PHYSICAL REVIEW A VOLUME 35, NUMBER 3 FEBRUARY 1, 1987

Many-electron energy-density-functional theory: Point transformations and one-electron densities

Eugene S. Kryachko
Institute for Theoretical Physics, Kiev, USSR 252130

Eduardo V. Ludeña
Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 21827,
Caracas 1020-A, Venezuela

(Received 7 July 1986)

A novel approach to energy-density-functional theory, based on point transformations in coordinate three-dimensional space, is advanced. These point transformations are discussed in the context of one-electron densities and many-electron wave functions. In particular, the group properties of these transformations are discussed and it is shown by incorporating some of the topological properties of the one-electron density, as discussed by Bader *et al.*, that the n-representability conditions for densities may be reformulated. This is done in this paper for atoms. As a simple application of this method, the local-density approximation is obtained by computing the point transformation for a slowly varying density. Also the relationship between this method and the one based in equidensity orbitals is discussed.

I. INTRODUCTION

At present, density-functional theory (DFT) has become a powerful and rather popular approach for studying diverse properties of atoms (including ions), molecules, and solids.[1-7] A rigorous formulation of DFT has not been achieved so far[1-9] and the problem of constructing the correct energy functional remains unsolved.[10,11]

The basic idea of DFT is that of reformulating the stationary nonrelativistic quantum-mechanical Schrödinger principle for the ground states of many-electron systems in terms of a single variable, the one-electron density $\rho(\mathbf{r})$ [or $\rho(\mathbf{r},\sigma)$, when spin is included].[1-11]

It has been stressed in the works of Blokhintsev,[12] Macke,[13] and Rennert,[14] March and Young,[15(a)] and Percus[15(b)] that point transformations in coordinate space may be of importance for attaining a rigorous formulation of the energy variational principle in DFT. It should be emphasized, however, that the class of point transformations employed in these works has not been sufficiently general and hence, it has had a restricted range of applicability.[16-22] Spatial transformations of the most general type,[23] have been used rarely in quantum chemistry.[24-27]

A novel approach,[28-30] based on general point transformations in coordinate three-dimensional space, coupled to the method of orbits[31] introduced on a set of one-electron densities, with respect to such transformations, has been recently developed. A rigorous formulation of the variational principle for ground-state many-electron systems, within the framework of DFT, may be achieved by this new method. In addition, this method has turned out to be rather fruitful as well as sufficiently simple, in a computational sense, for processing data on $\rho(\mathbf{r})$ obtained on crystals.[32]

Based on these concepts, the primary goal of the present series of papers is to develop a unified approach to DFT. In particular, the present paper is devoted to the study of point transformations on a set of one-electron densities. In Sec. II we discuss the most general type of point transformations in coordinate space as applied to the set of one-electron densities. In Sec. III we discuss the case of n-electron wave functions. In Sec. IV the group-theoretical properties of these point transformations are investigated and we show by introducing some of the topological properties of $\rho(\mathbf{r})$ which have been established by Bader *et al.*, that the n-representability problem for $\rho(\mathbf{r})$ may be reformulated in terms of conditions on these general point transformations. In the present paper this reformulation is restricted to the atomic case. In Sec. V these results are discussed and illustrated by comparing them to approaches based on equidensity orbitals.

II. POINT TRANSFORMATIONS AND ONE-ELECTRON DENSITIES

Let us define a set of all functions of a type $\rho(\mathbf{r})$ which are given everywhere on the three-dimensional real vector space $\mathbb{R}^3$ and which satisfy the following conditions.

(i) Non-negativity: $\rho(\mathbf{r})\geq 0$ everywhere in $\mathbb{R}^3$.

(ii) Normalization

$$\int_{\mathbb{R}^3} d\mathbf{r}\rho(\mathbf{r}) < \infty \ , \tag{1}$$

i.e., $[\rho(\mathbf{r})]^{1/2}\in L^2(\mathbb{R}^3)$.

(iii) $\rho(\mathbf{r})$ is a continuously differentiable function for all $\mathbf{r}\in\mathbb{R}^3$. We designate a set of all ρ's which satisfy conditions (i)–(iii), by $\mathcal{N}_{\rm HKL}$ following Hohenberg and Kohn[33] and Lieb.[17] One can impose the subsidiary conditions on $\mathcal{N}_{\rm HKL}$, leading to the subset $\mathcal{N}^n_{\rm HKL}$ consisting of $\rho(\mathbf{r})\in\mathcal{N}_{\rm HKL}$ and for which $\int_{\mathbb{R}^3} d\mathbf{r}\rho(\mathbf{r})=n$ with an arbitrary integer n. It is clear that the set $\mathcal{N}^n_{\rm HKL}$ is convex; that is, if $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ belong to it, so does

$$\rho(\mathbf{r})\equiv\alpha\rho_1(\mathbf{r})+(1-\alpha)\rho_2(\mathbf{r})$$

with $0<\alpha<1$. We can further interpret the elements of

$\mathcal{N}^n_{\mathrm{HKL}}$ as one-electron densities of n-electron systems, although realistic $\rho(\mathbf{r})$'s satisfy also some additional conditions (see Sec. IV).

Let us define the point transformations in the vector space $\mathbb{R}^3$ as a mapping of $\mathbb{R}^3$ into itself: for an arbitrary and fixed vector $\mathbf{r}\in\mathbb{R}^3$ the mapping (point transformation) $\mathcal{R}$ transforms it, in general, into a new vector $\mathbf{R}\in\mathbb{R}^3$ by the following rule:

$$\mathbf{r}\equiv(x,y,z)\overset{\mathcal{R}}{\longmapsto}\mathbf{R}\equiv(X,Y,Z)\equiv\mathbf{R}(\mathbf{r}) , \tag{2}$$

where x,y,z and X,Y,Z are the Cartesian coordinates of $\mathbf{r}$ and $\mathbf{R}$, respectively. Moreover, the transformation (2) is such that the inverse transformation $\mathcal{R}^{-1}$ is defined and exists in some neighborhood of $\mathbf{r}\in\mathbb{R}^3$. It is well known that in order for the inverse transformation to exist in a neighborhood of $\mathbf{r}\in\mathbb{R}^3$, it is sufficient that the Jacobian of the transformation (2),

$$D_{\mathcal{R}}\big|_{\mathbf{r}\in R^3}\equiv D_{\mathbf{R}(\mathbf{r})}\equiv\frac{D(X,Y,Z)}{D(x,y,z)}\equiv\begin{vmatrix}\dfrac{\partial X}{\partial x} & \dfrac{\partial X}{\partial y} & \dfrac{\partial X}{\partial z}\\ \dfrac{\partial Y}{\partial x} & \dfrac{\partial Y}{\partial y} & \dfrac{\partial Y}{\partial z}\\ \dfrac{\partial Z}{\partial x} & \dfrac{\partial Z}{\partial y} & \dfrac{\partial Z}{\partial z}\end{vmatrix} , \tag{3}$$

be nonzero at $\mathbf{r}\in\mathbb{R}^3$: $D_{\mathbf{R}(\mathbf{r})}\neq 0$. Due to the inverse function theorem, the mapping $\mathcal{R}$ is one to one in some neighborhood of $\mathbf{r}\in\mathbb{R}^3$.

One should notice that the mapping $\mathcal{R}$ of the type (2) is the most general one; in particular, it is not required that it necessarily preserve any metric in $\mathbb{R}^3$, such as, for example, distances, angles, or other geometrical characteristics. The sole constraint imposed on the class of transformations under study is that the mapping must be one to one everywhere in $\mathbb{R}^3$. In other words, the Jacobian $D_{\mathcal{R}}$ is distinct from zero everywhere in $\mathbb{R}^3$. In a sense, the transformation $\mathcal{R}$ of the type (2) supposes the existence of three differentiable functions: $X_{\mathcal{R}}=X_{\mathcal{R}}(x,y,z)$, $Y_{\mathcal{R}}=Y_{\mathcal{R}}(x,y,z)$, and $Z_{\mathcal{R}}=Z_{\mathcal{R}}(x,y,z)$.

The mappings $\mathcal{R}$ of the type (2), such that $D_{\mathcal{R}}\neq 0$ everywhere in $\mathbb{R}^3$, generate the group $\mathcal{P}$ of point transformations of the vector space $\mathbb{R}^3$. The unit element of the group, $\mathcal{E}\in\mathcal{P}$, is defined as the identical mapping

$$\mathbf{r}\overset{\mathcal{E}}{\longmapsto}\mathbf{E}(\mathbf{r})\equiv\mathbf{r}\quad\text{for all}\quad\mathbf{r}\in\mathbb{R}^3 .$$

For a given pair of elements $\mathcal{R}_1$ and $\mathcal{R}_2$ of $\mathcal{P}$, their group product $\mathcal{R}\equiv\mathcal{R}_1\cdot\mathcal{R}_2$ is defined as follows:

$$\mathcal{R}(\mathbf{r})\equiv\mathcal{R}_1(\mathcal{R}_2(\mathbf{r})) \tag{4}$$

for any $\mathbf{r}\in\mathbb{R}^3$. It is fairly easy to prove that with the given definition of the group composition law, the associativity rules are satisfied. An inverse element to any $\mathcal{R}\in\mathcal{P}$, defined as $\mathcal{R}^{-1}\in\mathcal{P}$, exists by definition. Hence, $\mathcal{P}$ is, in fact, a group. Further, we assume that the group involves only those transformations $\mathcal{R}$ whose Jacobians are positive definite on $\mathbb{R}^3$.

We define the action of the group $\mathcal{P}$ on the given set $\mathcal{N}^n_{\mathrm{HKL}}$ in the following way: for given $\mathcal{R}\in\mathcal{P}$ and $\rho(\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$

$$\rho(\mathbf{r})\overset{\mathcal{R}}{\longmapsto}\mathcal{R}(\rho(\mathbf{r}))\equiv\rho(\mathbf{R}(\mathbf{r}))D_{\mathbf{R}(\mathbf{r})} . \tag{5}$$

It is proved trivially that under rather general assumptions on the form of the functions $X_{\mathcal{R}}(x,y,z)$, $Y_{\mathcal{R}}(x,y,z)$, and $Z_{\mathcal{R}}(x,y,z)$ the new function

$$\mathcal{R}(\rho(\mathbf{r}))\equiv\rho_{\mathcal{R}}(\mathbf{r})\equiv\rho(\mathbf{R}(\mathbf{r}))D_{\mathbf{R}(\mathbf{r})} \tag{6}$$

satisfies conditions (i)—(iii) of the definitions of $\mathcal{N}^n_{\mathrm{HKL}}$ for any $\mathcal{R}\in\mathcal{P}$, i.e., an action of the group $\mathcal{P}$ on $\mathcal{N}^n_{\mathrm{HKL}}$, defined by (5), does not come outside of the boundaries of $\mathcal{N}^n_{\mathrm{HKL}}$. In other words, the new function $\rho_{\mathcal{R}}(\mathbf{r})$ is also the density. Generally speaking, if $\mathcal{R}\neq\mathcal{E}$, the one-electron density $\rho_{\mathcal{R}}(\mathbf{r})$ differs from its $\mathcal{R}$ preimage, i.e., it represents a new electron density belonging to $\mathcal{N}^n_{\mathrm{HKL}}$ which has the same value at $\mathbf{R}(\mathbf{r})$ as the reference one-electron density $\rho(\mathbf{r})$ at $\mathbf{r}$ scaled by the magnitude of the corresponding Jacobian $D_{\mathcal{R}}$ at $\mathbf{r}\in\mathbb{R}^3$. Notice that the definition of action of $\mathcal{P}$ on $\mathcal{N}^n_{\mathrm{HKL}}$, defined above in (5), somewhat differs from the traditional one, accepted in mathematics where one assumes that under transformation $\mathcal{R}\in\mathcal{P}$ a volume element $d\mathbf{r}$ transforms to $D_{\mathbf{R}(\mathbf{r})}d\mathbf{r}$. Our definition of the action of the group $\mathcal{P}$ on the set of one-electron densities seems to be more natural in view of the quantum theory of many-electron systems [see, for example, (34) and (35)], as it is generally assumed that under the so-called dilation transformation $\mathcal{R}^{\mu}_{d}$ which transforms any $\mathbf{r}\in\mathbb{R}^3$ to $\mu\mathbf{r}\in\mathbb{R}^3$ for positive $\mu\in\mathbb{R}^1_+$, a given one-electron density $\rho(\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$ is transformed into $\rho_\mu(\mathbf{r})\equiv\mu^3\rho(\mu\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$.

Let an arbitrary one-electron density $\rho(\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$ be given. We designate by $\mathcal{P}_\rho$ the set of point transformations, belonging to $\mathcal{P}$, which leaves $\rho(\mathbf{r})$ unchanged, i.e.,

$$\mathcal{P}_\rho\equiv\{\mathcal{R}\in\mathcal{P}\mid\rho_{\mathcal{R}}(\mathbf{r})=\rho(\mathbf{r})\ \ \forall\ \ \mathbf{r}\in\mathbb{R}^3\} . \tag{7}$$

It is clear that $\mathcal{P}_\rho$ is a subgroup of $\mathcal{P}$, because if $\mathcal{R}_1$ and $\mathcal{R}_2$ belong to $\mathcal{P}_\rho$, so does $\mathcal{R}=\mathcal{R}_1\cdot\mathcal{R}_2$, since

$$\begin{aligned}\mathcal{R}_1\cdot\mathcal{R}_2(\rho(\mathbf{r}))&=R_1(\rho_{\mathcal{R}_2}(\mathbf{r}))=\mathcal{R}_1(\rho(\mathbf{r}))\\ &=\rho_{\mathcal{R}_1}(\mathbf{r})=\rho(\mathbf{r}) .\end{aligned} \tag{8}$$

Obviously, the group $\mathcal{P}$ for the atomic case contains all the transformations of the special three-dimensional rotation group SO(3). In that case the Jacobian of any transformation $\mathcal{R}\in\mathrm{SO}(3)$ is equal to unity, and the transformation (5) is just the well-known operation of "rotation of one-electron densities." Therefore, for a given $\rho(\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$ the group $\mathcal{P}_\rho$ contains all the transformations of the point-symmetry group of $\rho(\mathbf{r})$. One can define, naturally, $\mathcal{P}_\rho$ as the stationary group of $\rho(\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$, or isotropy subgroup of $\mathcal{P}$.

III. POINT TRANSFORMATIONS AND n-ELECTRON WAVE FUNCTIONS

Let an n-electron system with the total Hamiltonian

$$\hat{H}=\hat{T}+\hat{V} \tag{9}$$

be given. In Eq. (9) $\hat{T}$ is the kinetic energy operator (in atomic units)

$$\hat{T}=\sum_{i=1}^{n}-\tfrac{1}{2}\nabla_i^2 \tag{10a}$$

and $\hat{V}$ is the potential-energy operator (in the Born-Oppenheimer approximation the constant term, corresponding to the nuclear-nuclear repulsion energy, can be omitted)

$$\hat{V}=\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}|\mathbf{r}_i-\mathbf{r}_j|^{-1}+\sum_{i=1}^{n}v(\mathbf{r}_i)\,, \tag{10b}$$

where $v(\mathbf{r}_i)$ is the external potential acting on the ith electron and possessing a multiplicative one-electron nature. For an isolated electron system, $v(\mathbf{r})$ corresponds to the electron-nuclear attraction energy.

Let $\mathcal{H}_A^n$ be the Hilbert space of n-particle antisymmetric wave functions

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)\in L^2(\mathbb{R}^{3n})$$

such that $\langle\Psi|\hat{T}|\Psi\rangle<\infty$. We define the subset $W^n\subset\mathcal{H}_A^n$ as the set of $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)$, belonging to $\mathcal{H}_A^n$ and whose norm $||\Psi||$,

$$\int_{\mathbb{R}^3}d\mathbf{r}_1\cdots\int_{\mathbb{R}^3}d\mathbf{r}_n\,|\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)|^2=1\,. \tag{11}$$

Designating by $\mathcal{P}^n$ the internal or diagonal product of groups

$$\mathcal{P}^n\equiv\otimes\mathcal{P}\equiv\{\underbrace{(\mathcal{R},\mathcal{R},\ldots,\mathcal{R})}_{n\text{ times}}\,|\,\mathcal{R}\in\mathcal{P}\}\,,$$

let us determine the action of the group $\mathcal{P}^n$ on W^n in the following manner: for arbitrary elements

$$\mathcal{R}^n\equiv(\mathcal{R},\mathcal{R},\ldots,\mathcal{R})\in\mathcal{P}^n$$

and

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_n)\in W^n\,,$$

we define[30]

$$\mathcal{R}^n(\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n))\equiv\Psi(\mathbf{R}(\mathbf{r}_1),\mathbf{R}(\mathbf{r}_2),\ldots,\mathbf{R}(\mathbf{r}_n))\left[\prod_{i=1}^{n}D_{\mathbf{R}(\mathbf{r}_i)}\right]^{1/2}. \tag{12}$$

It is clear that the actions of the group $\mathcal{P}^n$ on W^n and the group $\mathcal{P}$ on $\mathcal{N}^n_{\mathrm{HKL}}$ are consistent in the sense that if the action of an element $\mathcal{R}^n\in\mathcal{P}^n$ on $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)\in W^n$ is given by Eq. (12), the action of $\mathcal{R}\in\mathcal{P}$ on

$$\rho_\Psi(\mathbf{r})\equiv n\int_{\mathbb{R}^3}d\mathbf{r}_2\cdots\int_{\mathbb{R}^3}d\mathbf{r}_n\,|\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)|^2\in\mathcal{N}^n_{\mathrm{HKL}} \tag{13}$$

is given by Eq. (5). The operation of reduction, Eq. (13), can be interpreted as a mapping of W^n into $\mathcal{N}^n_{\mathrm{HKL}}$. Let us define the preimage of $\rho(\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$ under this mapping as the subset $W^n_\rho\subset W^n$:[36]

$$W^n_\rho\equiv\left\{\Psi\in W^n\,|\,\rho(\mathbf{r})=n\int_{\mathbb{R}^3}d\mathbf{r}_2\cdots\int_{\mathbb{R}^3}d\mathbf{r}_n\,|\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)|^2\right\}. \tag{14}$$

For any $\rho(\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$, the set W^n_ρ is certainly nonempty and, in fact, there is a many-to-one correspondence between wave functions $\Psi\in W^n$ and the density $\rho(\mathbf{r})$. This statement, which is equivalent to saying that $\rho(\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$ is pure-state n-representable follows from a theorem first proved by Gilbert[37] and later on extended by Harriman[2,16] (see also Ref. 17). In either case, however, there is an infinity of single-determinant wave functions or, equivalently, of reduced first-order density operators which yield a given particle density. The selection of the optimal density for a given physical system may be accomplished by imposing additional constraints which may be incorporated through a variational or a nonvariational procedure.[38] In Sec. IV we shall discuss how topological properties of $\rho(\mathbf{r})$ may be incorporated in order to restrict the search for the density to a smaller set containing densities which are not only n representable but which also satisfy the topological requirements dictated by the physical situation.

Consider now an electron density $\rho_0(\mathbf{r})\in\mathcal{N}^n_{\mathrm{HKL}}$ and its corresponding subset $W^n_{\rho_0}\subset W^n$. Let $\mathcal{P}_{\rho_0}$ be the stationary group of $\rho_0(\mathbf{r})$. Then the action of the subgroup $\mathcal{P}^n_{\rho_0}\equiv\otimes\mathcal{P}_{\rho_0}\subset\mathcal{P}^n$ on $W^n_{\rho_0}$ partitions $W^n_{\rho_0}$ into nonintersecting, or disjoint, subsets, the so-called orbits, which are transitive with respect to the action of the group $\mathcal{P}^n_{\rho_0}$

$$W^n_{\rho_0}=\bigcup_\alpha W^n_{\rho_0}[\alpha]\,, \tag{15a}$$

such that

$$W^n_{\rho_0}[\alpha]\cap W^n_{\rho_0}[\beta]=\phi\quad\text{if }\alpha\neq\beta \tag{15b}$$

and

$$\otimes^n\mathcal{P}_{\rho_0}(W^n_{\rho_0}[\alpha])=W^n_{\rho_0}[\alpha]\,. \tag{15c}$$

In a sense, the partitioning of $W^n_{\rho_0}$ into $\mathcal{P}^n_{\rho_0}$ orbits means that the symmetry group [the stationary subgroup of $\mathcal{P}$ (isotropy subgroup),[31] as defined by (5)] of one-electron densities is smaller that the symmetry group [the stationary subgroup of $\mathcal{P}^n$ in the sense of (12)] of any wave function $\Psi^{[\alpha]}_{\rho_0}\in W^n_{\rho_0}[\alpha]$.

IV. STRUCTURE OF THE GROUP $\mathcal{P}$

A rigorous formulation of the ground-state variational principle for many-electron systems within the framework of energy-density-functional theory could be developed by establishing a one-to-one correspondence between point transformations in $\mathbb{R}^3$ and one-electron densities (naturally, to within a stationary subgroup). In that sense, the group $\mathcal{P}$ of point transformations of the type (2) seems to be overcomplete. In fact, an arbitrary transformation $\mathcal{R}\in\mathcal{P}$ is determined uniquely, in general, by three independent functions $X_{\mathcal{R}},Y_{\mathcal{R}},Z_{\mathcal{R}}$, each of which depends on $\mathbf{r}\in\mathbb{R}^3$. Moreover, the set $\mathcal{N}^n_{\mathrm{HKL}}$, defined as consisting of "densities" is not adequately characterized since in addition to the conditions imposed above, realistic one-electron densities $\rho(\mathbf{r})$ of many-electron isolated systems possess other important properties, which are traditionally omitted in the energy-density-functional theory literature and which have been determined on the basis of extensive analyses of real one-electron densities, carried out by

Bader and co-workers.[39] These conditions refer to properties of $\rho(\mathbf{r})$, its associated vector field $\nabla\rho(\mathbf{r})$, and its Laplacian $\nabla^2\rho(\mathbf{r})$. In what follows, we single out one of these conditions, the fact that $\rho(\mathbf{r})$ must generate a closed curve in $\mathbb{R}^3$, as we are interested in developing, at this particular stage, a density-functional theory applicable to atoms. It is clear that for molecules, the paths generated by $\rho(\mathbf{r})$, although closed, satisfy additional constraints and thus we find in that case that there arise closed density curves surrounding several nuclei, but that there also exist others which only surround a subset of nuclei, until finally, in the inner regions of the virial fragments, such curves only surround a single nucleus.

Let C be an arbitrary non-negative number $C\in\mathbb{R}^1_+$, where $\mathbb{R}^1_+$ is the positive part of $\mathbb{R}^1$, including zero. Then a set of vectors $\mathbf{r}\in\mathbb{R}^3$ such that $\rho(\mathbf{r})=C$, generates for a given one-electron density $\rho(\mathbf{r})$ a closed curve in $\mathbb{R}^3$, or a path

$$\mathscr{L}_C[\rho(\mathbf{r})]\equiv\{\mathbf{r}\in\mathbb{R}^3\,|\,\rho(\mathbf{r})=C\in\mathbb{R}^1_+\}\ . \tag{16}$$

We also define for a given one-electron density $\rho(\mathbf{r})$ its set (domain) of values

$$\mathscr{M}[\rho(\mathbf{r})]\equiv\{C\in\mathbb{R}^1_+\,|\,\rho(\mathbf{r})=C,\mathbf{r}\in\mathbb{R}^3\}\ . \tag{17}$$

Let us redefine $\mathscr{N}^n_{\text{HKL}}$ as the set of densities satisfying conditions (i)—(iii) given in Sec. II, and for which any path $\mathscr{L}_C[\rho(\mathbf{r})]$ for any $C\in\mathscr{M}[\rho(\mathbf{r})]$ is a continuously differentiable function of $\mathbf{r}\in\mathbb{R}^3$ and is a closed one. We denote this subset of $\mathscr{N}^n_{\text{HKL}}$ as $\widetilde{\mathscr{N}}^n_{\text{HKL}}$.

The condition of closeness of a path $\mathscr{L}_C[\rho(\mathbf{r})]$ for an arbitrary density $\rho(\mathbf{r})\in\widetilde{\mathscr{N}}^n_{\text{HKL}}$ and for any $C\in\mathscr{M}[\rho(\mathbf{r})]$ is obviously equivalent to the following one. Let a radius vector $\mathbf{r}_0\in\mathbb{R}^3$ be given and fixed. It determines the unit vector $\mathbf{e}[\hat{\mathbf{r}}_0]\equiv\mathbf{r}/|\mathbf{r}|$ defined in the spherical coordinates by the angular part $\hat{\mathbf{r}}_0\in\Omega$ of the vector $\mathbf{r}_0$. Then, it is clear that

$$\mathscr{M}[\rho(\mathbf{r})]=\{\rho(\mathbf{r})\,|\,\mathbf{r}=r\mathbf{e}[\hat{\mathbf{r}}_0]\ \ \forall\ r\in\mathbb{R}^1\}\ .$$

In other words, selecting the unit vector in $\mathbb{R}^3$ and taking into account all values of $\rho(\mathbf{r})$ along it, one obtains the whole $\mathscr{M}[\rho(\mathbf{r})]$ for $\rho(\mathbf{r})\in\widetilde{\mathscr{N}}^n_{\text{HKL}}$.

Therefore, choosing and fixing any unit vector $\mathbf{e}_0\equiv\mathbf{e}[\hat{\mathbf{r}}_0]\in\Omega$, one can represent two arbitrary one-electron densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$, belonging to $\widetilde{\mathscr{N}}^n_{\text{HKL}}$ by one-parameter curves

$$\hat{\rho}_1(r)\equiv\rho_1(r,\mathbf{e}[\hat{\mathbf{r}}_0])$$

and

$$\hat{\rho}_2(r)=\rho_2(r,\mathbf{e}[\hat{\mathbf{r}}_0])\ .$$

It follows from the definition of $\widetilde{\mathscr{N}}^n_{\text{HKL}}$ that these curves $\hat{\rho}_1(r)$ and $\hat{\rho}_2(r)$ are continuously differentiable functions of $r\in\mathbb{R}^1$. Hence, $\hat{\rho}_1(r)$ and $\hat{\rho}_2(r)$ are homotopically equivalent, i.e., there exists such a transformation, or deformation, which transforms $\hat{\rho}_1(r)$ into $\hat{\rho}_2(r)$. By varying $\mathbf{e}[\hat{\mathbf{r}}_0]$ over the whole Ω, as a result we obtain the point transformation $\mathscr{R}$ from the group $\mathscr{P}$ of the following type:

$$\mathbf{r}\overset{\mathscr{R}}{\longmapsto}\mathbf{R}\equiv|\mathbf{R}|\,\mathbf{e}[\hat{\mathbf{r}}]\ , \tag{18}$$

where $|\mathbf{R}|$ is the length of the radius vector $\mathbf{R}\in\mathbb{R}^3$. It is clear that the transformations of the type (18) generate the subgroup $\mathscr{F}$ of the group $\mathscr{P}$ which was introduced in Refs. 28, 30, and 32.

Therefore, we prove that restrictions may be imposed on the set of one-electron densities by means of transformations of the group $\mathscr{F}$. It is clear that the transformation (18) takes the vector $\mathbf{r}\in\mathbb{R}^3$ with the Cartesian coordinates x,y,z into the vector $\mathbf{R}\in\mathbb{R}^3$ with the coordinates

$$\begin{aligned}X(x,y,z)&=\frac{x}{r}R(x,y,z)\ ,\\ Y(x,y,z)&=\frac{y}{r}R(x,y,z)\ ,\\ Z(x,y,z)&=\frac{z}{r}R(x,y,z)\ .\end{aligned} \tag{19}$$

The Jacobian of the transformation $\mathscr{R}\in\mathscr{F}$ of the type (18) becomes[28,30]

$$\begin{aligned}D_{\mathbf{R}(\mathbf{r})}=&\begin{vmatrix}\frac{1}{r}R-\frac{x^2}{r^3}R+\frac{x}{r}\frac{\partial R}{\partial x} & -\frac{xy}{r^3}R+\frac{x}{r}\frac{\partial R}{\partial y} & -\frac{xz}{r^3}R+\frac{x}{r}\frac{\partial R}{\partial z}\\ -\frac{xy}{r^3}R+\frac{y}{r}\frac{\partial R}{\partial x} & \frac{1}{r}R-\frac{y^2}{r^3}R+\frac{y}{r}\frac{\partial R}{\partial y} & -\frac{yz}{r^3}R+\frac{y}{r}\frac{\partial R}{\partial z}\\ -\frac{xz}{r^3}R+\frac{z}{r}\frac{\partial R}{\partial x} & -\frac{yz}{r^3}R+\frac{z}{r}\frac{\partial R}{\partial y} & \frac{1}{r}R-\frac{z^2}{r^3}R+\frac{z}{r}\frac{\partial R}{\partial z}\end{vmatrix}=\frac{R^2}{r^3}\left[x\frac{\partial R}{\partial x}+y\frac{\partial R}{\partial y}+z\frac{\partial R}{\partial z}\right]\\ &=\frac{1}{3r^3}\left[x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right]R^3\\ &=\frac{1}{3r^3}\mathbf{r}\cdot\nabla R^3\ .\end{aligned} \tag{20}$$

Since we fix the unit vector $\mathbf{e}[\hat{\mathbf{r}}]$, which is defined in spherical coordinates by the angles θ and ϕ, it is convenient to express the Jacobian $D_{\mathscr{R}}$ of the transformation (18) in the same coordinates. One obtains

$$D_{\mathbf{R}(\mathbf{r})}=\frac{1}{3r^2}\frac{\partial}{\partial r}R^3(r,\theta,\phi)=\left[\frac{R(r,\theta,\phi)}{r}\right]^2\frac{\partial R(r,\theta,\phi)}{\partial r}\ . \tag{21}$$

Hence, choosing $\mathscr{R}$ to belong to the group $\mathscr{F}$ and taking Eq. (21) into account, one can rewrite relation (6) in the following way:

$$\begin{aligned}\mathscr{R}(\rho(\mathbf{r}))\equiv\rho_{\mathscr{R}}(\mathbf{r})&=\left[\frac{R(\mathbf{r})}{r}\right]^2\frac{\partial R(\mathbf{r})}{\partial r}\rho(\mathbf{R}(\mathbf{r}))\\&=\left[\frac{R(r,\theta,\phi)}{r}\right]^2\frac{\partial R(r,\theta,\phi)}{\partial r}\\&\quad\times\rho(R(r,\theta,\phi),\theta,\phi)\ ,\\&\qquad\qquad\rho(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}\ .\end{aligned}\tag{22}$$

In particular, if $\rho(\mathbf{r})$ is represented in the form of the spherical-harmonic expansion series,

$$\rho(\mathbf{r})=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\rho_{lm}(r)Y_{lm}(\theta,\phi)\ ,$$

$\rho_{\mathscr{R}}(\mathbf{r})$ for $\mathscr{R}\in\mathscr{F}$ takes the following form:

$$\begin{aligned}\rho_{\mathscr{R}}(\mathbf{r})&=\rho_{\mathscr{R}}(r,\theta,\phi)\\&=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left[\frac{R(r,\theta,\phi)}{r}\right]^2\\&\qquad\times\frac{\partial R(r,\theta,\phi)}{\partial r}\rho_{lm}(R(r,\theta,\phi))Y_{lm}(\theta,\phi)\ .\end{aligned}\tag{23}$$

For fixed $\theta=\theta_0$ and $\phi=\phi_0$ from Ω, or $\mathbf{e}[\hat{\mathbf{r}}]\in\Omega$, the relation (22) can be represented as follows:[30]

$$\begin{aligned}\rho_{\mathscr{R}}(r,\theta_0,\phi_0)&=\left[\frac{R(r,\theta_0,\phi_0)}{r}\right]^2\frac{\partial R(r,\theta_0,\phi_0)}{\partial r}\\&\qquad\times\rho(R(r,\theta_0,\phi_0),\theta_0,\phi_0)\ .\end{aligned}\tag{24}$$

Therefore, it is shown that the transformations of the space $\mathbb{R}^3$ from the group $\mathscr{F}$, which were denoted in previous papers[28,30,32] as local-scaling transformations, are rather general, in the sense that $\mathscr{P}\supset\mathscr{F}$, and that they uniquely determine electron densities from $\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$.

Theorem 1. Let an arbitrary one-electron density $\rho_0(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ with the corresponding stationary subgroup $\mathscr{F}_{\rho_0}\subset\mathscr{F}$ be given. There exists a one-to-one correspondence between the representatives of cosets $\mathscr{F}/\mathscr{F}_{\rho_0}$ and one-electron densities $\rho(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ under which the unit class (1) corresponds to $\rho_0(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$.

Proof. It proceeds by *reductio ad absurdum.* Let us assume that the transformations $\mathscr{R}_1$ and $\mathscr{R}_2$ from $\mathscr{F}$ belong to different cosets of $\mathscr{F}/\mathscr{F}_{\rho_0}$, and for a given $\rho(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$

$$\rho(\mathbf{r})=\mathscr{R}_1(\rho_0(\mathbf{r}))=\mathscr{R}_2(\rho_0(\mathbf{r}))$$

then

$$\rho_0(\mathbf{r})=\mathscr{R}_1^{-1}\mathscr{R}_2(\rho_0(\mathbf{r}))\ ,$$

i.e., $\mathscr{R}_1^{-1}\mathscr{R}_2\in\mathscr{F}_{\rho_0}$. A contradiction results. Further, it is clear that any element of the form $\mathscr{R}(\rho_0(\mathbf{r}))$ belongs to $\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ under the conditions that $\mathscr{R}\in\mathscr{F}$ and that $\rho_0\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$. Let us prove now that for any electron density $\rho(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ there exists a transformation $\mathscr{R}$ from $\mathscr{F}$ such that $\rho(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$. For this purpose, we choose an arbitrary unit vector $\mathbf{e}_0=\mathbf{e}_0[\hat{\mathbf{r}}_0]\in\Omega$ and fix it. We define the transformation $\mathscr{R}\in\mathscr{F}$ on the ray $\mathbf{e}_0\in\Omega$, determined by the angles θ_0 and ϕ_0, as the solution of the following first-order nonlinear differential equation:

$$\frac{d}{dr}R^3(r,\theta_0,\phi_0)=\frac{3r^2\rho(r,\theta_0,\phi_0)}{\rho_0(R(r,\theta_0,\phi_0),\theta_0,\phi_0)}\ ,\tag{25}$$

which satisfies the condition of Theorem 1 of Ref. 40 due to the properties of $\rho(\mathbf{r})$ and $\rho_0(\mathbf{r})\neq\rho(\mathbf{r})$ from $\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$. Therefore, Eq. (25) has a solution, i.e., the required transformation $\mathscr{R}\in\mathscr{F}/\mathscr{F}_{\rho_0}$ along the fixed ray $\mathbf{e}_0\in\Omega$, and this solution is unique. Varying θ_0 and ϕ_0 over the whole space Ω, due to the properties of $\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$, we obtain the total required transformation $\mathscr{R}\in\mathscr{F}$ which transforms $\rho_0(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ into $\rho(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ Q.E.D.

It should be noticed that the proof of Theorem 1 is due partially to the results of Refs. 28 and 30. As follows from Theorem 1, for any $\rho_0(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$

$$\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}=\mathscr{F}/\mathscr{F}_{\rho_0}(\rho_0(\mathbf{r}))\ .\tag{26}$$

Theorem 1 provides a possibility of reformulating the conditions of n-representability of one-electron densities[2,16,37,17] belonging to $\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$. We emphasize here that this is a reformulation as the n-representability problem for one-electron densities has been solved some time ago by Gilbert,[37] using a very particular construction for $\rho(\mathbf{r})$, and more generally by Harriman,[2,16] using equidensity orbitals (see also Ref. 17). By definition (see, for example, Refs. 41 and 17), a given one-electron density $\rho(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ is pure-state n representable if there exists an n-electron wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)\in W^n$ such that the associated density $\rho_\Psi(\mathbf{r})$ is just $\rho(\mathbf{r})$. As a first step we formulate the statement whose proof is trivial.

Theorem 2. The set of n-particle antisymmetric wave functions is represented as a union of $\mathscr{F}^n/\mathscr{F}^n_{\rho_0}$ $[\equiv(\mathscr{F}/\mathscr{F}_{\rho_0})^n]$ orbits

$$W^n=\bigcup_{\alpha}W^n[\alpha]\ ,\tag{27}$$

where $\rho_0(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ and

$$W^n[\alpha]\equiv\mathscr{F}^n/\mathscr{F}^n_{\rho_0}(\Psi^{[\alpha]}_{\rho_0})$$

with $\Psi^{[\alpha]}_{\rho_0}\in W^n_{\rho_0}$. In the frame of each $\mathscr{F}^n/\mathscr{F}^n_{\rho_0}$ orbit of W^n there exists to one-to-one correspondence between (i) n-electron wave functions from $W^n[\alpha]$ and one-electron densities from $\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$—in the sense of the mapping (13), (ii) n-electron wave functions from $W^n[\alpha]$ and transformations from $\mathscr{F}^n/\mathscr{F}^n_{\rho_0}$ with fixed $\rho_0(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$—in the sense of the action (12).

Corollary 1. The definition of the orbits of W^n with respect to the group $\mathscr{F}^n/\mathscr{F}^n_{\rho_0}$ is independent of the choice of the reference electron density $\rho_0(\mathbf{r})\in\widetilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$.

This statement follows trivially from the fact that for a given $\rho_0(\mathbf{r})\in\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$ and $\mathcal{R}\in\mathcal{F}$ the density $\rho(\mathbf{r})\equiv\mathcal{R}(\rho_0(\mathbf{r}))$ possesses the stationary subgroup $\mathcal{F}_\rho=\mathcal{R}\mathcal{F}_{\rho_0}\mathcal{R}^{-1}$.

Corollary 2. Each orbit $W^n[\alpha]$ contains a unique n-particle antisymmetric wave function whose one-electron density is just $\rho(\mathbf{r})\in\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$ (to within the group $\mathcal{F}^n_\rho$).

In order to reformulate the n-representability conditions for $\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$ of one-electron densities, let us consider an orbit $W^n[\alpha]\subset W^n$ with respect to $\mathcal{F}^n$. One can assume that a given orbit $W^n[\alpha]$ is generated by a given n-electron wave function $\Psi_0^{[\alpha]}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)$ ("the generator configuration") with the associated one-electron density $\rho_0(\mathbf{r})\in\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$. Naturally, one can suggest the existence of one-electron density $\rho(\mathbf{r})\in\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$ different from $\rho_0(\mathbf{r})$. Solving the nonlinear first-order differential equation (25) for all pairs $(\theta_0,\phi_0)\in\Omega$, one obtains the transformation $\mathcal{R}\in\mathcal{F}/\mathcal{F}_{\rho_0}$ such that $\rho(\mathbf{r})=\mathcal{R}(\rho_0(\mathbf{r}))$.

Then the following n-electron wave function

$$\Psi^{[\alpha]}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)\equiv\Psi_0^{[\alpha]}(\mathbf{R}(\mathbf{r}_1),\mathbf{R}(\mathbf{r}_2),\ldots,\mathbf{R}(\mathbf{r}_n))\times\left[\prod_{i=1}^{n}D_{\mathbf{R}(\mathbf{r}_i)}\right]^{1/2},\qquad(28)$$

belongs to the orbit $W^n[\alpha]$ and has the one-electron density $\rho(\mathbf{r})$. Hence, due to the arbitrariness of the choice of $\rho(\mathbf{r})\in\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$ we prove the following.

Theorem 3. Any one-electron density $\rho(\mathbf{r})\in\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$ is pure-state n representable.

It should be emphasized that above we have proved the statement that any one-electron density belonging to $\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$ is n representable inside an arbitrary orbit $W^n[\alpha]\subset W^n$, a fact that would guarantee pure-state n representability, as in general, for a mixed state, the different wave functions $|\Psi_i\rangle$ making up the expansion of an ensemble nth-order density operator

$$\hat{\Gamma}^n=\sum_i\omega_i\,|\Psi_i\rangle\langle\Psi_i\,|$$

would in principle fall into different orbits. In other words, the preimage of the reduction mapping of W^n into $\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$, determined by Eq. (13), exists and is unique (within a stationary group) in each orbit $W^n[\alpha]$.

V. DISCUSSION

In the present paper, some of the ideas already introduced in previous works,[28,30] have been further developed. The main advantage of the method employed here, which was initially proposed by Petkov and Stoitsov,[28] consists in that an explicit use is being made of the Jacobian transformation involved in the definition of the transformation of the vector space $\mathbb{R}^3$ on $\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$ and W^n. This provides the possibility of applying some rigorous statements of the theory of ordinary first-order differential equations, to the quantum chemical energy-density-functional theory. In addition, we have made an incipient connection between these point transformations with the topological properties of $\rho(\mathbf{r})$, which as discussed by Bader *et al.*,[39] provides a very adequate framework for the description of chemical phenomena.

It is important at this point to establish the relationship between the results of this paper and the transformations, considered by other authors, generated by Slater determinants consisting of plane-wave orbitals. An important work in this respect is that of Zumbach and Maschke.[21] It may seem, however, that the orbits introduced by these authors are a particular case of the orbits defined by Eq. (27), although rigorously speaking, the term "orbit" in the former case is not justified and applicable, because the set of transformations given by Eq. (3) and in Appendix A of Ref. 21, does not form a group, since it does not contain unit and inverse elements.

We show in what follows how the ideas developed in the present paper may be applied in order to obtain a local-density approximation and equidensity orbitals.[16,22,42,43] Consider the Slater determinant

$$\Psi_0^{\{\mathbf{k}_i\}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)=(n!)^{-1/2}\det[\phi_{\mathbf{k}_1}(\mathbf{r}_1),\phi_{\mathbf{k}_2}(\mathbf{r}_2),\ldots,\phi_{\mathbf{k}_n}(\mathbf{r}_n)]\,,\qquad(29)$$

where the single-particle functions are plane-wave orbitals

$$\phi_{\mathbf{k}_i}(\mathbf{r}_i)=V^{-1/2}\exp(i\mathbf{k}_i\cdot\mathbf{r}_i)$$

and V is the normalization volume. The Slater determinant given by Eq. (29) generates in W^n the orbit $W^n_{P-W}[\{\mathbf{k}_i\}]$, determined uniquely by the set of wave vectors $\{\mathbf{k}_i\}_{i=1}^n$ and the volume V and consisting of the following determinants:

$$\Psi_{\mathcal{R}_\rho}^{\{\mathbf{k}_i\}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)=(n!)^{-1/2}\det[\psi_{\mathbf{k}_1}^{\mathcal{R}_\rho}(\mathbf{r}_1)\psi_{\mathbf{k}_2}^{\mathcal{R}_\rho}(\mathbf{r}_2)\cdots\psi_{\mathbf{k}_n}^{\mathcal{R}_\rho}(\mathbf{r}_n)]\,,\qquad(30)$$

where

$$\psi_{\mathbf{k}}^{\mathcal{R}_\rho}(\mathbf{r})=\left[\left(\frac{R_\rho(\mathbf{r})}{r}\right)^2\frac{\partial R_\rho(\mathbf{r})}{\partial r}\right]^{1/2}V^{-1/2}\exp[i\mathbf{k}\cdot\mathbf{R}_\rho(\mathbf{r})]\qquad(31)$$

and

$$R_\rho(r,\theta,\phi)=\left[\frac{3V}{n}\int_0^r dr'(r')^2\rho(r',\theta,\phi)\right]^{1/3},\qquad(32)$$

with $\rho(\mathbf{r})\in\widetilde{\mathcal{N}}^n_{\mathrm{HKL}}$ and $\mathcal{R}_\rho\in\mathcal{F}$. In Eq. (32) the lower boundary of integration is taken as zero, for simplicity.

Equation (32) is just the restatement of Eqs. (21) and (22)

$$\frac{1}{3r^2}\frac{\partial}{\partial r}R^3(r,\theta,\phi)=\frac{\rho_R(\mathbf{r})}{\rho[R(r,\theta,\phi),\theta,\phi]}\,,\qquad(33)$$

where we assume that the density in the denominator is constant and is given by n/V. Integrating Eq. (33), one obtains Eq. (32).

If we assume that $\rho(r',\theta,\phi)$ of Eq. (32) is spherically symmetric and also that it varies slowly with r (for example, as in the Thomas-Fermi model[35]), then we may take $\rho(r',\theta,\phi)$ outside the integral sign and obtain

$$R_\rho(\mathbf{r}) \cong \left[\frac{V}{n}\rho(\mathbf{r})\right]^{1/3} r, \quad \rho(\mathbf{r}) \in \tilde{\mathscr{N}}^{n}_{\mathrm{LDA}}\ , \tag{34}$$

where in view of the fact that these conditions define a subset $\tilde{\mathscr{N}}^{n}_{\mathrm{LDA}}$ of $\tilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ which corresponds to a local-density approximation (LDA), the $\rho(\mathbf{r})$ of Eq. (34) belongs to this subset. The orbital $\psi_{\mathbf{k}}^{\overset{\mathscr{R}}{\rho}}(\mathbf{r})$ takes the following form:

$$\psi_{\mathbf{k}}^{\overset{\mathscr{R}}{\rho}}(\mathbf{r}) = \left[\frac{\rho(\mathbf{r})}{n}\right]^{1/2} \exp\left[i\left[\frac{V}{n}\rho(\mathbf{r})\right]^{1/3} \mathbf{k}\cdot\mathbf{r}\right]\ . \tag{35}$$

One may conclude, therefore, that all the results of Refs. 12—19 and 21—22 refer to the class of orbits of the plane-wave type. It is also interesting to notice that the orbitals given by Eq. (31) are equidensity orbitals since they satisfy the relation

$$|\psi_{\mathbf{k}}^{\overset{\mathscr{R}}{\rho}}(\mathbf{r})|^2 = \rho(\mathbf{r})/n\ . \tag{36}$$

As a final consideration, let us take an arbitrary one-electron density $\rho_0(\mathbf{r}) \in \tilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ represented in terms of its natural orbital expansion $\{\chi_i(\mathbf{r}), i=1,\ldots,m; m>n\}$

$$\rho_0(\mathbf{r}) = \sum_{i=1}^{m} \lambda_i |\chi_i(\mathbf{r})|^2\ . \tag{37}$$

For a fixed $\rho(\mathbf{r}) \in \tilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$, one obtains the transformation $\mathscr{R}_i \in \mathscr{F}$ such that

$$\rho(\mathbf{r})/n = \left[\frac{R_i(\mathbf{r})}{r}\right]^2 \frac{\partial R_i(\mathbf{r})}{\partial r} |\chi_i(R_i(\mathbf{r}))|^2\ , \tag{38}$$

where i runs over the whole sum in Eq. (37). Obviously, the orbital

$$\psi_i(\mathbf{r}) = \left[\left[\frac{R_i(\mathbf{r})}{r}\right]^2 \frac{\partial R_i(\mathbf{r})}{\partial r}\right]^{1/2} \chi_i(R_i(\mathbf{r})) \tag{39}$$

satisfies the relation

$$|\psi_i(\mathbf{r})|^2 = \rho(r)/n\ , \tag{40}$$

i.e., it is an equidensity orbital. It follows that if $\rho(\mathbf{r}) \in \tilde{\mathscr{N}}^{n}_{\mathrm{HKL}}$ is represented by a single Slater determinant

$$\rho(\mathbf{r}) = \sum_{i=1}^{n} |\psi_i(\mathbf{r})|^2\ , \tag{41}$$

then

$$\begin{aligned} \rho_0(\mathbf{r}) &= \sum_{i=1}^{m} \lambda_i \left[\left[\frac{R_i}{r}\right]^2 \frac{\partial R_i}{\partial r}\right]^{-1} |\psi_i(\mathbf{r})|^2 \\ &= \frac{\rho(\mathbf{r})}{n} \sum_{i=1}^{m} \lambda_i \left[\left[\frac{R_i}{r}\right]^2 \frac{\partial R_i}{\partial r}\right]^{-1}\ . \end{aligned} \tag{42}$$

If we select the arbitrary $\rho(\mathbf{r})$ to be precisely $\rho_0(\mathbf{r})$, then it follows that the necessary condition for a density which was originally represented by an expansion such as (37), which is obtain generally from a linear combination of Slater determinants, to be exactly represented by a single Slater determinant with orbitals $\{\psi_i\}$ is that

$$\sum_{i=1}^{m} \lambda_i \left[\left[\frac{R_i}{r}\right]^2 \frac{\partial R_i}{\partial r}\right]^{-1} = n\ . \tag{43}$$

However, the representation in this case is not unique, as any n of the m equidensity orbitals ψ_i may be selected to fulfill Eq. (41).

ACKNOWLEDGMENT

One of the authors (E.S.K.) is indebted to I. Zh. Petkov and M. V. Stoitsov for fruitful discussions.

---

[1] J. C. Slater, Adv. Quantum Chem. **6**, 1 (1972).

[2] *Density Functional Theory,* Vol. 187 of *Lecture Notes in Physics,* edited by J. Keller and J. L. Gazquez (Springer-Verlag, Berlin, 1983).

[3] *Local Density Approximations in Quantum Chemistry and Solid State Physics,* edited by J. P. Dahl and J. Avery (Plenum, New York, 1984).

[4] *Density Functional Methods in Physics,* edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985).

[5] (a) J. Callaway and N. H. March, Solid State Phys. **38**, 315 (1984); (b) W. Kohn and P. Vashishta, in *Theory of the Inhomogeneous Electron Gas,* edited by S. Lundqvist and N. H. March (Plenum, New York, 1983), p. 79.

[6] A. S. Bamzai and B. M. Deb, Rev. Mod. Phys. **53**, 95 (1981); S. R. Ghosh and B. M. Deb, Phys. Rep. **92**, 1 (1982); R. G. Parr, Ann. Rev. Phys. Chem. **34**, 631 (1983).

[7] E. S. Kryachko and E. V. Ludeña, *Energy Density Functional Theory in Quantum Chemistry* (Reidel, Dordrecht, 1987).

[8] H. Primas and M. Schleicher, Int. J. Quantum Chem. **9**, 855 (1975).

[9] I. M. Reznik and V. M. Shatalov, Ukr. Phys. J. **26**, 1187 (1981).

[10] B. M. Deb, Ref. 3, p. 75; J. R. Sabin and S. B. Trickey, *ibid.* p. 333.

[11] T. T. Nguyen-Dang, R. F. W. Bader, and M. Essén, Int. J. Quantum Chem. **22**, 1049 (1982); R. F. W. Bader and M. Essén, Ref. 3, p. 129.

[12] D. I. Blokhintsev, Zh. Eksp. Teor. Fiz. **9**, 1166 (1939).

[13] W. Macke, Ann. Phys. (N.Y.) **17**, 1 (1955); Phys. Rev. **100**, 992 (1955).

[14] W. Macke and P. Rennert, Ann. Phys. (Leipzig) **12**, 84 (1963).

[15] (a) N. H. March and W. N. Young, Proc. Phys. Soc. London **72**, 182 (1958); (b) J. K. Percus, Int. J. Quantum Chem. **13**, 89 (1978).

[16] J. E. Harriman, Phys. Rev. **24**, 680 (1981); Ref. 2, p. 37.

[17] E. H. Lieb, in *Physics as Natural Philosophy: Essays in Honor of Laszlo Tisza on His 75th Birthday,* edited by A. Shimony and M. Feshbach (MIT, Cambridge, Mass., 1982), p. 111; Int. J. Quantum Chem. **24**, 243 (1983).

[18] M. K. M. Siedentop, Z. Phys. **A302**, 213 (1981).

[19] V. Yu. Kolmanovich and I. M. Reznik, Dokl. Acad. Sci. USSR, Earth Sci. Sect. **258**, 1100 (1981).

[20] P. W. Payne, Proc. Nat. Acad. Sci. USA, **77**, 6293 (1980).

[21] G. Zumbach and K. Maschke, Phys. Rev. A **28**, 544 (1983); **29**, 1585(E) (1984).

[22] J. F. Capitani, B. Chang, and J. E. Harriman, J. Chem. Phys., **81**, 349 (1984).

[23] R. B. Wolf, Rev. Mex. Fis. **22**, 45 (1973).

[24] S. T. Epstein and J. O. Hirschfelder, Phys. Rev. **123**, 1495 (1961).

[25] S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic, New York, 1974).

[26] N. M. Witriol, Int. J. Quantum Chem. **6**, 145 (1972).

[27] B. I. Zhilinsky and N. F. Stepanov, Teor. Mat. Fiz. **15**, 146 (1973).

[28] I. Zh. Petkov and M. V. Stoitsov, Teor. Mat. Fiz. **55**, 407 (1983).

[29] E. S. Kryachko, Ref. 3, p. 207.

[30] I. Zh. Petkov, M. V. Stoitsov, and E. S. Kryachko, Int. J. Quantum Chem. **29**, 149 (1986).

[31] D. J. Rowe, A. Ryman, and G. Rosensteel, Phys. Rev. A **22**, 2362 (1980); see also A. J. Coleman, Int. J. Quantum Chem. **13**, 67 (1978), Sec. 6.

[32] E. S. Kryachko, I. Zh. Petkov, and M. V. Stoitsov, Ukr. Phys. J. **31**, N5 (1986).

[33] P. Hohenberg and W. Kohn, Phys. Rev. **136B**, 864 (1964).

[34] V. Fock, Z. Phys **63**, 855 (1930).

[35] P. Gombás, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Springer, Wien, 1949).

[36] S. M. Valone, J. Chem. Phys. **73**, 4653 (1980).

[37] T. L. Gilbert, Phys. Rev. B **12**, 2111 (1975).

[38] G. A. Henderson, Int. J. Quantum Chem. **13**, 143 (1978).

[39] R. F. W. Bader and T. T. Nguyen-Dang, Adv. Quantum Chem. **14**, 63 (1981).

[40] L. S. Pontrjagin, *Ordinary Differential Equations* (Nauka, Moscow, 1974).

[41] M. Levy, Proc. Nat. Acad. Sci. USA **76**, 6062 (1975).

[42] J. E. Harriman, J. Chem. Phys. **83**, 6283 (1985).

[43] E. V. Ludeña, J. Chem. Phys. **79**, 6174 (1985); Ref. 3, p. 287; E. V. Ludeña and A. Sierraalta, Phys. Rev. A **32**, 19 (1985).