some advantages but their calculation is considerably more complicated. It may only be justified if divergencies appear in the calculation of the matrix elements $W_{\mu,\mu'}$ or if serious problems of convergence prevent an expansion with respect to Bloch-functions.

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[1] Hydrogen in Metals I and II, G. Alefeld and J. Völkl (eds.), Topics in Applied Physics, Vol. 28 and 29, Springer-Verlag, Berlin, New York 1978. — H. Peisl, Wasserstoff in Metallen, in: Physik in unserer Zeit, Nr. 2, 1978. H. Buchner Chemietechik (1978) 371-377.

[2] See, for example: The Hydrogen Energy System, Proc. of the 2nd World Hydrogen Energy Conference, Zürich 1978, T. N. Veziroglu, W. Seifritz (eds.), Pergamon Press, London 1979.

[3] See, for example, the contributions of K. W. Kehr, A. C. Switendick, and H. Wagner in: Hydrogen in Metals I.

[4] C. A. Sholl and P. V. Smith, J. Phys. F: Metal Physics, Vol. **7**, No. 5, 789 and 799 (1977).

[5] H. Stumpf, Quantentheorie der Ionenkristalle, Springer-Verlag, Berlin 1961.

[6] F. Wahl, Z. Naturforsch. **30a**, 1333 (1975), und W. Feist, Diplomarbeit, Tübingen 1979.

[7] H. P. Dürr and F. Wagner, Nuovo Cim. **X**, 46, 223 (1966).

[8] H. Krauß, Diplomarbeit, Tübingen 1977.

[9] H. Rampacher, H. Stumpf, and F. Wagner, Fortschritte der Physik **13**, 385 (1965), § 20. J. Schwinger, Proc. Nat. Acad. Sci. USA **37**, 452, 455 (1951).