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New approach to the calculation of density functionals

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The density-functional theory relates the ground-state properties of an N-electron system to a universal functional of the charge density. In this paper we discuss a functional which avoids the problems of the Hohenberg-Kohn theory. We show that this functional can be calculated exactly, at least in principle. We present an upper bound for this functional, which is applied to the case $N=1$ and to the jellium problem. This upper bound is exact for $N=1$.

I. INTRODUCTION

The density-functional theory (DFT), which was first formulated by Hohenberg and Kohn in 1964,[1] claims that the ground-state properties of a many-electron system are related to a unique functional of the electronic charge density. Within this theory the ground state for a given system is obtained by a variational calculation, which minimizes the total energy of the system by varying the charge density. This approach to the many-body problem has stimulated research in many branches of theoretical physics, such as atomic, molecular, and solid-state physics.

Very recently, however, Levy[2] and Lieb[3] have shown independently that the original formulation of the DFT by Hohenberg and Kohn (HK) contains some very serious problems. In particular, it is shown that the HK functional (i) does not exist for all charge densities, and (ii) does not have the desired property of convexity which is generally assumed in practical applications. Levy and Lieb propose some new functionals which have the desired properties. Unfortunately, however, the new functionals cannot be calculated directly. In this work we first present an approximation to one of the new functionals. In this approximation we obtain an upper bound for the total energy of the N-electron system. The theory is then applied to the case $N=1$ and to the interacting electron gas. We further outline a general method which in principle allows an exact calculation of the density functional.

II. DENSITY FUNCTIONALS

A. Formulation of the problem

We search for the ground state of an interacting N-electron system in an external potential. We have to solve the Schrödinger equation

$$H\,|\Psi\rangle=E\,|\Psi\rangle\ ,$$

where $H=H_0+V$, with

$$H_0=K+U=\sum_i \frac{p_i^2}{2m}+\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\ ,$$

$$V=\sum_i v(\vec{r}_i)\ .$$

Ψ is a normalized and antisymmetric N-particle wave function $\Psi(z_1,\ldots,z_N)$, where $z=(\vec{r},\sigma)$ with space coordinates $\vec{r}$ and spin coordinate σ. E is the lowest eigenvalue of the Hamiltonian H.

In the following we use "natural" units ($e=1$, $m=\frac{1}{2}$, $\hbar=1$), i.e.,

$$H_0=-\sum_i \Delta_i+\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}\frac{1}{|\vec{r}_i-\vec{r}_j|}\ .$$

The electronic charge density is defined by

$$\rho(\vec{r})=N\sum_\sigma \int |\Psi(z,z_2,\ldots,z_N)|^2 d\vec{r}_2\cdots d\vec{r}_N\ ; \qquad (1)$$

$\rho(\vec{r})$ is a real, semidefinite positive function which is normalized to N. For later purposes it is important to define a convenient, physical set of functions $\rho(\vec{r})$ on which we can apply the variational principle. Following Lieb,[3] we define the set[4]

$$A_N=\{\rho\,|\,\rho\geq 0,\ \sqrt{\rho}\in H^1,\ \int \rho\, d\vec{r}=N\}\ , \qquad (2)$$

where the Hilbert space H^1 is defined with the inner product

$$(f,g)=\int f^*(\vec{r})g(\vec{r})d\vec{r}+\int [\vec{\nabla}f(\vec{r})]^*\vec{\nabla}g(\vec{r})d\vec{r}\ .$$

This somewhat unusual definition guarantees that the kinetic energy exists. We emphasize that A_N has some important properties.

(i) A_N is a convex set, i.e., if $\rho_1,\rho_2\in A_N$, and $\rho=\lambda\rho_1+(1-\lambda)\rho_2$, with $0\leq\lambda\leq 1$, then $\rho\in A_N$.

(ii) If $\rho\in A_N$, then there exists at least one Ψ which yields ρ according to Eq. (1), i.e., $\Psi\rightarrow\rho$. We will see later that there exists even an infinite number of Ψ's which satisfy this condition.

(iii) There exists a $\rho\in A_N$, which does not come from a ground state Ψ of a Hamiltonian $H=H_0+V$, where v may be an arbitrary external potential.[5] This is the problem of v representability [see, also, Ref. 2].

The DFT is based on the following theorem of HK: If Ψ_1 (Ψ_2) is a ground state for the external potential v_1 (v_2), and $v_1\neq v_2+\text{const}$, then $\rho_1\neq\rho_2$. This shows that $\rho(r)$ is a parameter which can be used to characterize the system.

B. Hohenberg-Kohn functional $F_{\mathrm{HK}}(\rho)$

Hohenberg and Kohn define the functional

$$F_{\mathrm{HK}}(\rho)=\langle\Psi\,|\,(K+U)\,|\,\Psi\rangle\ ,$$

where ρ comes from the ground state Ψ of the Hamiltonian $H=H_0+V$. More explicitly, for a given $\rho(r)$, take the unique potential v which is related to ρ by the Hohenberg-Kohn theorem, search for the ground state Ψ of the Hamiltonian H, and calculate $\langle\Psi\,|\,(K+U)\,|\,\Psi\rangle$.

From this construction it is evident that the set of the admitted densities ρ is restricted to

$$a_N=\{\rho\,|\,\rho \text{ comes from a ground state}\}\ ,$$

i.e., ρ comes from a Ψ which is a ground state for an arbitrary v. The above construction of F_{HK} suffers from the following defects.

(i) The set a_N is unknown, and $a_N\subset A_N$ and $a_N\neq A_N$. In other words, if we choose a ρ from the well-defined set A_N [Eq. (2)], it is impossible to decide *a priori* whether it is included in the set a_N. This excludes a well-defined variational calculation which is based on $F_{\mathrm{HK}}(\rho)$. Moreover, a_N is not a convex set.

(ii) Lieb shows that the functional F_{HK} is not convex. Here, convexity of a functional $F(\rho)$ means that if $\rho=\lambda\rho_1+(1-\lambda)\rho_2$, with $0\leq\lambda\leq1$, then

$$F(\rho)\leq\lambda F(\rho_1)+(1-\lambda)F(\rho_2)\ .$$

The nonconvexity of the functional is not very convenient for practical calculations.

(iii) As will be explicitly shown in what follows, for a given $\rho\in A_N$, there exists an infinite number of functions Ψ which yield ρ by Eq.(1).

C. Functional $\tilde{F}(\rho)$

Levy[2] and Lieb[3] propose a new functional $\tilde{F}(\rho)$ which is defined on the well-defined set A_N:

For all $\rho\in A_N$,

$$\tilde{F}(\rho)=\inf\{\langle\Psi\,|\,H_0\,|\,\Psi\rangle\,|\,\Psi\rightarrow\rho\}\ .$$

This definition is rather subtle and merits translation into common language: For a given ρ, search all normalized antisymmetric N-particle wave functions Ψ, such that $\Psi\rightarrow\rho$. Then, calculate for all those Ψ's the numbers $\langle\Psi\,|\,H_0\,|\,\Psi\rangle$. The smallest of these numbers gives $\tilde{F}(\rho)$.

The difficulty with this definition is to find *all* functions Ψ which correspond to a given ρ. It is rather obvious that

$$\tilde{F}(\rho)=F_{\mathrm{HK}}(\rho)\ \text{ if }\ \rho\in a_N\ .$$

Thus $\tilde{F}$ is an extension of F_{HK} over the well-defined set A_N. However, $\tilde{F}(\rho)$ is still a nonconvex functional.

Lieb has shown that one can define a functional over A_N which is convex. However, it appears that this functional cannot be calculated in practice. In this paper, we shall, therefore, restrict our discussion to $\tilde{F}(\rho)$.

D. Calculation of the ground-state energy

For a given external potential v, the ground-state energy is obtained from

$$E(v)=\inf\left\{F(\rho)+\int\rho v\,|\,\rho\in\mathscr{g}\right\}\ ,$$

where $\mathscr{g}$ represents the "good set" and where F is one of the functionals F_{HK} or $\tilde{F}$ discussed above, and good set means a_N for F_{HK} and A_N for $\tilde{F}$. Because of the bad properties of F_{HK}, it will be replaced in what follows by $\tilde{F}$.

We shall search upper bounds for $\tilde{F}$. Let us first discuss the meaning of a ground-state—energy calculation based on the approximated density functionals. If we denote the approximate functional by F', and the exact one by F, we have

$$F'(\rho)\geq F(\rho)\ ,$$

$$E(v)=\inf\left\{F(\rho)+\int\rho v\,|\,\rho\in A_N\right\}\ ,$$

which is the exact energy, and

$$E'(v)=\inf\left\{F'(\rho)+\int\rho v\,|\,\rho\in A_N\right\}\ ,$$

which is the approximated energy, and

$$E'(v)\geq E(v)\ .$$

Proof. We have the following:

$$\begin{aligned}E'(v)&=\inf\left\{F'(\rho)+\int\rho v\right\}\\&=F'(\rho^0)+\int\rho^0v\geq F(\rho^0)\\&\quad+\int\rho^0v\geq\inf\left\{F(\rho)+\int\rho v\right\}=E(v)\ .\end{aligned}$$

III. UPPER BOUND FOR $\tilde{F}(\rho)$

As already mentioned, the exact calculation of $\tilde{F}$ presents a serious difficulty, which is to find *all* Ψ such that $\Psi\rightarrow\rho$. It is not obvious how to find all these Ψ's, and in practice we are, thus, restricted to a limited subspace. This implies that we will obtain an upper bound, $\tilde{F}'(\rho)$, of $\tilde{F}(\rho)$.

A. Construction of determinants Ψ such that $\Psi\rightarrow\rho$ for spinless fermions

We construct a basis of one-electron functions $\varphi^k(r)$ which depend on the density $\rho(r)$. The N-particle wave function Ψ is then given by a determinant of the φ^k's. We have the following theorem.

Theorem 1. For all $\rho(r)\in A_N$, and if $\vec{\mathrm{R}}(\vec{\mathrm{r}})=(R_1(\vec{\mathrm{r}}),R_2(\vec{\mathrm{r}}),R_3(\vec{\mathrm{r}}))$,

$$R_1(\vec{\mathrm{r}})=R_1(x,y,z)=2\pi\frac{\int_{-\infty}^{x}dx'\rho(x',y,z)}{\int_{-\infty}^{\infty}dx'\rho(x',y,z)}\ ,$$

$$R_2(\vec{\mathrm{r}})=R_2(y,z)=2\pi\frac{\int_{-\infty}^{y}dy'\int_{-\infty}^{\infty}dx'\rho(x',y',z)}{\int_{-\infty}^{\infty}\int dx'dy'\rho(x',y',z)}\ ,\tag{3}$$

$$R_3(\vec{r})=R_3(z)$$

$$=\frac{2\pi}{N}\int_{-\infty}^{z}dz'\int_{-\infty}^{\infty}\int dy'dx'\rho(x',y',z)\ ,$$

then the functions $\varphi^{\vec{k}}(\vec{r})=[\rho(\vec{r})/N]^{1/2}e^{i\vec{k}\cdot\vec{R}}$ form an orthonormal basis, i.e.,

$$\langle\varphi\vec{k}'\,|\,\varphi^{\vec{k}}\rangle=\delta_{\vec{k}\vec{k}'},\quad\sum_{\vec{k}}|\varphi^{\vec{k}}\rangle\langle\varphi^{\vec{k}}|=1\ ,$$

with $\vec{k}=(k_1,k_2,k_3)$, where the k_i are signed integer numbers. The proof of this theorem is given in Appendix A together with the following one.

Theorem 2. For all $\rho(\vec{r})\in A_N$, and if

$$\Psi(\vec{r}_1,\ldots,\vec{r}_N)=\frac{1}{\sqrt{N!}}\det[\varphi^{\vec{k}}(\vec{r}_j)],\quad\vec{k}_i\neq\vec{k}_j$$

for all $i\neq j$, then

$$N\int|\Psi(\vec{r}_1,\ldots,\vec{r}_N)|^2d\vec{r}_2\cdots d\vec{r}_N=\rho(\vec{r})\ .$$

The above theorems generalize the construction of Ψ given by Harriman[6] and Lieb. We note the following.

(i) $\vec{k}$ is generally *not* a "good" quantum number because it is not associated to an operator which commutes with H. Thus $\vec{k}$ does not, in general, contain any physical significance.

(ii) For a finite volume V and $\rho(r)=N/V=\text{const}$, the functions $\varphi^{\vec{k}}(\vec{r})$ become plane waves $V^{-1/2}e^{i\vec{k}\cdot\vec{r}}$.

(iii) Some permutations are possible in the definition of $\vec{R}$, Eq. (3). (a) We may permute the components R_1, R_2, and R_3. This does not lead to any new set of functions because it is equivalent to a different choice of the k_i. (b) We may permute the order of integrations: For example, in the definition of R_1 we integrate over y instead of x, for R_2 over y and z, and for R_3 over y, z and x. Thus we can define $\vec{R}$ in six different ways.

(iv) The set $\{\vec{k}\}$ in the definition of Ψ is any subset of the set Z^3, where Z is the set of (positive and negative) integers. Even if we restrict ourself to the subset

$$\{\vec{k}\}\subset\{-(N-1),\ldots,-1,0,1,\ldots,N-1\}^3\ ,\tag{4}$$

which will be reasonable in most cases, the number of possible choices N_c "explodes" with N. If we include the permutations discussed under (iii), it is given by

$$N_c=6\left[\begin{matrix}(2N-1)^3\\N\end{matrix}\right].$$

One obtains $N_c(N=1)=6$, $N_c(N=2)=2106$, $N_c(N=3)=3\,813\,000$. This example shows that even under the above restriction the map $\Psi\to\rho$ is not at all one-to-one.

(v) It is evident that the same construction of Ψ can be performed using other orthogonal coordinate systems. In this way it is possible to take advantage of the symmetry of the problem, e.g., we can use spherical coordinates for an atom.

B. Upper bound for $\widetilde{F}$ for spinless fermions

We now calculate $\langle\Psi\,|\,H_0\,|\,\Psi\rangle$ with the Ψ's constructed above. We obtain

$$\widetilde{F}'(\rho)=\inf\{T(\rho)+U(\rho)\}\ ,$$

$$T(\rho)=\int(\vec{\nabla}\sqrt{\rho})^2d\vec{r}+\frac{1}{N}\int\rho(\vec{r})\sum_{\{\vec{k}\}}\{\vec{\nabla}[\vec{k}\cdot\vec{R}(\vec{r})]\}^2d\vec{r}\ ,$$

$$U(\rho)=\tfrac{1}{2}\int d\vec{r}\int d\vec{r}'\frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}[1-\epsilon_x(\{\vec{k}\},\vec{r},\vec{r}')]\ ,$$

$$\epsilon_x(\{\vec{k}\},\vec{r},\vec{r}')=\frac{1}{N^2}\left|\sum_{\{\vec{k}\}}e^{i\vec{k}\cdot[\vec{R}(\vec{r})-\vec{R}(\vec{r}')]}\right|^2 .$$

The infimum is performed over all possible sets $\{\vec{k}\}$.

C. Choice of the phase of Ψ

We still may choose a phase of the function Ψ. In fact, if $\Psi\to\rho$, and if

$$\Psi'=\exp\left[i\sum_j\theta(\vec{r}_j)\right]\Psi\ ,$$

then $\Psi'\to\rho$, and Ψ is still an antisymmetric N-particle wave function. For a given Ψ, the possible free choice of phase thus yields an infinite number of new wave functions. The only term in $\widetilde{F}(\rho)$ which is affected by the phase is the kinetic energy. We thus have to investigate whether we can lower the kinetic energy by a judicious choice of $\theta(r)$. This is, in fact, the case. The lowest kinetic energy is found for

$$\theta(\vec{r})=-\frac{1}{N}\sum_{\{\vec{k}\}}(\vec{k}\cdot\vec{R})\ .$$

We obtain

$$T(\rho)=\int(\vec{\nabla}\sqrt{\rho})^2d\vec{r}+\frac{1}{N}\int\rho(\vec{r})\left[\sum_{\{\vec{k}\}}[\vec{\nabla}(\vec{k}\cdot\vec{R})]^2-\frac{1}{N}\left(\sum_{\{\vec{k}\}}\vec{\nabla}(\vec{k}\cdot\vec{R})\right)^2\right]d\vec{r}\ .\tag{5}$$

This relation is proven in Appendix B.

D. Case $N=1$

As shown in Appendix C, we have for $N=1$

$$\widetilde{F}'(\rho)=\widetilde{F}(\rho)\ .$$

The proof is based on the fact that for one particle we can construct *all* Ψ such that $\Psi\to\rho$. The approximation $\widetilde{F}'$ is thus exact in the one-particle case. In other words, the problem of self-interaction (see, e.g., Ref. 7) does not exist in our approach.

E. Upper bound for $\widetilde{F}$ for fermions with spin $s=\frac{1}{2}$

The extension of the above construction of Ψ to the spin case is immediate. We define

$$\varphi^{\vec{k}s}=(\rho/N)^{1/2}e^{i(\vec{k}\cdot\vec{R})}s\ ,$$

where s is either up or down.

The set $\varphi^{\vec{k}s}$ is still an orthonormal basis:

$$\langle \varphi^{\vec{k}s} | \varphi^{\vec{k}'s'} \rangle = \delta_{\vec{k}\vec{k}'} \delta_{ss'} ,$$

$$\sum_{s} \sum_{\vec{k}} | \varphi^{\vec{k}s} \rangle \langle \varphi^{\vec{k}s} | = 1 .$$

As before, Ψ is given by the determinant

$$\Psi = \frac{1}{\sqrt{N!}} \det[\varphi^{\vec{k}s}(\vec{r}_j)] .$$

The set $\{\vec{k}\}$ can be decomposed

$$\{\vec{k}\} = \{\vec{k}\}_{\text{up}} + \{\vec{k}\}_{\text{down}}, \quad \{\vec{k}\}_{\text{up}}, \{\vec{k}\}_{\text{down}} \subset Z^3 .$$

Similarly, $N = N_{\text{up}} + N_{\text{down}}$. $\tilde{F}'(\rho)$ is constructed as before

$$\begin{aligned} \tilde{F}'(\rho) &= \inf\{T(\rho) + U(\rho)\} , \\ T(\rho) &= \int (\vec{\nabla}\sqrt{\rho})^2 d\vec{r} \\ &\quad + \frac{1}{N} \int \rho(\vec{r}) \left[\sum_{\{\vec{k}\}} [\vec{\nabla}(\vec{k}\cdot\vec{R})]^2 - \frac{1}{N} \left[\sum_{\{\vec{k}\}} \vec{\nabla}(\vec{k}\cdot\vec{R}) \right]^2 \right] d\vec{r} , \\ U(\rho) &= \tfrac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} \\ &\quad \times [1 - \epsilon_x(\{\vec{k}\}_{\text{up}}, \{\vec{k}\}_{\text{down}}, \vec{r}, \vec{r}')] , \end{aligned} \tag{6}$$

$$\epsilon_x = \frac{1}{N^2} \left| \sum_{\{\vec{k}\}_{\text{up}}} e^{i\vec{k}\cdot\vec{\alpha}} \right|^2 + \frac{1}{N^2} \left| \sum_{\{\vec{k}\}_{\text{down}}} e^{i\vec{k}\cdot\vec{\alpha}} \right|^2 ,$$

$$\vec{\alpha} = \vec{R}(\vec{r}) - \vec{R}(\vec{r}') .$$

F. Comparison with Hartree-Fock theory

As in the Hartree-Fock (HF) theory, our wave functions Ψ which are used to define the upper bound $\tilde{F}'$ of $\tilde{F}$ are single determinants. However, it must be noted that in our case all the single-particle functions have the same modulus $(\rho/N)^{1/2}$, i.e., we are in a subspace of the HF function space.[8] Therefore, $E'(\rho) \le E_{\text{HF}}(\rho)$, where E_{HF} is the HF energy obtained by a fully variational calculation. Usually HF calculations start from the self-consistent HF equations which yield a stationary solution of $\langle \Psi_{\text{HF}} | H | \Psi_{\text{HF}} \rangle$. It should be noted, however, that an infimum (i.e., the lowest value) is not necessarily a stationary point (i.e., the first derivative is equal to 0). Therefore, *a priori* the respective energies cannot be compared.

G. Thermodynamic limit

Even if we restrict ourselves to the set $\{\vec{k}\}$ as proposed in Eq. (4), the number of possible subsets $\{\vec{k}_1, \ldots, \vec{k}_N\}$ explodes with N. In certain cases a reasonable choice will be given by

$$\{\vec{k}\} = \{\vec{k} \mid |\vec{k}| \le k_F\} , \tag{7}$$

i.e., k is restricted to a Fermi sphere. We must remember that, in general, $\vec{k}$ has no physical meaning. The justification of the above choice becomes, however, evident in the case of the jellium problem.

We now want to calculate $\tilde{F}'$ in the thermodynamic limit:

$$N \to \infty, \quad V = L^3 \to \infty, \quad N/V = \text{const} .$$

In this case we can substitute, as usual,

$$\sum_{|\vec{k}| \le k_F} \to \frac{V}{(2\pi)^3} \int_{|\vec{k}| \le k_F} d\vec{k} .$$

As we want to compare our results based on $\tilde{F}'$ with the well-known results for the jellium problem, it is convenient to redefine $\vec{k}$ and $\vec{R}$

$$\frac{2\pi}{L}\vec{k} \to \vec{k}, \quad \frac{2\pi}{L} k_F \to k_F, \quad \frac{L}{2\pi}\vec{R} \to \vec{R} . \tag{8}$$

We obtain immediately from Eq. (6)

$$\begin{aligned} \tilde{F}'(\rho) &= T(\rho) + U(\rho) , \\ T(\rho) &= \int (\vec{\nabla}\sqrt{\rho})^2 d\vec{r} \\ &\quad + \frac{V}{(2\pi)^3 N} \int d\vec{r} \rho(\vec{r}) \int d\vec{k} [\vec{\nabla}(\vec{k}\cdot\vec{R})]^2 , \\ U(\rho) &= \tfrac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} [1 - \epsilon_x(k_F, \vec{r}, \vec{r}')] , \\ \epsilon_x &= \frac{V^2}{(2\pi)^6 N^2} \left| \int d\vec{k}\, e^{i\vec{k}\cdot[\vec{R}(\vec{r}) - \vec{R}(\vec{r}')]} \right|^2 . \end{aligned} \tag{9}$$

The above expressions depend only on k_F. The infimum in the expression for $\tilde{F}'$ has disappeared because we are considering only one function which corresponds to the choice of $\{\vec{k}\}$ in Eq. (7). The integrals over $\vec{k}$ can be calculated analytically.

The functional F must be extensive. As the charge neutrality of the system is only guaranteed in the presence of the external potential, the term $U(\rho)/N$, which contains only the electronic contributions, diverges. This divergence must be eliminated in the standard way by including a neutralizing homogeneous background charge density in $\rho(\vec{r})$. As shown in Appendix D we finally obtain

$$\begin{aligned} F'(\rho) &= T(\rho) + U(\rho) , \\ T(\rho) &= \int (\vec{\nabla}\sqrt{\rho})^2 d\vec{r} + \frac{k_F^2}{5} \int d\vec{r} \rho(\vec{r}) [(\vec{\nabla}R_1)^2 + (\vec{\nabla}R_2)^2 \\ &\quad + (\vec{\nabla}R_3)^2] , \\ U(\rho) &= \tfrac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} [1 - \epsilon_x(k_F, \vec{r}, \vec{r}')] , \\ \epsilon_x &= \begin{cases} F^2(k_F\alpha), & \text{for spinless fermions} \\ \tfrac{1}{2} F^2(k_F\alpha), & \text{for fermions with spin} \end{cases} \\ \alpha &= |\vec{R}(\vec{r}) - \vec{R}(\vec{r}')| , \\ F(x) &= \frac{3}{x^2} \left[\cos x - \frac{\sin x}{x} \right] . \end{aligned} \tag{10}$$

H. Application to the case of a periodic jellium

We shall now discuss the case of a periodic jellium in a box of volume $V=L^3$ with a periodic charge density. In this case the term $\int \rho v$ is constant and drops out of the ground-state—energy calculation. Therefore, the minimum of $E(v)$ is given directly by the absolute minimum of $F(\rho)$. The periodic charge density is chosen to be

$$\rho(\vec{r})=\frac{N}{V}[1-\alpha\cos(2lx)][1-\alpha\cos(2ly)][1-\alpha\cos(2lz)],\quad 0\leq\alpha\leq 1,\quad l=m\pi/L,\quad m \text{ integer}\ . \tag{11}$$

We have already seen that for $\alpha=0$ (i.e., $\rho=N/V$), Ψ is given by a determinant of plane waves. For $\alpha=0$, we must therefore obtain the well-known result for the plane-waves jellium. For $\alpha=1$, we have a cubic lattice with the lattice constant L/m

$$\rho(\vec{r})=(8N/V)\sin^2(lx)\sin^2(ly)\sin^2(lz)\ .$$

We introduce the dimensionless parameter $\xi=2l/k_F=1/\mu$. The system can then be characterized by the three parameters k_F, ξ, and α.

As shown in Appendix E, we obtain for the ground-state energy in the thermodynamic limit

$$\frac{E(\rho)}{N}=\tfrac{3}{5}k_F^2-\frac{3}{4\pi}k_F+k_F^2\{\tfrac{9}{10}\alpha^2+\tfrac{3}{4}\xi^2[1-(1-\alpha^2)^{1/2}]\}$$
$$+\frac{2k_F\alpha}{\pi}\left[\frac{1}{\xi^2}-\frac{1}{8\pi}f(\xi)+\alpha\left[\frac{1}{2\xi^2}-\frac{1}{8\pi}f(\sqrt{2}\xi)\right]+\frac{\alpha^2}{3}\left[\frac{1}{3\xi^2}-\frac{1}{8\pi}f(\sqrt{3}\xi)\right]\right]\ , \tag{12}$$

where $f(K)$ is the Fourier transform of $F^2(x)/|x|$.

The first two terms give the result for the plane-waves jellium. The following term represents the kinetic-energy correction which is always positive for $0<\alpha\leq 1$. The last terms represent the Coulomb-energy correction, which is positive, because $1/\xi^2-(1/8\pi)f(\xi)$ is always positive. This shows that the introduced inhomogeneity of the electronic charge increases the ground-state energy, i.e., we do not observe any tendency towards the formation of a Wigner lattice. It can be shown that this result is valid for any periodic charge density and is not produced by our particular choice of $\rho(r)$, Eq. (11). This can be understood if we remember that our map $\rho\rightarrow\Psi$ accepts only determinantal Ψ's and, thus, excludes any correlation effects.

IV. EXACT CALCULATION OF $\widetilde{F}(\rho)$

In our previous approximation of $\widetilde{F}$, we started from a single-particle basis $\varphi^{\vec{k}}$ corresponding to the charge density ρ. We then constructed antisymmetric N-particle functions Ψ by forming determinants. The set of all these N-particle functions Ψ, which is obtained by antisymmetrization of the product of the basis $\varphi^{\vec{k}}$, forms a complete basis ψ in the N-particle space. We, thus, can develop any N-particle function Ψ within this basis. The only problem left is to find the condition under which a given function Ψ satisfies $\Psi\rightarrow\rho$. We have the following theorem.

Theorem 3. For all $\rho(\vec{r})\in A_N$, and with

$$\varphi^{\vec{k}s}(\vec{r})=[\rho(\vec{r})/N]^{1/2}e^{i(\vec{k}\cdot\vec{R})}s\ ,$$

a one-particle basis,

$$\psi_{\{\vec{k},s\}_i}=\frac{1}{\sqrt{N!}}\det{}_{\{\vec{k},s\}_i}(\varphi^{\vec{k}s})\ ,$$

an N-particle basis, where

$$\mathscr{C}(\{\vec{k},s\}_i)=N\ ,$$

and $\mathscr{C}$ represents cardinality, and for

$$\Psi=\sum_i\lambda_i\psi_{\{\vec{k},s\}_i}\ ,$$

an N-particle wave function, where

$$\sum_i|\lambda_i|^2=1\ .$$

If for all i,j with $i\neq j$, the set $\{\vec{k},s\}_i$ differs from the set $\{\vec{k},s\}_j$ (a) by at least one spin, or (b) if all spins are equal, by at least two $\vec{k}$, then

$$\Psi\rightarrow\rho\ .$$

The proof of this theorem is given in Appendix F.

This powerful theorem allows us to obtain *all* Ψ's which satisfy $\Psi\rightarrow\rho$. It is thus, in principle, possible to calculate the functional $\widetilde{F}(\rho)$ exactly. We obtain for $\widetilde{F}(\rho)$

$$\widetilde{F}(\rho)=\inf\{T(\rho)+U(\rho)\}\ ,$$
$$T(\rho)=\int(\vec{\nabla}\sqrt{\rho})^2d\vec{r}+\frac{1}{N}\int\rho(\vec{r})\sum_i|\lambda_i|^2\left[\sum_{\{\vec{k},s\}_i}[\vec{\nabla}(\vec{k}\cdot\vec{R})]^2-\frac{1}{N}\left[\sum_{\{\vec{k},s\}_i}\vec{\nabla}(\vec{k}\cdot\vec{R})\right]^2\right]d\vec{r}\ ,$$
$$U(\rho)=\tfrac{1}{2}\int d\vec{r}\int d\vec{r}\,'\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}[1-\epsilon_{\rm xc}(\{\{\vec{k},s\}_i\},\vec{r},\vec{r}\,')]\ , \tag{13}$$

$$\epsilon_{\mathrm{xc}}=\sum_j |\lambda_j|^2\frac{1}{N^2}\left[\left|\sum_{\{\vec{\mathrm{k}},s=\mathrm{up}\}_j} e^{i\vec{\mathrm{k}}\cdot\vec{\alpha}}\right|^2+\left|\sum_{\{\vec{\mathrm{k}},s=\mathrm{down}\}_j} e^{i\vec{\mathrm{k}}\cdot\vec{\alpha}}\right|^2\right]$$

$$-\frac{1}{N^2}\sum_{i,j}{}'\lambda_i\lambda_j^*\left(e^{-i(\vec{\mathrm{q}}_i\cdot\vec{\mathrm{R}}+\vec{\mathrm{q}}_i'\cdot\vec{\mathrm{R}}'-\vec{\mathrm{q}}_j\cdot\vec{\mathrm{R}}-\vec{\mathrm{q}}_j'\cdot\vec{\mathrm{R}}')}-e^{-i(\vec{\mathrm{q}}_i\cdot\vec{\mathrm{R}}'+\vec{\mathrm{q}}_i'\cdot\vec{\mathrm{R}}-\vec{\mathrm{q}}_j\cdot\vec{\mathrm{R}}-\vec{\mathrm{q}}_j\cdot\vec{\mathrm{R}}')}\delta_{s_is_i'}\right),$$

$$\vec{\mathrm{R}}=\vec{\mathrm{R}}(\vec{\mathrm{r}}),\quad \vec{\mathrm{R}}'=\vec{\mathrm{R}}(\vec{\mathrm{r}}'),\quad \vec{\alpha}=\vec{\mathrm{R}}-\vec{\mathrm{R}}'\ . \tag{13}$$

The sum $\sum'$ runs over all i,j $(i\neq j)$ for which the sets $\{\vec{\mathrm{k}},s\}_i$ and $\{\vec{\mathrm{k}},s\}_j$ differ by exactly two elements $\vec{\mathrm{k}}$, i.e., the elements $(\vec{\mathrm{q}}_i,s_i)$, $(\vec{\mathrm{q}}_i',s_i')$ in $\{\vec{\mathrm{k}},s\}_i$ are replaced by $(\vec{\mathrm{q}}_j,s_i)$, $(\vec{\mathrm{q}}_j',s_i')$ in $\{\vec{\mathrm{k}},s\}_j$. Note that the spin part is unchanged. If we restrict ourselves to a finite basis set $\psi_{\{\vec{\mathrm{k}},s\}_i}$ we will obtain an upper bound for $\tilde{F}(\rho)$. This upper bound can be successively improved by extension of the basis set.

V. CONCLUSIONS

In order to avoid the inherent difficulties of the HK theory, Levy and Lieb have proposed a new functional $\tilde{F}(\rho)$. We have shown in this paper, that this functional can be calculated in principle. Following our method it is possible to approach $\tilde{F}$ by an upper bound. The accuracy can be pushed to any desired degree. In a first approximation to $\tilde{F}$ we have shown that this functional allows to treat the case $N=1$ exactly. We have further applied a thermodynamic limit of $\tilde{F}(\rho)$ to the jellium problem.

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APPENDIX A: CONSTRUCTION OF THE BASIS $\varphi^{\vec{\mathrm{k}}}(\vec{\mathrm{r}})$

We define

$$\vec{\mathrm{R}}(\vec{\mathrm{r}})=(R_1(x,y,z),R_2(y,z),R_3(z))$$

with

$$R_1(x,y,z)=2\pi\frac{\int_{-\infty}^{x}dx'\rho(x',y,z)}{\int_{-\infty}^{\infty}dx'\rho(x',y,z)},\quad 0\le R_1\le 2\pi\ ,$$

$$R_2(y,z)=2\pi\frac{\int_{-\infty}^{y}dy'\int_{-\infty}^{\infty}dx'\rho(x',y',z)}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dx'dy'\rho(x',y',z)}\ ,\qquad 0\le R_2\le 2\pi\ ,$$

$$R_3(z)=\frac{2\pi}{N}\int_{-\infty}^{z}dz'\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dx'dy'\rho(x',y',z')\ ,\qquad 0\le R_3\le 2\pi\ ,$$

R_1, R_2, and R_3 increase monotonously with x, y, and z, respectively. The above relations give a one-to-one map[9] between $(x,y,z)\in R^3$ and $(R_1,R_2,R_3)\in[0,2\pi]^3$. Points at infinity in R^3 correspond to points on the surface of the cube $[0,2\pi]^3$. The latter property is important for the limits of integration. We obtain

$$\frac{\partial R_1(x,y,z)}{\partial x}=2\pi\rho(\vec{\mathrm{r}})\frac{1}{\int_{-\infty}^{\infty}dx'\rho(x',y,z)}\ ,$$

$$\frac{\partial R_2(y,z)}{\partial y}=2\pi\int_{-\infty}^{\infty}dx'\rho(x',y,z)\times\frac{1}{\int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dy'\rho(x',y',z)}\ ,$$

$$\frac{\partial R_2(y,z)}{\partial x}=0\ ,$$

$$\frac{\partial R_3(z)}{\partial z}=\frac{2\pi}{N}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dx'dy'\rho(x',y',z)\ ,$$

$$\frac{\partial R_3(z)}{\partial x}=\frac{\partial R_3(z)}{\partial y}=0\ ,$$

$$\frac{\partial R_1(x,y,z)}{\partial x}\frac{\partial R_2(y,z)}{\partial y}\frac{\partial R_3(z)}{\partial z}=\frac{(2\pi)^3}{N}\rho(x,y,z)\ .$$

The Jacobian of the transformation $\vec{\mathrm{R}}\rightarrow\vec{\mathrm{r}}$ is

$$\frac{D(R_1,R_2,R_3)}{D(x,y,z)}=\begin{vmatrix}\frac{\partial R_1}{\partial x} & \frac{\partial R_1}{\partial y} & \frac{\partial R_1}{\partial z}\\ \frac{\partial R_2}{\partial x} & \frac{\partial R_2}{\partial y} & \frac{\partial R_2}{\partial z}\\ \frac{\partial R_3}{\partial x} & \frac{\partial R_3}{\partial y} & \frac{\partial R_3}{\partial z}\end{vmatrix}$$

$$=\frac{\partial R_1}{\partial x}\frac{\partial R_2}{\partial y}\frac{\partial R_3}{\partial z}=\frac{(2\pi)^3}{N}\rho(\vec{\mathrm{r}})\ .$$

We define

$$\varphi^{\vec{\mathrm{k}}}(\vec{\mathrm{r}})=\left[\frac{\rho(\vec{\mathrm{r}})}{N}\right]^{1/2}e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{R}}},\quad \vec{\mathrm{k}}\in Z^3\ .$$

Orthogonality of the basis is shown as follows:

$$\langle\varphi^{\vec{\mathrm{k}}'}|\varphi^{\vec{\mathrm{k}}}\rangle=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dx\,dy\,dz\frac{\rho(\vec{\mathrm{r}})}{N}e^{i(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\cdot\vec{\mathrm{R}}}$$

$$=\frac{1}{(2\pi)^3}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi}dR_1dR_2dR_3e^{i(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\cdot\vec{\mathrm{R}}}=\delta_{\vec{\mathrm{k}},\vec{\mathrm{k}}'}\ .$$

Completeness of the basis is shown as follows. We use the completeness of the plane-wave basis $\langle \vec{q} \,|$,

$$q(\vec{r})=\frac{1}{\sqrt{V}}e^{i\vec{q}\cdot\vec{r}}\,,$$

$$\sum_{\vec{k}} |\varphi^{\vec{k}}\rangle\langle\varphi^{\vec{k}}| = \sum_{\vec{q},\vec{q}\,'}\sum_{\vec{k}} |\vec{q}\rangle\langle\vec{q}\,|\varphi^{\vec{k}}\rangle\langle\varphi^{\vec{k}}\,|\vec{q}\,'\rangle\langle\vec{q}\,'|\,,$$

$$\langle\vec{q}\,|\varphi^{\vec{k}}\rangle=\int d^3r\, e^{-i\vec{q}\cdot\vec{r}}\left[\frac{\rho(\vec{r})}{NV}\right]^{1/2} e^{i\vec{k}\cdot\vec{R}}\,,$$

$$\begin{aligned}\sum_{\vec{k}}\langle\vec{q}\,|\varphi^{\vec{k}}\rangle\langle\varphi^{\vec{k}}\,|\vec{q}\,'\rangle &= \sum_{\vec{k}}\int\int \frac{d^3r\,d^3r'}{NV}[\rho(\vec{r})\rho(\vec{r}\,')]^{1/2}e^{i\vec{q}\,'\cdot\vec{r}\,'-\vec{q}\cdot\vec{r})}e^{i\vec{k}\cdot(\vec{R}-\vec{R}\,')}\\ &=\int\int d^3r\,d^3r'\frac{[\rho(\vec{r})\rho(\vec{r}\,')]^{1/2}}{NV}e^{i(\vec{q}\,'\cdot\vec{r}\,'-\vec{q}\cdot\vec{r})}V\delta(\vec{R}-\vec{R}\,')\\ &=\int d^3r\frac{[\rho(\vec{r})]^{1/2}}{N}e^{-i\vec{q}\cdot\vec{r}}\int d^3r' e^{i\vec{q}\,'\cdot\vec{r}\,'}[\rho(\vec{r}\,')]^{1/2}\delta(\vec{R}(\vec{r})-\vec{R}(\vec{r}\,'))\,.\end{aligned}$$

We have

$$\int d^3r\, g(\vec{r})\delta(\vec{f}(\vec{r}))=\sum_{\vec{r}_0} g(\vec{r}_0)\frac{1}{(D\vec{f}/D\vec{r})\,|_{\vec{r}=\vec{r}_0}}\,\vec{f}(\vec{r}_0)=0\,,$$

where $D\vec{f}/D\vec{r}$ is the Jacobian. In our case, $\vec{f}(\vec{r})=\vec{R}(\vec{r})-\vec{R}(\vec{r}\,')$,

$$\vec{R}(\vec{r})-\vec{R}(\vec{r}\,')=0 \Longrightarrow \vec{r}=\vec{r}\,'$$

because $\vec{R}$ is a regular and monotonously increasing function. This gives us

$$\begin{aligned}&\int d^3r\frac{[\rho(\vec{r})]^{1/2}}{N}e^{-i\vec{q}\cdot\vec{r}}\int d^3r' e^{i\vec{q}\,'\cdot\vec{r}\,'}[\rho(\vec{r}\,')]^{1/2}\delta(\vec{R}(\vec{r})-\vec{R}(\vec{r}\,'))\\ &\qquad=\int d^3r\frac{[\rho(\vec{r})]^{1/2}}{N}e^{-i\vec{q}\cdot\vec{r}}[\rho(\vec{r})]^{1/2}\frac{e^{i\vec{q}\,'\cdot\vec{r}}}{\frac{(2\pi)^3}{N}\rho(\vec{r})}=\int d^3r\frac{e^{i(\vec{q}\,'-\vec{q})\cdot\vec{r}}}{(2\pi)^3}=\delta(\vec{q}\,'-\vec{q})\end{aligned}$$

$$\sum_{\vec{k}}|\varphi^{\vec{k}}\rangle\langle\varphi^{\vec{k}}| = \sum_{\vec{q},\vec{q}\,'}\delta(\vec{q}\,'-\vec{q})\,|\vec{q}\rangle\langle\vec{q}\,'| = \sum_{\vec{q}}|\vec{q}\rangle\langle\vec{q}\,| = \mathbb{1}\,.$$

Proof of theorem 2: Construction of ψ. We define $\psi_{\{\vec{k}\}}=(1/\sqrt{N}!)\det[\phi^{\vec{k}}(\vec{r})]$. If ψ is a determinant, $\rho'(\vec{r})$ is given by

$$\rho'(\vec{r})=\sum_{\vec{k}}|\phi^{\vec{k}}(\vec{r})|^2=\frac{\rho(\vec{r})}{N}\sum_{\vec{k}}1=\rho(\vec{r})\,.$$

Thus $\psi\rightarrow\rho(\vec{r})$.

APPENDIX B: CHOICE OF THE PHASE OF ψ

We start with

$$\psi=\frac{1}{\sqrt{N!}}\det(\varphi^k)\,.$$

We define

$$\begin{aligned}\psi'&=\exp\left[i\sum_{j=1}^{N}\theta(\vec{r}_j)\right]\psi\\ &=\frac{1}{\sqrt{N!}}\det\left[\left[\frac{\rho}{N}\right]^{1/2}e^{i(\vec{k}\cdot\vec{R}+\theta)}\right]\,.\end{aligned}$$

The phase changes only the kinetic energy:

$$\begin{aligned}T(\rho)=&\int(\vec{\nabla}\sqrt{\rho})^2d^3r\\ &+\frac{1}{N}\int\rho(\vec{r})\sum_{\{\vec{k}\}}\{\nabla[\vec{k}\cdot\vec{R}+\theta(\vec{r})]\}^2d^3r\,.\end{aligned}$$

We define

$$G(\theta)=\frac{1}{N}\int\rho(\vec{r})\sum_{\{\vec{k}\}}[\vec{\nabla}(\vec{k}\cdot\vec{R}+\theta)]^2d^3r\,.$$

$T(\rho)$ becomes extremal for stationary $G(\theta)$:

$$\begin{aligned}\delta G(\theta)&=\frac{1}{N}\int\rho(\vec{r})\sum_{\{\vec{k}\}}2\vec{\nabla}(\vec{k}\cdot\vec{R}+\theta)\vec{\nabla}\delta\theta\, d^3r\\ &=0\,.\end{aligned}$$

The solution is $\sum_{\{\vec{k}\}} \vec{\nabla}(\vec{k}\cdot\vec{R}+\theta)=0$:

$$\vec{\nabla}\theta(\vec{r})=-\frac{1}{N}\sum_{\{\vec{k}\}}\vec{\nabla}(\vec{k}\cdot\vec{R}) .$$

It corresponds to a minimum of the kinetic energy given by Eq. (5).

APPENDIX C: PROOF THAT $\tilde{F}'(\rho)=\tilde{F}(\rho)$ FOR $N=1$

$\tilde{F}'(\rho)$ is calculated as follows:

$$\tilde{F}'(\rho)=\inf\{T(\rho)+U(\rho)\}$$

$$=\inf\left\{\int(\vec{\nabla}\sqrt{\rho})^2d^3r+\int\rho(\vec{r})[\vec{\nabla}(\vec{k}\cdot\vec{R})]^2d^3r\right.$$

$$+\int\int\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

$$\left.\times(1-|e^{i\vec{k}\cdot(\vec{R}-\vec{R}\,')}|^2)d^3r\,d^3r'\right\} .$$

The infimum is obtained for $\vec{k}=(0,0,0)$:

$$\tilde{F}'(\rho)=\int(\vec{\nabla}\sqrt{\rho})^2d^3r .$$

$\tilde{F}(\rho)$ is calculated as follows. For $N=1$, we can construct *all* ψ such that $\psi\rightarrow\rho$:

$$\psi=[\rho(\vec{r})]^{1/2}e^{i\theta(\vec{r})},\quad \theta(\vec{r})\text{ arbitrary} .$$

Thus $\tilde{F}(\rho)$ can be calculated exactly:

$$\vec{\nabla}\psi=(\vec{\nabla}\sqrt{\rho}+i\sqrt{\rho}\vec{\nabla}\theta)e^{i\theta} ,$$

$$\langle\psi|H_0|\psi\rangle=\langle\psi|p^2|\psi\rangle=\int(\vec{\nabla}\sqrt{\rho})^2d^3r+\int\rho(\vec{\nabla}\theta)^2d^3r$$

$$\tilde{F}=\inf\{\langle\psi|H_0|\psi\rangle\ |\ \psi\rightarrow\rho\}$$

$$=\inf\left\{\int(\vec{\nabla}\sqrt{\rho})^2d^3r+\int\rho(\vec{\nabla}\theta)^2d^3\right\}$$

$$=\int(\nabla\sqrt{\rho})^2d^3r .$$

It thus follows that $\tilde{F}'(\rho)=\tilde{F}(\rho)$.

APPENDIX D: THE THERMODYNAMIC LIMIT

In the following we treat the case of fermions with spins $\frac{1}{2}$. We start from Eq. (6). We make the following assumptions:

$$N_\uparrow=N_\downarrow=\frac{N}{2} ,$$

$$N_\uparrow=N_\downarrow=\frac{N}{2} ,$$

$$\{\vec{k}\}_\uparrow=\{\vec{k}\}_\downarrow .$$

The latter defines a Fermi sphere, such that

$$\sum_{\{\vec{k}\}}=2\sum_{\{\vec{k}\}_\uparrow},\quad \frac{N}{V}=\frac{k_F^3}{3\pi^2} .$$

Changing the variables $\vec{k},k_F,\vec{R}$ according to Eq. (8), we obtain

$$\tilde{F}'(\rho)=T(\rho)+U(\rho) ,$$

$$T(\rho)=\int(\vec{\nabla}\sqrt{\rho})^2d^3r$$

$$+\frac{2V}{(2\pi)^3N}\int d^3r\,\rho(\vec{r})\int\{\vec{\nabla}[\vec{k}\cdot\vec{R}(\vec{r})]\}^2d^3k ,$$

$$U(\rho)=\tfrac{1}{2}\int\int d^3r\,d^3r'\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}(1-\epsilon_x) ,$$

$$\epsilon_x=\frac{2V^2}{N^2(2\pi)^6}\left|\int d^3k\,e^{i\vec{k}\cdot\vec{\alpha}}\right|^2 ,$$

$$\vec{\alpha}=\vec{R}(\vec{r})-\vec{R}(\vec{r}\,') .$$

Kinetic term. We start with

$$\vec{R}=(R_1,R_2,R_3),\quad \vec{k}=(k_1,k_2,k_3) ,$$

$$[\vec{\nabla}(\vec{k}\cdot\vec{R})]^2=k_1^2(\vec{\nabla}R_1)^2+k_2^2(\vec{\nabla}R_2)^2$$

$$+(k_3)^2(\vec{\nabla}R_3)^2+\cdots ,$$

where the ellipsis represents cross terms. The cross terms vanish after the integration by symmetry. With $\int_{|\vec{k}|\le k_F}d^3k\,k_1^2=(4\pi/15)k_F^5$ we obtain

$$\frac{2V}{(2\pi)^3N}\int d^3r\,\rho(\vec{r})\int[\vec{\nabla}(\vec{k}\cdot\vec{R})]^2d^3k$$

$$=\tfrac{1}{5}k_F^2\int d^3r\,\rho(\vec{r})[(\vec{\nabla}R_1)^2+(\vec{\nabla}R_2)^2+(\vec{\nabla}R_3)^2] .$$

Exchange term. With

$$\int_{|\vec{k}|\le k_F}d^3k\,e^{i\vec{k}\cdot\vec{\alpha}}=-\frac{4\pi}{\alpha^2}\left[k_F\cos(k_F\alpha)-\frac{\sin(k_F\alpha)}{\alpha}\right]$$

we obtain

$$\epsilon_x=\tfrac{1}{2}F^2(k_F\alpha)$$

with

$$F(x)=\frac{3}{x^2}\left[\cos x-\frac{\sin x}{x}\right] .$$

Thus we obtain Eq. (10).

APPENDIX E: THE PERIODIC JELLIUM

From Eq. (3) we obtain, together with Eq. (11) and Eq. (8),

$$R_1=x-\frac{\alpha}{2l}\sin(2lx),\quad R_2=y-\frac{\alpha}{2l}\sin(2ly),\quad R_3=z-\frac{\alpha}{2l}\sin(2lz) .$$

Kinetic energy. We calculate the terms of Eq. (10):

$$\int (\vec{\nabla}\sqrt{\rho})^2 d^3r = \int \frac{(\vec{\nabla}\rho)^2}{4\rho} d^3r = \tfrac{3}{4} \int \frac{\left[\dfrac{\partial\rho}{\partial x} \right]^2}{\rho} d^3r$$

$$= \frac{3N}{4V}(2l\alpha)^2 \int_0^L \frac{\sin^2(2lx)}{1-\alpha\cos(2lx)} dx \left[\int_0^L [1-\alpha\cos(2ly)]dy \right]^2$$

$$= \frac{3}{4}\frac{N}{L}\frac{(2l\alpha)^2}{2l} \int_0^{2\pi m} \frac{1-\cos 2x}{1-\alpha\cos x} dx = \tfrac{3}{4}Nk_F^2\xi^2[1-(1-\alpha^2)^{1/2}] ,$$

$$\frac{T(\rho)}{N} = \tfrac{3}{5}k_F^2 + k_F^2\{\tfrac{9}{10}\alpha^2 + \tfrac{3}{4}\xi^2[1-(1-\alpha^2)^{1/2}]\}.$$

$$= \tfrac{3}{5}k_F^2 \int d^3r \frac{N}{V}[1-\alpha\cos(2lx)]^3[1-\alpha\cos(2ly)][1-\alpha\cos(2lz)] = \tfrac{3}{5}k_F^2 N \left[1 + \frac{3\alpha^2}{2} \right] ,$$

$$\frac{T(\rho)}{N} = \tfrac{3}{5}k_F^2 + k_F^2\{\tfrac{9}{10}\alpha^2 + \tfrac{3}{4}\xi^2[1-(1-\alpha^2)^{1/2}]\}.$$

Coulomb energy. We have the following.
(a) The exchange integral

$$E_x = \tfrac{1}{4} \int \int d^3r\, d^3r' \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} F^2(k_F a) ,$$

$$a = |\vec{R}(\vec{r}) - \vec{R}(\vec{r}\,')|$$

$$= \left| \vec{r} - \vec{r}\,' - \frac{\alpha}{2l}(\sin(2lx)-\sin(2lx'), \sin(2ly)-\sin(2ly'), \sin(2lz)-\sin(2lz')) \right| .$$

We approximate a by $a = |\vec{r}-\vec{r}\,'|$. This approximation is valid if m [Eq. (11)] is large, i.e., if the number of periods is sufficiently large in the volume $V = L^3$.

As $\rho(\vec{r})$ is periodic, the exchange integral can be calculated by Fourier expansion:

$$\rho(\vec{r}) = \sum_{n,l,p=0}^{m-1} \rho(\vec{R}_{nlp} + \vec{\xi}), \quad \vec{R}_{nlp} = \frac{L}{m}(n,l,p), \quad \vec{\xi} \in \left[0, \frac{L}{m} \right]^3 ,$$

the latter being one period. We then obtain

$$E_x(\rho) = \sum_{n,l,p} \sum_{n',l',p'} \frac{k_F}{4} \int \int d^3\xi\, d^3\xi' \frac{\rho(\vec{R}_{nlp}+\vec{\xi})\rho(\vec{R}_{n'l'p'}+\vec{\xi}\,')}{k_F|\vec{R}_{nlp}-\vec{R}_{n'l'p'}+\vec{\xi}-\vec{\xi}\,'|} F^2(k_F|\vec{R}_{nlp}-\vec{R}_{n'l'p'}+\xi-\vec{\xi}\,'|)$$

$$= \sum_{n,l,p} \sum_{n',l',p'} \int \int d^3\xi\, d^3\xi' \rho(\vec{R}_{nlp}+\vec{\xi})\rho(\vec{R}_{n'l'p'}+\vec{\xi}\,')$$

$$\times \frac{1}{k_F^2} \int \frac{d^3k}{(2\pi)^3} \left[\frac{F^2(\vec{x})}{|\vec{x}|} \right]^{\sim} e^{-i\vec{k}\cdot[k_F(\vec{R}_{nlp}-\vec{R}_{n'l'p'}+\vec{\xi}-\vec{\xi}\,')]}$$

$$= \int d^3k \frac{1}{4k_F^2(2\pi)^3} \int \int d^3\xi\, d^3\xi' \rho(\vec{\xi})\rho(\vec{\xi}\,') \left[\frac{F^2(\vec{x})}{|\vec{x}|} \right]^{\sim} e^{-i\vec{k}\cdot[k_F(\vec{\xi}-\vec{\xi}\,')]} \sum_{n,l,p} \sum_{n',l',p'} e^{i\vec{k}\cdot[k_F(\vec{R}_{nlp}-\vec{R}_{n',l'p'})]}$$

$$= \sum_{\vec{K}} \frac{1}{k_F^2} \frac{V}{4} \int d^3\xi \rho(\vec{\xi}) e^{-i\vec{K}\cdot\vec{\xi}} \int d^3\xi' \rho(\vec{\xi}\,') e^{i\vec{K}\cdot\vec{\xi}\,'} \left[\frac{F(\vec{x})}{|\vec{x}|} \right]^{\sim}$$

$$= \frac{V}{4k_F^2} \sum_{\vec{K}} |\rho(\vec{K})|^2 f(\vec{K}) ,$$

$$f(\vec{K}) = \int \frac{F^2(\vec{x})}{|\vec{x}|} e^{i\vec{K}\cdot\vec{x}} d^3x = \left[\frac{F^2(\vec{x})}{|\vec{x}|} \right]^{\sim} .$$

$\vec{K}$ is the reciprocal-lattice vector in units of k_F:

$$\vec{K}_{nlp}=\frac{2\pi m}{Lk_F}(n,l,p)\ .$$

We have still to calculate $f(\vec{K})$ and $\rho(\vec{K})$. $\rho(\vec{K})$ can be calculated immediately from Eq. (11):

$$|\vec{K}|=0,\ \ \rho(|\vec{K}|=0)=\frac{N}{V}\ \ \text{(one term)}\ ;$$

$$|\vec{K}|=\frac{2l}{k_F}=\xi,\ \ \rho(|\vec{K}|=\xi)=-\alpha\frac{N}{V}\ \ \text{(three terms)}\ ;$$

$$|\vec{K}|=\sqrt{2}\frac{2l}{k_F}=\sqrt{2}\xi,\ \ \rho(\sqrt{2}\xi)=\alpha^2\frac{N}{V}\ \ \text{(three terms)}\ ;$$

$$|\vec{K}|=\sqrt{3}\frac{2l}{k_F}=\sqrt{3}\xi,\ \ \rho(\sqrt{3}\xi)=-\alpha^3\frac{N}{V}\ \ \text{(one term)}\ .$$

For $\vec{K}=0$ we have

$$f(\vec{K}=0)=9\pi\ ,$$

$$E_x=\frac{V}{4k_F^2}\left|\frac{N}{V}\right|^2 9\pi=Nk_F\frac{3}{4\pi}\ .$$

This is exactly the well-known result for the exchange term for the plane-waves jellium. For $\vec{K}\neq 0$, we have

$$\frac{V}{4k_F^2}\sum_{\vec{K}\neq 0}|\rho(\vec{K})|^2 f(\vec{K})=\frac{Nk_F}{4\pi^2}\left[\alpha f(\xi)+\alpha^2 f(\sqrt{2}\xi)+\frac{\alpha^3}{3}f(\sqrt{3}\xi)\right]\ ,$$

$$\frac{E_x}{N}=k_F\frac{3}{4\pi}+\frac{k_F}{4\pi^2}\left[\alpha f(\xi)+\alpha^2 f(\sqrt{2}\xi)+\frac{\alpha^3}{3}f(\sqrt{3}\xi)\right]\ .$$

(b) Classical Coulomb term. The calculation is very similar to that of the exchange integral. We have only to replace $f(\vec{K})$ by the Fourier transform of $1/|\vec{x}|$, which is $4\pi/|\vec{K}|^2$:

$$U_D=\frac{2\pi V}{k_F^2}\sum_{\vec{K}}|\rho(\vec{K})|^2\frac{1}{|\vec{K}|^2}\ .$$

For $\vec{K}=0$ we obtain the classical Coulomb interaction term of the plane-waves jellium. This term is compensated by the contribution of the homogeneous background, which guarantees the charge neutrality. For $\vec{K}\neq 0$ we obtain

$$U_D=\frac{2N}{\pi}k_F\frac{\alpha}{\xi^2}\left[1+\frac{\alpha}{2}+\frac{\alpha^2}{9}\right]\ .$$

Total energy. Summing up, we find the total energy of the periodic jellium, Eq. (12).

APPENDIX F: PROOF OF THEOREM 3. CONSTRUCTION OF ALL Ψ SUCH THAT $\psi\to\rho$

We have

$$\Psi=\sum_i \lambda_i\psi_{\{\vec{k},s\}_i},\ \ \sum_i|\lambda_i|^2=1\ ,$$

(a) follows from the spin orthogonality. The necessity of (b) is shown in the following way: If $\{\vec{k},s\}_i$ differs from $\{\vec{k},s\}_j$ by only one $\vec{k}$ element ($\vec{q}_i$ and $\vec{q}_j$),

$$\begin{aligned}\rho(\vec{r})&=N\sum_{\sigma}\int d^3r_2\cdots d^3r_N\sum_{i,j}\lambda_i\lambda_j^*\psi_{\{\vec{k},s\}_i}\psi_{\{\vec{k},s\}_j}\\&=\sum_i\sum_{\{\vec{k},s\}_i}|\lambda i|^2|\varphi^{\vec{k}s}|^2+\sum_{\substack{i,j\\ i\neq j}}\lambda_i\lambda_j^*\varphi^{\vec{q}_is}(\varphi^{\vec{q}_js})^*\\&=\rho(r)+\rho(r)\sum_{\substack{i,j\\ i\neq j}}\frac{\lambda_i\lambda_j^*}{N}e^{i(\vec{q}_i-\vec{q}_j)\cdot\vec{R}(\vec{r})}\ .\end{aligned}$$

It is obvious that the second term is zero for all r, if and only if only one of the coefficients λ_i differs from zero.

The proof of sufficiency is trivial.

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[4] To be rigorous, the set A_N must be restricted by the following condition: There exists no finite volume Ω for which $\int_{\Omega} \rho(\vec{r}) d\vec{r} = 0$. This property is used for the proof in Appendix A.

[5] For a rigorous definition of the admissible functional subspace of the external potentials, see Ref. 3.

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[8] The limitation to equal-density orbitals is not very restrictive: One can construct nearly equal-density orbitals from the HF orbitals by a unitary transformation as was shown by R. G. Parr and M. B. Chen, Proc. Natl. Acad. Sci. U.S.A. 78, 1323 (1981).

[9] If $\rho(\vec{r}) = 0$ along a line or on a surface (see also Ref. 4) care has to be taken to preserve the uniqueness of the map.