

Foundations of a Theory Concerning Hydrogen Centres in Metals

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The present work is an attempt to treat hydrogen storage in metals with the aid of field theoretical methods. Starting with the many-body Schrödinger equation, an adiabatic decomposition yields an electronic system, a protonic system and a host lattice system. We define a storage energy consisting of a lattice contribution and an electronic part. The latter one will be evaluated by the New Tamm-Dancoff (NTD) procedure. This formalism is a method to compute differences of eigenvalues in quantum mechanical problems. As an example we derive a one-particle equation describing a single hydrogen atom in a metal crystal.

Introduction

In recent years, energy storage systems have attracted great interest. We treat metal hydrides as a very promising example. Our theoretical description is based on first principles. In §§ 1 and 2 we develop a consideration of the electronic and elastic problem of hydrogen storage in metals. In § 3 we define the storage energy as a difference energy between hydrided and dehydrided metal crystals. This storage energy consists of an electronic and an elastic part. We are exclusively interested in the computation of the electronic energy difference. The appropriate tool to calculate such energy differences will be the New Tamm-Dancoff (NTD) procedure illustrated in §§ 4, 5 and 6. In § 7 we present a so-called zeroth order NTD-approximation applied to a single hydrogen centre.

§ 1. Twofold adiabatic decomposition (Born-Oppenheimer approximation) of the total problem. Definition of a reference system

The starting point of our investigation is the many-particle Schrödinger equation of a host crystal disturbed by stored hydrogen atoms

$$\mathcal{H}_H \psi(\mathbf{x}, \mathbf{Y}, \mathbf{X}) = E \psi(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \quad (1.1)$$

and of a reference system describing the eventually deformed host crystal without hydrogen centres

$$\mathcal{H}_R \psi_R(\mathbf{x}, \mathbf{X}) = E_R \psi_R(\mathbf{x}, \mathbf{X}). \quad (1.2)$$

The labels \mathbf{x} , \mathbf{X} and \mathbf{Y} represent the set of electron coordinates \mathbf{x}_μ , the set of nuclear coordinates of the host lattice atoms $\mathbf{X}_{m,i}$ and the coordinates of the

absorbed protons \mathbf{Y}_n , respectively. We split the Hamiltonian into three parts

$$\mathcal{H}_H = \mathcal{H}^e + \mathcal{H}^p + \mathcal{H}^w \quad (1.3)$$

with

$$\begin{aligned} \mathcal{H}^e = & - \sum_{\mu} \frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial \mathbf{x}_{\mu}^2} + \frac{1}{2} \sum'_{\mu, \mu'} \frac{e^2}{|\mathbf{x}_{\mu} - \mathbf{x}_{\mu'}|} \\ & - \sum_{\mu, n} \frac{e^2}{|\mathbf{x}_{\mu} - \mathbf{Y}_n|} + \sum_{\mu, m, i} V_i(\mathbf{x}_{\mu} - \mathbf{X}_{m, i}), \end{aligned} \quad (1.4)$$

$$\begin{aligned} \mathcal{H}^p = & - \sum_n \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \mathbf{Y}_n^2} + \frac{1}{2} \sum'_{n, n'} \frac{e^2}{|\mathbf{Y}_n - \mathbf{Y}_{n'}|} \\ & + \sum_{n, m, i} U_i(\mathbf{Y}_n - \mathbf{X}_{m, i}), \end{aligned} \quad (1.5)$$

$$\begin{aligned} \mathcal{H}^w = & - \sum_{m, i} \frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial \mathbf{X}_{m, i}^2} \\ & + \frac{1}{2} \sum'_{\substack{m, i \\ m', i'}} W_{i, i'}(\mathbf{X}_{m, i} - \mathbf{X}_{m', i'}), \end{aligned} \quad (1.6)$$

where m_e , M and M_i denote the mass of the electron, the mass of the proton and the mass of the host lattice ion, respectively. (\sum' means: $\mu = \mu'$ excluded.)

The particular terms in (1.4) to (1.6) are the kinetic energies followed by the coulombic interactions. For our purpose it is best to consider the atomic cores rather than the nuclei of the host lattice. Therefore the coordinates \mathbf{x}_{μ} represent the degrees of freedom of the explicitly treated N valence electrons in the metallic crystal, and those of the n additional electrons absorbed by the host lattice together with the n protons. The potentials $V_i(\mathbf{x}_{\mu} - \mathbf{X}_{m, i})$, $U_i(\mathbf{Y}_n - \mathbf{X}_{m, i})$ and $W_{i, i'}(\mathbf{X}_{m, i} - \mathbf{X}_{m', i'})$ characterize the nucleus-electron interaction, the

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nucleus-additional proton interaction and the nucleus-nucleus interaction, respectively.

For the Hamiltonian of the reference system we suppose

$$\mathcal{H}_R = \mathcal{H}_R^e + \mathcal{H}_R^w \quad (1.7)$$

with

$$\begin{aligned} \mathcal{H}_R^e = & - \sum_{\mu} \frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial \mathbf{x}_{\mu}^2} + \frac{1}{2} \sum'_{\mu, \mu'} \frac{e^2}{|\mathbf{x}_{\mu} - \mathbf{x}_{\mu'}|} \\ & + \sum_{\mu, m, i} V_i(\mathbf{x}_{\mu} - \mathbf{X}_{m, i}^R), \end{aligned} \quad (1.8)$$

$$\begin{aligned} \mathcal{H}_R^w = & - \sum_{m, i} \frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial \mathbf{X}_{m, i}^2} \\ & + \frac{1}{2} \sum'_{\substack{m, i \\ m', i'}} W_{i, i'}(\mathbf{X}_{m, i}^R - \mathbf{X}_{m', i'}^R). \end{aligned} \quad (1.9)$$

In the following we suitably choose the coordinates $\mathbf{X}_{m, i}^R$.

The mobility of the electrons compared with that of the protons and nuclei is very high. Furthermore the protons are very mobile compared with the nuclei. By these facts we are encouraged to apply an adiabatic approximation (Born-Oppenheimer approximation) [1, 2] in two steps. For this purpose we express the total wavefunction in (1.1) in the form

$$\psi(\mathbf{x}, \mathbf{Y}, \mathbf{X}) = \psi^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \chi(\mathbf{Y}, \mathbf{X}) \Phi(\mathbf{X}). \quad (1.10)$$

Analogously we decompose the reference system

$$\psi_R(\mathbf{x}, \mathbf{X}^R) = \psi^N(\mathbf{x}, \mathbf{X}^R) \Phi(\mathbf{X}^R). \quad (1.11)$$

The adiabatic decoupling of the total system can be achieved if we start with a Schrödinger equation for the electronic subsystem of the form

$$\mathcal{H}^e \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) = \varepsilon_{\alpha}^{N+n}(\mathbf{Y}, \mathbf{X}) \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}). \quad (1.12)$$

The index α denotes a set of appropriate quantum numbers. We treat the coordinates \mathbf{Y} and \mathbf{X} as parameters, i.e. the electronic states have to be calculated as functions of the instantaneous positions of protons and lattice ions.

Inserting (1.10) into (1.1) leads to

$$\begin{aligned} & \{\chi(\mathbf{Y}, \mathbf{X}) \Phi(\mathbf{X}) \mathcal{H}^e \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \\ & + \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \Phi(\mathbf{X}) \mathcal{H}^p \chi(\mathbf{Y}, \mathbf{X}) \\ & + \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \chi(\mathbf{Y}, \mathbf{X}) \mathcal{H}^w \Phi(\mathbf{X})\} \\ & = E \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \chi(\mathbf{Y}, \mathbf{X}) \Phi(\mathbf{X}) + F_y + F_x \end{aligned} \quad (1.13)$$

with

$$\begin{aligned} F_y = & \frac{\hbar^2}{2M} \sum_n \left\{ \chi(\mathbf{Y}, \mathbf{X}) \Phi(\mathbf{X}) \frac{\partial^2}{\partial \mathbf{Y}_n^2} \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \right. \\ & \left. + 2 \Phi(\mathbf{X}) \frac{\partial \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X})}{\partial \mathbf{Y}_n} \cdot \frac{\partial \chi(\mathbf{Y}, \mathbf{X})}{\partial \mathbf{Y}_n} \right\} \end{aligned} \quad (1.14)$$

and

$$\begin{aligned} F_x = & \sum_{m, i} \frac{\hbar^2}{2M_i} \left\{ \chi(\mathbf{Y}, \mathbf{X}) \Phi(\mathbf{X}) \frac{\partial^2}{\partial \mathbf{X}_{m, i}^2} \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \right. \\ & + 2 \Phi(\mathbf{X}) \frac{\partial \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X})}{\partial \mathbf{X}_{m, i}} \cdot \frac{\partial \chi(\mathbf{Y}, \mathbf{X})}{\partial \mathbf{X}_{m, i}} \\ & + 2 \chi(\mathbf{Y}, \mathbf{X}) \frac{\partial \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X})}{\partial \mathbf{X}_{m, i}} \cdot \frac{\partial \Phi(\mathbf{X})}{\partial \mathbf{X}_{m, i}} \\ & + 2 \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \frac{\partial \chi(\mathbf{Y}, \mathbf{X})}{\partial \mathbf{X}_{m, i}} \cdot \frac{\partial \Phi(\mathbf{X})}{\partial \mathbf{X}_{m, i}} \\ & \left. + \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \Phi(\mathbf{X}) \frac{\partial^2 \chi(\mathbf{Y}, \mathbf{X})}{\partial \mathbf{X}_{m, i}^2} \right\}. \end{aligned} \quad (1.15)$$

Neglecting the terms (1.14) and (1.15), which describe interactions of the subsystems, we gain the twofold adiabatic approximation. The energy eigenvalues $\varepsilon_{\alpha}^{N+n}(\mathbf{Y}, \mathbf{X})$ of (1.12) play the role of an additional potential for the proton system

$$\{\mathcal{H}^p + \varepsilon_{\alpha}^{N+n}(\mathbf{Y}, \mathbf{X})\} \chi_{\alpha\beta}(\mathbf{Y}, \mathbf{X}) = E_{\alpha\beta}^{N+n}(\mathbf{X}) \chi_{\alpha\beta}(\mathbf{Y}, \mathbf{X}). \quad (1.16)$$

Furthermore \mathbf{X} is treated as parameter.

Using $\varepsilon_{\alpha}^{N+n}(\mathbf{Y}, \mathbf{X})$ of (1.12) and $E_{\alpha\beta}^{N+n}(\mathbf{X})$ of (1.16) in the left-hand side of (1.13), we get the Schrödinger problem for the cores of the host lattice:

$$\begin{aligned} & \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \Phi(\mathbf{X}) \{\mathcal{H}^p + \varepsilon_{\alpha}^{N+n}(\mathbf{Y}, \mathbf{X})\} \chi_{\alpha\beta}(\mathbf{Y}, \mathbf{X}) \\ & + \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \chi_{\alpha\beta}(\mathbf{Y}, \mathbf{X}) \mathcal{H}^w \Phi(\mathbf{X}) \\ & = \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \chi_{\alpha\beta}(\mathbf{Y}, \mathbf{X}) \{\mathcal{H}^w + E_{\alpha\beta}^{N+n}(\mathbf{X})\} \Phi_{\alpha\beta\gamma}(\mathbf{X}) \\ & = E^{N+n} \Phi_{\alpha\beta\gamma}(\mathbf{X}) \psi_{\alpha}^{N+n}(\mathbf{x}, \mathbf{Y}, \mathbf{X}) \chi_{\alpha\beta}(\mathbf{Y}, \mathbf{X}) + F_y + F_x. \end{aligned} \quad (1.17)$$

If the adiabatic approximation is a realistic one, the eigenvalue of the host lattice system

$$\{\mathbf{H}^w + E_{\alpha\beta}^{N+n}\} \Phi_{\alpha\beta\gamma}(\mathbf{X}) = E_{\alpha\beta\gamma}^{N+n} \Phi_{\alpha\beta\gamma}(\mathbf{X}) \quad (1.18)$$

is an approach to the energy of the total system

$$E^{N+n} \approx E_{\alpha\beta\gamma}^{N+n}. \quad (1.19)$$

The reference system (1.2) is decomposed in the same way. We get two subsystems, namely the electronic equation

$$\mathcal{H}_R^e \psi_{\alpha}^N(\mathbf{x}, \mathbf{X}^R) = \varepsilon_{\alpha}^N(\mathbf{X}^R) \psi_{\alpha}^N(\mathbf{x}, \mathbf{X}^R) \quad (1.20)$$

and the equation for the host lattice

$$\{\mathcal{H}_R^w + \varepsilon_x^N(\mathbf{X}^R)\} \Phi_{x',y'}(\mathbf{X}^R) = E_{x',y'}^N \Phi_{x',y'}(\mathbf{X}^R). \quad (1.21)$$

Again we have neglected the coupling term

$$F_x^R = \sum_{m,i} \frac{\hbar^2}{2M_i} \left\{ \Phi(\mathbf{X}^R) \frac{\partial^2 \psi_x^N(\mathbf{x}, \mathbf{X}^R)}{\partial \mathbf{X}_{m,i}^2} + 2 \frac{\partial \psi_x^N(\mathbf{x}, \mathbf{X}^R)}{\partial \mathbf{X}_{m,i}^R} \cdot \frac{\partial \Phi(\mathbf{X}^R)}{\partial \mathbf{X}_{m,i}^R} \right\}. \quad (1.22)$$

$E_{x',y'}^N$ is considered as an approach to the reference energy E_R .

§ 2. The static and dynamic problem of protons and host lattice ions

When treating a crystal with stored hydrogen atoms we start with the assumption that both the protons and the lattice ions are localized at equilibrium positions, $\tilde{\mathbf{Y}}_n$ and $\tilde{\mathbf{X}}_{m,i}$, respectively, oscillating about them. With that it is possible to formulate a lattice statics and a lattice dynamics and to derive a system of force equations in two steps. First we separate the proton coordinates into equilibrium positions $\tilde{\mathbf{Y}}_n$ and displacements \mathbf{y}_n

$$\mathbf{Y}_n = \tilde{\mathbf{Y}}_n + \mathbf{y}_n. \quad (2.1)$$

Hence, from the proton equation (1.16) we obtain

$$\begin{aligned} & \left\{ -\frac{\hbar^2}{2M} \sum_n \frac{\partial^2}{\partial \mathbf{Y}_n^2} + \frac{e^2}{2} \sum_{n,n'}' \left(\frac{1}{|\tilde{\mathbf{Y}}_n - \tilde{\mathbf{Y}}_{n'} + \mathbf{y}_n - \mathbf{y}_{n'}|} - \frac{1}{|\tilde{\mathbf{Y}}_n - \tilde{\mathbf{Y}}_{n'}|} \right) \right. \\ & + \sum_{n,m,i} (U_i(\tilde{\mathbf{Y}}_n - \mathbf{X}_{m,i} + \mathbf{y}_n) - U_i(\tilde{\mathbf{Y}}_n - \mathbf{X}_{m,i})) \\ & \left. + \varepsilon_x^{N+n}(\tilde{\mathbf{Y}} + \mathbf{y}, \mathbf{X}) - \varepsilon_x^{N+n}(\tilde{\mathbf{Y}}, \mathbf{X}) \right\} \chi_{x\beta}(\tilde{\mathbf{Y}} + \mathbf{y}, \mathbf{X}) \\ & = \left\{ E_{x\beta}^{N+n}(\mathbf{X}) - \left(\frac{1}{2} \sum_{n,n'}' \frac{e^2}{|\tilde{\mathbf{Y}}_n - \tilde{\mathbf{Y}}_{n'}|} + \sum_{n,m,i} U_i(\tilde{\mathbf{Y}}_n - \mathbf{X}_{m,i}) + \varepsilon_x^{N+n}(\tilde{\mathbf{Y}}, \mathbf{X}) \right) \right\} \chi_{x\beta}(\tilde{\mathbf{Y}} + \mathbf{y}, \mathbf{X}). \end{aligned} \quad (2.2)$$

Due to our semi-classical view-point the energy eigenvalue $E_{x\beta}^{N+n}(\mathbf{X})$ depends on the equilibrium position $\tilde{\mathbf{Y}}$.

$$E_{x\beta}^{N+n}(\mathbf{X}) \equiv E_{x\beta}^{N+n}(\tilde{\mathbf{Y}}, \mathbf{X}) \quad (2.3)$$

which has to be evaluated by equilibrium conditions. Computing the expectation value with $\chi_{x\beta}^*(\tilde{\mathbf{Y}} + \mathbf{y}, \mathbf{X})$ normalized by

$$\int |\chi_{x\beta}(\tilde{\mathbf{Y}} + \mathbf{y}, \mathbf{X})|^2 d^3y = 1 \quad \text{for all } \mathbf{X} \quad (2.4)$$

we find

$$E_{x\beta}^{N+n}(\tilde{\mathbf{Y}}, \mathbf{X}) = H_{x\beta}(\tilde{\mathbf{Y}}, \mathbf{X}) + \frac{1}{2} \sum_{n,n'}' \frac{e^2}{|\tilde{\mathbf{Y}}_n - \tilde{\mathbf{Y}}_{n'}|} + \sum_{n,m,i} U_i(\tilde{\mathbf{Y}}_n - \mathbf{X}_{m,i}) + \varepsilon_x^{N+n}(\tilde{\mathbf{Y}}, \mathbf{X}). \quad (2.5)$$

Here $H_{x\beta}(\tilde{\mathbf{Y}}, \mathbf{X})$ denotes the expectation value of the left-hand side of (2.2).

In the second step, we consider the host lattice system (1.18). Dividing

$$\mathbf{X}_{m,i} = \tilde{\mathbf{X}}_{m,i} + \mathbf{u}_{m,i} \quad (2.6)$$

($\tilde{\mathbf{X}}_{m,i}$ = equilibrium position of host lattice cores) and inserting (2.5) into (1.18), we have the lattice vibration problem

$$\begin{aligned} & \left\{ -\sum_{m,i} \frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial \mathbf{u}_{m,i}^2} + \frac{1}{2} \sum_{\substack{m,i \\ m',i'}}' (W_{i,i'}(\tilde{\mathbf{X}}_{m,i} - \tilde{\mathbf{X}}_{m',i'} + \mathbf{u}_{m,i} - \mathbf{u}_{m',i'}) - W_{i,i'}(\tilde{\mathbf{X}}_{m,i} - \tilde{\mathbf{X}}_{m',i'})) \right. \\ & \left. + E_{x\beta}^{N+n}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}} + \mathbf{u}) - E_{x\beta}^{N+n}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) \right\} \Phi_{x\beta\gamma}(\tilde{\mathbf{X}} + \mathbf{u}) \\ & = \left\{ E_{x\beta\gamma}^{N+n} - \frac{1}{2} \sum_{\substack{m,i \\ m',i'}}' W_{i,i'}(\tilde{\mathbf{X}}_{m,i} - \tilde{\mathbf{X}}_{m',i'}) - E_{x\beta\gamma}^{N+n}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) \right\} \Phi_{x\beta\gamma}(\tilde{\mathbf{X}} + \mathbf{u}). \end{aligned} \quad (2.7)$$

Corresponding to (2.5), the energy eigenvalue $E_{x\beta\gamma}^{N+n}$ is found by computing the expectation value of (2.7) with $\Phi_{x\beta\gamma}^*(\tilde{\mathbf{X}} + \mathbf{u})$ normalized by

$$\int |\Phi_{x\beta\gamma}(\tilde{\mathbf{X}} + \mathbf{u})|^2 d^3u = 1. \quad (2.8)$$

It results in

$$\begin{aligned} E_{x\beta\gamma}^{N+n}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) &= \frac{1}{2} \sum_{n,n'}' \frac{e^2}{|\tilde{\mathbf{Y}}_n - \tilde{\mathbf{Y}}_{n'}|} + \sum_{n,m,i} U_i(\tilde{\mathbf{Y}}_n - \tilde{\mathbf{X}}_{m,i}) \\ &+ \frac{1}{2} \sum_{\substack{m,i \\ m',i'}}' W_{i,i'}(\tilde{\mathbf{X}}_{m,i} - \tilde{\mathbf{X}}_{m',i'}) + \varepsilon_x^{N+n}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) + H_{x\beta}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) \\ &+ K_{x\beta\gamma}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}), \end{aligned} \quad (2.9)$$

where $H_{\alpha\beta}(\tilde{Y}, \tilde{X})$ represents the vibration energy of the hydrogen centres

$$H_{\alpha\beta}(\tilde{Y}, \tilde{X}) = \int d^3y \chi_{\alpha\beta}^*(\tilde{Y} + y, \tilde{X}) \left\{ - \sum_n \frac{\hbar^2}{2M} \frac{\partial^2}{\partial y_n^2} + \frac{e^2}{2} \sum_{n,n'}' \left(\frac{1}{|\tilde{Y}_n - \tilde{Y}_{n'} + y_n - y_{n'}|} - \frac{1}{|\tilde{Y}_n - \tilde{Y}_{n'}|} \right) + \sum_{n,m,i} (U_i(\tilde{Y}_n - \tilde{X}_{m,i} + y_n) - U_i(\tilde{Y}_n - \tilde{X}_{m,i})) + \varepsilon_{\alpha}^{N+n}(\tilde{Y} + y, \tilde{X}) - \varepsilon_{\alpha}^{N+n}(\tilde{Y}, \tilde{X}) \right\} \chi_{\alpha\beta}(\tilde{Y} + y, \tilde{X}) \quad (2.10)$$

and $K_{\alpha\beta\gamma}(\tilde{Y}, \tilde{X})$ the vibration energy of the host lattice

$$K_{\alpha\beta\gamma}(\tilde{Y}, \tilde{X}) = \int d^3u \phi_{\alpha\beta\gamma}^*(\tilde{X} + u) \left\{ - \sum_{m,i} \frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial u_{m,i}^2} + \frac{1}{2} \sum_{\substack{m,i \\ m',i'}}' (W_{i,i'}(\tilde{X}_{m,i} - \tilde{X}_{m',i'} + u_{m,i} - u_{m',i'}) - W_{i,i'}(\tilde{X}_{m,i} - \tilde{X}_{m',i'})) + E_{\alpha\beta}^{N+n}(\tilde{Y}, \tilde{X} + u) - E_{\alpha\beta}^{N+n}(\tilde{Y}, \tilde{X}) \right\} \phi_{\alpha\beta\gamma}(\tilde{X} + u). \quad (2.11)$$

The equilibrium positions \tilde{Y} and \tilde{X} can be obtained by the coupled force equations systems

$$\nabla_{\tilde{Y}_n} E_{\alpha\beta\gamma}^{N+n}(\tilde{Y}, \tilde{X}) = 0, \quad (2.12a)$$

$$\nabla_{\tilde{X}_{m,i}} E_{\alpha\beta\gamma}^{N+n}(\tilde{Y}, \tilde{X}) = 0. \quad (2.12b)$$

§ 3. Definition of storage energy and force equations to determine equilibrium positions

By taking (1.21) and treating it in the same way as we did in § 2, we find for the eigenvalue of the reference system

$$E_{\alpha'\gamma'}^N \equiv E_{\alpha'\gamma'}(\tilde{X}^R) = \frac{1}{2} \sum_{\substack{m,i \\ m',i'}}' W_{i,i'}(\tilde{X}_{m,i}^R - \tilde{X}_{m',i'}^R) + \varepsilon_{\alpha'}^N(\tilde{X}^R) + K_{\alpha'\gamma'}(\tilde{X}^R) \quad (3.1)$$

with

$$K_{\alpha'\gamma'}(\tilde{X}^R) = \int d^3u \phi_{\alpha'\gamma'}^*(\tilde{X}^R + u) \left\{ - \sum_{m,i} \frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial u_{m,i}^2} + \frac{1}{2} \sum_{\substack{m,i \\ m',i'}}' (W_{i,i'}(\tilde{X}_{m,i}^R - \tilde{X}_{m',i'}^R + u_{m,i} - u_{m',i'}) - W_{i,i'}(\tilde{X}_{m,i}^R - \tilde{X}_{m',i'}^R)) + \varepsilon_{\alpha'}^N(\tilde{X}^R + u) - \varepsilon_{\alpha'}^N(\tilde{X}^R) \right\} \phi_{\alpha'\gamma'}(\tilde{X}^R + u). \quad (3.2)$$

Now we take as the reference system the ideal lattice in its ground state, i.e. the lattice coordinates $\tilde{X}_{m,i}^R$ are the equilibrium positions $\tilde{X}_{m,i}^0$ and the energy $E_{\alpha'\gamma'}^N$ is the ground state energy E_g^N

$$\tilde{X}_{m,i}^R \equiv \tilde{X}_{m,i}^0, \quad (3.3a)$$

$$E_{\alpha'\gamma'}^N \equiv E_g^N. \quad (3.3b)$$

Then the storage energy is defined by

$$\Delta E = E^{N+n} - E_R^N \approx E_{\alpha\beta\gamma}^{N+n}(\tilde{Y}, \tilde{X}) - E_g^N(\tilde{X}^0). \quad (3.4)$$

It is possible to split up this energy into two parts each with a clear physical meaning. For this purpose, we compute the ground state energy $E_g^N(\tilde{X}^R)$ from (3.1) for those displaced lattice coordinates \tilde{X}^R which are identical with the equilibrium positions \tilde{X} (determined by (2.12)) in the distorted system

$$\tilde{X}^R = \tilde{X}. \quad (3.5)$$

Now we add and subtract $E_g^N(\tilde{X})$ in (3.4) and get

$$\Delta E \approx Q_{\alpha\beta\gamma}^{(n)}(\tilde{Y}, \tilde{X}) + \Delta(\tilde{X}), \quad (3.6)$$

where

$$Q_{\alpha\beta\gamma}^{(n)}(\tilde{Y}, \tilde{X}) = E_{\alpha\beta\gamma}^{N+n}(\tilde{Y}, \tilde{X}) - E_g^N(\tilde{X}) \quad (3.7)$$

and

$$\Delta(\tilde{X}) = E_g^N(\tilde{X}) - E_g^N(\tilde{X}^0). \quad (3.8)$$

$\Delta(\tilde{X})$ denotes the change of the total energy of the crystal, i.e. elastic and electronic energy, caused by the lattice distortions due to hydrogen centres. $Q_{\alpha\beta\gamma}^{(n)}(\tilde{Y}, \tilde{X})$ may be interpreted as interaction energy between the hydrogen centres and the distorted metal lattice.

With (2.9) and (3.1) we verify

$$Q_{\alpha\beta\gamma}^{(n)}(\tilde{Y}, \tilde{X}) = \frac{1}{2} \sum_{n,n'}' \frac{e^2}{|\tilde{Y}_n - \tilde{Y}_{n'}|} + \sum_{n,m,i} U_i(\tilde{Y}_n - \tilde{X}_{m,i}) + \varepsilon_{\alpha}^{N+n}(\tilde{Y}, \tilde{X}) - \varepsilon_g^N(\tilde{X}) + H_{\alpha\beta}(\tilde{Y}, \tilde{X}) + K_{\alpha\beta\gamma}(\tilde{Y}, \tilde{X}) - K_g(\tilde{X}) \quad (3.9)$$

and

$$\Delta(\tilde{X}) = \frac{1}{2} \sum_{\substack{m,i \\ m',i'}}' (W_{i,i'}(\tilde{X}_{m,i} - \tilde{X}_{m',i'}) - W_{i,i'}(\tilde{X}_{m,i}^0 - \tilde{X}_{m',i'}^0)) + K_g(\tilde{X}) - K_g(\tilde{X}^0) + \varepsilon_g^N(\tilde{X}) - \varepsilon_g^N(\tilde{X}^0). \quad (3.10)$$

The subscript g denotes a set of ground state quantum numbers as in (3.3). For more interpretation of the terms W and ε_g^N , see [3].

Differentiating the storage energy (3.6), we obtain the force equations

$$\frac{\partial}{\partial \tilde{\mathbf{X}}_{q,1}} \Delta E = \frac{\partial}{\partial \tilde{\mathbf{X}}_{q,1}} (Q_{\alpha\beta\gamma}^{(n)}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) + \Delta(\tilde{\mathbf{X}})) = 0, \quad (3.11)$$

$$\frac{\partial}{\partial \tilde{\mathbf{Y}}_p} \Delta E = \frac{\partial}{\partial \tilde{\mathbf{Y}}_p} Q_{\alpha\beta\gamma}^{(n)}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) = 0. \quad (3.12)$$

These expressions correspond to the system (2.12) of coupled nonlinear equations. They permit, in principle, the determination of the equilibrium positions $\tilde{\mathbf{Y}}$ and $\tilde{\mathbf{X}}$. (3.11) and (3.12) yield the proton coordinates depending on the positions of the lattice cores

$$\tilde{\mathbf{Y}}_n = \tilde{\mathbf{Y}}_n(\tilde{\mathbf{X}}). \quad (3.13)$$

Inserting (3.13) into (3.11), we get a lattice equilibrium system

$$\frac{\partial}{\partial \tilde{\mathbf{X}}_{q,1}} \Delta(\tilde{\mathbf{X}}) = - \frac{\partial}{\partial \tilde{\mathbf{X}}_{q,1}} Q_{\alpha\beta\gamma}^{(n)}(\tilde{\mathbf{Y}}(\tilde{\mathbf{X}}), \tilde{\mathbf{X}}). \quad (3.14)$$

We interpret the right-hand side in (3.14) as “external” forces acting on the ions of the host lattice. Obviously, these forces themselves depend on the displacements $\tilde{\mathbf{X}}$. Therefore, we are left with a self-consistent problem.

For the rest of this paper, our main interest will be the computation of the electronic energy difference between the total system and the reference system

$$\omega(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) := \varepsilon_x^{N+n}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) - \varepsilon_g^N(\tilde{\mathbf{X}}) \quad (3.15)$$

which is an important term in $Q_{\alpha\beta\gamma}^{(n)}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}})$ in (3.9). We treat this energy difference (3.15) by the New Tamm-Dancoff (NTD) procedure, which is well known in field theory [4, 5]. To prepare for the discussion of the NTD-formalism, we start with a mathematical introduction.

§ 4. The CAR-tensor product

Using the quantum field theoretical formulation, we introduce electron creation and destruction operators $\psi_s^+(\mathbf{x})$, $\psi_s(\mathbf{x})^*$. Due to the Fermi statistics, these field operators obey the following canonical anticommutation relations (CAR)

$$\begin{aligned} \{\psi_s(\mathbf{x}), \psi_{s'}(\mathbf{x}')\}_+ &= \{\psi_s^+(\mathbf{x}), \psi_{s'}^+(\mathbf{x}')\}_+ = 0; \\ \{\psi_s(\mathbf{x}), \psi_{s'}^+(\mathbf{x}')\}_+ &= \delta(\mathbf{x} - \mathbf{x}') \cdot \delta_{ss'}. \end{aligned} \quad (4.1)$$

* The index s denoting spin-components will be suppressed provided it is not necessary to treat it explicitly.

We consider the algebra \mathcal{A}_ψ , induced by ψ^+ and ψ , and note that our physical observables are special elements of this algebra. Let $|O_\psi\rangle$ be the bare vacuum state. An arbitrary state $|\Phi\rangle$ in Fock space H_ψ may be written as

$$\begin{aligned} |\Phi\rangle &= \sum_{j=0}^{\infty} \frac{1}{j!} \int d^3x_1 \dots d^3x_j \varphi(\mathbf{x}_1, \dots, \mathbf{x}_j) \\ &\quad \cdot \psi^+(\mathbf{x}_1) \dots \psi^+(\mathbf{x}_j) |O_\psi\rangle \\ &= \Phi(\psi^+) |O_\psi\rangle \quad \text{with} \quad \Phi(\psi^+) \in \mathcal{A}_\psi. \end{aligned} \quad (4.2)$$

In analogy, we define vacuum states $|O_v\rangle$ and $|O_w\rangle$ with corresponding field operators $v^+(\mathbf{x})$, $v(\mathbf{x})$ and $w^+(\mathbf{x})$, $w(\mathbf{x})$. Again these operators generate CAR-algebras \mathcal{A}_v , \mathcal{A}_w and Fock spaces H_v , H_w .

To achieve an efficient representation, we combine the three systems by forming the tensor product. We obtain

the algebra

$$\mathcal{A}_\psi \otimes \mathcal{A}_v \otimes \mathcal{A}_w, \quad (4.3a)$$

the vacuum

$$|O_{\psi v w}\rangle = |O_\psi\rangle \otimes |O_v\rangle \otimes |O_w\rangle, \quad (4.3b)$$

the Fock space

$$H_\psi \otimes H_v \otimes H_w. \quad (4.3c)$$

(For a detailed discussion, see [6, 7].)

Because of the independence of the three subsystems, we have, for instance, the commutation relation

$$[\psi(\mathbf{x}), v(\mathbf{x}')]_- = 0. \quad (4.4)$$

For abbreviation, we have written

$$\begin{aligned} \psi(\mathbf{x}) &= \psi(\mathbf{x}) \otimes \mathbb{1} \otimes \mathbb{1}, \\ v(\mathbf{x}) &= \mathbb{1} \otimes v(\mathbf{x}) \otimes \mathbb{1}. \end{aligned} \quad (4.5)$$

Now the intention is to consider only one kind of commutation relations. For that purpose, we define the so-called “CAR-tensor product” [6, 7]:

$\mathcal{A}_\psi \otimes \mathcal{A}_v \otimes \mathcal{A}_w$ is called a CAR-tensor product of \mathcal{A}_ψ , \mathcal{A}_v and \mathcal{A}_w , if there are mappings

$$\begin{aligned} f_\psi: \mathcal{A}_\psi &\rightarrow \mathcal{A}_\psi \hat{\otimes} \mathcal{A}_v \hat{\otimes} \mathcal{A}_w, \\ f_v: \mathcal{A}_v &\rightarrow \mathcal{A}_\psi \hat{\otimes} \mathcal{A}_v \hat{\otimes} \mathcal{A}_w, \\ f_w: \mathcal{A}_w &\rightarrow \mathcal{A}_\psi \hat{\otimes} \mathcal{A}_v \hat{\otimes} \mathcal{A}_w \end{aligned} \quad (4.6)$$

with the properties

I) f_ψ , f_v and f_w are linear, multiplicative, isometric and

$$\begin{aligned} f_\psi(A^+) &= f_\psi(A)^+ \quad \text{for all } A \in \mathcal{A}_\psi, \\ f_v(B^+) &= f_v(B)^+ \quad \text{for all } B \in \mathcal{A}_v, \\ f_w(C^+) &= f_w(C)^+ \quad \text{for all } C \in \mathcal{A}_w. \end{aligned} \quad (4.7)$$

II) The images of the CAR-operators ψ^+ , ψ , v^+ , v , w^+ , w under the mappings f_ψ , f_v , f_w

$$\begin{aligned} \tilde{\psi}^+(\mathbf{x}) &= f_\psi(\psi^+(\mathbf{x})) & \tilde{\psi}(\mathbf{x}) &= f_\psi(\psi(\mathbf{x})) \\ \tilde{v}^+(\mathbf{x}) &= f_v(v^+(\mathbf{x})) & \tilde{v}(\mathbf{x}) &= f_v(v(\mathbf{x})) \\ \tilde{w}^+(\mathbf{x}) &= f_w(w^+(\mathbf{x})) & \tilde{w}(\mathbf{x}) &= f_w(w(\mathbf{x})) \end{aligned} \quad (4.8)$$

are anticommuting operator families, i.e.

$$\begin{aligned} \{\tilde{\psi}_s(\mathbf{x}), \tilde{\psi}_{s'}^+(\mathbf{x}')\}_+ &= \delta(\mathbf{x} - \mathbf{x}') \delta_{ss'} \\ \{\tilde{v}_s(\mathbf{x}), \tilde{v}_{s'}^+(\mathbf{x}')\}_+ &= \delta(\mathbf{x} - \mathbf{x}') \delta_{ss'} \\ \{\tilde{w}_s(\mathbf{x}), \tilde{w}_{s'}^+(\mathbf{x}')\}_+ &= \delta(\mathbf{x} - \mathbf{x}') \delta_{ss'} \end{aligned} \quad (4.9)$$

and

$$\begin{aligned} \{\tilde{\psi}_s(\mathbf{x}), \tilde{v}_{s'}(\mathbf{x}')\}_+ &= \{\tilde{\psi}_s^+(\mathbf{x}), \tilde{v}_{s'}^+(\mathbf{x}')\}_+ = 0; \\ \{\tilde{\psi}_s(\mathbf{x}), \tilde{w}_{s'}(\mathbf{x}')\}_+ &= \{\tilde{\psi}_s^+(\mathbf{x}), \tilde{w}_{s'}^+(\mathbf{x}')\}_+ = 0; \\ \{\tilde{v}_s(\mathbf{x}), \tilde{w}_{s'}(\mathbf{x}')\}_+ &= \{\tilde{v}_s^+(\mathbf{x}), \tilde{w}_{s'}^+(\mathbf{x}')\}_+ = 0, \text{ etc.} \end{aligned} \quad (4.10)$$

III) The images of the CAR-operators ψ^+ , ψ under f_ψ and v^+ , v under f_v and w^+ , w under f_w generate the CAR-tensor product

$$\mathcal{A}_{\tilde{\psi}} \hat{\otimes} \mathcal{A}_{\tilde{v}} \hat{\otimes} \mathcal{A}_{\tilde{w}} = \text{norm-completion} \quad (4.11)$$

$$\langle \{\tilde{\psi}^+(\mathbf{x}), \tilde{\psi}(\mathbf{x}), \tilde{v}^+(\mathbf{x}), \tilde{v}(\mathbf{x}), \tilde{w}^+(\mathbf{x}), \tilde{w}(\mathbf{x})\} \cup \{\mathbf{1}\} \rangle.$$

We are left with the problem to define the action of CAR-tensor product operators. Let

$$\begin{aligned} A \in \mathcal{A}_\psi, \quad B \in \mathcal{A}_v, \quad C \in \mathcal{A}_w \\ f_\psi(A) = \tilde{A}, \quad f_v(B) = \tilde{B}, \quad f_w(C) = \tilde{C}. \end{aligned} \quad (4.12)$$

Then

$$\begin{aligned} \tilde{A} \tilde{B} \tilde{C} |O_\psi\rangle \hat{\otimes} |O_v\rangle \hat{\otimes} |O_w\rangle \\ := |AO_\psi\rangle \hat{\otimes} |BO_v\rangle \hat{\otimes} |CO_w\rangle. \end{aligned} \quad (4.13)$$

(sequence)

Closing Remark

From here on we will disregard the difference between the image and the inverse image of the embedding isomorphisms f_ψ , f_v , f_w and suppress the \sim .

§ 5. The fundamental equation of the NTD-procedure

When treating a many-body system one faces the problem of a “difference of large numbers”. To avoid this difficulty we use the New Tamm-Dancoff (NTD) procedure.

We start with the field theoretical formulation of the electronic problem. The Hamiltonian of the reference system may be denoted by

$$\begin{aligned} \mathcal{H}_R^e \equiv \mathbb{H}_R(\psi^+, \psi) &= \sum_s \int d^3x \psi_s^+(\mathbf{x}) H(\mathbf{x}, \tilde{\mathbf{X}}) \psi_s(\mathbf{x}) \\ &+ \sum_{s,s'} \frac{1}{2} \int d^3x d^3x' \psi_s^+(\mathbf{x}) \psi_{s'}^+(\mathbf{x}') W(\mathbf{x}, \mathbf{x}') \psi_{s'}(\mathbf{x}') \psi_s(\mathbf{x}). \end{aligned} \quad (5.1)$$

The single particle contribution is

$$\begin{aligned} H(\mathbf{x}, \tilde{\mathbf{X}}) &:= -\frac{\hbar^2}{2m_e} \Delta + V(\mathbf{x}, \tilde{\mathbf{X}}) \quad \text{with} \\ V(\mathbf{x}, \tilde{\mathbf{X}}) &:= \sum_{m,i} V_i(\mathbf{x} - \tilde{\mathbf{X}}_{m,i}) \end{aligned} \quad (5.2)$$

and the two-particle interaction is represented by the Coulomb potential

$$W(\mathbf{x}, \mathbf{x}') := \frac{e^2}{|\mathbf{x} - \mathbf{x}'|}. \quad (5.3)$$

In the following we use an extended Einstein convention, i.e. one has to integrate multiple arguments as well as to sum up the same spin indices. Thus (5.1) rewrites

$$\begin{aligned} \mathbb{H}_R(\psi^+, \psi) &= \psi^+(\mathbf{x}) H(\mathbf{x}, \tilde{\mathbf{X}}) \psi(\mathbf{x}) \\ &+ \frac{1}{2} \psi^+(\mathbf{x}) \psi^+(\mathbf{x}') W(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}') \psi(\mathbf{x}). \end{aligned} \quad (5.4)$$

If it is possible we suppress the arguments.

To obtain the Hamiltonian of the total system including hydrogen absorption, we have to add the potential of the stored protons

$$V_H(\mathbf{x}, \tilde{\mathbf{Y}}) = - \sum_n e^2 / |\mathbf{x} - \tilde{\mathbf{Y}}_n| \quad (5.5)$$

and achieve

$$\mathbb{H}_H(\psi^+, \psi) = \mathbb{H}_R(\psi^+, \psi) + \psi^+(\mathbf{x}) V_H(\mathbf{x}, \tilde{\mathbf{Y}}) \psi(\mathbf{x}). \quad (5.6)$$

According to Haken [8] our further description will not be based on the so-called “bare vacuum” $|O_\psi\rangle$ but on a physical vacuum $|\Omega_\psi\rangle$. For this physical vacuum we choose the ground state of the N valence electrons in the ideal crystal.

Moreover, let $S_0(\mathbf{x}, \mathbf{x}')$ and $S_1(\mathbf{x}, \mathbf{x}')$ be two abstract projection operators fulfilling the relations

$$S_i(\mathbf{x}, \mathbf{y}) S_j(\mathbf{y}, \mathbf{x}') = S_i(\mathbf{x}, \mathbf{x}') \delta_{ij}, \quad i, j \in \{0, 1\}, \quad (5.7)$$

$$S_0(\mathbf{x}, \mathbf{x}') + S_1(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'), \quad (5.8)$$

$$S_i^+(\mathbf{x}, \mathbf{x}') = S_i^*(\mathbf{x}', \mathbf{x}) = S_i(\mathbf{x}, \mathbf{x}'), \quad i = 0, 1. \quad (5.9)$$

Interpreting with respect to $|\Omega_\psi\rangle$

$$\psi^+(\mathbf{x}') S_1(\mathbf{x}', \mathbf{x}), \quad \text{as particle creation operator,}$$

$$S_0(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}'), \quad \text{as hole creation operator,}$$

$$S_1(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}'), \quad \text{as particle destruction operator,}$$

$$\psi^+(\mathbf{x}') S_0(\mathbf{x}', \mathbf{x}), \quad \text{as hole destruction operator,}$$

we conclude

$$\psi^+(\mathbf{x}') S_0(\mathbf{x}', \mathbf{x}) |\Omega_\psi\rangle = 0, \quad (5.10a)$$

$$S_1(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}') |\Omega_\psi\rangle = 0. \quad (5.10b)$$

To receive an impression of $|\Omega_\psi\rangle$ and the operators $S_0(\mathbf{x}, \mathbf{x}')$ and $S_1(\mathbf{x}, \mathbf{x}')$, we consider the Hamiltonian of the ideal crystal

$$\begin{aligned} \mathbb{H}_0(\psi^+, \psi) &= \psi^+(\mathbf{x}) H_0(\mathbf{x}, \tilde{\mathbf{X}}^0) \psi(\mathbf{x}) \\ &\quad + \frac{1}{2} \psi^+(\mathbf{x}) \psi^+(\mathbf{x}') W(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}') \psi(\mathbf{x}) \end{aligned} \quad (5.11)$$

with

$$H_0(\mathbf{x}, \tilde{\mathbf{X}}^0) = -\frac{\hbar^2}{2m_e} \Delta + \sum_{\mathbf{m}, i} V_i(\mathbf{x} - \tilde{\mathbf{X}}_{\mathbf{m}, i}^0), \quad (5.12)$$

where $\tilde{\mathbf{X}}^0$ denotes the positions of the ideal lattice cores. Then $|\Omega_\psi\rangle$ may be built up with the aid of one-particle wavefunctions $b_k(\mathbf{x})$ (Bloch functions) as the Slater determinant

$$\begin{aligned} |\Omega_\psi\rangle &= \frac{1}{N!} \int d^3x_1 \dots d^3x_N \det(b_{k_1}(\mathbf{x}_1) \dots b_{k_N}(\mathbf{x}_N)) \\ &\quad \cdot \psi^+(\mathbf{x}_1) \dots \psi^+(\mathbf{x}_N) |\Omega_\psi\rangle. \end{aligned} \quad (5.13)$$

The projection operators $S_0(\mathbf{x}, \mathbf{x}')$ and $S_1(\mathbf{x}, \mathbf{x}')$ would be given by

$$S_0(\mathbf{x}, \mathbf{x}') = \sum_{k \text{ occ.}} b_k(\mathbf{x}) b_k^*(\mathbf{x}'), \quad (5.14a)$$

$$S_1(\mathbf{x}, \mathbf{x}') = \sum_{k \text{ unocc.}} b_k(\mathbf{x}) b_k^*(\mathbf{x}'). \quad (5.14b)$$

Hence $S_0(\mathbf{x}, \mathbf{x}')$ projects onto occupied states and $S_1(\mathbf{x}, \mathbf{x}')$ maps onto the complement, that is unoccupied states.

We return to the problem of calculating the electronic energy difference $\omega(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}})$ of (3.15). The elec-

tron states $|H\rangle$, $|R\rangle$ and the energies E_H , E_R are defined by the eigenvalue problems

$$\mathbb{H}_H |H\rangle = E_H |H\rangle, \quad (5.15a)$$

$$\mathbb{H}_R |R\rangle = E_R |R\rangle. \quad (5.15b)$$

As in the preceding sections, the labels R and H represent the reference system and the total system disturbed by stored hydrogen atoms, respectively. In the CAR-tensor product space $\mathcal{A}_\psi \hat{\otimes} \mathcal{A}_r \hat{\otimes} \mathcal{A}_w$, introduced in § 4, we define the generating operator*

$$\Gamma := e^{i w^\dagger S_0 \psi} e^{-i \psi^\dagger S_1 r^\dagger} e^{i \psi^\dagger S_1 w} e^{-i r S_0 \psi} e^{i w^\dagger S_1 \psi} e^{-i \psi^\dagger S_0 r^\dagger} \quad (5.16)$$

stressing that the creation and destruction operators ψ^+ , ψ , ... fulfill anticommutation relations and refer to the equations (4.9) and (4.10). If Φ' is an arbitrary element of $\mathbb{1} \hat{\otimes} \mathcal{A}_r \hat{\otimes} \mathcal{A}_w$, the fundamental equation of the NTD-procedure is written as

$$\begin{aligned} \langle R \hat{\otimes} \Phi' O_{rw} (\Gamma \mathbb{H}_H - \mathbb{H}_R \Gamma) H \hat{\otimes} O_{rw} \rangle \\ = (E_H - E_R) \langle R \hat{\otimes} \Phi' O_{rw} \Gamma H \hat{\otimes} O_{rw} \rangle \\ =: \omega_{HR} \langle R \hat{\otimes} \Phi' O_{rw} \Gamma H \hat{\otimes} O_{rw} \rangle. \end{aligned} \quad (5.17)$$

In contrast to (4.3b) we now use the new physical vacuum state

$$|\Omega\rangle = |\Omega_\psi\rangle \hat{\otimes} |O_r\rangle \hat{\otimes} |O_w\rangle = |\Omega_\psi\rangle \hat{\otimes} |O_{rw}\rangle. \quad (5.18)$$

§ 6. The development of the NTD-formalism

Our physical problem is represented by H_R , $H_H \in \mathcal{A}_\psi \hat{\otimes} \mathbb{1} \hat{\otimes} \mathbb{1}$. We will specify a mapping of the quantum mechanical content of $\mathcal{A}_\psi \hat{\otimes} \mathbb{1} \hat{\otimes} \mathbb{1}$ onto $\mathbb{1} \hat{\otimes} \mathcal{A}_r \hat{\otimes} \mathcal{A}_w$.

For that purpose, we write the states $|H\rangle$ and $|R\rangle$ as

$$\begin{aligned} |H\rangle &= \chi_H(\psi^+ S_1, S_0 \psi) |\Omega_\psi\rangle \\ &= \sum_{n=0}^{\infty} \frac{1}{(n+J)! n!} \psi^+(y_1) S_1(y_1, x_1) \dots \\ &\quad \dots \psi^+(y_{n+J}) S_1(y_{n+J}, x_{n+J}) \\ &\quad \cdot f(x_{n+J}, \dots, x_1 | x'_1, \dots, x'_n) S_0(x'_n, y'_n) \psi(y'_n) \dots \\ &\quad \dots S_0(x'_1, y'_1) \psi(y'_1) |\Omega_\psi\rangle. \end{aligned} \quad (6.1)$$

* Remember our extended Einstein convention, for instance,

$$w^\dagger S_0 \psi = \sum_s \iint d^3x d^3x' w_s^\dagger(\mathbf{x}) S_0(\mathbf{x}, \mathbf{x}') \psi_s(\mathbf{x}').$$

and

$$\begin{aligned} |R\rangle &= \chi_R(\psi^+ S_1, S_0 \psi) |\Omega_\psi\rangle \\ &= \sum_{n=0}^{\infty} \frac{1}{(n+J')! n!} \psi^+(y_1) S_1(y_1, x_1) \dots \\ &\quad \dots \psi^+(y_{n+J'}) S_1(y_{n+J'}, x_{n+J'}) \\ &\quad \cdot g(x_{n+J'}, \dots, x_1 | x'_1, \dots, x'_n) \cdot S_0(x'_n, y'_n) \psi(y'_n) \dots \\ &\quad \dots S_0(x'_1, y'_1) \psi(y'_1) |\Omega_\psi\rangle. \end{aligned} \quad (6.2)$$

According to even or odd values of J or J' we define so-called “even” or “odd” states. $J > 0$ describes a state with J excess electrons, while $J < 0$ corresponds to a state with J defect electrons (holes). Because there are no states with negative particle numbers, in the case of $J < 0$, $|J|$ may not exceed the particle number of the physical vacuum state $|\Omega_\psi\rangle$.

Due to the special combinations of the field operators ψ^+ , ψ and the projection operators S_0 , S_1 in (6.1), (6.2), we have the following properties: if both J and J' are either even or odd, the operators $\chi_H(\psi^+ S_1, S_0 \psi)$ and $\chi_R(\psi^+ S_1, S_0 \psi)$ will commute. If J is even and J' is odd, or vice versa, χ_H and χ_R will anticommute. Subsequently, we note that the states $|H\rangle$ and $|R\rangle$ may be chosen independently.

To convert the NTD-equation (5.17) into a functional equation, we need the operator equations

$$\Gamma \psi \Gamma^{-1} = S_1 \psi + i v^+ - i S_1 w, \quad (6.3)$$

$$\Gamma \psi^+ \Gamma^{-1} = \psi^+ S_0 + i w^+ - i v S_0, \quad (6.4)$$

and the identities

$$i \psi^+ \Gamma |\Omega\rangle = (v S_1 + w^+ S_0) \Gamma |\Omega\rangle, \quad (6.5)$$

$$i \psi \Gamma |\Omega\rangle = (S_0 w + S_1 v^+) \Gamma |\Omega\rangle. \quad (6.6)$$

The result is a functional equation in the form of a linear eigenvalue problem

$$\mathbb{B} |\Phi_{HR}\rangle = \omega_{HR} |\Phi_{HR}\rangle \quad (6.7)$$

with

$$|\Phi_{HR}\rangle = [\chi_R(i v S_1, i S_0 w)]^+ \chi_H(i w^+ S_1, i S_0 v^+) |O_{vw}\rangle \quad (6.8)$$

$$\begin{aligned} \mathbb{B} &= \mathbb{H}_H(i w^+ S_1 - i v S_0, i S_0 v^+ - i S_1 w) \\ &\quad - \mathbb{H}_R(i S_0 w + i S_1 v^+, -i v S_1 - i w^+ S_0). \end{aligned} \quad (6.9)$$

Hence, the quantum mechanical problem is mapped in the $H_c \hat{\otimes} H_w$ -space mentioned above. Because of the new arguments in \mathbb{H}_H and \mathbb{H}_R , it is easy to see that these particle number conserving Hamiltonians commute:

$$[\mathbb{H}_H, \mathbb{H}_R]_- = 0. \quad (6.10)$$

In χ_H , the arguments $\psi^+ S_1$ and $S_0 \psi$ are transformed into $i w^+ S_1$ and $i S_0 v^+$. In the same way, the variables $\psi^+ S_1$ and $S_0 \psi$ in χ_R are converted to $[i v S_1]^+ = -i S_1 v^+$ and $[i S_0 w]^+ = -i w^+ S_0$.

A normal ordering of creation and destruction operators yields the following representation of the first term of \mathbb{B} :

$$\begin{aligned} \mathbb{H}_H(i w^+ S_1 - i v S_0, i S_0 v^+ - i S_1 w) \\ = \mathbb{H}_H^{(0)} + \mathbb{H}_H^{(1)} + \mathbb{H}_H^{(1)+} + \mathbb{H}_H^{(2)} + \mathbb{H}_H^{(2)+}, \end{aligned} \quad (6.11)$$

$$\begin{aligned} \mathbb{H}_H^{(0)} &= w^+(y) S_1(y, x) (D(x, x') + V_H(x, \tilde{Y}) \delta(x - x')) S_1(x', y') w(y') \\ &\quad - v^+(y) S_0^*(y, x) (D^*(x, x') + V_H^*(x, \tilde{Y}) \delta(x - x')) S_0^*(x', y') v(y') + \text{Tr} [V_H(x, \tilde{Y}) S_0(x, x)] \\ &\quad + \frac{1}{2} w^+(y) S_1(y, x) w^+(y') S_1(y', x') \frac{e^2}{|x - x'|} S_1(x', y'') w(y'') S_1(x, y''') w(y''') \\ &\quad + \frac{1}{2} v^+(y) S_0^*(y, x) v^+(y') S_0^*(y', x') \frac{e^2}{|x - x'|} S_0^*(x', y'') v(y'') S_0^*(x, y''') v(y''') \\ &\quad + w^+(y) S_1(y, x) S_0(x, y') v^+(y') \frac{e^2}{|x - x'|} v(y'') S_0(y'', x') S_1(x', y''') w(y''') \\ &\quad - w^+(y) S_1(y, x) v^+(y') S_0^*(y', x') \frac{e^2}{|x - x'|} S_0^*(x', y'') v(y'') S_1(x, y''') w(y'''), \end{aligned} \quad (6.12)$$

and

$$\begin{aligned} \mathbb{H}_H^{(1)} &= -w^+(y) S_1(y, x) (D(x, x') + V_H(x, \tilde{Y}) \delta(x - x')) S_0(x', y') v^+(y') \\ &\quad - w^+(y) S_1(y, x) w^+(y') S_1(y', x') \frac{e^2}{|x - x'|} S_0(x', y'') v^+(y'') S_1(x, y''') w(y''') \\ &\quad + v^+(y) S_0^*(y, x) w^+(y') S_1(y', x') \frac{e^2}{|x - x'|} S_0(x', y'') v^+(y'') S_0^*(x, y''') v(y''') \end{aligned} \quad (6.13)$$

as well as

$$\mathbb{H}_H^{(2)} = \frac{1}{2} w^+(y) S_1(y, x) w^+(y') S_1(y', x') \frac{e^2}{|x - x'|} S_0(x', y'') v^+(y'') S_0(x, y''') v^+(y'''). \quad (6.14)$$

The reference Hamiltonian in (6.9) is obtained by a suitable procedure:

$$\mathbb{H}_R(i S_0 w + i S_1 v^+, -i v S_1 - i w^+ S_0) = \mathbb{H}_R^{(0)} + \mathbb{H}_R^{(1)} + \mathbb{H}_R^{(1)+} + \mathbb{H}_R^{(2)} + \mathbb{H}_R^{(2)+} \quad (6.15)$$

with

$$\begin{aligned} \mathbb{H}_R^{(0)} &= v^+(y) S_1^*(y, x) D^*(x, x') S_1^*(x', y') v(y') - w^+(y) S_0(y, x) D(x, x') S_0(x', y') w(y') \\ &+ \frac{1}{2} v^+(y) S_1^*(y, x) v^+(y') S_1^*(y', x') \frac{e^2}{|x - x'|} S_1^*(x', y'') v(y'') S_1^*(x, y''') v(y''') \\ &+ \frac{1}{2} w^+(y) S_0(y, x) w^+(y') S_0(y', x') \frac{e^2}{|x - x'|} S_0(x', y'') w(y'') S_0(x, y''') w(y''') \\ &+ w^+(y) S_0(y, x) S_1(x, y') v^+(y') \frac{e^2}{|x - x'|} v(y'') S_1(y'', x') S_0(x', y''') w(y''') \\ &- w^+(y) S_0(y, x) v^+(y') S_1^*(y', x') \frac{e^2}{|x - x'|} S_1^*(x', y'') v(y'') S_0(x, y''') w(y''') \end{aligned} \quad (6.16)$$

and

$$\begin{aligned} \mathbb{H}_R^{(1)} &= -w^+(y) S_0(y, x) D(x, x') S_1(x', y') v^+(y') \\ &+ w^+(y) S_0(y, x) w^+(y') S_0(y', x') \frac{e^2}{|x - x'|} S_1(x', y'') v^+(y'') S_0(x, y''') w(y''') \\ &- v^+(y) S_1^*(y, x) w^+(y') S_0(y', x') \frac{e^2}{|x - x'|} S_1(x', y'') v^+(y'') S_1^*(x, y''') v(y''') \end{aligned} \quad (6.17)$$

as well as

$$\mathbb{H}_R^{(2)} = \frac{1}{2} w^+(y) S_0(y, x) w^+(y') S_0(y', x') \frac{e^2}{|x - x'|} S_1(x', y'') v^+(y'') S_1(x, y''') v^+(y'''). \quad (6.18)$$

The term $D(x, x')$ in (6.12) to (6.17) is in the form of a Hartree-Fock operator*

$$D(x, x') = \left\{ H(x, \tilde{X}) + e^2 \int d^3y \, 2 \frac{S_0(y, y)}{|x - y|} \right\} \delta(x - x') - e^2 \frac{S_0(x, x')}{|x - x'|} =: D(x, x', \tilde{X}) \quad (6.19)$$

with $H(x, \tilde{X})$ from (5.2), Coulomb interaction

$$e^2 \int d^3y \, 2 \frac{S_0(y, y)}{|x - y|} \quad \text{and exchange interaction} \quad -e^2 \frac{S_0(x, x')}{|x - x'|}$$

which is easily recognized if an expansion of the type (5.14) is introduced for $S_0(x, x')$.

* Due to spin degeneration, the factor 2 originates from formal contractions, e.g., $\sum_s w_s(x) w_s^+(x') = 2 \delta(x - x')$
 $-\sum_s w_s^+(x') w_s(x).$

In order to get more familiar with the structure of the Hamiltonians (6.11) and (6.15), we make some useful identifications: In \mathbb{H}_H we interpret the operators $w(\mathbf{x})$ and $v(\mathbf{x})$ as field operators $a(\mathbf{x})$ of electrons, and as $d(\mathbf{x})$ of defect electrons (holes), respectively, in the following way

$$\begin{aligned} i w^+(\mathbf{y}) S_1(\mathbf{y}, \mathbf{x}) &\equiv a^+(\mathbf{x}); & -i S_1(\mathbf{x}, \mathbf{y}) w(\mathbf{y}) &\equiv a(\mathbf{x}); \\ i S_0(\mathbf{x}, \mathbf{y}) v^+(\mathbf{y}) &\equiv d^+(\mathbf{x}); & -i v(\mathbf{y}) S_0(\mathbf{y}, \mathbf{x}) &\equiv d(\mathbf{x}). \end{aligned} \quad (6.20)$$

On the other hand, we define in \mathbb{H}_R

$$\begin{aligned} -i S_1(\mathbf{x}, \mathbf{y}) v^+(\mathbf{y}) &\equiv a^+(\mathbf{x}); & i v(\mathbf{y}) S_1(\mathbf{y}, \mathbf{x}) &\equiv a(\mathbf{x}); \\ -i w^+(\mathbf{y}) S_0(\mathbf{y}, \mathbf{x}) &\equiv d^+(\mathbf{x}); & i S_0(\mathbf{x}, \mathbf{y}) w(\mathbf{y}) &\equiv d(\mathbf{x}). \end{aligned} \quad (6.21)$$

If we expand $a(\mathbf{x})$ and $d(\mathbf{x})$ with respect to a complete set of one-particle wavefunctions $b_k(\mathbf{x})$

$$a_s(\mathbf{x}) = \sum_{k \text{ unocc.}} a_{k,s} b_k(\mathbf{x}), \quad d_s(\mathbf{x}) = \sum_{k \text{ occ.}} d_{k,s} b_k^*(\mathbf{x}) \quad (6.22)$$

then, apart from a constant term and the additional proton potential, \mathbb{H}_H can be written in accordance with the Hamiltonian obtained by Haken [8] due to an electron-hole transformation. The reference system can be treated in a similar way.

Interpreting $a_k^+ d_k^+$ as creation operator of an electron-hole pair, i.e. attaching d_k^+ the eigenvalue (-1) of the number operator, the particle number conservation is guaranteed. With the above identifications we gain

$$\begin{aligned} \chi_H |O_{vw}\rangle &= \sum_{n=0}^{\infty} \frac{(-1)^n i^J}{(n+J)! n!} w^+(y_1) S_1(y_1, x_1) \dots w^+(y_{n+J}) S_1(y_{n+J}, x_{n+J}) \\ &\quad \cdot f(x_{n+J}, \dots, x_1 | x'_1, \dots, x'_n) S_0(x'_n, y'_n) v^+(y'_n) \dots S_0(x'_1, y'_1) v^+(y'_1) |O_{vw}\rangle \\ &= \sum_{n=0}^{\infty} \frac{1}{(n+J)! n!} \sum_{\substack{k_1, \dots, k_{n+J} \\ k'_1, \dots, k'_n}} a_{k_1}^+ \dots a_{k_{n+J}}^+ f_{k_1, \dots, k_{n+J} k'_1, \dots, k'_n} d_{k'_n}^+ \dots d_{k'_1}^+ |O_{vw}\rangle \end{aligned} \quad (6.23)$$

$$\begin{aligned} \chi_R^+ |O_{vw}\rangle &= \sum_{n=0}^{\infty} \frac{(-1)^{n+J'} i^{J'}}{(n+J')! n!} S_1(x_1, y_1) v^+(y_1) \dots S_1(x_{n+J'}, y_{n+J'}) v^+(y_{n+J'}) \\ &\quad \cdot g^*(x_{n+J'}, \dots, x_1 | x'_1, \dots, x'_n) w^+(y'_n) S_0(y'_n, x'_n) \dots w^+(y'_1) S_0(y'_1, x'_1) |O_{vw}\rangle \\ &= \sum_{n=0}^{\infty} \frac{1}{(n+J')! n!} \sum_{\substack{k_1, \dots, k_{n+J'} \\ k'_1, \dots, k'_n}} a_{k_1}^+ \dots a_{k_{n+J'}}^+ g_{k_1, \dots, k_{n+J'} k'_1, \dots, k'_n}^* d_{k'_n}^+ \dots d_{k'_1}^+ |O_{vw}\rangle. \end{aligned} \quad (6.24)$$

We return to the functional equation (6.7). Instead of solving equation (6.7), we can achieve the same effect by calculating the solution of

$$\langle \Phi' | \mathbb{B} \Phi_{HR} \rangle = \omega_{HR} \langle \Phi' | \Phi_{HR} \rangle \quad (6.25)$$

for all states $|\Phi'\rangle = \Phi' |O_{vw}\rangle$ with $\Phi' \in \mathbf{1} \hat{\otimes} \mathcal{A}_v \hat{\otimes} \mathcal{A}_w$. If we select special states of the form *

$$\begin{aligned} |\Phi'\rangle &\equiv |\Phi^{m+J, m'+J'}(\mathbf{x}, \mathbf{x}', \mathbf{x}'', \mathbf{x}'')\rangle \\ &= \prod_{i=0}^{m+J} w^+(y_i) S_1(y_i, x_i) \prod_{j=0}^m v^+(y'_j) S_0^*(y'_j, x'_j) \prod_{i'=0}^{m'+J'} v^+(y'_{i'}) S_1^*(y'_{i'}, x'_{i'}) \\ &\quad \cdot \prod_{j'=0}^{m'} w^+(y'_{j'}) S_0(y'_{j'}, x'_{j'}) |O_{vw}\rangle \end{aligned} \quad (6.26)$$

we can build up from (6.25) a hierarchy of coupled many-body Schrödinger equations corresponding to fixed J and J' . m and J denote the number of electron-hole pairs and the number of excess electrons, respec-

* We note that the factors corresponding to $i=0$ (or $j=0$ or $i'=0$ or $j'=0$) are defined as unity operator $\mathbf{1}$.

tively. Now the so-called “NTD-approximations” result from a quadratic cut-off procedure applied to such a system of equations.

The easiest way to calculate approximations is to define projection operators

$$\mathbb{P}^{M+J, M'+J'} := \sum_{m=0}^M \sum_{m'=0}^{M'} \mathbb{P}^{m+J, m'+J'} \quad (6.27)$$

with

$$\mathbb{P}^{m+J, m'+J'} := \int d^3x d^3x' d^3x'' d^3x''' |\Phi^{m+J, m'+J'}(\mathbf{x}, \mathbf{x}', \mathbf{x}'', \mathbf{x}''')\rangle \frac{1}{(m+J)! m! (m'+J')! m'!} \cdot \langle \Phi^{m+J, m'+J'}(\mathbf{x}, \mathbf{x}', \mathbf{x}'', \mathbf{x}''')| \quad (6.28)$$

and the properties

$$\sum_{J, J'=0}^{\infty} \lim_{\substack{M \rightarrow \infty \\ M' \rightarrow \infty}} \mathbb{P}^{M+J, M'+J'} = \mathbb{1} \quad (\text{unity operator}) \quad (6.29)$$

$$\langle \Phi^{m+J, m'+J'}(\mathbf{x}, \mathbf{x}', \mathbf{x}'', \mathbf{x}''') | \mathbb{P}^{M+J, M'+J'} = \langle \Phi^{m+J, m'+J'}(\mathbf{x}, \mathbf{x}', \mathbf{x}'', \mathbf{x}''') | \quad (6.30)$$

for all m, m' with $m \leq M, m' \leq M'$

which are inserted in equation (6.25)

$$\langle \Phi^{m+J, m'+J'} | \mathbb{P}^{M+J, M'+J'} \mathbb{B} \mathbb{P}^{M+J, M'+J'} \Phi_{HR} \rangle = \omega_{HR} \langle \Phi^{m+J, m'+J'} | \mathbb{P}^{M+J, M'+J'} \Phi_{HR} \rangle. \quad (6.31)$$

Using (6.30), we get

$$\langle \Phi^{m+J, m'+J'} | \mathbb{B} \mathbb{P}^{M+J, M'+J'} \Phi_{HR} \rangle = \omega_{HR} \langle \Phi^{m+J, m'+J'} | \Phi_{HR} \rangle \quad \text{with } m \leq M, m' \leq M'. \quad (6.32)$$

Given fixed integers J, J' and M, M' we obtain with $m = 0, 1, \dots, M$ and $m' = 0, 1, \dots, M'$ a finite system of coupled equations for approximate computations of J -particle states in the H -system and J' -particle states in the reference system.

§ 7. One-centre problem

We consider a physical model by putting one single proton in the position $\tilde{\mathbf{Y}}$ and one single additional electron into the metal crystal. These particles induce a polarization field. One can describe it by adding particle-hole pairs to the Hartree-Fock initial state, but the treatment of such effects is beyond the topic of this paper. Likewise, we choose the simplest reference state, namely the N -electron Hartree-Fock problem of a disturbed metal lattice. Hence, in (6.32) we set $M = M' = 0$ and $J = 1, J' = 0$. This radical cut-off can be considered as a kind of zeroth order approximation. Using (6.11) and (6.15), equation (6.32) can be rewritten in a non-local one particle Schrödinger equation

$$\begin{aligned} S_1(\mathbf{z}, \mathbf{x}) & \left(D(\mathbf{x}, \mathbf{x}', \tilde{\mathbf{X}}) - \frac{e^2}{|\mathbf{x} - \tilde{\mathbf{Y}}|} \delta(\mathbf{x} - \mathbf{x}') \right) \\ & \cdot S_1(\mathbf{x}', \mathbf{y}') h_s(\mathbf{y}') \\ & = (\omega(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) - \text{Tr}[V_H(\mathbf{x}, \tilde{\mathbf{Y}}) S_0(\mathbf{x}, \mathbf{x})]) h_s(\mathbf{z}) \quad (7.1) \end{aligned}$$

with

$$h_s(\mathbf{z}) := \langle \Phi_s^{0+1,0+0}(\mathbf{z}) | \Phi_{HR} \rangle. \quad (7.2)$$

The (divergent) constant

$$\text{Tr}[V_H(\mathbf{x}, \tilde{\mathbf{Y}}) S_0(\mathbf{x}, \mathbf{x})] = -e^2 \int d^3x \, 2 \frac{S_0(\mathbf{x}, \mathbf{x})}{|\mathbf{x} - \tilde{\mathbf{Y}}|} \quad (7.3)$$

represents the screened proton potential and is subtracted from the energy difference value ω . Inserting (6.19) into (7.1) and expanding the projection operators $S_0(\mathbf{x}, \mathbf{x}')$, $S_1(\mathbf{x}, \mathbf{x}')$ with respect to Bloch functions $b_k^0(\mathbf{x})$ of the ideal crystal, i.e. with respect to solutions of the Hartree-Fock problem

$$\begin{aligned} D(\mathbf{x}, \mathbf{x}', \tilde{\mathbf{X}}^0) b_k^0(\mathbf{x}') & = \left\{ \left(-\frac{\hbar^2}{2m_e} \Delta + V(\mathbf{x}, \tilde{\mathbf{X}}^0) \right. \right. \\ & \quad \left. \left. + e^2 \sum_{l \text{ occ.}} \int d^3y \, 2 \frac{b_l^0(\mathbf{y}) b_l^{0*}(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \right) \delta(\mathbf{x} - \mathbf{x}') \right. \\ & \quad \left. - e^2 \sum_{l \text{ occ.}} \frac{b_l^0(\mathbf{x}) b_l^{0*}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \right\} b_k^0(\mathbf{x}') = \varepsilon_k b_k^0(\mathbf{x}) \quad (7.4) \end{aligned}$$

we are left with the Schrödinger equation

$$\sum_{l,l' \text{ unocc.}} b_l^0(\mathbf{z}) \left\{ \varepsilon_l \delta_{ll'} + \int d^3x b_l^{0*}(\mathbf{x}) \cdot \left[\sum_{m,i} (V_i(\mathbf{x} - \tilde{\mathbf{X}}_{m,i}) - V_i(\mathbf{x} - \tilde{\mathbf{X}}_{m,i}^0)) - \frac{e^2}{|\mathbf{x} - \tilde{\mathbf{Y}}|} \right] b_l^0(\mathbf{x}) \right\} b_{l'}^{0*}(\mathbf{x}') h_s(\mathbf{x}') = \lambda^{(1)}(\tilde{\mathbf{X}}, \tilde{\mathbf{Y}}) h_s(\mathbf{z}), \quad (7.5)$$

where

$$\lambda^{(1)}(\tilde{\mathbf{X}}, \tilde{\mathbf{Y}}) := \omega(\tilde{\mathbf{X}}, \tilde{\mathbf{Y}}) + e^2 \sum_{l \text{ occ.}} \int d^3y 2 \frac{b_l^0(\mathbf{y}) b_l^{0*}(\mathbf{y})}{|\mathbf{y} - \tilde{\mathbf{Y}}|}. \quad (7.6)$$

The index (1) corresponds to one single hydrogen proton in the crystal.

We end this section with a transformation of the Schrödinger problem (7.5) into an integral equation. For this purpose we state (7.5) in the following way

$$\sum_l b_l^0(\mathbf{z}) (g_l \varepsilon_l - \lambda^{(1)}) b_l^{0*}(\mathbf{x}') h_s(\mathbf{x}') = A_s(\mathbf{z}) \quad (7.7)$$

with

$$A_s(\mathbf{z}) = - \sum_{l,l' \text{ unocc.}} b_l^0(\mathbf{z}) b_l^{0*}(\mathbf{x}) \cdot \left[\sum_{m,i} (V_i(\mathbf{x} - \tilde{\mathbf{X}}_{m,i}) - V_i(\mathbf{x} - \tilde{\mathbf{X}}_{m,i}^0)) - \frac{e^2}{|\mathbf{x} - \tilde{\mathbf{Y}}|} \right] \cdot b_{l'}^0(\mathbf{x}) b_{l'}^{0*}(\mathbf{x}') h_s(\mathbf{x}') \quad (7.8)$$

and

$$g_l := \begin{cases} 0 & \text{if } l \in \{\text{occupied states}\} \\ 1 & \text{if } l \in \{\text{unoccupied states}\} \end{cases}. \quad (7.9)$$

We obtain the inversion of the left-hand side of (7.7) with the aid of the Green function

$$G(\mathbf{y}, \mathbf{z}, \lambda^{(1)}) = \sum_q \frac{b_q^0(\mathbf{y}) b_q^{0*}(\mathbf{z})}{g_q \varepsilon_q - \lambda^{(1)}}. \quad (7.10)$$

The result is

$$h_s(\mathbf{y}) = - \sum_q b_q^0(\mathbf{y}) \frac{1}{g_q \varepsilon_q - \lambda^{(1)}} b_q^0(\mathbf{z}) A_s(\mathbf{z}) = - \sum_q \frac{b_q^0(\mathbf{y}) g_q b_q^{0*}(\mathbf{x})}{\varepsilon_q - \lambda^{(1)}} \cdot \left[\sum_{m,i} (V_i(\mathbf{x} - \tilde{\mathbf{X}}_{m,i}) - V_i(\mathbf{x} - \tilde{\mathbf{X}}_{m,i}^0)) - \frac{e^2}{|\mathbf{x} - \tilde{\mathbf{Y}}|} \right] \cdot S_1(\mathbf{x}, \mathbf{z}) h_s(\mathbf{z}). \quad (7.11)$$

Multiplying from the left by $S_0(\mathbf{x}, \mathbf{y})$ and integrating over all \mathbf{y} (note our extended Einstein convention of § 5), we get

$$S_0(\mathbf{x}, \mathbf{y}) h_s(\mathbf{y}) = 0 \quad (7.12)$$

as a consequence of (5.7). The same procedure with $S_1(\mathbf{x}, \mathbf{y})$ instead of $S_0(\mathbf{x}, \mathbf{y})$ leads to the integral equation

$$\varphi_s(\mathbf{x}) - K(\mathbf{x}, \mathbf{z}, \lambda^{(1)}) \varphi_s(\mathbf{z}) = 0 \quad (7.13)$$

with a kind of “pseudo function”

$$\varphi_s(\mathbf{x}) := S_1(\mathbf{x}, \mathbf{y}) h_s(\mathbf{y}) \quad (7.14)$$

and the kernel*

$$K(\mathbf{x}, \mathbf{z}, \lambda) = - \sum_q \frac{b_q^0(\mathbf{x}) g_q b_q^{0*}(\mathbf{z})}{\varepsilon_q - \lambda} \cdot \left[\sum_{m,i} (V_i(\mathbf{z} - \tilde{\mathbf{X}}_{m,i}) - V_i(\mathbf{z} - \tilde{\mathbf{X}}_{m,i}^0)) - \frac{e^2}{|\mathbf{z} - \tilde{\mathbf{Y}}|} \right]. \quad (7.15)$$

The integral representation allows the inclusion of special lattice properties in the problem, because it could be more simple to compute the Green function (7.10) with respect to realistic Bloch functions (even with Bloch functions of displaced lattice cores) than to solve the differential equation (7.5). So, in simple metals, one can use pseudo-potentials to approximate the lattice potential $V(\mathbf{x}, \tilde{\mathbf{X}})$ and to compute appropriate Bloch functions with the aid of the perturbation theory. Essentially, the formulation of the Green function is then only a problem of integration. On expanding the kernel of the integral equation, for instance with respect to hydrogen wavefunctions, and applying a qualified cut-off criterion, one is left with an integral kernel of finite rank. Obviously, introducing a delta function into (7.13) and representing it as a completeness relation relative to hydrogen wavefunctions ψ_{nlms} , we can multiply (7.13) with $\psi_{nlms}^*(\mathbf{x})$ and integrate over all \mathbf{x} . Hence, we obtain an algebraic eigenvalue equation

$$\begin{aligned} \psi_{nlms}^*(\mathbf{x}) (\varphi_s(\mathbf{x}) - K(\mathbf{x}, \mathbf{z}, \lambda) \delta(\mathbf{z} - \mathbf{z}') \varphi_s(\mathbf{z}')) \\ = \psi_{nlms}^*(\mathbf{x}) \varphi_s(\mathbf{x}) - \psi_{nlms}^*(\mathbf{x}) K(\mathbf{x}, \mathbf{z}, \lambda) \\ \cdot \sum_{n', l', m'} \psi_{n' l' m'}(\mathbf{z}) \psi_{n' l' m'}^*(\mathbf{z}') \varphi_s(\mathbf{z}') \\ = c_{nlms} - \sum_{n', l', m'} K_{nlms, n' l' m'}(\lambda) c_{n' l' m'} = 0, \end{aligned} \quad (7.16)$$

* In this place, we renounce on our extended Einstein convention.

where the c_{nlms} denote the expansion coefficients with respect to hydrogen wavefunctions

$$c_{nlms} = \int \psi_{nlms}^*(\mathbf{x}) \varphi_s(\mathbf{x}) d^3x \quad (7.17)$$

and $K_{nlms, n'l'm's}(\lambda)$ represents the matrix elements

$$K_{nlms, n'l'm's}(\lambda) = \int \psi_{nlms}^*(\mathbf{x}) K(\mathbf{x}, \mathbf{z}, \lambda) \psi_{n'l'm's}(\mathbf{z}) d^3x d^3z. \quad (7.18)$$

An extended investigation of the one-centre problem based on (7.5) is already done. We have calculated the electronic ground state energy and the

resulting distortion forces with respect to host lattice displacements. Using the equilibrium conditions for distorting and reacting forces the new lattice positions are fixed which enables us to compute the volume extension.

A current work is concerned with the n -centre problem. The great importance of diffusion of hydrogen in metals forces us to take into account the non-adiabatic terms F_y and F_x in (1.14) and (1.15).

Both points will be topics of subsequent papers.

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