

# Electron Density Distribution of a Single Hydrogen Perturbation in a Metal Lattice

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Z. Naturforsch. **42 a**, 431–437 (1987); received January 23, 1987

The electronic structure of hydrogen centres stored in a metal crystal is described by a microscopic theory based on a functional energy difference method. That formalism works in a suitably chosen tensor product space built on a physical quasi-particle vacuum state. A transformation back to a bare Fock space representation is shown. This transformation operator divides the functional eigenvalue equation into a difference of two Schrödinger problems. The resulting state vectors can be used to calculate the electronic density distribution of a hydrogen excess electron in a metal lattice. The density function is obtained in a higher order approximation which considers the influence of three-particle correlations. A numerical solution is discussed for the case of a single hydrogen centre in a magnesium crystal. The plot shows that the excess electron is mainly localized in the surroundings of the corresponding hydrogen core. But with increasing host lattice extension there is more and more a non-vanishing probability to find the hydrogen electron dipped into the Fermi sea of metal electrons.

## Introduction

In a preceding paper we computed the electronic contribution to the storage energy of a single hydrogen impurity in a metal crystal [1]. The calculation was performed in a higher order approximation which considered the coupling between one-electron wavefunctions and three-particle amplitudes. The foundations of this theory were based on a functional energy difference method presented in [2].

As a follow-on study, the intention of the current work is to determine the influence of three-particle correlations on the electron density distribution in the surroundings of an interstitial hydrogen centre. These evaluations are easy to do as long as we stay in the valence band representation considered in [1]. But the contribution of our higher order approximation takes only effect if the wavefunctions are transformed back into the original Fock space representation built on a bare vacuum state. After a brief summary of the theoretical background of our formalism, we derive an explicit expression for that reverse transformation. Applied to the wavefunctions which correspond to the energy eigenvalues

obtained in [1], we get the effective radial density distribution of a single hydrogen excess electron in a metal hydride, and in addition its alterations due to three-particle interactions.

## 1. Review on the General Formalism

Originally, the electronic subsystem of stored hydrogen atoms in a metal lattice is characterized by two many-particle Schrödinger equations:

$$\begin{aligned} \mathbb{H}_H(\psi^+, \psi) \chi_H(\psi^+) |O_\psi\rangle &= E_H \chi_H(\psi^+) |O_\psi\rangle, \\ \mathbb{H}_R(\psi^+, \psi) \chi_R(\psi^+) |O_\psi\rangle &= E_R \chi_R(\psi^+) |O_\psi\rangle. \end{aligned} \quad (1.1)$$

For notations and abbreviations, as e.g. our extended Einstein convention, we refer to [1].

According to the particle-hole formulation of Haken [3], we pass from the Fock space representation corresponding to the bare vacuum state  $|O_\psi\rangle$  into a kind of valence band representation where the vacuum state vector  $|\Omega_\psi\rangle$  is identified with a physical quasi-particle vacuum in a completely occupied valence band [4].

Besides, the system (1.1) is rewritten in [1, 2]:

$$\begin{aligned} \mathbb{H}_H(\psi^+, \psi) \chi_H(\psi^+ S_1, S_0 \psi) |\Omega_\psi\rangle &= E_H \chi_H(\psi^+ S_1, S_0 \psi) |\Omega_\psi\rangle \\ \mathbb{H}_R(\psi^+, \psi) \chi_R(\psi^+ S_1, S_0 \psi) |\Omega_\psi\rangle &= E_R \chi_R(\psi^+ S_1, S_0 \psi) |\Omega_\psi\rangle. \end{aligned} \quad (1.2)$$

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The main advantage of this macroscopic transition is that we do not have to consider the interaction of conduction electrons neither in the H-system nor in the R-system. Both are reciprocally compensated when we calculate the energy difference

$$\omega := E_H - E_R. \quad (1.3)$$

With the help of the generating operator [1, 2]

$$\Gamma = e^{i(w^+ - v)S_0\psi} e^{i(v^+ - w)S_1^\dagger\psi^+} e^{i(w^+ + v)S_1\psi} e^{i(v^+ + w)S_0^\dagger\psi^+} \quad (1.4)$$

we achieve a reformation of (1.2) in form of a functional equation [1, 2]

$$\mathbb{B}|\Phi_{HR}\rangle = \omega|\Phi_{HR}\rangle, \quad (1.5)$$

where  $\mathbb{B}$  denotes a functional difference Hamiltonian

$$\begin{aligned} \mathbb{B} = & \mathbb{H}_H(iw^+S_1 - ivS_0, iS_0v^+ - iS_1w) \\ & - \mathbb{H}_R(iS_0w + iS_1v^+, -ivS_1 - iw^+S_0) \end{aligned} \quad (1.6)$$

and  $|\Phi_{HR}\rangle$  is the corresponding eigenvector

$$|\Phi_{HR}\rangle = [\chi_R(-ivS_1, iS_0w)]^+ \chi_H(iw^+S_1, iS_0v^+) |O_{vw}\rangle \quad (1.7)$$

acting in a CAR-tensor product space built on a vacuum state

$$|O_{vw}\rangle = |O_v\rangle \otimes |O_w\rangle. \quad (1.8)$$

Wahl and Feist [4] showed that calculating the solution of (1.5) in  $v$ - $w$ -space is equivalent to solving the system (1.1) in  $\psi$ -space.

A numerical solution of (1.5) has been achieved by Göbel [1, 5] when treating one additional hydrogen excess electron in a hexagonal magnesium lattice. For this case we considered a Fock space expansion of  $|\Phi_{HR}\rangle$  with respect to one-centre base states  $|\Phi^{m+1, m'+0}\rangle$  ([1], (1.13)):

$$\begin{aligned} |\Phi_{HR}\rangle & \approx |\Phi\rangle := |\Phi_{HR}^{(1,1)}\rangle \\ & = h^{0,0} |\Phi^{0+1,0+0}\rangle + h^{1,0} \frac{1}{2!} |\Phi^{1+1,0+0}\rangle. \end{aligned} \quad (1.9)$$

This series expansion (1.9) represents a higher order approximation because three-particle correlations in the metal hydride are included. Interactions with the R-system are neglected. The expansion coefficients  $h^{v,v'}$  ([1], (2.1)) have been computed [5] and the corresponding energy eigenvalues  $\omega$  are plotted as a function of host lattice displacements  $s$  [1].

For the calculation of an electron density distribution the obtained eigenvectors  $|\Phi_{HR}\rangle$  according to (1.7) are not suitable because they represent a

sort of difference wavefunctions and cannot be identified with real Schrödinger amplitudes. To ensure an interpretation as a normal many-particle wavefunction we have to split  $|\Phi_{HR}\rangle$  into a direct decomposition of states  $|\Phi_v\rangle$  belonging to  $v$ -space and  $|\Phi_w\rangle$  belonging to  $w$ -space:

$$|\Phi_{HR}\rangle \rightarrow |\Phi_v\rangle \otimes |\Phi_w\rangle. \quad (1.10)$$

Returning to the original formulation as in (1.1),  $|\Phi_v\rangle$  and  $|\Phi_w\rangle$  have to be built on a bare vacuum state. In our formalism it is easy to pass back to a bare Fock space representation because the occupation of states is described by the projectors  $S_0(\mathbf{x}, \mathbf{x}')$  and  $S_1(\mathbf{x}, \mathbf{x}')$ , respectively ([2], (5.14a, b)). If we choose

$$S_0(\mathbf{x}, \mathbf{x}') \equiv 0 \quad \text{and} \quad S_1(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'), \quad (1.11)$$

we obtain from (1.4) a reduced generating operator:

$$\Gamma^0 = e^{i(v^+ - w)\psi^+} e^{i(w^+ + v)\psi}. \quad (1.12)$$

The functional operator  $\mathbb{B}$  in (1.16) is then rewritten as a difference of two Hartree-Fock Hamiltonians in usual shape [3]:

$$\mathbb{B}^0 = \mathbb{H}_H^0(iw^+, -iw) - \mathbb{H}_R^0(iv^+, -iv) \quad (1.13)$$

with ([2], (6.9)–(6.19))

$$\begin{aligned} \mathbb{H}_H^0(iw^+, -iw) = & w_s^+(\mathbf{x}) \{D(\mathbf{x}, \mathbf{x}') + V_H(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')\} \\ & \cdot w_s(\mathbf{x}') + \frac{1}{2} w_s^+(\mathbf{x}) w_{s'}^+(\mathbf{x}') \frac{e^2}{|\mathbf{x} - \mathbf{x}'|} w_{s'}(\mathbf{x}') w_s(\mathbf{x}) \end{aligned} \quad (1.14)$$

and

$$\begin{aligned} \mathbb{H}_R^0(iv^+, -iv) = & v_s^+(\mathbf{x}) D(\mathbf{x}, \mathbf{x}') v_s(\mathbf{x}') \\ & + \frac{1}{2} v_s^+(\mathbf{x}) v_{s'}^+(\mathbf{x}') \frac{e^2}{|\mathbf{x} - \mathbf{x}'|} v_{s'}(\mathbf{x}') v_s(\mathbf{x}). \end{aligned} \quad (1.15)$$

The state vector  $|\Phi_{HR}\rangle$  in (1.7) becomes

$$|\Phi_{HR}^0\rangle = \chi_R(iv^+) |O_v\rangle \otimes \chi_H(iw^+) |O_w\rangle, \quad (1.16)$$

which means a complete decomposition between  $v$ -space and  $w$ -space.

The purpose of the next chapter is therefore to find a transformation  $T$  such that

$$\mathbb{B}^0 = T\mathbb{B}T^{-1} \quad (1.17)$$

and such that (1.5) is transformed into a functional equation of the form

$$\mathbb{B}^0|\Phi_{vw}\rangle = \omega|\Phi_{vw}\rangle, \quad (1.18)$$

which is trivially equivalent to the system (1.1).

## 2. Reverse Transformation

We will show now the

*Theorem:* The transformation  $T$  leading us back from our physical quasi-particle space into a bare Fock space representation is given by

$$T = e^{v S_0 w} e^{-w^+ S_0 v^+} e^{v S_0 w}. \quad (2.1)$$

With this transformation operator (1.17) is fulfilled and (1.18) is reached.

*Proof:* The main task in proving (2.1) is to show the relation

$$\Gamma^{(-)} = e^{v S_0 w} e^{-w^+ S_0 v^+} e^{v S_0 w} \Gamma e^{-2v S_0 w}. \quad (2.2)$$

To prove (2.2) we use (1.4) and rewrite the right side of (2.2) in the form

$$e^{v S_0 w} e^{-w^+ S_0 v^+} e^{v S_0 w} \Gamma e^{-2v S_0 w} = \Gamma^{(+)} \cdot \Gamma^{(-)} \quad (2.3)$$

with the definitions

$$\Gamma^{(+)} := e^{i(v^+ - w) S_1^*} \psi^+ e^{i(w^+ + v) S_1} \psi, \quad (2.4)$$

$$\Gamma^{(-)} := e^{v S_0 w} e^{-w^+ S_0 v^+} \{ e^{v S_0 w} e^{i(w^+ - v) S_0} \psi \cdot e^{i(v^+ + w) S_0^*} \psi^+ e^{-v S_0 w} \} e^{-v S_0 w}. \quad (2.5)$$

$\Gamma^{(+)}$  consists of all terms containing  $S_1$ . Therefore,  $\Gamma^{(+)}$  commutes ([1], (1.3)) with all other terms which contain  $S_0$  and which are collected in  $\Gamma^{(-)}$ . The idea is now to modify  $\Gamma^{(-)}$  until an expression of the form

$$\Gamma^{(-)} = e^{i(v^+ - w) S_0^*} \psi^+ e^{i(w^+ + v) S_0} \psi \quad (2.6)$$

is reached. This term would then be the complement for  $\Gamma^{(+)}$  to obtain  $\Gamma^0$  in (1.12) ([1], (1.4)):

$$\Gamma^{(+)} \cdot \Gamma^{(-)} = e^{i(v^+ - w) \psi^+} e^{i(w^+ + v) \psi} = \Gamma^0. \quad (2.7)$$

Indeed, we insert a unity operator

$$\mathbb{1} = e^{-v S_0 w} e^{v S_0 w} \quad (2.8)$$

in the middle of the braces in (2.5). Using the operator identity

$$e^A e^B = e^{[A, B]} e^B e^A \quad (2.9)$$

whose prerequisites

$$[A, [A, B]] = [B, [A, B]] = 0 \quad (2.10)$$

are fulfilled in our case, we get

$$\Gamma^{(-)} = e^{v S_0 w} e^{-w^+ S_0 v^+} \{ e^{i w^+ S_0} \psi e^{-i \psi^+ S_0 v^+} \} e^{-v S_0 w}. \quad (2.11)$$

Applying (2.9) again to the braces in (2.11), we obtain

$$\Gamma^{(-)} = e^{v S_0 w} e^{-i \psi^+ S_0 v^+} e^{i w^+ S_0} \psi e^{-v S_0 w}. \quad (2.12)$$

With (2.8) we are led to

$$\Gamma^{(-)} = \{ e^{v S_0 w} e^{-i \psi^+ S_0 v^+} e^{-v S_0 w} \} \{ e^{v S_0 w} e^{i w^+ S_0} \psi e^{-v S_0 w} \} \quad (2.13)$$

which results with (2.9) in (2.6). Thus, (2.2) is proved.

With that connexion in mind it is easy to find (2.1) because we will need  $\Gamma^0$  and  $\Gamma$  only in application to the vacuum state  $|O_{vw}\rangle$  which implies immediately

$$\Gamma^0 |O_{vw}\rangle = T \Gamma |O_{vw}\rangle \quad (2.14)$$

with  $T$  as shown in (2.1).

To prove (1.17) we have to consider the transformation behaviour of  $w^+$ ,  $w$  and  $v^+$ ,  $v$ , respectively. Using a special case of the well-known Campbell-Baker-Hausdorff formula

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2!} [A, [A, B]] + \dots \quad (2.15)$$

we get

$$T w T^{-1} = S_1 w + S_0 v^+, \quad (2.16a)$$

$$T w^+ T^{-1} = w^+ S_1 + v S_0, \quad (2.16b)$$

$$T v T^{-1} = v S_1 - w^+ S_0, \quad (2.16c)$$

$$T v^+ T^{-1} = S_1 v^+ - S_0 w. \quad (2.16d)$$

With these relations it is not a great task to compute the transformed functional Hamilton operator. The result is (1.17):

$$T B T^{-1} = B^0. \quad (2.17)$$

The state vector  $|\Phi_{HR}\rangle$  in (1.7) is transformed in

$$|\Phi_{vw}\rangle := T |\Phi_{HR}\rangle \quad (2.18)$$

$$= [\chi_R(-i v S_1, i S_0 v^+)]^+ \chi_H(i w^+ S_1, -i S_0 w) T |O_{vw}\rangle,$$

which is again a complete decoupling between  $v$ -contributions and  $w$ -parts contained in the wavefunctions.

Equation (1.18) is reached with the aid of (2.17), (2.18), and (1.5):

$$B^0 |\Phi_{vw}\rangle = T B T^{-1} T |\Phi_{HR}\rangle = T \omega |\Phi_{HR}\rangle = \omega |\Phi_{vw}\rangle \quad (2.19)$$

This finishes the proof of our theorem.

The next chapter shows the influence of  $T$  on the electron density distribution.

### 3. Electron Density Distribution

Let  $w^+$  and  $w$  be Fermi operators describing an electron field. The density operator is then defined by [3]

$$\varrho(\mathbf{r}, \sigma) := w_\sigma^+(\mathbf{r}) \omega_\sigma(\mathbf{r}). \quad (3.1)$$

We want to emphasize in particular that we desist now from our extended Einstein convention [1, 2], i.e. multiple appearing variables or indices are no longer integrated or summed up, respectively. Integrations and sums will be noted explicitly.

First, let us investigate the expectation value of  $\varrho$  belonging to the non-transformed states (1.9) as considered in our higher order approximation [1]:

$$\overline{\varrho(\mathbf{r}, \sigma)} = \langle \Phi | w_\sigma^+(\mathbf{r}) \omega_\sigma(\mathbf{r}) | \Phi \rangle. \quad (3.2)$$

In order that (3.2) makes sense as a “particle-density”,  $|\Phi\rangle$  has to be normalized:

$$\langle \Phi | \Phi \rangle = 1. \quad (3.3)$$

This requirement is fulfilled by

$$|\tilde{\Phi}\rangle := \left[ |h^{0,0}|^2 + \frac{1}{2!} |h^{1,0}|^2 \right]^{-1/2} \cdot |\Phi\rangle. \quad (3.4)$$

The mean value (3.2) describing the non-transformed electron density distribution in higher order is then given by

$$\begin{aligned} \overline{\varrho(\mathbf{r}, \sigma)} &= \left[ |h^{0,0}|^2 + \frac{1}{2!} |h^{1,0}|^2 \right]^{-1} \\ &\cdot \left\{ h^{0,0} * \begin{pmatrix} \mathbf{r} \\ \sigma \end{pmatrix} h^{0,0} \begin{pmatrix} \mathbf{r} \\ \sigma \end{pmatrix} + \sum_{\sigma_2 \sigma_3} \int d^3 z_2 \int d^3 z_3 \right. \\ &\cdot \left. h^{1,0} * \begin{pmatrix} \mathbf{r} & \mathbf{z}_2 & \mathbf{z}_3 \\ \sigma & \sigma_2 & \sigma_3 \end{pmatrix} \cdot h^{1,0} \begin{pmatrix} \mathbf{r} & \mathbf{z}_2 & \mathbf{z}_3 \\ \sigma & \sigma_2 & \sigma_3 \end{pmatrix} \right\}. \end{aligned} \quad (3.5)$$

We expect that the main contribution to the density function is due to the one-particle amplitude  $h^{0,0}$  which we obtained in lowest order approximation [6] and which is represented by the first term in (3.5). Figure 1 shows the typical radial density distribution

$$\int h^{0,0} * \begin{pmatrix} \mathbf{r} \\ \sigma \end{pmatrix} h^{0,0} \begin{pmatrix} \mathbf{r} \\ \sigma \end{pmatrix} r^2 d\Omega_r \quad (3.6)$$

for a single hydrogen excess electron in a magnesium crystal. It is obvious that the hydrogen electron is mainly localized in the surroundings of the corre-

sponding hydrogen core sitting in the centre of a metal ion tetrahedron [1]. But there are also contributions of excited states in the density function which increase if the host lattice volume is extended. This implies a non-vanishing probability to find the excess electron outside the tetrahedron because the distance between Mg ions and hydrogen proton is about 3.7 atomic units (a.u.).

Let us compute now the densities after applying the reverse transformation operator  $T$  to the approximate state vector  $|\tilde{\Phi}\rangle$ :

$$\overline{\varrho_T(\mathbf{r}, \sigma)} = \langle T\tilde{\Phi} | w_\sigma^+(\mathbf{r}) \omega_\sigma(\mathbf{r}) | T\tilde{\Phi} \rangle. \quad (3.7)$$

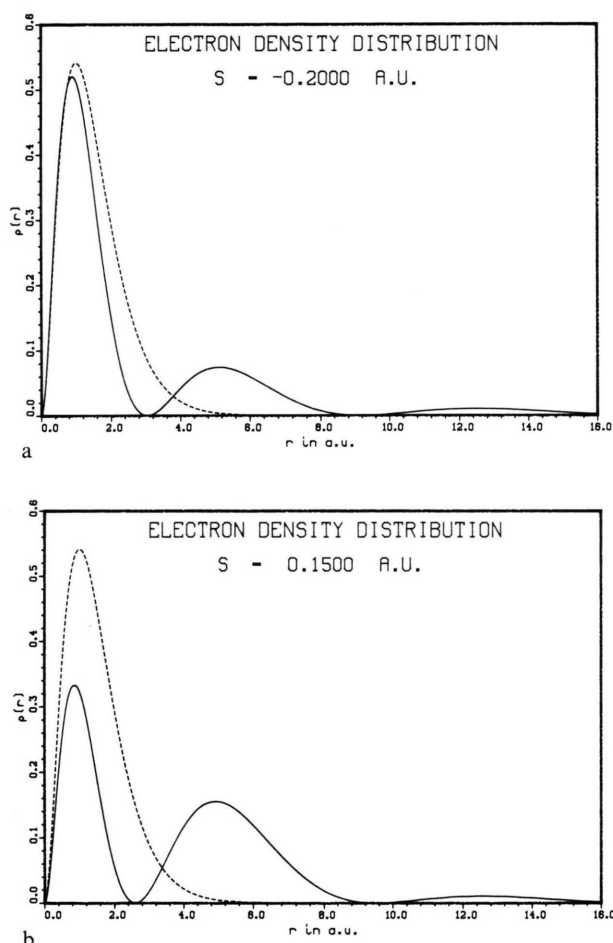


Fig. 1. Radial density distribution  $\varrho(r)$  (solid line) of an interstitial hydrogen electron in Mg compared with the ground state density of a free electron (dashed line) plotted as a function of the distance  $r$  between hydrogen electron and corresponding proton for different values of host lattice distortions  $s$ : a)  $s = -0.20$  a.u. (lattice compression); b)  $s = +0.15$  a.u. (lattice extension).

It is easy to show that  $T$  is norm preserving such that  $|T\tilde{\Phi}\rangle$  is normalized, too:

$$\langle T\tilde{\Phi} | T\tilde{\Phi} \rangle = \langle O_{vw} | T^+ T | O_{vw} \rangle = 1. \quad (3.8)$$

A proof of (3.8) is given in the appendix. With (3.4), (1.9), and [1] (1.13) we get from (3.7):

$$\begin{aligned} \overline{\varrho_T} = & \left\{ h^{0,0*} \cdot h^{0,0} \cdot \langle O_{vw} | S_1 w T^+ w^+ w T w^+ S_1 | O_{vw} \rangle \right. \\ & \left. + h^{1,0*} \cdot h^{1,0} \cdot \frac{1}{2!} \frac{1}{2!} \langle O_{vw} | S_0^* v S_1 w S_1 w T^+ w^+ w T w^+ S_1 w^+ S_1 v^+ S_0^* | O_{vw} \rangle \right\} \left[ |h^{0,0}|^2 + \frac{1}{2!} |h^{1,0}|^2 \right]^{-1}. \end{aligned} \quad (3.9)$$

The expectation values in (3.9) are easy to evaluate using the relations (2.16). They result in

$$\begin{aligned} \overline{\varrho_T}(\mathbf{r}, \sigma) = & \left[ |h^{0,0}|^2 + \frac{1}{2!} |h^{1,0}|^2 \right]^{-1} \cdot \left\{ h^{0,0*} \left( \begin{matrix} \mathbf{r} \\ \sigma \end{matrix} \right) h^{0,0} \left( \begin{matrix} \mathbf{r} \\ \sigma \end{matrix} \right) \right. \\ & + \left[ \sum_s \int d^3z h^{0,0*} \left( \begin{matrix} \mathbf{z} \\ s \end{matrix} \right) h^{0,0} \left( \begin{matrix} \mathbf{z} \\ s \end{matrix} \right) \right] \cdot S_0(\mathbf{r}, \mathbf{r}) \delta_{\sigma\sigma} \\ & + \sum_{\sigma_2 \sigma_3} \int d^3z_2 d^3z_3 h^{1,0*} \left( \begin{matrix} \mathbf{r} & \mathbf{z}_2 & \mathbf{z}_3 \\ \sigma & \sigma_2 & \sigma_3 \end{matrix} \right) h^{1,0} \left( \begin{matrix} \mathbf{r} & \mathbf{z}_2 & \mathbf{z}_3 \\ \sigma & \sigma_2 & \sigma_3 \end{matrix} \right) \\ & + \left[ \frac{1}{2!} \sum_{\sigma_1 \sigma_2 \sigma_3} \int d^3z_1 d^3z_2 d^3z_3 h^{1,0*} \left( \begin{matrix} \mathbf{z}_1 & \mathbf{z}_2 & \mathbf{z}_3 \\ \sigma_1 & \sigma_2 & \sigma_3 \end{matrix} \right) h^{1,0} \left( \begin{matrix} \mathbf{z}_1 & \mathbf{z}_2 & \mathbf{z}_3 \\ \sigma_1 & \sigma_2 & \sigma_3 \end{matrix} \right) \right] \cdot S_0(\mathbf{r}, \mathbf{r}) \delta_{\sigma\sigma} \\ & \left. - \frac{1}{2!} \sum_{\sigma_1 \sigma_2} \int d^3z_1 d^3z_2 h^{1,0*} \left( \begin{matrix} \mathbf{z}_1 & \mathbf{z}_2 & \mathbf{r} \\ \sigma_1 & \sigma_2 & \sigma \end{matrix} \right) h^{1,0} \left( \begin{matrix} \mathbf{z}_1 & \mathbf{z}_2 & \mathbf{r} \\ \sigma_1 & \sigma_2 & \sigma \end{matrix} \right) \right\}. \end{aligned} \quad (3.10)$$

The first and the third terms in (3.10) represent exactly the density (3.5) of the non-transformed system. The second and the fourth terms can be simplified because the existing prefactors are compensated with the normalisation term. In an electron gas model, they both lead to the constant underground of Fermi sea electrons. The last term is interpreted as a hole density with negative sign. Summarized we obtain

$$\begin{aligned} \overline{\varrho_T}(\mathbf{r}, \sigma) = & \overline{\varrho}(\mathbf{r}, \sigma) + S_0(\mathbf{r}, \mathbf{r}) \delta_{\sigma\sigma} - \left[ |h^{0,0}|^2 + \frac{1}{2!} |h^{1,0}|^2 \right]^{-1} \\ & \cdot \left[ \frac{1}{2} \sum_{\sigma_1 \sigma_2} \int d^3z_1 \int d^3z_2 h^{1,0*} \left( \begin{matrix} \mathbf{z}_1 & \mathbf{z}_2 & \mathbf{r} \\ \sigma_1 & \sigma_2 & \sigma \end{matrix} \right) h^{1,0} \left( \begin{matrix} \mathbf{z}_1 & \mathbf{z}_2 & \mathbf{r} \\ \sigma_1 & \sigma_2 & \sigma \end{matrix} \right) \right]. \end{aligned} \quad (3.11)$$

Concluding our results we state: As a consequence of the transformation back to a bare Fock space representation, we have to correct the electron density distribution in two ways: First, the underlying metal electron density has to be added, and second, we observe that there is a negative contribution due to three-particle correlations leading at certain positions  $\mathbf{r}$  to a reduction of the density.

For the numerical evaluation we mention that the three-particle amplitudes  $h^{1,0}$  can be reduced to

one-particle wavefunctions  $h^{0,0}$  using [1] (6.6):

$$\begin{aligned} & h^{1,0} \left( \begin{matrix} \mathbf{z}_1 & \mathbf{z}_2 & \mathbf{r} \\ \sigma_1 & \sigma_2 & \sigma \end{matrix} \right) \\ & = - \sum_s \int d^3y_1 \int d^3y_2 \int d^3y_3 \int d^3x G^{1,0}(\mathbf{z}_1 \mathbf{z}_2 \mathbf{r}; y_1 y_2 y_3) \\ & \quad \cdot B^{1,0}_{0,0} \left( \begin{matrix} y_1 & y_2 & y_3 & \mathbf{x} \\ \sigma_1 & \sigma_2 & \sigma & s \end{matrix} \right) h^{0,0} \left( \begin{matrix} \mathbf{x} \\ s \end{matrix} \right), \end{aligned} \quad (3.12)$$



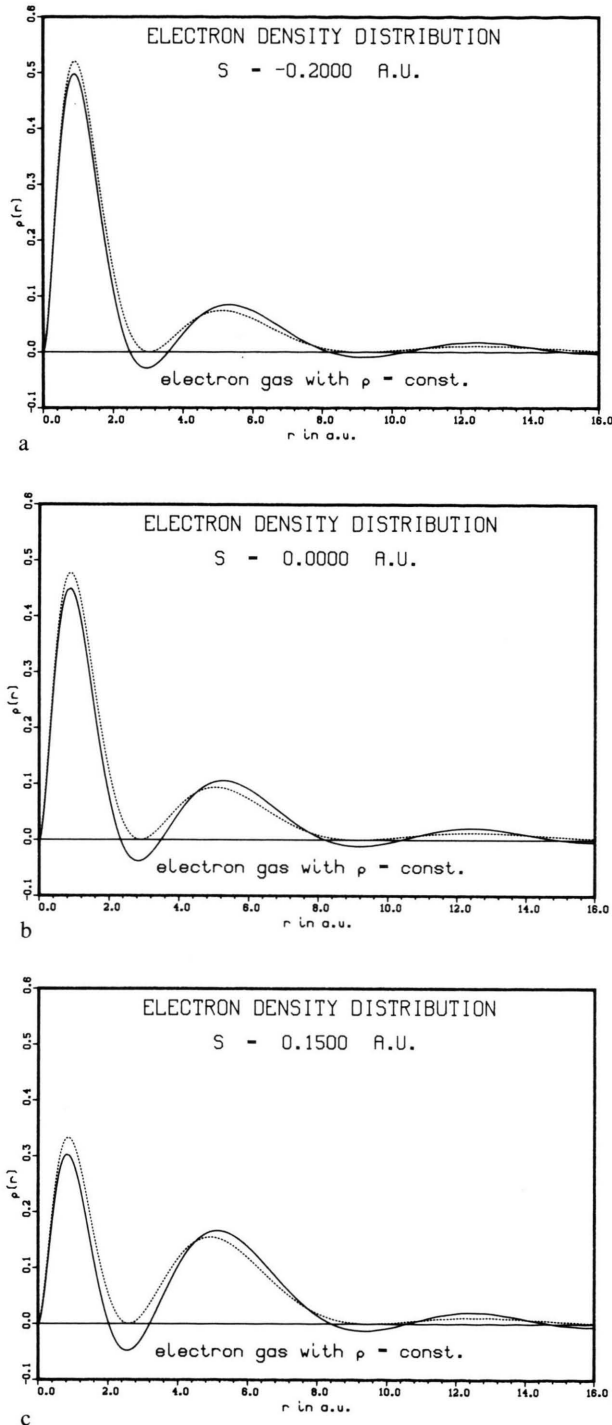


Fig. 2. Back transformed effective radial density distribution by one-particle amplitudes (dotted line) compared with the density induced by one-particle amplitudes (solid line) for different values of metal lattice distortions  $s$  in Mg: a)  $s = -0.20$  a.u. (lattice compression); b)  $s = 0.00$  a.u. (no volume change); c)  $s = +0.15$  a.u. (lattice extension).

The calculation of products of three-particle amplitudes as contained in (3.11) is really hard because products of Green's functions matrix elements arise which cannot be reduced on known matrix elements as computed in HN ([1], (7.2)). In a random phase approximation we obtained the numerical results for a hydrogen centre in Mg as shown in Figure 2. It can be seen that the main density maxima decrease compared with the non-transformed densities while the minor maxima grow and are shifted to larger distances. This means that the probability to find the hydrogen electron outside the tetrahedron is increased due to the interactions between excess electron and Fermi sea underground. Furtheron, there are minima which dip in the electron gas. As the nearest neighbours are shifted outwards, the depth of these minima increases. This is a direct consequence of three-particle correlations and has been computed before by Nørskov [7] who used a combination of density functional theory and Green's function method. Nørskov considered aluminium as an example and calculated the induced electron density of a hydrogen perturbation in a jellium model. Qualitatively we are in good agreement with the results obtained in [7].

We want to mention that there are several attempts in the literature to treat perturbations in solid. Most of them are based on a density functional theory as e.g. [8, 9]. Also correlation effects have been studied using local density functionals and/or pseudo potentials [10, 11, 12], especially in application on metal hydrides [13, 14, 15, 16].

Nevertheless, there are some important advantages of our method compared with all other theories: Firstly, we are able to determine exactly the contributions to energy and electron density arising from three-particle correlations. Other theories only calculate the total influence of many-particle interactions. Second, we keep the host lattice distortion as a parameter in our model. Thus, as the case may be, determining the volume change of a metal hydride either by experiment [17] or by theoretical investigations [18], we are able to calculate the corresponding energy and density distribution. Last not least, we are independent of phenomenological theories because our formalism is based on "first principles" as introduced by Heisenberg [19, 20] and further developed to a functional quantum mechanics by Stumpf [21].

## Appendix

We prove that

$$\langle O_{vw} | T^+ T | O_{vw} \rangle = 1 \quad (\text{A.1})$$

with  $T$  as defined in (2.1):

$$T = e^{v S_0 w} e^{-w^+ S_0 v^+} e^{v S_0 w}. \quad (\text{A.2})$$

*Proof:* Because  $|O_{vw}\rangle$  is a (normalized) vacuum state, all we have to show is

$$\langle O_{vw} | e^{-v S_0 w} e^{w^+ S_0 v^+} e^{v S_0 w} e^{-w^+ S_0 v^+} | O_{vw} \rangle = 1. \quad (\text{A.3})$$

With (2.15) we get

$$\begin{aligned} e^{w^+ S_0 v^+} e^{v S_0 w} e^{-w^+ S_0 v^+} \\ = e^{v S_0 w} + [w^+ S_0 v^+, e^{v S_0 w}] \\ + \frac{1}{2!} [w^+ S_0 v^+, [w^+ S_0 v^+, e^{v S_0 w}]] + \dots \quad (\text{A.4}) \end{aligned}$$

The evaluation for the first commutator in (A.4) is easy. We obtain

$$[w^+ S_0 v^+, e^{v S_0 w}] = -S_0 + v^+ S_0 v + w^+ S_0 w. \quad (\text{A.5})$$

Thus we get for the second commutator in (A.4)

$$[w^+ S_0 v^+, [w^+ S_0 v^+, e^{v S_0 w}]] = 2v^+ S_0 w^+. \quad (\text{A.6})$$

This implies that all higher commutators become zero. Therefore we have

$$\begin{aligned} e^{w^+ S_0 v^+} e^{v S_0 w} e^{-w^+ S_0 v^+} | O_{vw} \rangle \\ = \left\{ e^{v S_0 w} + (-S_0 + v^+ S_0 v + w^+ S_0 w) \right. \\ \left. + \frac{1}{2!} 2v^+ S_0 w^+ \right\} | O_{vw} \rangle \\ = \{1 - S_0 + v^+ S_0 v + w^+ S_0 w\} | O_{vw} \rangle. \quad (\text{A.7}) \end{aligned}$$

The left side in (A.3) is then rewritten in

$$\begin{aligned} \langle O_{vw} | e^{-v S_0 w} e^{w^+ S_0 v^+} e^{v S_0 w} e^{-w^+ S_0 v^+} | O_{vw} \rangle \\ = \langle O_{vw} | e^{-v S_0 w} | O_{vw} \rangle - \langle O_{vw} | e^{-v S_0 w} S_0 | O_{vw} \rangle \\ + \langle O_{vw} | e^{-v S_0 w} v^+ S_0 w^+ | O_{vw} \rangle \quad (\text{A.8}) \\ = 1 - S_0 + \langle O_{vw} | e^{-v S_0 w} v^+ S_0 w^+ e^{v S_0 w} e^{-v S_0 w} | O_{vw} \rangle. \end{aligned}$$

Applying (2.15) to the last term in (A.8) we get

$$\begin{aligned} \langle O_{vw} | e^{-v S_0 w} v^+ S_0 w^+ e^{v S_0 w} | O_{vw} \rangle \\ = \langle O_{vw} | v^+ S_0 w^+ + (S_0 - v^+ S_0 v - w^+ S_0 w) \\ + \frac{1}{2!} 2v S_0 w | O_{vw} \rangle = S_0. \quad (\text{A.9}) \end{aligned}$$

Insertion of (A.9) into (A.8) proves (A.3).

## Acknowledgement

The authors are highly indebted to the Friedrich Flick Förderungstiftung for the financial support received for this work.

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