Noninteracting v-Representable Subspaces of Orbitals in the Kohn–Sham Method

Viktor N. Staroverov

Western University, vstarove@uwo.ca

Follow this and additional works at: https://ir.lib.uwo.ca/chempub

Citation of this paper:
Noninteracting υ-Representable Subspaces of Orbitals in the Kohn–Sham Method

Viktor N. Staroverov*
Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada
(Dated: July 14, 2022)

The notion of noninteracting υ-representability is extended from electron densities to finite-dimensional linear subspaces of orbitals. Unlike electron densities, orbital subspaces can be tested for noninteracting υ-representability using a transparent necessary condition: the subspace must be invariant under the action of some one-electron Kohn–Sham Hamiltonian. This condition allows one to determine in principle, and sometimes in practice, whether a given one-electron basis set can represent an N-electron density within the Kohn–Sham method and to find the corresponding Kohn–Sham effective potential υ if it exists. If the occupied Kohn–Sham orbitals form linearly independent products, then their subspace is determined by the corresponding ground-state electron density. This means that the Kohn–Sham effective potential corresponding to certain finite-basis-set electron densities can be deduced from the basis set itself.

In the Kohn–Sham density-functional theory1 (DFT), the ground-state electron density ρ(r) of a many-electron system of interest is constructed as the ground-state density of an auxiliary system of noninteracting electrons with a suitable external potential υ(r). Assuming a closed-shell noninteracting system with N electrons and a nondegenerate ground state, the potential υ(r) and the density are related through the Kohn–Sham equations

$$\left[ -\frac{1}{2} \nabla^2 + \nu(r) \right] \phi_i(r) = \epsilon_i \phi_i(r) \quad (1)$$

and

$$\rho(r) = 2 \sum_{i=1}^{n} |\phi_i(r)|^2 \quad (2)$$

where the summation is over the n = N/2 lowest-energy eigenfunctions φ_i(r), i.e., the occupied Kohn–Sham orbitals. For degenerate ground states and for spin-polarized systems, eqs 1 and 2 can be generalized accordingly,2 but such extensions fall outside the scope of this work.

Densities that can be generated by some physically reasonable potential υ(r) through eqs 1 and 2 as written are said to be noninteracting υ-representable by a single Slater determinant. It is well known that many reasonable densities are not so representable.3–8 Although this fact is of little consequence for Kohn–Sham calculations where electron densities are generated using explicit density-functional approximations, it cannot be ignored in discussing DFT foundations9 or in the context of Kohn–Sham inversion methods where one attempts to find the effective potential υ(r) associated with a given ρ(r) (see ref 10 for a comprehensive review of various inversion techniques). Densities used as inputs for Kohn–Sham inversions are often generated using arbitrary partitions into subsystems or by approximation methods and may well not be noninteracting υ-representable. Particular suspicion has been cast on densities generated using finite basis sets. For instance, de Silva and Wesolowski11 argued that the presence of nodes in the lowest-lying finite-basis-set Kohn–Sham orbital φ_1(r) signals that the corresponding density |φ_1(r)|^2 is not noninteracting υ-representable within a complete basis set. More recently, Mayer et al.12,13 pointed out that finite-basis-set ab initio densities derived from a nonidempotent (correlated) one-electron reduced density matrices (1-RDM) cannot be represented exactly by Kohn–Sham orbitals expanded in the same finite basis set; one can say then that such densities are not noninteracting υ-representable within the chosen basis set.

To facilitate the analysis of such problems and υ-representability in general, we propose here to extend the concept of noninteracting υ-representability to linear spaces spanned by subsets of Kohn–Sham orbitals. We will show that this concept makes it possible to determine whether a given one-electron basis set can be used to represent a noninteracting υ-representable electron density and to find the associated Kohn–Sham effective potential υ(r) if it exists.

Let us begin with definitions. Consider a set of m arbitrary linearly independent square-integrable complex-valued one-electron functions (orbitals), f_i(r). These functions form a basis for an m-dimensional vector space F^m over the field of complex numbers. We say that F^m is n-state (1 ≤ n ≤ m) noninteracting υ-representable if there exists a one-electron Kohn–Sham Hamiltonian

$$\hat{h} = -\frac{1}{2} \nabla^2 + \nu(r) \quad (3)$$

whose n lowest-energy eigenfunctions f_i are contained in F^m. The restriction to the lowest-lying orbitals is introduced for consistency with the definition of υ-representable densities, which pertains to ground states. For the purposes of this work, the symbol υ(r) in eq 3 refers to the equivalence class of effective potentials that differ from one another by an arbitrary constant.

Using the symbol V^n to denote an n-dimensional linear space spanned by n lowest occupied Kohn–Sham orbitals, the above definition can be restated as follows: An orbital space F^m is n-state noninteracting υ-representable if there exists a subspace V^n of n lowest-lying Kohn–Sham orbitals such that V^n ⊆ F^m. An orbital space F^m that is n-state noninteracting υ-representable is simultaneously k-state representable by the same υ for
all $k < n$. A space $F^m$ may be $n$-state noninteracting $v$-representable by one potential and simultaneously $k$-state representable ($k \leq m - n$) by another.

Both $v$-representable and non-$v$-representable spaces of orbitals are common and easy to come by. For instance, every $F^m$ containing at least one nodeless real-valued square-integrable function, say $\phi$, is 1-state noninteracting $v$-representable by the potential

$$v(r) = \frac{1}{2} \nabla^2 \phi(r) + \epsilon$$

which follows from eqs 1 and 2 for $n = 1$. A space spanned by the two lowest-energy nondegenerate eigenfunctions of some $\hat{h}$ is 2-state $v$-representable, whereas a space spanned by two nodeless lowest-energy eigenfunctions of different Kohn–Sham Hamiltonians is only 1-state $v$-representable, in two different ways. This is because every Kohn–Sham eigenfunction determines $v(r)$ uniquely through eq 4,14 and no ground-state eigenfunction of one Hamiltonian with an external potential $v(r)$ can be simultaneously the ground-state eigenfunction of another for the same interaction strength.15–17

Now we can formulate a necessary condition for $n$-state noninteracting $v$-representability of orbital subspaces: If a linear space $F^m$ is $n$-state noninteracting $v$-representable, then there exists a subspace $V^n \subseteq F^m$ that is invariant under the action of some Kohn–Sham Hamiltonian $\hat{h}$. Indeed, every $n$-state noninteracting $v$-representable space $F^m$ contains a subspace $V^n$ of the occupied Kohn–Sham orbitals of some $\hat{h}$, and every $k$-dimensional space ($k \geq 1$) spanned by $k$-fold degenerate eigenfunctions of $\hat{h}$ is invariant under the action of $\hat{h}$ by the definition of eigenspaces. The subspace $V^n$ is a direct sum of such invariant eigenspaces, so it is also invariant under $\hat{h}$.

The converse of this criterion is not true in general. An invariant subspace of an operator may be the null space rather than an eigenspace. Moreover, even when $V^n$ is an eigenspace, the eigenfunctions spanning it may not be the ones with the lowest eigenvalues. Thus, invariance of $V^n$ is necessary but not sufficient for noninteracting $v$-representability. This fact highlights two distinct aspects of noninteracting $v$-representable orbital subspaces and electron densities: invariance of the orbitals under the action of $\hat{h}$ and restriction to their being the lowest-energy eigenfunctions of $\hat{h}$.

The necessary condition formulated above can be put to practical use to identify $m$-dimensional orbital spaces that are not $n$-state noninteracting $v$-representable. For the sake of clarity, we will first explain the method for $m = n$ in relation to one-dimensional (1D) systems and then generalize to $m > n$ and 3D.

Consider a closed-shell system of $N = 2n$ noninteracting electrons moving in 1D. Let us choose a finite basis set of $n$ linearly independent square-integrable differentiable functions $f_i(x)$ ($i = 1, 2, \ldots, n$), which is the minimal number needed to represent the occupied Kohn–Sham orbitals of this system. The question whether the space $F^n$ is $n$-state noninteracting $v$-representable amounts to the following: Does there exist a Kohn–Sham Hamiltonian

$$\hat{h} = -\frac{1}{2} \frac{d^2}{dx^2} + v(x)$$

whose exact eigenfunctions $\phi_i(x)$ are given by

$$\phi_i(x) = \sum_{j=1}^{n} c_{ij} f_j(x)$$

with some coefficients $c_{ij}$? If such a Hamiltonian exists, then the space $F^n$ is invariant under the action of $\hat{h}$. This means that for every $f_i(x)$, the function defined by

$$q_i(x) = \hat{h} f_i(x)$$

must be a linear combination of all $f_i(x)$, that is,

$$q_i(x) = \sum_{j=1}^{n} \lambda_{ij} f_j(x)$$

where $\lambda_{ij}$ are some coefficients. Equation 8 can be satisfied only if there exists a $v(x)$ which makes every set of $n+1$ functions $\{f_1, f_2, \ldots, f_n, q_i\} (i = 1, 2, \ldots, n)$ linearly dependent.

The question of linear dependence of a set of functions can be answered by considering their Wronskians

$$W_i(x) = \begin{vmatrix} f_1(x) & f_2(x) & \cdots & f_n(x) & q_i(x) \\ f_1'(x) & f_2'(x) & \cdots & f_n'(x) & q_i'(x) \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ f_1^{(n)}(x) & f_2^{(n)}(x) & \cdots & f_n^{(n)}(x) & q_i^{(n)}(x) \end{vmatrix}$$

where the primes and subscripts in parentheses indicate the order of the derivatives. If the functions $\{f_1, f_2, \ldots, f_n, q_i\}$ are linearly dependent, then their Wronskian $W_i(x)$ vanishes at every point. The converse is not true in general but does hold for continuous functions with continuous derivatives of order up to $n-1$.18–20

In that case, the simultaneous vanishing of all $n$ Wronskians

$$W_i(x) = 0 \quad (i = 1, 2, \ldots, n)$$

implies that the functions $\{f_1, f_2, \ldots, f_n, q_i\}$ are linearly dependent.

If there is no $v(x)$ that solves eq 10 for all $i$, then $F^n$ is not $v$-representable. If such a $v(x)$ exists, then $F^n$ is invariant under some Kohn–Sham Hamiltonian $\hat{h}$. To settle the question whether $F^n$ is also $n$-state noninteracting $v$-representable, find the $n$ lowest-energy eigenfunctions of $\hat{h}$ with $v(x)$ and check if they span the same space as $F^n$.

To test for $n$-state noninteracting $v$-representability of a space $F^m$ with $m \geq n$, the prescription is to set up and solve equations $W_i(x) = 0$ for $i = 1, 2, \ldots, m$. If there is a
that simultaneously solves $n$ of the $m$ equations and if the $n$ lowest-energy eigenfunctions of the corresponding $h$ are contained in $F^m$, then $F^m$ is $n$-state noninteracting $v$-representable.

Finally, if the basis functions of $F^m$ are analytic and defined on 3D domains, then a necessary and sufficient condition for eq 10 to hold is that all generalized Wronskians associated with the sets $\{f_1, f_2, \ldots, f_n, q_i\}$ vanish identically.\textsuperscript{19,20} (Generalized Wronskians involve partial derivatives of the functions tested). This makes it possible, at least in principle, to determine which spaces of Gaussian-type basis functions are $v$-representable.

For Gaussian-type basis functions in 1D, eq 10 turns out to be solvable in closed form. By way of illustration, consider an orbital space $F^m$ spanned by three ($m = 3$) unnormalized basis functions:

$$
\begin{align*}
  f_1(x) &= e^{-\alpha x^2} \\
  f_2(x) &= xe^{-\alpha x^2} \\
  f_3(x) &= x^2 e^{-\alpha x^2}
\end{align*}
$$

where $-\infty < x < \infty$ and $\alpha > 0$, so the functions are square-integrable. This space $F^m$ can be at most 3-state noninteracting $v$-representable. The three functions $q_i(x)$ generated by the action of $h$ with an unknown $v(x)$ on the orbitals $f_i(x)$ are

$$
\begin{align*}
  q_1(x) &= [v(x) - 2\alpha^2 x^2 + \alpha] e^{-\alpha x^2} \\
  q_2(x) &= [v(x)x - 2\alpha^2 x^3 + 3\alpha x] e^{-\alpha x^2} \\
  q_3(x) &= [v(x)x^2 - 2\alpha^2 x^4 + 5\alpha x^2 - 1] e^{-\alpha x^2}
\end{align*}
$$

Evaluation of the first Wronskian of eq 9 gives

$$
W_1(x) = 2e^{-4\alpha x^2} \frac{d^3 v}{dx^3}
$$

This Wronskian vanishes everywhere if and only if $v(x)$ satisfies the equation $d^3 v/dx^3 = 0$, whose general solution is

$$
v(x) = A_1 x^2 + A_2 x + A_3
$$

where $A_1$, $A_2$, and $A_3$ are arbitrary constants. Similarly, one finds that

$$
W_2(x) = 2e^{-4\alpha x^2} \left( x \frac{d^3 v}{dx^3} + 3 \frac{d^2 v}{dx^2} - 12\alpha^2 \right)
$$

and solve the differential equation $W_2(x) = 0$ to obtain the general solution

$$
v(x) = 2\alpha^2 x^2 + B_1 x + B_2 + \frac{B_3}{x}
$$

where $B_1$, $B_2$, and $B_3$ are arbitrary constants. Finally, $W_3(x)$ and the general solution of the equation $W_3(x) = 0$ is

$$
v(x) = 2\alpha^2 x^2 + C_1 + \frac{C_2}{x} + \frac{C_3}{x^2}
$$

where $C_1$, $C_2$, and $C_3$ are arbitrary constants.

The requirement that $W_1(x)$, $W_2(x)$, and $W_3(x)$ vanish simultaneously can be met only if $A_1 = 2\alpha^2$, $A_2 = B_1 = B_3 = C_2 = C_3 = 0$, and $A_3 = B_2 = C_1 = C$. The only compatible potential is therefore

$$
v(x) = 2\alpha^2 x^2 + C
$$

where $C$ is an arbitrary constant. This is precisely the confining potential of noninteracting harmonic oscillators. The normalized lowest-energy eigenfunctions of the corresponding $h$ happen to be

$$
\begin{align*}
  \phi_1(x) &= \left( \frac{2\alpha}{\pi} \right)^{1/4} f_1(x) \\
  \phi_2(x) &= 2 \left( \frac{2\alpha^3}{\pi} \right)^{1/4} f_2(x) \\
  \phi_3(x) &= \left( \frac{\alpha}{2\pi} \right)^{1/4} [4\alpha f_3(x) - f_1(x)]
\end{align*}
$$

Thus, $F^m$ is 3-state noninteracting $v$-representable by the potential of eq 19.

Now consider a basis set of three unnormalized Gaussian-type functions with different exponents:

$$
\begin{align*}
  f_1(x) &= e^{-\alpha x^2} \\
  f_2(x) &= xe^{-\beta x^2} \\
  f_3(x) &= x^2 e^{-\gamma x^2}
\end{align*}
$$

where $\alpha, \beta, \gamma > 0$ and $\alpha \neq \beta \neq \gamma$. Proceeding as above, we evaluate the three Wronskians and solve eq 10 to obtain the following three general solutions:

$$
\begin{align*}
  v(x) &= 2\alpha^2 x^2 + A_1 x^2 e^{(\alpha-\gamma)x^2} + A_2 x e^{(\alpha-\beta)x^2} + A_3 \\
  v(x) &= 2\beta^2 x^2 + B_1 x e^{(\beta-\gamma)x^2} + B_2 e^{(\beta-\alpha)x^2} + B_3 \\
  v(x) &= 2\gamma^2 x^2 + C_1 e^{(\gamma-\beta)x^2} + C_2 e^{(\gamma-\alpha)x^2} + \frac{1}{x^2} + C_3
\end{align*}
$$

where $A_k$, $B_k$, and $C_k$ ($k = 1, 2, 3$) are arbitrary constants. These solutions are compatible with one another only if $\alpha = \beta = \gamma$, $A_1 = A_2 = B_1 = B_2 = C_1 = 0$, $C_2 = -1$, and $A_3 = B_3 = C_3 = C$. In that case, we have a 3-state noninteracting $v$-representable $F^m$ with the potential of eq 19. When only two of the three exponents are equal, say, $\alpha = \beta \neq \gamma$, then at most two equations $W_i(x) = 0$ can be made compatible, so the corresponding $F^m$ is 2-state noninteracting $v$-representable. For $\alpha \neq \beta \neq \gamma$, there is no $v(x)$ which simultaneously solves eq 10 for all $i$. This means the space $F^m$ spanned by Gaussian-type functions with three different exponents is at most 1-state noninteracting $v$-representable. Similarly,
one can show that an \( m \)-dimensional linear space spanned by the basis function \( f_i(x) = e^{-\alpha x^2} \), where all \( \alpha_i > 0 \) are distinct, is only 1-state noninteracting \( \nu \)-representable, in \( m \) different ways.

The remainder of this Letter describes several insights afforded by the concept of noninteracting \( \nu \)-representable orbital subspaces. First, situations where the Kohn–Sham potential exists only for a subset of the occupied Kohn–Sham orbitals can have significant numerical consequences for the evaluation of properties defined by reference to two or more eigenstates of \( \hat{h} \). In particular, when Kohn–Sham orbitals \( \phi_i \) cease to become exact eigenfunctions of \( \hat{h} \) above a certain \( i \), the result could be an imbalanced description of ionization potentials, electron affinities, and excitation energies.

Second, orbital subspaces are closely related to idempotent 1-RDMs. Specifically, every closed-shell Kohn–Sham system of \( N = 2n \) noninteracting electrons is in a one-to-one correspondence with an idempotent \( \sigma \)-spin \((\sigma = \alpha \text{ or } \beta)\) 1-RDM

\[
P_\sigma(r, r') = \sum_{i=1}^{n} \phi_i(r)\phi_i^*(r')
\]

where \( \phi_i(r) \) are orthonormal canonical occupied Kohn–Sham orbitals or any of their unitary transformations. Viewed as a kernel of a linear integral operator, \( P_\sigma(r, r') \) acts as a projector into the \( n \)-dimensional subspace \( V^n \) spanned by the occupied Kohn–Sham orbitals. The one-to-one correspondence between \( P_\sigma(r, r') \) and the orbital subspace \( V^n \) means that, for noninteracting systems with nondegenerate ground states, \( n \)-state noninteracting \( \nu \)-representability of the occupied Kohn–Sham orbital subspace is equivalent to noninteracting \( \nu \)-representability of the corresponding idempotent 1-RDM. This equivalence allows one in principle to determine whether a given 1-RDM is noninteracting \( \nu \)-representable, by using the following procedure. First, check whether \( P_\sigma(r, r') \) is idempotent; if so, determine the natural orbitals and use them as a basis for the subspace \( V^n \). Then solve eq 10 for \( \nu(r) \) to determine whether this subspace is invariant under the action of some Kohn–Sham Hamiltonian. If so, find the \( n \) lowest-energy eigenfunctions of \( \hat{h} \) and check whether their linear span is identical with \( F^n \). Note the issue of \( \nu \)-representability of nonidempotent 1-RDM is considerably more involved than for idempotent 1-RDMs.

The third illustration demonstrates the possibility of exact Kohn–Sham inversion for certain finite-basis-set densities. In terms of the occupied canonical Kohn–Sham orbitals, the \( \sigma \)-spin electron density of a spin-compensated \( N \)-electron system is given by

\[
\rho_\sigma(r) = P_\sigma(r, r') = \sum_{i=1}^{n} |\phi_i(r)|^2
\]

where \( n = N/2 \). More generally, if \( f_i(r) \) are nonorthogonal but linearly independent complex-valued basis functions for the space of the occupied Kohn–Sham orbitals, then

\[
\rho_\sigma(r) = \sum_{i=1}^{n} \sum_{j=1}^{n} P_{ij} f_i(r) f_j^*(r)
\]

where \( P_{ij} \) are coefficients. Following Harriman, we regard \( ij \) as a collective index and treat the 1-RDM as an expansion

\[
P_\sigma(r, r') = \sum_{ij=1}^{n^2} a_{ij} F_{ij}(r, r')
\]

in products of basis functions

\[
F_{ij}(r, r') = f_i(r) f_j^*(r')
\]

Then the density of eq 25 is an expansion

\[
\rho_\sigma(r) = \sum_{ij=1}^{n^2} a_{ij} g_{ij}(r)
\]

where

\[
g_{ij}(r) = F_{ij}(r, r) = f_i(r) f_j^*(r)
\]

are the “collapses” of \( F_{ij}(r, r') \). If the basis functions \( f_i(r) \) are linearly independent, the functions \( F_{ij}(r, r') \) are also linearly independent (Lemma 1 in the Appendix), whereas the collapsed functions \( g_{ij}(r) \) may or may not be. If the functions \( g_{ij}(r) \) are linearly independent, the functions \( f_i(r) \) are said to form a linearly independent product (LIP) basis set. Note that the functions \( g_{ij}(r) \) preserve their linear independence under nonsingular linear transformations of the underlying basis set \( \{f_i\} \) (Lemma 2 in the Appendix).

Harriman pointed out that if the collapsed functions \( g_{ij}(r) \) happen to be linearly independent, then there exists an invertible one-to-one mapping between electron densities and the corresponding 1-RDMs within the basis set \( \{f_i\} \). This mapping is effected by the system of linear equations

\[
\sum_{kl=1}^{n^2} \Omega_{i,j,kl} a_{kl} = \rho_{ij}
\]

where

\[
\Omega_{i,j,kl} = \int g_{ij}^*(r) g_{kl}(r) \, dr
\]

and

\[
\rho_{ij} = \int g_{ij}^*(r) \rho(r) \, dr
\]

If \( \{f_i\} \) is a LIP basis set, the overlap matrix \( \Omega \) is nonsingular and eq 30 has a solution. For a known density of eq 25 this solution would be \( a_{ij} = F_{ij} \). For LIP basis sets of real functions \( f_i(r) \), eqs 26, 28, and 30 would contain
only \( M = n(n + 1)/2 \) terms with \( k \leq l \) and \( i \leq j \) but otherwise would be unchanged.

The above argument shows that a density expanded in a LIP basis set unambiguously determines the corresponding finite-basis-set 1-RDM. Actual 1-RDM reconstructions of this type have been reported.\textsuperscript{24,25} Although standard Gaussian basis sets of nucleus-centered functions almost never form LIPs,\textsuperscript{25–28} sets of occupied Roothaan–Hall self-consistent-field orbitals routinely do so for small atoms and molecules.\textsuperscript{26,29} Thus, the 1-RDM reconstruction is feasible for systems of chemical interest.

We see that the Kohn–Sham inversion problem for LIP-basis set densities has the following formal exact solution: Infer the \( n \)-dimensional orbital subspace \( V^n \) of the 1-RDM from \( \rho(r) \) and then solve eq \( 10 \) to find the corresponding potential \( v(r) \) if it exists. This is clearly not a general or even practical method because it applies only within LIP basis sets and requires solving high-order partial differential equations arising from the Wronskians. Nevertheless, it puts the Kohn–Sham inversion problem into a broader perspective.

It is unlikely that standard atomic basis sets of quantum chemistry form multidimensional noninteracting \( v \)-representable orbital spaces, i.e., that they can represent more than one Kohn–Sham orbital exactly for the same system. This does not mean, however, that many-electron densities expanded in such basis sets cannot be noninteracting \( v \)-representable. To see why, consider an example motivated by the work of Aryasetiawani and Stott.\textsuperscript{30,31} Given a two-electron \( \sigma \)-spin density \( \rho_\sigma(r) \), one can take any nodeless real-valued function as the presumed first Kohn–Sham orbital \( \phi_1(r) \) and then the second occupied orbital is automatically given by \( \phi_2(r) = \sqrt{\rho_\sigma(r) - \phi_1^2(r)} \). Different nonorthogonal pairs \( \phi_1(r) \) and \( \phi_2(r) \) constructed in this manner are not related to one another through linear transformations and therefore span different two-dimensional orbital subspaces. According to the Hohenberg–Kohn theorem, at most one of those subspaces can be noninteracting \( v \)-representable by a single Slater determinant.\textsuperscript{32} The concept of \( v \)-representable orbital subspaces allows one to test any particular orbital subspace for consistency with \( \rho_\sigma(r) \) but, unfortunately, offers little help in finding the target subspace if it exists.

In conclusion, we have shown that by extending the concept of noninteracting \( v \)-representability from electron densities to finite-dimensional linear spaces of orbitals one can determine in principle, and sometimes in practice, whether a given set of one-electron basis functions can generate a noninteracting \( v \)-representable density and, if so, to find the corresponding Kohn–Sham potential \( v(r) \). If the occupied Kohn–Sham orbitals form LIPs, the expansion of the corresponding density in terms of those orbitals implies the corresponding Kohn–Sham 1-RDM. In such cases, solution of eq \( 10 \) may be interpreted as a Kohn–Sham inversion procedure in which the potential \( v(r) \) is determined from the Kohn–Sham 1-RDM. As a consequence, the unique mapping from ground-state electron densities to Kohn–Sham potentials, which generally does not exist within finite basis sets,\textsuperscript{16,17,33} is effectively restored within minimal LIP basis sets of occupied Kohn–Sham orbitals. It is anticipated that the concept of noninteracting \( v \)-representability of orbital spaces will be useful in these and other contexts of electronic structure theory.

**APPENDIX**

**Lemma 1.** If \( n \) complex-valued functions \( f_i(r) \) are linearly independent, then the \( n^2 \) products \( f_i(r)f_j^*(r') \) are also linearly independent.

**Proof.** The functions \( f_i(r) \) may or may not be orthogonal. If they are orthogonal, then the products \( f_i(r)f_j^*(r') \) are obviously orthogonal and therefore linearly independent. If the linearly independent functions \( f_i(r) \) are not orthogonal, they can always be regarded as nonsingular linear transformations of some \( n \) orthonormal complex-valued functions \( \phi_i(r) \) spanning the same \( n \)-dimensional vector space, that is,

\[
    f_i(r) = \sum_{k=1}^{n} A_{ik} \phi_k(r) \quad (A1)
\]

where \( A \) is the transformation matrix. Every product of such functions is given by

\[
    f_i(r)f_j^*(r') = \sum_{k=1}^{n} \sum_{l=1}^{n} A_{ik} A_{jl}^* \phi_k(r) \phi_l^*(r') \quad (A2)
\]

The transformation matrix from the basis \( \phi_k(r) \phi_l^*(r') \) to \( f_i(r)f_j^*(r') \) is the direct (Kronecker) matrix product\textsuperscript{34}

\[
    U = A \otimes A^* \quad (A3)
\]

which is a square \( n \times n \) matrix with elements

\[
    U_{ij,kl} = A_{ik} A_{jl}^* \quad (A4)
\]

One can show\textsuperscript{34} that the determinant of \( U \) is

\[
    \det U = (\det A)^n (\det A^*)^n = |\det A|^{2n} \quad (A5)
\]

Thus, if \( A \) is nonsingular, \( U \) is also nonsingular. This means that the products \( f_i(r)f_j^*(r') \) are linearly independent and concludes the proof.

**Lemma 2.** Let \( f_i(r) \) be \( n \) linearly independent complex-valued functions and \( \tilde{f}_i(r) = \sum_{j=1}^{n} A_{ij} f_j(r) \) their linear transformations by a nonsingular matrix \( A \). If the \( n^2 \) products \( f_i(r)f_j^*(r') \) are linearly independent, then the products \( \tilde{f}_i(r)f_j^*(r') \) are also linearly independent.

**Proof.** The argument is exactly the same as in Lemma 1 starting with eq \( A2 \) in which the products \( \phi_k(r)\phi_l^*(r') \) and \( f_i(r)f_j^*(r') \) are replaced with \( f_k(r)f_l^*(r) \) and \( \tilde{f}_i(r)f_j^*(r') \), respectively.
ACKNOWLEDGMENTS

The author acknowledges the support of the Natural Sciences and Engineering Research Council of Canada (NSERC) through the Discovery Grants Program (Application RGPI-2020-06420).