In practical implementations of density–functional theory, the only term where an orbital description
is needed is the kinetic one. Even this term in principle depends on the density only, but its explicit
form is unknown. We provide a novel solution of the N-representability problem for an
extended system, which implies an explicit form for the Kohn–Sham kinetic energy in terms of the
density. Our approach is based on a periodic coordinate mapping, uniquely defined by the Fourier
coefficients of the metric. The density functional is thus expressed as an explicit functional of the
metric tensor: since N-representability is enforced, our constructive recipe provides a variational
approximation. Furthermore, we show that our geometric viewpoint is quite naturally related to
the electron localization function (ELF), which provides a very informative analysis of the electron
distribution. Studies of ELF, as obtained from accurate Kohn–Sham orbitals in real materials,
allow an appraisal of the variational approximate density functional. We show that the value of
an approximate functional—either the present geometric–based one or some previous ones based
on different constructive recipes—strongly depends on the nature of the chemical bonding in the
material.

I. INTRODUCTION

The celebrated basic tenet of density–functional theory (DFT) states that an exact description of a
many–electron system is in principle possible in terms of a single scalar field, namely the electron density \(n(\mathbf{r})\).
The N-electron wavefunction contains instead redundant information; in extendend systems, it does not even
have a defined thermodynamic limit. However, the Hohenberg–Kohn theorem (upon which DFT is based)
does not provide a constructive scheme: for any given \(N\), the exact functional is indeed accessible only through the
many–body wavefunction.

The enormous success of DFT resides in approximate schemes which are constructive, and do not
make explicit recourse to the many–body wavefunction. These schemes—implemented using first–principles
ingredients—have proved over the years their astonishingly accurate predictive power for many physical properties,
in many different materials. In all these schemes the only wavefunction needed is a wavefunction of noninteracting
electrons, which is uniquely defined by the manifold of the occupied Kohn–Sham (KS) single–particle orbitals
or equivalently by the KS one–body reduced density matrix. The eponymous density functional \(F[n]\),
Eq. (10) below, is the sum of a few terms: all of them but one are almost invariably approximated as explicit functionals of the
density. The only term where the KS orbitals (or the density matrix) are actually needed is \(T_s\),
the kinetic energy of the noninteracting system, which is a functional of the density in an implicit way. This qualitative
difference is of course responsible for most of the computer workload in practical calculations, hindering
amongst other things the linear scaling of computations with the size of the system. There is therefore a quest for
approximate (though accurate enough) expressions for \(T_s\) as explicit functionals of the density.

Historically, the first approximate form for the kinetic energy of a system of noninteracting electrons in
terms of their density is the Thomas–Fermi (TF) one, which predates DFT by several decades and is a very crude one; it is however exact for an extended system of free electrons. We focus here on a different class of approximations, which are—at variance with TF—
variational: this feature is intimately linked to the problem of N-representability. In fact, whenever the approximate \(T_s\) coincides with the true kinetic energy of an arbitrary independent–electron wavefunction, then the variational theorem ensures that it must be no smaller
that the exact \(T_s\) of the given system. The requisite of N-representability is equivalent to requiring that \(T_s\) ob-
tains from a density matrix which is idempotent. There is clearly an infinity of idempotent density matrices, all
yielding the same given density: amongst these infinite solutions of the N-representability problem, one searches
for the one having the lowest \(T_s\) at the given density.

In order to provide an explicit approximate (and variational) expression for \(T_s\) one has, first of all, to provide
a constructive recipe which, starting from a given density, produces an idempotent density matrix. Ex-
plicit solutions of this problem have been provided by several authors in the literature, amongst whom we only
quote Harriman, Zumbach and Maschke and Ludeña and coworkers. The present paper may thus be con-
sidered as a continuation and a generalization of this earlier work, where the elements of novelty are basically the
following. (i) At variance with previous work, we are interested in extended systems. We therefore solve the N–
representability problem for a system of \(N\) noninteracting electrons in a box of volume \(V\), where periodic (Born-von

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Kärnänen) conditions are assumed at the boundary. Our approximate solution coincides with the exact one for the electron gas. (ii) Our construction uses in an essential way a periodic coordinate mapping, in the same spirit as the one advocated by Gygi in electronic structure calculations. This provides an elegant and symmetric treatment; some of the results obtained in the previous literature assume here an interesting geometric meaning. The electronic energy is variationally expressed in terms of the metric tensor as the independent variable. (iii) Our geometric approach naturally partitions \( T_s \) into the sum of two terms: very roughly speaking “bosonic” and “Pauli”. We show that these two terms coincide with the sum of two terms: very roughly speaking “bosonic” and “Pauli”. We show that these two terms coincide with the volume integrals of two local functions which are used in the literature as the main ingredients of the electron localization function \( \rho_0(\xi, \xi') \) (ELF).

Our solution of the \( N \)-representability problem—as well as the explicit approximate density functional based upon such solution—is therefore fundamentally linked in a very natural way to the ELF concept. Since ELF provides a very informative analysis of the electron distribution, the published results for real materials—obtained \textit{a-posteriori} from accurate density matrices—help understanding what is good and what is bad in the approximate forms of \( T_s \). We find that the quality of the approximation provided by our constructive recipe strongly depends on the kind of bonding involved in the many–electron system. We give evidence that both the Zumbach–Maschke recipe and our own one provide a reasonable \( T_s \) for simple metals in the pseudopotential approximation, while they significantly overestimate \( T_s \) whenever covalent bonding is present. The possible directions for improvement on this point are sketched.

The present paper is organized as follows. In Sec. II we present our novel solution to the \( N \)-representability problem, essentially based on a coordinate mapping, which transforms a reference uniform system into the actual nonuniform one. In Sec. III we apply such solution to the construction of a functional which is a variational approximation to the exact one: this functional is an explicit functional of the metric tensor. In Sec. IV we review the fundamental properties of ELF, a powerful tool used in the quantum–chemistry community to analyze the electron distribution in various real systems: we show that ELF is intimately related to basic features of the functional. Finally, in Sec. V we outline our conclusions and perspectives, based on some ELF analyses for real materials.

\section*{II. CURVILINEAR COORDINATES AND \( N \)-REPRESENTABILITY}

For a system of independent electrons in a closed–shell configuration the wavefunction is a single determinant: knowledge of the one–particle reduced density matrix is equivalent to a complete knowledge of the wavefunction. The spin–integrated matrix \( \rho(\mathbf{r}, \mathbf{r}') \) is twice a projector, which indeed projects over the (doubly occupied) one–particle orbitals. We consider a system of \( N \) electrons in a box of volume \( V \), obeying periodic boundary conditions. The average density is \( n_0 = N/V \), the density is \( n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r}) \), and the idempotency condition is written:

\[
\int_V d\mathbf{r}'' \rho(\mathbf{r}, \mathbf{r}'') \rho(\mathbf{r}'', \mathbf{r}') = 2 \rho(\mathbf{r}, \mathbf{r}').
\]  

(1)

We start with a homogeneous system of \( N \) non–interacting electrons at the same density \( n_0 \), for which we use \( \xi \) as a space coordinate. For this system the canonical orbitals are, by symmetry, the plane waves \( e^{i\mathbf{k} \cdot \xi}/\sqrt{V} \), where \( \mathbf{k} \) are the reciprocal vectors determined by the boundary conditions. By choosing to occupy the \( N/2 \) orbitals of lowest energy, the density matrix is:

\[
\rho_0(\xi, \xi') = \frac{2}{V} \sum_{l=1}^{N/2} e^{i\mathbf{k}_l \cdot (\xi - \xi')}.
\]  

(2)

which is obviously idempotent and yields a constant density. In the thermodynamic limit (\( N \to \infty \) and \( V \to \infty \) at constant \( n_0 \)) the \( \mathbf{k}_l \) set becomes dense. Occupying the \( \mathbf{k} \)-vectors within the Fermi sphere (\( |\mathbf{k}| < k_F \) Eq. \( \xi \)) yields the well known electron–gas result:

\[
\rho_0(\xi, \xi') = n_0 \frac{3j_1(k_F|\xi - \xi'|)}{k_F|\xi - \xi'|}.
\]  

(3)

At this point we introduce a generic curvilinear coordinate precisely of the same kind as introduced by Gygi in the field of electronic–structure calculations. We therefore define a twice differentiable invertible map \( \xi \to \mathbf{r}(\xi) \), periodic over \( V \), whose Riemannian metric tensor is:

\[
g_{ij} = \frac{\partial r^k}{\partial \xi^i} \frac{\partial r^k}{\partial \xi^j}.
\]  

(4)

Summation over repeated indices is understood throughout. A generic plane wave of momentum \( \mathbf{k} \) is transformed as:

\[
\frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \xi} \to \chi_\mathbf{k}(\mathbf{r}) = \frac{1}{\sqrt{V}} g^{-\frac{1}{2}}(\mathbf{r}) e^{i\mathbf{k} \cdot \xi(\mathbf{r})},
\]  

(5)

where \( g = \det\{g_{ij}\} \), and \( g^{-\frac{1}{2}} \) is the Jacobian \( |\partial \xi/\partial \mathbf{r}| \) of the inverse transformation. Notice that the orbitals \( \chi_\mathbf{k}(\mathbf{r}) \) have a \( \mathbf{k} \)-independent density and are therefore “equidensity orbitals” in Harriman’s nomenclature. The density matrix in the new coordinates is:

\[
\rho(\mathbf{r}, \mathbf{r}') = \rho_0(\xi(\mathbf{r}), \xi(\mathbf{r}')) = \frac{2}{V} \frac{1}{g^{-\frac{1}{2}}(\mathbf{r}) g^{-\frac{1}{2}}(\mathbf{r}')} \sum_{l=1}^{N/2} e^{i\mathbf{k}_l \cdot (\xi(\mathbf{r}) - \xi(\mathbf{r}'))}.
\]  

(6)

The corresponding transformed density is
In the novel coordinates we thus have a nonhomogeneous system, with the same average density as the homogeneous one, and whose density matrix is idempotent by construction.

We are now ready to attribute physical content to the above mathematics. Suppose that the density $n(\mathbf{r})$ of an electronic system is given. Then we may look for a coordinate transformation $\xi \rightarrow \mathbf{r}(\xi)$ which maps the uniform density into the given density: a necessary and sufficient condition is Eq. (7). The solution is nonunique, since several different maps share the same Jacobian $g^{-\frac{1}{2}}$: we will argue below about an optimal solution, using a variationally adaptive metric in the sense of Gyorffy.  

Replacement into Eq. (6) yields the explicit form:

$$\rho(\mathbf{r}, \mathbf{r}') = \frac{2}{N} n^\frac{\frac{1}{2}}{n} n(\mathbf{r})^{\frac{1}{2}}(\mathbf{r}')^{\frac{1}{2}} \sum_{i=1}^{N/2} e^{i\xi_i(\mathbf{r})-\xi_i(\mathbf{r}')}].$$  (8)

In one dimension the solution of Eq. (7) is unique, and we get here the periodic analogue of the Harriman construction. In three dimensions, our result is related to the work of Zumbach and Maschke the differences being that we deal with periodic systems, and we provide a more general explicit construction. A coordinate mapping, similar in spirit to the present one (and called "local scaling transformation"), has been previously introduced by Ludeña and coworkers for spherical atoms.

### III. DENSITY FUNCTIONAL

The energy of the electronic system in the external potential $v_{\text{ext}}$ is written, within DFT, as:

$$E[n] = \int_V d\mathbf{r} \ n(\mathbf{r})v_{\text{ext}}(\mathbf{r}) + F[n];$$  (9)

$$F[n] = T_s[n] + \frac{1}{2} \int_V d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n],$$  (10)

where atomic Hartree units have been used. As already anticipated, basically all the available constructive approximations to DFT provide $E_{\text{xc}}$ as an explicit functional of the density $n(\mathbf{r})$, while instead the kinetic energy term $T_s$ is:

$$T_s = \frac{1}{2} \int_V d\mathbf{r} \nabla \cdot \nabla' \rho(\mathbf{r}, \mathbf{r}') \bigg|_{\mathbf{r} = \mathbf{r}'}.$$  (11)

The ground electronic energy, Eq. (8), is therefore an explicit functional of the density matrix, which has to be minimized under the constraints of idempotency, Eq. (3), and electron number.

Replacement of our ansatz density matrix, Eq. (3), in the above expressions provides an upper bound to the electronic energy, explicitly expressed solely in terms of the density and of the metric. The approximate kinetic energy is:

$$\hat{T}_s = \sum_{i=1}^{N/2} \int_V d\mathbf{r} |\nabla \chi_i(\mathbf{r})|^2.$$  (12)

Using then Eq. (7) of Ref. [12] the expectation value of the kinetic energy over a $\chi_k$ orbital is the sum of two positive terms:

$$\langle \chi_k | T | \chi_k \rangle = \frac{k_ik_j}{2V} \int d\xi g^{ij} + \frac{1}{2V} \int d\xi A_i g^{ij} A_j,$$  (13)

where the "gauge potential" is:

$$A_i = \frac{1}{4} \frac{\partial \ln g}{\partial \xi_i}.$$  (14)

After summing over the $N/2$ doubly occupied states, we get:

$$\hat{T}_s[n] = \hat{T}_P[n] + T_B[n],$$  (15)

where the reason for the notations will be clear in a moment.

Using Eq. (3), we cast the gauge term as:

$$T_B[n] = \frac{n_0}{32} \int_V d\mathbf{r} g^{-\frac{\frac{1}{2}}{2}}(\mathbf{r}) |\nabla g(\mathbf{r})|^2 = \frac{1}{8} \int_V d\mathbf{r} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}.$$  (16)

In the latter expression, we notice that the metric formally disappears from the gauge term, which is indeed identical to the so-called von Weizsäcker energy functional. This energy coincides with the kinetic energy of a system of noninteracting bosons in their ground state, having the given density $n(\mathbf{r})$: with this specific meaning, we may refer to $T_B$ as to the "bosonic" energy. It is easy to prove that $T_B$ is a lower bound to the kinetic energy $T_s$ of a system of noninteracting fermions and coincides with $T_s$ only in the trivial case $N = 2$, where the Pauli principle has no effect (we are considering singlets only). In all the interesting cases, there is an excess kinetic energy $T_P$ due to the Pauli principle:

$$T_P = \frac{1}{2} \int_V d\mathbf{r} \nabla \cdot \nabla' \rho(\mathbf{r}, \mathbf{r}') \bigg|_{\mathbf{r} = \mathbf{r}'} - \frac{1}{8} \int_V d\mathbf{r} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}.$$  (17)

Our expression for $\hat{T}_P[n]$ as a function of the metric shall therefore be a variational approximation to the true excess Pauli energy $T_P$.

The sum over the occupied states in $\hat{T}_P$ is most easily evaluated if we assume a cubic box. If we define $E_0$ as the kinetic energy of the homogeneous system:

$$E_0 = \sum_{i=1}^{N/2} |k_i|^2,$$  (18)
it is then easy to recast $\tilde{T}_p[n]$ as:

$$\tilde{T}_p[n] = \frac{E_0}{3V} \int_V d\mathbf{r} \ g^{-\frac{1}{2}} \ tr\{g^{ij}\}.$$  \hspace{1cm} (19)

We further notice that in the thermodynamic limit one has:

$$E_0 = \frac{3}{10} N k_F^2 = c_F V n_0^2,$$  \hspace{1cm} (20)

where $c_F = \frac{2}{15} (3\pi^2)^{\frac{2}{3}}$.

Putting all the previous formulas together and approximating $T_s$ in Eq. (10) with $T_{s0}$, we obtain an approximate $F[n]$ as an explicit functional of the density and of the metric tensor. Since the density—owing to Eq. (7)—is in turn a function of the metric tensor, we use the latter as the independent variable. Eventually, the electronic energy of the system, Eq. (8), is a variational explicit functional of the metric tensor. Since the density—owing to Eq. (7)—is everywhere positive, and coincides with the choice made in the ELF literature.

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Finally, we end this section just noting that in the trivial case $\tau_{ext}(\mathbf{r}) = 0$ all of the kinetic energy is due to $T_p$, since the density is constant and $T_{1B}$ vanishes. Furthermore the metric is the identity and the approximate kinetic energy equals the exact one: $\tilde{T}_s = T_s = E_0$, Eq. (20). The approximate functional $F[n]$ coincides with the exact one, including its exchange–correlation term if the exact electron–gas data are used therein (as usual). This suggests that the approximate functional should work reasonably well for a system close enough to the electron gas, such as a simple metal within a pseudopotential scheme.

**IV. ELECTRON LOCALIZATION FUNCTION**

The kinetic energy $T_s$ can be thought of as the integral over $V$ of a kinetic energy density $\tau(\mathbf{r})$. It is well known that the expression for $\tau(\mathbf{r})$ is not unique: we use the form suggested by Eq. (17), namely,

$$\tau(\mathbf{r}) = \left. \frac{1}{2} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho(\mathbf{r}, \mathbf{r}') \right|_{\mathbf{r} = \mathbf{r}'};$$  \hspace{1cm} (21)

which is everywhere positive, and coincides with the choice made in the ELF literature. By analogy, one defines the Pauli excess density energy, after Eq. (17), as:

$$\tau_p(\mathbf{r}) = \left. \frac{1}{2} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho(\mathbf{r}, \mathbf{r}') \right|_{\mathbf{r} = \mathbf{r}'} - \frac{1}{8} \frac{]\nabla n(\mathbf{r})^2}{n(\mathbf{r})}.$$  \hspace{1cm} (22)

This function is the main ingredient of ELF in the formulation due to Savin et al. who write the function as:

$$\mathcal{E}(\mathbf{r}) = \left\{ 1 + \frac{\tau_p(\mathbf{r})}{c_F n(\mathbf{r})} \right\}^{-1}.$$  \hspace{1cm} (23)

This function by design takes values between zero and one: several of its features are remarkable. In the homogeneous electron gas, owing to Eq. (20), the ELF equals $1/2$ at any density. In a non-homogenous system $\mathcal{E}(\mathbf{r})$ assumes values close to its upper bound 1 in the regions of space where there is an high probability of finding a pair of electrons with antiparallel spins (or an isolated electron) with this meaning, we may say that $\mathcal{E}(\mathbf{r})$ close to 1 characterizes space regions where the electron distribution is “bosonic”. Conversely, $\mathcal{E}(\mathbf{r})$ is close to 0 in low–density regions.

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**FIG. 1.** Pseudocharge density contour plot (upper panel) and the corresponding ELF (lower panel) for bulk silicon in the [110] crystal plane. The grey–scale is also shown: dark regions correspond to large ELF values. The maximum ELF value at the bond center is 0.96.
FIG. 2. Pseudocharge density contour plot (upper panel) and the corresponding ELF (lower panel) for bulk aluminum in the [100] crystalline plane. The maximum ELF value in the interatomic region is 0.61.

Detailed ELF analyses have been performed for many systems of chemical interest. For heavy atoms, the ELF perspicuously localizes in space the different electronic shells: furthermore, when the valence shell is considered, the ELF provides a very meaningful description of the chemical bonding. This is illustrated in the lower panels of Figs. (1) and (2), where we plot the function $E(r)$ for two paradigmatic crystalline materials: respectively, silicon and aluminum.

In the covalently bonded system of Fig. 1, the bond electron pairs forming the typical “zig-zag” chain in the [110] plane are clearly visible. The very dark regions in the lower panel indicate in fact the strong bosonic character of the charge density in the bond region. Actually, $E(r)$ attains the maximum value of 0.96 at the bond center, thus indicating an extremely strong pairing between opposite–spin electrons.

A completely different picture emerges for our simple metallic system, Fig 2. The ELF plot in the lower panel shows—outside the core regions—a large grey area, which correspond to a jellium–like (or Thomas–Fermi) ELF value. Actually, the maximum value attained by $E(r)$ is only 0.61. This is agreement with the usual picture of a simple metal, where the (pseudo) electrons are excluded from the core region, while behaving essentially as free particles in the rest of the material.

Comparison of the two ELF plots provides therefore the most significant and perspicuous visualization of the important qualitative difference between the covalent bond and the metallic one. In the two classes of materials the Pauli principle plays quite a different role. At variance with the ELF, the corresponding charge density plots, (upper panels in Figs. 1 and 2) are much less informative, and do not qualitatively discriminate between the two different kinds of chemical bonds.

V. CONCLUSIONS AND PERSPECTIVES

The experience gained in investigating the ELF in real materials helps understanding the meaning and the limits of the approximate density functional such as the Zumbach–Maschke one, as well as of the generalization proposed here in Sec. III.

Our explicit ansatz of Eq. (8) leads to the Pauli excess energy $\tilde{T}_P$ of Eq. (13). It is interesting to see the consequences for the ELF, since the ansatz clearly leads to replacing the Pauli excess energy density, Eq. (22), with

$$\tilde{T}_P(r) = \frac{E_0}{3V} g^{-\frac{1}{2}} \text{tr} \{g^{ij}\} = \frac{1}{3} \epsilon_{π} n_π^\frac{5}{3} g^{-\frac{1}{2}} \text{tr} \{g^{ij}\},$$

where the thermodynamic limit, Eq. (20), has been used. Considering now the inequality

within a norm–conserving pseudopotential scheme this class includes simple metals, covalent semiconductors, simple ionic solids, and many other disparate materials. We have in this case by construction only a single shell (the valence $sp$ one of each atom involved), and the ELF allows a very meaningful analysis of the chemical bonding. Perhaps the most spectacular performance is the ability to perspicuously distinguish in a very clearcut way between metallic bonding and covalent bonding. This is illustrated in the lower panels of Figs. (1) and (2), where we plot the function $E(r)$ for two paradigmatic crystalline materials: respectively, silicon and aluminum.
we get for the approximate Pauli energy density the lower bound:

$$\tilde{\varepsilon}_p(r) \geq c_F n^\frac{5}{3}(r).$$  \hspace{1cm} (26)$$

Comparing with the ELF definition, Eq. (23), one easily realizes that even the optimal choice of the metric tensor will unavoidably provide values of $\mathcal{E}(r)$ which are smaller than $1/2$ everywhere.

In this work we have shown that a fundamental link exists between $N$-representability, approximate explicit functionals, and ELF. This link emerges very naturally within the geometric approach upon which our work is based. The same geometric approach, however, also indicates very clearly the limits of the approximate form of the kinetic energy for real materials which we have found here. In fact the final considerations of the previous paragraph imply that our constructive recipe, as well as the previous one of Zumbach and Maschke, are a good approximation only for systems where the bonding is metallic, while it necessarily overestimates the kinetic energy (and the total energy) whenever covalent bonding is present. Looking more closely, this major limitation owes to the occurrence of equidensity orbitals in our ansatz density matrix, Eq. (9), which occurrence can be further traced back to the choice of the uniform electron gas as the reference system upon which we perform the coordinate transformation. This naturally suggests the directions for improvements: one should start from a reference model system other than the uniform electron gas, having instead some covalent bonding features already built in. Interestingly, the use of a model reference system designed to reproduce—after coordinate mapping—some desirable features of the real one has been proposed in the most recent work of Ludeña and coworkers. These authors, however, focus on a spherical atom having several electronic shells: here instead we are discussing a condensed system with only one valence shell, within a pseudopotential scheme.

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