Trial Functions for the Two-Particle Density Functional Variational Method

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Z. Naturforsch. **53 a,** 833–840 (1998); received August 5, 1998

The N-particle quantum mechanical system in an external field is considered on the basis of two-particle density functions. The main point of the presented work is to reveal the advantages of the two-particle density formalism as compared to the common one-particle density formalism applied to a simple example. The two-particle density formalism permits us to take into account the exact two-particle interaction without additional models. The exchange and correlation effects can be considered by a proper choice of the trial function. By using the presented formalism we calculate the density of the electron gas on different metal surfaces. A simple trial function allowing for correlations gives us a more correct fit to the experimental data on the metal dipol barriers than corresponding calculations with the one-particle density formalism. It is also shown that a pertubation of the external potential can be effectively taken into account by a pertubation calculation for the trial function.

Key words: Quantum Theory; Two-particle Density; Density Functional; Metallic Surface.

1. Introduction

A well established method to calculate experimentally measurable properties of many-particle systems is the one-particle density functional theory [1, 2]. A difficulty of this approach is to deal with the exchange- and correlation energy of the system. To avoid this difficulty we proposed a more general method based on the many-particle density functionals [3, 4] to calculate properties of inhomogenous quantum systems. It was shown in [3] how the correlation properties in many-particle systems with two-body type interactions can be considered more exactly in the frame of two-particle density functional calculations. It was also shown that the problems arising with the consideration of two-body correlations on the basis of traditional one-particle density functional theory are met by the choice of the trial function in many-particle density functional calculations. We suggested to construct the trial function by using the general many-particle scattering theory [5].

In this paper we present an analysis of exchange and correlation properties of particles in a many-particle system with two-body interactions for a simple example, the electron density in the presence of a metallic surface. This analysis is done in the frame of two-body density functionals with a proper choice of the two-particle density trial function. We also consider the dependence of the trial function on a pertubation of the potential and develop for this a pertubation method on the basis of the Lagrange-Euler equation of the variational calculation.

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2. The Influence of the Trial Function on Correlation Properties

We consider an N-Fermi-particle quantum system with two-body interaction in an external force field. This system is represented by the Hamiltonian

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_{k=1}^{N}\nabla_{\boldsymbol{r}_k}^2 + \sum_{k=1}^{N} V(\boldsymbol{r}_k) + \frac{e^2}{4\pi\varepsilon_0}\sum_{k<j}^{N}\frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_j|}, \tag{1}$$

where the explicite spin dependence is neglected.

To calculate the ground state energy of the system we use the two-particle density method which

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we briefly sketch in the following. The two-particle density of the system in a state ψ is defined as the diagonal part of the reduced density matrix of second order

$$n_2(\boldsymbol{r}_1,\boldsymbol{r}_2) = \gamma_2(\boldsymbol{r}_1\boldsymbol{r}_2,\boldsymbol{r}_1\boldsymbol{r}_2) \tag{2}$$

with

$$\gamma_2(\boldsymbol{r}_1\boldsymbol{r}_2,\boldsymbol{r}_1'\boldsymbol{r}_2') = \frac{N(N-1)}{2} \cdot \tag{3}$$

$$\cdot \int \psi(\boldsymbol{r}_1\boldsymbol{r}_2\boldsymbol{r}_3\cdots\boldsymbol{r}_N)\psi^*(\boldsymbol{r}_1'\boldsymbol{r}_2'\boldsymbol{r}_3\cdots\boldsymbol{r}_N)\,\mathrm{d}^3\boldsymbol{r}_3\cdots\mathrm{d}^3\boldsymbol{r}_N.$$

Similarly to one-particle density functional theory [1], the ground state energy of a quantum system can be proved to be a definite functional of the ground state two-particle density n_2. The kinetic energy functional is defined by

$$T[n_2] := \inf_{\psi\mapsto n_2} \langle\psi|\mathcal{T}|\psi\rangle, \tag{4}$$

where $\mathcal{T}$ is the kinetic energy operator

$$\mathcal{T} = -\frac{\hbar^2}{2m}\sum_{k=1}^{N}\nabla^2_{\boldsymbol{r}_k}, \tag{5}$$

and the infimum is taken over all states ψ with two-particle density n_2. An energy functional can then be defined as

$$\begin{aligned} E[n_2] &= T[n_2] \\ &+ \frac{1}{N-1}\int (V(\boldsymbol{r}_1)+V(\boldsymbol{r}_2))n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2 \\ &+ \frac{e^2}{4\pi\varepsilon_0}\int \frac{n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2. \end{aligned} \tag{6}$$

Further there is a variational principle for the ground state energy

$$E_0 = \min_{\text{all allowed } n_2} E[n_2], \tag{7}$$

where minimization over "all allowed n_2" means minimization over all functions $f : \mathbb{R}^3 \times \mathbb{R}^3 \longrightarrow \mathbb{R}$, which arise as two-particle densities of an N-Fermion quantum system. The corresponding functional for the one-particle density formalism was developed by Levy and Lieb [6 - 8]. For an application of the variational principle (7), the allowed two particle densities must be characterized intrinsically. This important problem of the so-called N-representability of integrable functions $f : \mathbb{R}^3 \times \mathbb{R}^3 \longrightarrow \mathbb{R}$ has not yet been solved satisfactorily.

In contrast to one-particle density functional theory, however, the suggested method has the great advantage of an exact interaction energy functional. Only in the kinetic energy part suitable approximations are necessary. Here we used the gradient expansion and especially the Kirzhnits method [9 - 11]. The result is a well known expansion

$$t_2[n_2] = t_2^{(0)}[n_2] + t_2^{(2)}[n_2] + \ldots \tag{8}$$

with vanishing odd terms for the kinetic energy density t_2, which is defined by

$$T = \int\int t_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2. \tag{9}$$

In the above mentioned expansion we have for the zeroth and second order terms

$$t_2^{(0)}[n_2] = \frac{\hbar^2}{m}\frac{1}{N}\frac{3}{5}(18\pi^4)^{1/3}n_2^{4/3}, \tag{10}$$

$$\begin{aligned} t_2^{(2)}[n_2] &= \frac{\hbar^2}{m}\frac{1}{72N}\left(\frac{(\nabla_1 n_2)^2}{n_2} + \frac{(\nabla_2 n_2)^2}{n_2}\right) \\ &- \frac{\hbar^2}{m}\frac{1}{12N}\left(\nabla_1^2 n_2 + \nabla_2^2 n_2\right). \end{aligned} \tag{11}$$

Now (6) and (10, 11) can be applied to an analysis of the electron gas on metal surfaces in the frame of the jellium model in the following way. We choose suitable parameter dependent trial functions for the two-electron density, and then minimize the functional with respect to these parameters. To show the dependence of the results on the special choice of the trial functions we use to different classes of them.

Firstly we use a very simple two-particle density trial function as a product of one-particle densities:

$$n_2^\alpha(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{2}n^\alpha(\boldsymbol{r}_1)n^\alpha(\boldsymbol{r}_2) \tag{12}$$

with

$$n^\alpha(\boldsymbol{r}) = \bar{n}_+ \cdot \begin{cases} \frac{1}{2}\exp(-\alpha z) & \text{if } z > 0, \\ 1 - \frac{1}{2}\exp(\alpha z) & \text{if } z < 0, \end{cases} \tag{13}$$

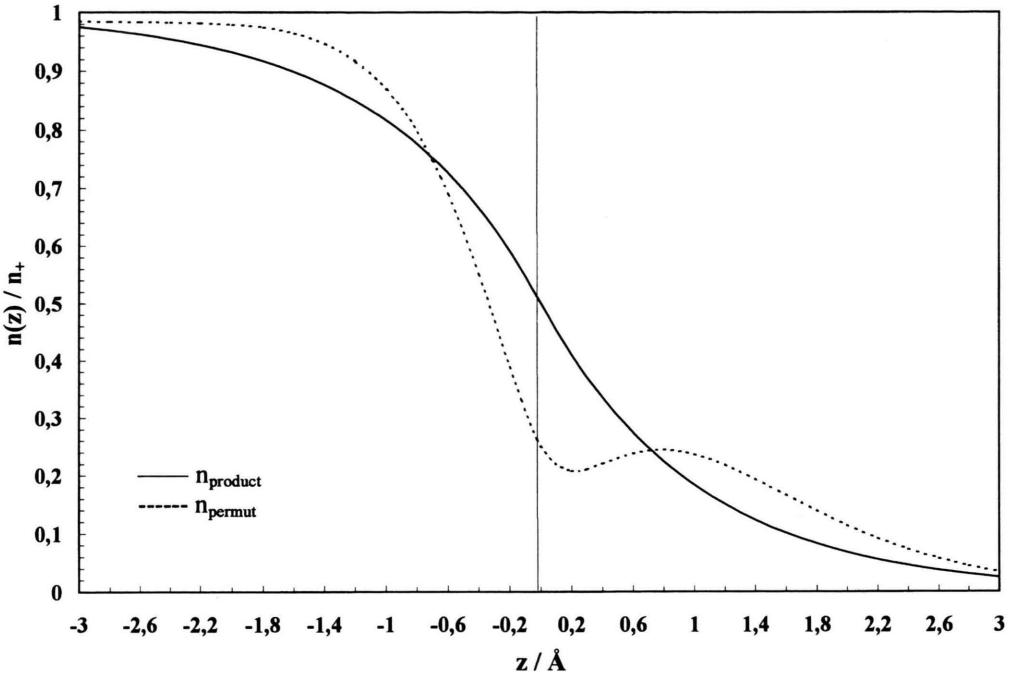

Fig. 1. One-particle densities of the product- and the permutation trial function.

where $\bar{n}_+$ is the constant density of the metal ions. In this approximation it is clear that correlation effects cannot occur, because there is only the electron-electron Coulomb repulsion as interaction energy. In a further step we choose a more complex kind of trial functions by taking into account some permutation properties of the system:

$$n_2^{\alpha_1,\alpha_2}(\boldsymbol{r}_1,\boldsymbol{r}_2) = C\left[\phi_1^2(\boldsymbol{r}_1)\phi_2^2(\boldsymbol{r}_2) + \phi_2^2(\boldsymbol{r}_1)\phi_1^2(\boldsymbol{r}_2) - \beta\phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2)\phi_2(\boldsymbol{r}_2)\right], \tag{14}$$

where

$$\phi_i(\boldsymbol{r}) = \frac{1}{2}\exp(-\alpha_i z)\theta(z) + \left(1 - \frac{1}{2}\exp(\alpha_i z)\right)\theta(-z), \tag{15}$$

$$\beta = \frac{3}{2}\frac{(\alpha_1+\alpha_2)^2}{\alpha_1^2+\alpha_2^2+\alpha_1\alpha_2} \tag{16}$$

and C is the normalization constant

$$C = \frac{1}{2}\frac{\bar{n}_+}{2-\beta}. \tag{17}$$

Table 1. Results for the dipole-barriere, calculated by the variational two-particle density formalism; $D_{\mathrm{th,pr}}$ are the results from using the product trial-function; $D_{\mathrm{th,per}}$ are the results from using the permutation trial-function; D_{exp} are the experimental data.

Metall	$\bar{n}_+$ /Å^{-3}	$\alpha_{0,\mathrm{pr}}$ /Å^{-1}	$D_{\mathrm{th,pr}}$ /eV	$\alpha_{0,\mathrm{pe}}$ /Å^{-1}	$D_{\mathrm{th,pe}}$ /eV	D_{exp} /eV
Rb	0.0119	1.690	0.752	1.929	0.579	0.80
Na	0.0266	2.033	1.163	2.294	0.915	0.50
Li	0.0465	2.309	1.580	2.582	1.263	0.90
Ag	0.1167	2.837	2.622	3.126	2.162	2.03
Cu	0.1693	3.081	3.226	3.373	2.693	3.50
Ca	0.0483	2.328	1.612	2.602	1.290	1.00
Mg	0.0867	2.655	2.224	2.940	1.820	2.17
Al	0.1818	3.130	3.358	3.422	2.810	3.87

The special form of (16) is required by charge conservation. We hope to see real correlation effects, because this class of trial functions differs strongly from a product of simple electron number densities. It was found that for all $\bar{n}_+$ the energy functional was minimized when $\alpha_1 = \alpha_2 =: \alpha$. In Fig. 1 the one-particle densities, as calculated from the two-particle density of both two-particle trial functions, are presented graphically. For a comparison with experimental data we also calculated the dipol barriere, which

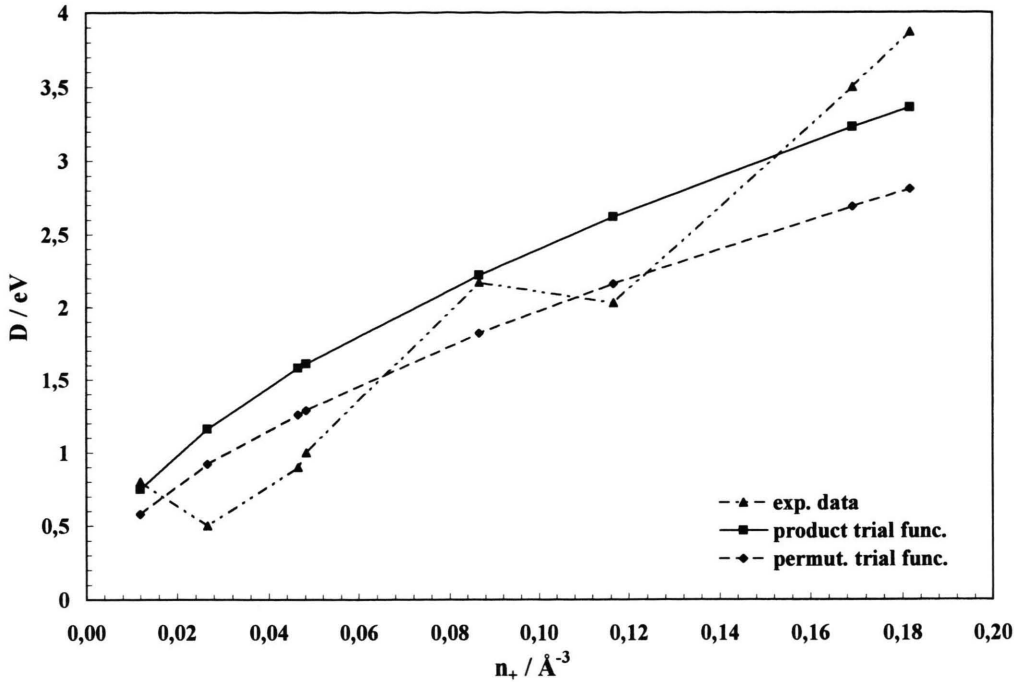

Fig. 2. Results for the dipole-barriere, calculated by the variational two-particle density formalism.

is defined by

$$D = e(\phi(-\infty) - \phi(\infty)). \tag{18}$$

Here ϕ is the electrostatic potential of the total charge distribution $\rho(\boldsymbol{r}) = e(-n(\boldsymbol{r}) + \bar{n}_+\theta(-z))$ derived by means of the poisson equation $\Delta\phi = (1/\varepsilon_0)\rho$. In Table 1 these results are listed for both trial functions, together with the experimental data taken from [12] for several metals. In Fig. 2 these data are additionally presented graphically. The analysis of our calculations shows that even in the frame of the simple jellium modell the variational calculation using the above presented two-particle density method gives a good agreement with experimental data if one takes into account more complex permutation properties of the electron system on the metal surface.

3. A Pertubation Calculation in the Two-Particle Density Functional Method

In this part of our work, we introduce a possibility to handle a more complicated external force field as that of a periodic solid by a pertubation calculation formalism which is based on the Euler-Lagrange equation of the two-particle density variational problem. Let us expand the external potential in a series

$$V = V^{(0)} + V^{(1)} + \cdots$$

If the minimization problem is solved for the zero order term $V^{(0)}$ the higher order terms immediately result from the hereafter introduced pertubation calculation.

As an example we apply this formalism to a solid with periodically located atoms. We use the variational calculation in the frame of the jellium model of Sect. 2 as a result of order zero and consider the lattice structure by the pertubation $V^{(1)}$. The starting point of the pertubation calculation is the Euler-Lagrange equation

$$\frac{\delta}{\delta n_2}\left(E[n_2] - \mu \int n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2\right) = 0, \tag{19}$$

where

$$\begin{aligned} E[n_2] &= T[n_2] \\ &+ \frac{1}{N-1}\int (V(\boldsymbol{r}_1) + V(\boldsymbol{r}_2))n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2 \\ &+ \int n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)W(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2, \end{aligned} \tag{20}$$

$$W(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{4\pi\varepsilon_0}\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}.$$

Executing the functional derivative in (19) one gets the identity

$$\frac{\delta T}{\delta n_2} + \frac{1}{N-1}(V(\boldsymbol{r}_1)+V(\boldsymbol{r}_2)) + W(\boldsymbol{r}_1,\boldsymbol{r}_2) - \mu = 0. \quad (21)$$

We assume that according to the potential the density n_2 and the multiplier μ can be expanded in a pertubation series

$$V = V^{(0)} + V^{(1)} + \ldots, \quad (22)$$

$$n_2 = n_2^{(0)} + n_2^{(1)} + \ldots, \quad (23)$$

$$\mu = \mu^{(0)} + \mu^{(1)} + \ldots, \quad (24)$$

where the first order terms are comparatively small. Collecting in (21) all terms order by order while taking into account that the interaction function W is completely considered in the order zero equation, one gets

$$\mu^{(0)} = \frac{\delta T}{\delta n_2^{(0)}} + \frac{1}{N-1}(V^{(0)}(\boldsymbol{r}_1) + V^{(0)}(\boldsymbol{r}_2)) + W(\boldsymbol{r}_1,\boldsymbol{r}_2), \quad (25)$$

$$\mu^{(1)} = \frac{\delta^2 T}{(\delta n_2^{(0)})^2} n_2^{(1)} + \frac{1}{N-1}(V^{(1)}(\boldsymbol{r}_1) + V^{(1)}(\boldsymbol{r}_2)). \quad (26)$$

In the kinetic energy functional of (26) we only consider $t_2^{(0)}$ according to (10) and find

$$\frac{\delta^2 T}{(\delta n_2^{(0)})^2} = \frac{\hbar^2}{m}\frac{4}{5N}(18\pi^4)^{1/3}\frac{1}{3}(n_2^{(0)})^{-2/3}. \quad (27)$$

Assuming that $n_2^{(0)}$ as an approximate solution of () is already known from calculations in the frame of the jellium model, the first order of the two-particle density is then

$$n_2^{(1)} = \left(\mu^{(1)} - \frac{1}{N-1}(V^{(1)}(\boldsymbol{r}_1) + V^{(1)}(\boldsymbol{r}_2))\right) \cdot \left(\frac{\hbar^2}{m}\frac{4}{5N}(18\pi^4)^{1/3}\frac{1}{3}\right)^{-1}(n_2^{(0)})^{2/3}. \quad (28)$$

In (28) the Lagrangian multiplier has to be calculated from the normalization condition for n_2. Certainly, $n_2^{(0)}$ has already the correct normalization so that the constraint condition is

$$\int n_2^{(1)}(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2 = 0. \quad (29)$$

Therefore we have

$$\int \left(\mu^{(1)} - \frac{2}{N-1}(V^{(1)}(\boldsymbol{r}_1) + V^{(1)}(\boldsymbol{r}_2))\right) \cdot \left(\frac{\hbar^2}{m}\frac{4}{5N}(18\pi^4)^{1/3}\frac{1}{3}\right)^{-1}(n_2^{(0)}(\boldsymbol{r}_1,\boldsymbol{r}_2))^{2/3}\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2 = 0$$

and we obtain the Lagrangian multiplier

$$\mu^{(1)} = \frac{2}{N-1}\int (V^{(1)}(\boldsymbol{r}_1) + V^{(1)}(\boldsymbol{r}_2)) \cdot (n_2^{(0)}(\boldsymbol{r}_1,\boldsymbol{r}_2))^{2/3}\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2 \cdot \left(\int (n_2^{(0)}(\boldsymbol{r}_1,\boldsymbol{r}_2))^{2/3}\,\mathrm{d}^3\boldsymbol{r}_1\mathrm{d}^3\boldsymbol{r}_2\right)^{-1}. \quad (30)$$

As an application of the pertubation calculation we consider a periodic lattice with lattice points located at $\boldsymbol{a}_{nml} := n\boldsymbol{a}_1 + m\boldsymbol{a}_2 + l\boldsymbol{a}_3$, where the $\boldsymbol{a}_i$ denote the three lattice vectors. For a function $f \in \mathcal{L}^1(\mathbb{R}^3)$ the following identity is well known:

$$F(\boldsymbol{r}) := \sum_{n,m,l\in\mathbb{Z}} f(\boldsymbol{r}-\boldsymbol{a}_{nml}) = \frac{(2\pi)^{3/2}}{V}\sum_{n,m,l\in\mathbb{Z}} \hat{f}(\boldsymbol{g}_{nml})e^{-i\boldsymbol{r}\boldsymbol{g}_{nml}}, \quad (31)$$

where $\hat{f}$ denotes the Fourier-transform of f, $\boldsymbol{g}_{nml}$ is a reciprocal lattice vector and $V = \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)$ is the volume of one cell. For a cubic lattice one has $\boldsymbol{g}_{nml} = (2\pi n/a1, 2\pi m/a2, 2\pi l/a3)$.

For a single-atom potential V_S decreasing sufficiently fast and for a lattice with plane surface at the hyperplane $x_3 = 0$ one can assume that

$$V_{\text{tot}}(\boldsymbol{r}) = M(-x_3 + a_3/2)\sum_{n,m,l\in\mathbb{Z}} V_S(\boldsymbol{r}-\boldsymbol{a}_{nml}) = M(-x_3 + a_3/2)\frac{(2\pi)^{3/2}}{V} \cdot \sum_{n,m,l\in\mathbb{Z}} \hat{V}_S(\boldsymbol{g}_{nml})e^{-i\boldsymbol{r}\boldsymbol{g}_{nml}}, \quad (32)$$

where M is a cut-off function like the Heaviside function. In the following we will see that no definite expression is required for M.

With respect to the pertubation formalism presented above, it is now possible to specify different orders of the lattice potential.

We shall only consider the terms of zero and first order of the expansion (32). We assume the lattice to be cubic and $a_1 = a_2 = a_3 =: a$. With these assumptions the pertubation term of the potential becomes

$$V^{(1)}(\boldsymbol{r}) = M\left(x_3 - \frac{a}{2}\right)\frac{(2\pi)^{3/2}}{V} \cdot \left[\hat{V}_S(0) + 2\hat{V}_S\left(\frac{2\pi}{a}\right)\left(\sum_{k=1}^{3}\cos\left(\frac{2\pi x_k}{a}\right)\right)\right]. \tag{33}$$

4. Application to the Calculation with the Product Trial Function

In this section, the formalism presented above is applied to the jellium model calculation with the product trial function

$$n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{2}n(\boldsymbol{r}_1)n(\boldsymbol{r}_2)$$

with

$$n(\boldsymbol{r}) = \bar{n}_+\begin{cases}\frac{1}{2}e^{-\alpha x_3}, & x_3 > 0,\\ 1 - \frac{1}{2}e^{\alpha x_3}, & x_3 \le 0,\end{cases}$$

Because of the special properties of the system, and with the condition that $M(-x + a/2) = 0$ for $x \ge 0$, one gets

$$\mu^{(1)} = \frac{2}{N-1}\frac{(2\pi)^{3/2}}{V}\hat{V}_S(0). \tag{34}$$

It is easy to show that

$$n^{(1)}(\boldsymbol{r}) = \left(\frac{2}{\bar{n}_+}\right)^{1/3}\frac{1}{C_{\text{kin}}}\left(n^{(0)}(\boldsymbol{r})\right)^{2/3} \cdot \left[\frac{(2\pi)^{3/2}}{V}\hat{V}_S(0) - V^{(1)}(\boldsymbol{r})\right], \tag{35}$$

$$C_{\text{kin}} = \frac{\hbar^2}{m}\frac{4}{15}\left(18\pi^4\right)^{1/3}. \tag{36}$$

Typical values of α show, that it is now possible to neglect the cut-off function M completely, because $n^{(0)}$ decreases quickly enough. So we may write

$$n^{(1)}(\boldsymbol{r}) = -\left(\frac{2}{\bar{n}_+}\right)^{1/3}\frac{1}{C_{kin}}\left(n^{(0)}(\boldsymbol{r})\right)^{2/3}\frac{(2\pi)^{3/2}}{V} \cdot \hat{V}_S\left(\frac{2\pi}{a}\right)\sum_{k=1}^{3}\cos\left(\frac{2\pi x_k}{a}\right). \tag{37}$$

In our model the pertubation is caused by neutral atoms placed at the lattice points as a correction to the homogeneous positive charge density. The ordering number of the atoms is assumed to be $Z - A$, where Z is the ordering number of the element which forms the lattice and A is the number of electrons with which this element contributes to the electron gas.

As the potential, built from neutral atoms at the lattice points, we take

$$V_S(r) = \begin{cases}0, & r < R_C,\\ -C\frac{1}{r}e^{-r/a_{\text{eff}}}, & r \ge R_C,\end{cases} \tag{38}$$

where $C = (Z - A)e^2/4\pi\varepsilon_0$ is the typical electrostatic constant, $a_{\text{eff}} = 0.886 \cdot a_B \cdot (Z - A)^{-1/3}$ is the so-called effective radius, R_C is the so-called core-radius, which takes into account Pauli-like repulsions of the electron hull of the atom. Here we used the ionic radius of the metals from [13].

The Fourier transform of this potential is

$$\hat{V}_S(k) = -\frac{e^2}{4\pi\varepsilon_0}\sqrt{\frac{2}{\pi}}\frac{e^{-R_C/a_{\text{eff}}}}{1/a_{\text{eff}}^2 + k^2} \cdot \left(\cos(kR_C) + \frac{1}{ka_{\text{eff}}}\sin(kR_C)\right). \tag{39}$$

In order to simplify (37) we introduce the abbreviations

$$C_{\text{spec}} := 3\frac{e^2}{4\pi\varepsilon_0}\frac{1}{C_{\text{kin}}}\frac{(2\pi)^{3/2}}{a^3} \cdot \hat{\hat{V}}_S\left(\frac{2\pi}{a}\right)(2\bar{n}_+)^{1/3}(Z - A), \tag{40}$$

$$\hat{\hat{V}}_S\left(\frac{2\pi}{a}\right) := \hat{V}_S\left(\frac{2\pi}{a}\right)\left[\frac{(Z - A)e^2}{4\pi\varepsilon_0}\right]^{-1}, \tag{41}$$

$$F(x_1, x_2, x_3) := \frac{1}{3}\sum_{i=1}^{3}\cos\left(\frac{2\pi x_i}{a}\right), \tag{42}$$

$$f := \frac{1}{\bar{n}_+}n^{(0)}. \tag{43}$$

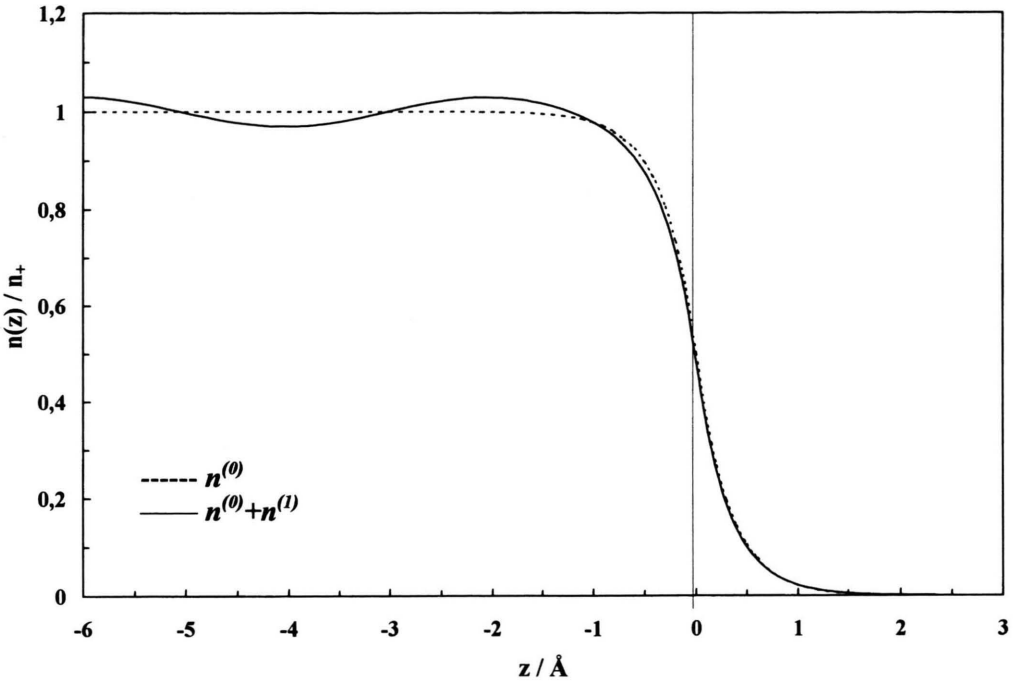

Fig. 3. Zero and first order of the electron density for Al.

Now we can write

$$n^{(1)}(\boldsymbol{r}) = -C_{\text{spec}} F(x_1, x_2, x_3) f^{2/3}(x_3) \tag{44}$$

C_{spec} characterizes the magnitude of the first order correction of the pertubation. In Table 2 C_{spec} in units of $\bar{n}_+$ is listed for those metals for which the variational calculation was carried out in the frame of the jellium model. Here one sees that the dominating factor in C_{spec} is the relation R_C/a_{eff} between the core- and the effective radius. In Fig. 3 the $x_1 - x_2$-mean of $n^{(0)} + n^{(1)}$ as a function of x_3 is presented graphically for Al as an example. To get the correction $\phi^{(1)}$ to the one electron potential it is now necessary to solve the Poisson equation for the pertubation charge density $\rho^{(1)} = -en^{(1)}$

$$\Delta\phi^{(1)} = \frac{e}{\varepsilon_0} n^{(1)}. \tag{45}$$

Therefore we first search for a solution of

$$\Delta G(x_1, x_2, x_3) = F(x_1, x_2, x_3) f^{2/3}(x_3). \tag{46}$$

Table 2. Results for C_{spec} that characterizes the magnitude of the first order correction of the pertubation

Metal	a/Å	$\bar{n}_+$/Å^{-3}	Z	R_C/Å	$C_{\text{spec}}/\bar{n}_+$	R_C/a_{eff}
Rb	5.62	0.0119	37	1.488	–0.0002	10.97
Na	4.30	0.0266	11	1.012	–0.0421	4.73
Li	3.50	0.0465	3	0.758	–0.1574	1.71
Ag	4.09	0.1167	47	1.011	–0.0024	7.74
Cu	3.61	0.1693	29	0.947	–0.0093	5.90
Ca	5.58	0.0483	20	1.051	–0.0109	5.37
Mg	3.20	0.0867	12	0.780	–0.0933	3.68
Al	4.04	0.1818	13	0.550	–0.0891	1.25

Only the behaviour in x_3-direction of G is of interest for later results. So we define a new potential by averaging over the x_1,x_2-coordinates:

$$\tilde{G}(x_3) := \int G(x_1, x_2, x_3)\, \mathrm{d}x_1 \mathrm{d}x_2. \tag{47}$$

This function satisfies the differential equation

$$\frac{\mathrm{d}^2\tilde{G}}{\mathrm{d}z^2} = \frac{1}{3} \cos\left(\frac{2\pi z}{a}\right) f^{2/3}(z). \tag{48}$$

The complete correction to the one-electron potential

Table 3. Results of the pertubation calculation with a periodic lattice for the first order of the dipol barriere D.

Metal	a/Å	$\bar{n}_+$Å^{-3}	Z	R_C/Å	$D^{(0)}$/eV	$D^{(1)}$/eV	$D^{(0)} + D^{(1)}$/eV	D_{exp}/eV
Rb	5.62	0.0119	37	1.488	0.752	0.0001	0.752	0.80
Na	4.30	0.0266	11	1.012	1.163	0.0303	1.193	0.50
Li	3.50	0.0465	3	0.758	1.579	0.1250	1.704	0.90
Ag	4.09	0.1167	47	1.011	2.622	0.0077	2.630	2.03
Cu	3.61	0.1693	29	0.947	3.226	0.0335	3.260	3.50
Ca	5.58	0.0483	20	1.051	1.612	0.0277	1.640	1.00
Mg	3.20	0.0867	12	0.780	2.224	0.1202	2.344	2.17
Al	4.04	0.1818	13	0.550	3.357	0.4458	3.803	3.87

is then

$$-e\phi^{(1)}(z) = \frac{e^2}{\varepsilon_0} C_{\text{spec}} G(z). \tag{49}$$

By averaging over the z-coordinate inside the solid one gets the correction to the dipol barrier $D^{(1)}$ listed in Table 3. We obtain these results by numerical integration of (48).

Compairing now the corrected values of the dipol barriere $D^{(0)} + D^{(1)}$ with the experimental data one sees that taking into account the lattice structure of the metal within a pertubation calculation gives no essential improvement of the variational calculation in the frame of the jellium model.

5. Conclusion

The presented results show that the two-particle density formalism of many-particle quantum mechanical systems may easily take into account correlation and exchange properties. By variational calculations based on the presented method, the two-particle densities can be chosen in a simple form by considering permutation properties of two body systems in external fields. The pertubation of external fields influences the trial functions. The corrections of the trial functions due to this effects can be estimated by the variational method based on the Euler-Lagrange equation.

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