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Multiplicative potentials for kinetic energy and exact exchange

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ABSTRACT

Harriman showed that within finite basis sets of one-electron functions that form linearly independent products (LIP), differential and integral operators can be represented exactly and unambiguously by multiplicative (local) potentials. Although almost no standard basis sets of quantum chemistry form LIPs in a numerical sense, occupied self-consistent field (SCF) orbitals routinely do so. Using minimal LIP basis sets of occupied SCF orbitals, we construct multiplicative potentials for electronic kinetic energy and exact exchange that reproduce the Hartree–Fock and Kohn–Sham Hamiltonian matrices and electron densities for atoms and molecules. The results highlight fundamental differences between local and nonlocal operators and suggest a practical possibility of developing exact kinetic energy functionals within finite basis sets by using effective local potentials.

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I. INTRODUCTION

Introduction of finite basis sets into quantum mechanics amounts to replacing operators on an infinite-dimensional Hilbert space with finite matrices that act within finite-dimensional subspaces. Although the eigenvalues and eigenvectors of a finite-dimensional matrix are generally different from those of the original operator, an agreement between the two sets of solutions can be improved systematically by enlarging the basis set. As a result, this discretization is sometimes viewed as a mere device for finding approximate solutions to eigenvalue problems.

In some situations, however, the use of finite basis sets gives rise to essentially new effects. For instance, the unique mapping from ground-state densities to external potentials generally does not exist within finite basis sets,[1] and the very Kohn–Sham scheme cannot be exact in general.[2] In a series of papers,[3–6] Harriman studied relationships between quantum-mechanical operators and their matrix representations and arrived at several striking conclusions for basis sets of a particular type, namely, those whose functions form linearly independent products (LIP). Within LIP basis sets (i) there is no distinction between local (multiplicative) potentials and nonlocal operators; (ii) multiplicative potentials can be reconstructed from their matrix representations; (iii) an electron density unambiguously implies the corresponding one-electron reduced density matrix (1-RDM); and (iv) unique mapping from densities to potentials $v(\mathbf{r})$ is restored.[7] These results have startling implications for quantum chemistry, e.g., the possibility of determining 1-RDMs from electron densities,[8,9] unambiguous reconstruction of Kohn–Sham potentials from their matrix representations,[10] and analytic Kohn–Sham inversion for many-electron densities.[7]

The initial wave of excitement generated by Harriman's results subsided when it was found[11–14] that almost no standard basis sets of quantum chemistry qualify as LIP sets. It turns out, however, that occupied self-consistent field (SCF) orbitals of small atoms and molecules routinely form LIPs.[10,11] This fact makes it possible to apply the LIP-basis-set machinery to a much broader range of chemically relevant systems than formerly recognized.

The construction of exchange-correlation potentials from their matrix representations was reported by us elsewhere.[10] Here, we construct and present multiplicative potentials by means of which one can faithfully reproduce every part of Hartree–Fock and Kohn–Sham Hamiltonians including the kinetic energy operator and the Fock exchange.

II. METHODOLOGY

We begin by reviewing the parts of Harriman's theory[3,4] that are relevant to our purposes. Afterwards, we derive the working equations, first for complex-valued orthonormal basis sets, then for real nonorthogonal basis functions.

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A. Complex-valued orthonormal basis functions

Consider a complex Hilbert space $\mathcal{H}$, finite- or infinite-dimensional, of one-electron position-dependent functions (orbitals) with an orthonormal basis $\{\phi_k\}$,

$$\int \phi_k^*(\mathbf{r})\phi_l(\mathbf{r})\,d\mathbf{r} = \delta_{kl}. \tag{1}$$

Any Hermitian spinless operator $\hat{G}$ from $\mathcal{H}$ to $\mathcal{H}$ is uniquely represented by an integral kernel $G(\mathbf{r},\mathbf{r}')$, and the operation $\hat{G}\phi = \psi$ $(\phi, \psi \in \mathcal{H})$ is then realized as

$$\int G(\mathbf{r},\mathbf{r}')\phi(\mathbf{r}')\,d\mathbf{r}' = \psi(\mathbf{r}). \tag{2}$$

In an infinite-dimensional $\mathcal{H}$, one can draw a clear distinction between local (multiplicative) and nonlocal operators. Integral kernels associated with local operators have the special form,

$$G(\mathbf{r},\mathbf{r}') = v(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}'), \tag{3}$$

where the function $v(\mathbf{r})$ is often referred to as a "local potential." This kernel is completely determined by $v(\mathbf{r})$.

When $\mathcal{H}$ is finite-dimensional, the distinction between local and nonlocal operators is blurred.[3] Consider a K-dimensional space with an orthonormal basis $\{\phi_k\}$ $(k = 1, 2, \ldots, K)$. The integral kernel of $\hat{G}$ on this space has finite rank and can be expanded as

$$G(\mathbf{r},\mathbf{r}') = \sum_{k=1}^{K}\sum_{l=1}^{K} G_{kl}\phi_k(\mathbf{r})\phi_l^*(\mathbf{r}'), \tag{4}$$

where

$$G_{kl} = \int d\mathbf{r}\int \phi_k^*(\mathbf{r})G(\mathbf{r},\mathbf{r}')\phi_l(\mathbf{r}')\,d\mathbf{r}'. \tag{5}$$

The Hermitian matrix $\mathbf{G}$ represents $\hat{G}$ in the basis set $\{\phi_k\}$. According to Harriman's theory, if $\{\phi_k\}$ is a LIP basis set, then there exists a *unique* local potential $\tilde{v}(\mathbf{r})$ associated with $G(\mathbf{r},\mathbf{r}')$, such that

$$\int \phi_k^*(\mathbf{r})\tilde{v}(\mathbf{r})\phi_l(\mathbf{r})\,d\mathbf{r} = \int d\mathbf{r}\int \phi_k^*(\mathbf{r})G(\mathbf{r},\mathbf{r}')\phi_l(\mathbf{r}')\,d\mathbf{r}' \tag{6}$$

for all k and l, whether $\hat{G}$ is multiplicative or not on the infinite-dimensional space. Our objective here is to calculate this $\tilde{v}(\mathbf{r})$ for various types of $\hat{G}$. Before we elaborate, let it be clear that $\tilde{v}(\mathbf{r}) \neq G(\mathbf{r},\mathbf{r})$ and that, for any finite basis set $\{\phi_k\}$, there are infinitely many local potentials whose matrix representations satisfy Eq. (6).[10,15] We are interested here in the unique potential $\tilde{v}(\mathbf{r})$ associated with $G(\mathbf{r},\mathbf{r}')$ through Harriman's theory.

Equation (6) is the key to understanding everything. Its right-hand side looks like a coefficient in the Fourier expansion of $G(\mathbf{r},\mathbf{r}')$ in orthonormal functions $\phi_k(\mathbf{r})\phi_l^*(\mathbf{r}')$, so the left-hand side leads one to consider an expansion of $\tilde{v}(\mathbf{r})$ in nonorthogonal products $\phi_k(\mathbf{r})\phi_l^*(\mathbf{r})$. This suggests treating $G(\mathbf{r},\mathbf{r}')$ as an element of a vector space $\mathcal{E}_r$ of integral-operator kernels on $\mathcal{H}$ and $\tilde{v}(\mathbf{r})$ as an element of a vector space $\mathcal{F}_r$ of potentials associated with those kernels. The former space is spanned by the orthogonal functions $\phi_k(\mathbf{r})\phi_l^*(\mathbf{r}')$, so its dimension is K^2. The space $\mathcal{F}_r$ contains the products $\phi_k(\mathbf{r})\phi_l^*(\mathbf{r})$ and its dimension depends on how many of these products are linearly independent, that is, on the underlying basis $\{\phi_k\}$. There is a mapping from $\mathcal{E}_r$ to $\mathcal{F}_r$ effected by the linear "collapse" operator $\hat{\delta}$ defined by

$$\hat{\delta}\Phi(\mathbf{r},\mathbf{r}') = \Phi(\mathbf{r},\mathbf{r}), \tag{7}$$

where $\Phi(\mathbf{r},\mathbf{r}')$ is an element of $\mathcal{E}_r$ and $\Phi(\mathbf{r},\mathbf{r})$ is the corresponding element of $\mathcal{F}_r$. In general, this mapping is many-to-one.

Now comes the crucial argument.[4] If the K^2 products $\phi_k(\mathbf{r})\phi_l^*(\mathbf{r})$ do happen to be linearly independent, then the dimensions of $\mathcal{E}_r$ and $\mathcal{F}_r$ are equal and the mapping from $\mathcal{E}_r$ to $\mathcal{F}_r$ is invertible, so it becomes possible to reconstruct $\tilde{v}(\mathbf{r})$ from $\mathbf{G}$.[4] Careful development of this idea requires properly symmetrized product functions.

The kernel $G(\mathbf{r},\mathbf{r}')$ is Hermitian-symmetric,

$$G(\mathbf{r},\mathbf{r}') = G^*(\mathbf{r}',\mathbf{r}), \tag{8}$$

but the K^2 functions $\phi_k(\mathbf{r})\phi_l^*(\mathbf{r}')$ with $k \neq l$ are not, so the actual dimension of $\mathcal{E}_r$ might be lower than K^2. A convenient properly symmetrized basis for $\mathcal{E}_r$ is

$$\Phi_{kl}(\mathbf{r},\mathbf{r}') = \begin{cases} \phi_k(\mathbf{r})\phi_k^*(\mathbf{r}') & (k=l) \\ \frac{1}{2}\left[\phi_k(\mathbf{r})\phi_l^*(\mathbf{r}') + \phi_l(\mathbf{r})\phi_k^*(\mathbf{r}')\right] & (k<l) \\ \frac{1}{2i}\left[\phi_k(\mathbf{r})\phi_l^*(\mathbf{r}') - \phi_l(\mathbf{r})\phi_k^*(\mathbf{r}')\right] & (k>l) \end{cases}, \tag{9}$$

where i is the imaginary unit. (Note that Harriman normalizes these functions to unity,[3] but we will see below that the factors chosen above lead to simpler working equations.) The K^2 Hermitian-symmetric functions $\Phi_{kl}(\mathbf{r},\mathbf{r}')$ are orthogonal, so the dimension of $\mathcal{E}_r$ is indeed K^2. In terms of this symmetrized basis, Eq. (4) becomes

$$G(\mathbf{r},\mathbf{r}') = \sum_{kl=1}^{K^2} \beta_{kl}\Phi_{kl}(\mathbf{r},\mathbf{r}'), \tag{10}$$

where kl is treated as a single collective index and

$$\beta_{kl} = \frac{\langle\Phi_{kl}|G\rangle}{\langle\Phi_{kl}|\Phi_{kl}\rangle} \tag{11}$$

are real coefficients. Note that Eq. (4) represents $G(\mathbf{r},\mathbf{r}')$ as a bilinear form, whereas Eq. (10) is a linear form.

The collapse operator transforms the functions $\Phi_{kl}(\mathbf{r},\mathbf{r}')$ into real one-electron functions,

$$g_{kl}(\mathbf{r}) = \begin{cases} \phi_k(\mathbf{r})\phi_k^*(\mathbf{r}) & (k=l) \\ \frac{1}{2}\left[\phi_k(\mathbf{r})\phi_l^*(\mathbf{r}) + \phi_l(\mathbf{r})\phi_k^*(\mathbf{r})\right] & (k<l) \\ \frac{1}{2i}\left[\phi_k(\mathbf{r})\phi_l^*(\mathbf{r}) - \phi_l(\mathbf{r})\phi_k^*(\mathbf{r})\right] & (k>l) \end{cases}, \tag{12}$$

where $g_{kl}(\mathbf{r}) \equiv \Phi_{kl}(\mathbf{r},\mathbf{r})$. By Lemma 1 of the Appendix, the functions $g_{kl}(\mathbf{r})$ are linearly independent if the products $\phi_k(\mathbf{r})\phi_l^*(\mathbf{r})$ are. Thus, if $\{\phi_k\}$ is a LIP basis set, then the dimension of $\mathcal{F}_r$ is also K^2 and the potential is given by

$$\tilde{v}(\mathbf{r}) = \sum_{kl=1}^{K^2} \alpha_{kl}g_{kl}(\mathbf{r}), \tag{13}$$

where α_{kl} are some real coefficients.

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In terms of the symmetry-adapted basis functions, Eq. (6) becomes

$$\langle g_{kl}|\tilde{v}\rangle = \langle \Phi_{kl}|G\rangle = \begin{cases} \mathrm{Re}\, G_{kl} & (k \le l) \\ \mathrm{Im}\, G_{kl} & (k > l) \end{cases}, \tag{14}$$

where we evaluated $\langle \Phi_{kl}|G\rangle$ by combining Eqs. (4) and (9). The prefactors of $\frac{1}{2}$ in Eq. (9) were chosen precisely so that the right-hand side of Eq. (14) contains matrix elements G_{kl} rather than their multiples.

Substitution of Eq. (13) into Eq. (14) gives

$$\sum_{kl=1}^{K^2} \langle g_{ij}|g_{kl}\rangle \alpha_{kl} = \begin{cases} \mathrm{Re}\, G_{kl} & (k \le l) \\ \mathrm{Im}\, G_{kl} & (k > l) \end{cases}. \tag{15}$$

This system of linear equations allows one to determine the coefficients α_{kl} from the matrix elements of **G**. Thus, within a LIP basis set, one can always recover $\tilde{v}(\mathbf{r})$ from **G**. If some products $\phi_k(\mathbf{r})\phi_l^*(\mathbf{r})$ are linearly dependent, then the mapping from $\mathcal{E}_r$ to $\mathcal{F}_r$ is many-to-one and cannot be inverted.

B. Real-valued nonorthogonal basis functions

For real and nonorthonormal basis sets, some of the equations of Sec. II A require nontrivial modifications. Consider a basis set of linearly independent real functions $f_k(\mathbf{r})$ $(k = 1, 2, \ldots, K)$ that are not necessarily orthogonal or normalized. The integral kernel of any Hermitian operator $\hat{G}$ in this basis is a symmetric function given by

$$G(\mathbf{r}, \mathbf{r}') = \sum_{k=1}^{K}\sum_{l=1}^{K} (\mathbf{S}^{-1}\mathbf{G}\mathbf{S}^{-1})_{kl} f_k(\mathbf{r}) f_l(\mathbf{r}'), \tag{16}$$

where **S** is the matrix of overlap integrals,

$$S_{kl} = \int f_k(\mathbf{r}) f_l(\mathbf{r})\, d\mathbf{r}, \tag{17}$$

and **G** is the matrix of $\hat{G}$ in the basis $\{f_k\}$, that is,

$$G_{kl} = \int f_k(\mathbf{r}) \hat{G} f_l(\mathbf{r})\, d\mathbf{r}. \tag{18}$$

Although the number of linearly independent functions $f_k(\mathbf{r}) f_l(\mathbf{r}')$ is K^2, only their $M = K(K+1)/2$ symmetrized combinations,

$$\Phi_{kl}(\mathbf{r}, \mathbf{r}') = \frac{1}{2}\left[f_k(\mathbf{r}) f_l(\mathbf{r}') + f_l(\mathbf{r}) f_k(\mathbf{r}')\right] \qquad (k \le l), \tag{19}$$

can contribute to the expansion,

$$G(\mathbf{r}, \mathbf{r}') = \sum_{kl=1}^{M} b_{kl} \Phi_{kl}(\mathbf{r}, \mathbf{r}'), \tag{20}$$

where kl is again a single collective subscript and b_{kl} are coefficients whose values are irrelevant for our purposes. Equation (20) shows that the dimension of $\mathcal{E}_r$ is now M. The same conclusion can be reached by inspecting Eq. (9) and noting that, for real basis sets, the functions $\Phi_{kl}(\mathbf{r}, \mathbf{r}')$ with $k > l$ become purely imaginary and, therefore, do not contribute.

The corresponding collapsed real functions $g_{kl}(\mathbf{r})$ are

$$g_{kl}(\mathbf{r}) = f_k(\mathbf{r}) f_l(\mathbf{r}) \quad (k \le l). \tag{21}$$

If these products are linearly independent, the dimension of $\mathcal{F}_r$ is also M and $G(\mathbf{r}, \mathbf{r}')$ is in a one-to-one correspondence with the potential,

$$\tilde{v}(\mathbf{r}) = \sum_{kl=1}^{M} a_{kl} g_{kl}(\mathbf{r}), \tag{22}$$

where a_{kl} are yet unknown coefficients, such that

$$G_{kl} = \int f_k(\mathbf{r}) \tilde{v}(\mathbf{r}) f_l(\mathbf{r})\, d\mathbf{r}. \tag{23}$$

It is essential that the functions $g_{kl}(\mathbf{r})$ do not lose their linear independence under any nonsingular linear transformation of $\{f_k\}$ (Lemma 2 in the Appendix).

The analog of Eq. (14) for real basis functions is

$$\langle g_{kl}|\tilde{v}\rangle = \langle \Phi_{kl}|G\rangle = G_{kl}. \tag{24}$$

After substituting Eq. (22) into Eq. (24), we obtain

$$\sum_{ij=1}^{M} W_{kl,ij} a_{ij} = G_{kl}, \tag{25}$$

where $i \le j$, $k \le l$, and

$$W_{ij,kl} = \langle g_{ij}|g_{kl}\rangle = \int f_i(\mathbf{r}) f_j(\mathbf{r}) f_k(\mathbf{r}) f_l(\mathbf{r})\, d\mathbf{r} \tag{26}$$

are elements of the four-center $M \times M$ overlap matrix **W**. As long as the basis functions $\{f_k\}$ form LIPs, **W** is nonsingular and Eq. (25) has a unique solution.

C. Local potentials for nonlocal operators

What happens if **G** is a matrix representation of a *nonlocal* operator such as the Hartree–Fock exchange or the differential operator for the kinetic energy? Within a LIP basis set, the solution of Eq. (25) will give a multiplicative potential $\tilde{v}(\mathbf{r})$ that faithfully reproduces the effect of $\hat{G}$ in that basis set. In fact, all operators within a LIP basis set can be represented by effective local potentials.[4]

From the computational point of view, there is no difference in applying Eq. (25) to matrices of local or nonlocal operators generated using the same LIP basis set. We will see, however, that multiplicative potentials for nonlocal operators tend to have rather complicated shapes.

D. LIP basis sets

Construction of unambiguous local potentials for nonlocal operators requires LIP basis sets. No complete (infinite) basis set can be a LIP basis[4,16] and, as mentioned above, virtually no standard finite basis set of Gaussian-type or Slater-type atomic orbitals (AO) has this property in a numerical sense. Fortunately, occupied canonical Hartree–Fock (HF) and Kohn–Sham (KS) SCF orbitals routinely form LIPs, at least for small atoms and molecules. Occupied SCF orbitals span only a small subspace of the original AO basis set but,

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within one-determinantal SCF methods, they are sufficient to reproduce exactly the ground-state electron density and total electronic energy of the original AO basis set, even if the latter is complete (infinite).

Here, we consider a set of functions to be a LIP basis set if the smallest eigenvalue of **W** (for normalized products) is above a threshold of $\lambda_{\min} = 10^{-9}$. For the systems reported here, we have $\lambda_{\min} \approx 3 \times 10^{-3}$ for Be, $\lambda_{\min} \approx 4 \times 10^{-4}$ for Ne, and $\lambda_{\min} \approx 5 \times 10^{-9}$ for HCN. The capacity of occupied SCF orbitals to form LIPs for a given system does not vary much with the size of the underlying AO basis set.[10]

III. IMPLEMENTATION

Construction of a multiplicative operator $\tilde{v}(\mathbf{r})$ reproducing the matrix of an arbitrary Hermitian operator $\hat{G}$ within a LIP basis set $\{\phi_i\}$ of occupied SCF orbitals amounts to solving the $M \times M$ system of linear equations,

$$\mathbf{W}\mathbf{a} = \mathrm{vech}(\mathbf{G}), \tag{27}$$

where $W_{ij,kl} = \langle \phi_i \phi_j | \phi_k \phi_l \rangle$, $G_{ij} = \langle \phi_i | \hat{G} | \phi_j \rangle$, and **a** is a column vector of expansion coefficients a_{kl} of $\tilde{v}(\mathbf{r})$ by Eq. (22) in terms of orbital products $g_{kl} = \phi_k \phi_l$. The operation vech() takes a symmetric matrix and stacks the rows of its upper triangular half into a single column vector.

To illustrate this method, we applied it to matrices of four different operators: the exchange-only potential $v_X(\mathbf{r})$ in the local density approximation (LDAx), the Fock exchange operator $\hat{K}$, the multiplicative exchange potential $v_X(\mathbf{r})$ generated from HF SCF wavefunctions by the modified method of Ryabinkin, Kohut, and Staroverov (HF-mRKS),[17–19] and the one-electron kinetic energy operator $\hat{t} = -\frac{1}{2}\nabla^2$ of the HF and KS SCF schemes. The LDAx potential represents local and semilocal exchange-correlation approximations the KS density-functional theory, $\hat{K}$ represents orbital-dependent integral operators, HF-mRKS represents optimized effective potentials (OEPs) for orbital-dependent functionals (it produces the same HF electron density as $\hat{K}$),[17–21] and $\hat{t}$ represents differential operators.

All HF and LDAx matrices were generated with the Psi4NumPy program.[22] HF-mRKS potentials $v_X(\mathbf{r})$, and their matrix representations were obtained by the method of Ref. 19. Overlap matrices **W** of canonical SCF orbitals were evaluated analytically by expanding each orbital in an AO basis and evaluating four-center AO overlap integrals using standard formulas.[23,24] We have also verified that, in each case, the calculated $\tilde{v}(\mathbf{r})$ has exactly the same matrix representation in the LIP basis set of occupied SCF orbitals as the parent operator $\hat{G}$.

IV. RESULTS

Multiplicative real-space potentials (e.g., external v_{ext}, Hartree v_H, LDAx v_X, and exact v_{XC}) constructed by standard SCF codes in the usual way will be referred to as "conventional." It is instructive to compare conventional potentials $v(\mathbf{r})$ to potentials $\tilde{v}(\mathbf{r})$ recovered from matrix representations of $v(\mathbf{r})$ in LIP basis sets.

We find that when one starts with a conventional local exchange potential $v_X(\mathbf{r})$, the potential $\tilde{v}_X(\mathbf{r})$ recovered from the matrix of $v_X(\mathbf{r})$ in a LIP basis set of occupied SCF orbitals is generally quite different from $v_X(\mathbf{r})$, especially near atomic nuclei. The dependence of $\tilde{v}_X(\mathbf{r})$ on the underlying AO basis set is not very strong but is more pronounced than for $v_X(\mathbf{r})$. This is seen in Figs. 1 and 2 for three standard Gaussian basis sets of increasing size: def2-SVP (small), def2-TZVP (medium), and def2-QZVP (large).[25]

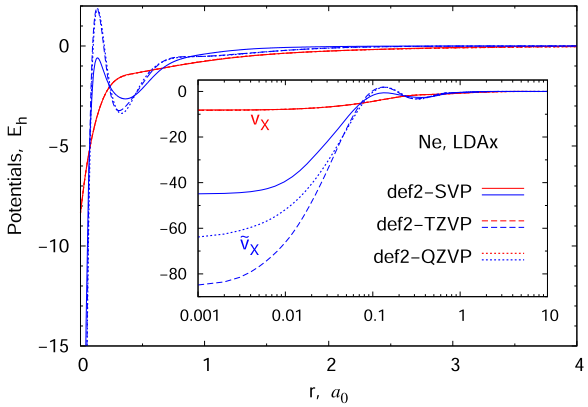


FIG. 1. LDAx potentials (v_X, red) of Ne and their reconstructions ($\tilde{v}_X$, blue) from the corresponding matrix representations of v_X in the basis of the occupied Kohn–Sham orbitals generated using AO basis sets of varying size. The inset shows the same data on the logarithmic *r*-scale.

Figure 1 shows three conventional LDAx potentials and their reconstructions from the occupied–occupied subblocks of the Kohn–Sham matrices generated using three different AO basis sets. The def2-QZVP $\tilde{v}_X(\mathbf{r})$ is closer to the def2-TZVP $\tilde{v}_X(\mathbf{r})$ than the latter is to the def2-SVP $\tilde{v}_X(\mathbf{r})$, which suggests that $\tilde{v}_X(\mathbf{r})$ is converging to the AO basis-set limit. Similar examples involving full exchange-correlation potentials may be found in our Ref. 10. Increasing the size of the LIP basis set (e.g., by including a few low-lying virtual orbitals) can improve the agreement between $\tilde{v}_X(\mathbf{r})$ and $v_X(\mathbf{r})$.[10]

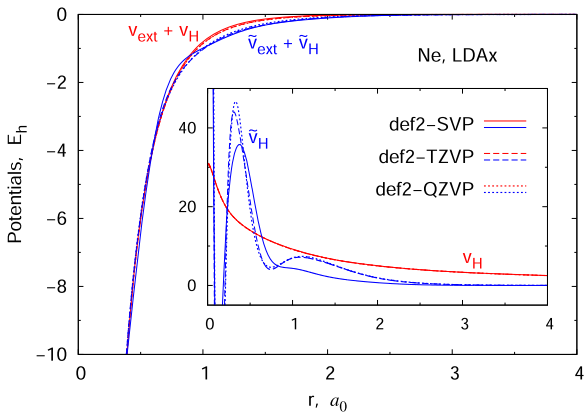


FIG. 2. External and conventional Hartree potentials (red) from LDAx SCF calculations for Ne and their reconstructions (blue) from the corresponding matrix representations in the basis of the occupied Kohn–Sham orbitals. The inset shows the Hartree potentials separately.

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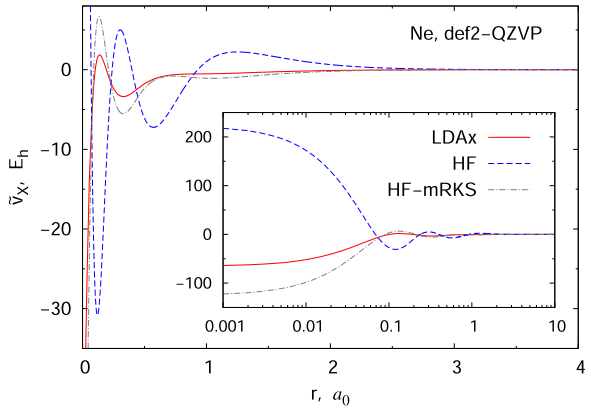


FIG. 3. Multiplicative potentials $\tilde{v}_X(\mathbf{r})$ reconstructed from the exchange parts of the LDAx, HF, and HF-mRKS matrices in the LIP basis set of the corresponding occupied SCF orbitals. The inset shows the same data on the logarithmic *r*-scale.

Figure 2 depicts analogous reconstructions for the external and Hartree potentials. Surprisingly, the agreement between the sums $v_{ext}(\mathbf{r}) + v_H(\mathbf{r})$ and $\tilde{v}_{ext}(\mathbf{r}) + \tilde{v}_H(\mathbf{r})$ is very good, even though each of $\tilde{v}_{ext}(\mathbf{r})$ and $\tilde{v}_H(\mathbf{r})$ separately is quite different from the respective original.

Potentials $\tilde{v}_X(\mathbf{r})$ recovered from matrices of the Fock exchange operator $\hat{K}$ are generally quite different from potentials $\tilde{v}_X(\mathbf{r})$ recovered from LDAx and HF-mRKS matrices (Fig. 3), as well as from conventional LDAx and OEP-like potentials.[26–28] Specifically, potentials $\tilde{v}_X(\mathbf{r})$ recovered from HF matrices exhibit oscillations absent in the analogous potentials recovered from LDAx and HF-mRKS Hamiltonian matrices. These oscillations are manifestations of the nonlocality of the operator $\hat{K}$.

Unlike the exchange, the one-electron kinetic energy operator $\hat{t}$ is always nonlocal in both HF and KS schemes. As a result, reconstructions $\tilde{v}_{kin}(\mathbf{r})$ of this operator from the kinetic energy parts of HF and KS matrices are very similar (Fig. 4).

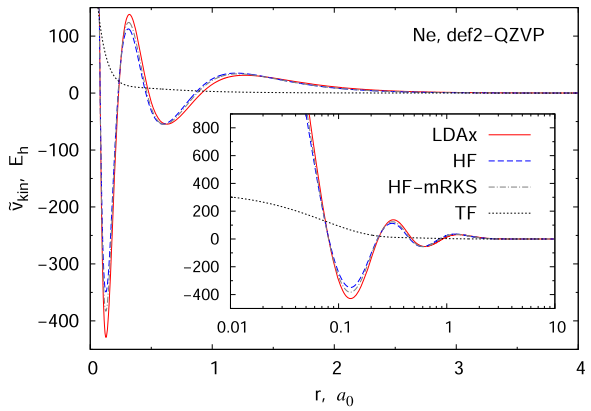


FIG. 4. Multiplicative potentials $\tilde{v}_{kin}(\mathbf{r})$ reconstructed from the kinetic-energy parts of the LDAx, HF, and HF-mRKS matrices in the LIP basis set of the corresponding occupied SCF orbitals. The inset shows the same data on the logarithmic *r*-scale.

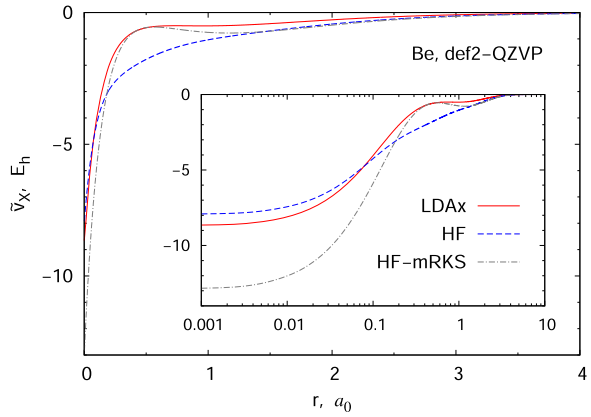


FIG. 5. Same as in Fig. 3 for the Be atom. The HF potential $\tilde{v}_X(\mathbf{r})$ again differs from the other two in the valence region, but to a lesser extent than in Fig. 3.

We also compared the multiplicative kinetic potentials $\tilde{v}_{kin}(\mathbf{r})$ to the functional derivative,

$$v_{TF}(\mathbf{r}) = \frac{\delta T_{TF}}{\delta \rho(\mathbf{r})}, \tag{28}$$

of the Thomas–Fermi (TF) kinetic energy functional,

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r}, \tag{29}$$

where $C_F = \frac{3}{10}(3\pi^2)^{2/3}$, evaluated for the LDAx SCF density (Fig. 4). There is very little resemblance between $v_{TF}(\mathbf{r})$ and $\tilde{v}_{kin}(\mathbf{r})$.

The shapes of $\tilde{v}_X(\mathbf{r})$ and $\tilde{v}_{kin}(\mathbf{r})$ vary considerably with the size of the LIP basis set. For Ne, there are five occupied SCF orbitals that form $M = 15$ distinct orbital products, of which only six ($1s1s$, $1s2s$, $2s2s$, $2p_x2p_x$, $2p_y2p_y$, and $2p_z2p_z$) actually contribute because of symmetry restrictions. For the Be atom, the SCF orbitals generate only $M = 3$ product basis functions ($1s1s$, $1s2s$, and $2s2s$). This

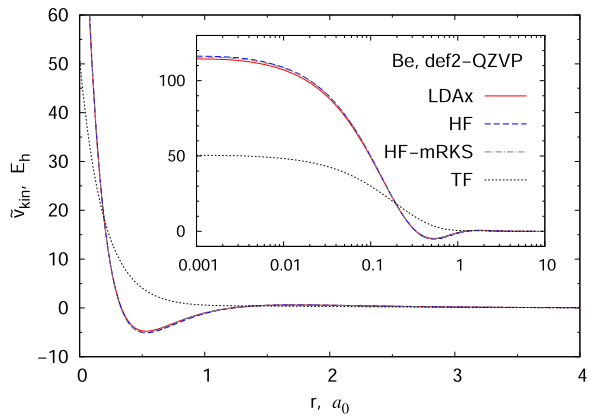


FIG. 6. Same as in Fig. 4 for the Be atom. In contrast to Fig. 5, the three reconstructed potentials are similar.

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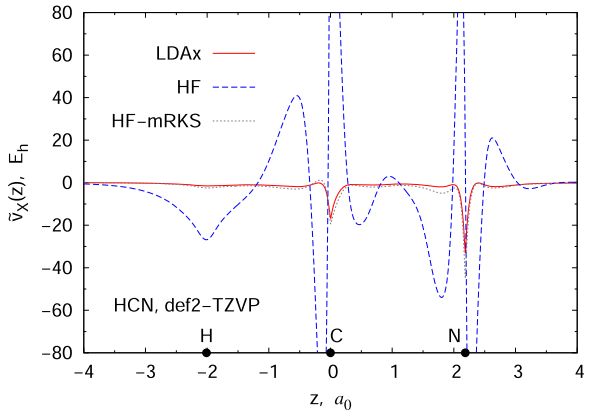


FIG. 7. Multiplicative exchange potentials $\tilde{v}_X(\mathbf{r})$ along the principal axis of HCN (R_{HC} = 2.011a_0, R_{CN} = 2.185a_0) recovered from the exchange parts of the LDAx, HF, and HF-mRKS matrices in the LIP basis set of the corresponding occupied SCF orbitals.

basis set is too small to reveal the fundamental differences between local and nonlocal potentials. As a consequence, the local exchange potential $\tilde{v}_X(\mathbf{r})$ for Be recovered from HF matrices shows less deviation from the corresponding LDAx and HF-mRKS potentials than for Ne (Fig. 5). The LDAx, HF, and HF-mRKS local kinetic potentials for Be (Fig. 6) are even closer to one another than they were for Ne.

The nonlocal nature of Fock exchange is revealed more clearly in calculations on many-electron molecules such as HCN (Figs. 7 and 8), where the number of occupied SCF orbitals is large enough to produce LIP basis sets of considerable size. For HCN, in particular, there are 14 occupied orbitals and M = 28. The local exchange potential extracted from the HF/def2-TZVP matrix for this system shows dramatic oscillations that are completely absent in potentials $\tilde{v}_X(\mathbf{r})$ obtained from LDAx and HF-mRKS matrices (Fig. 7). The local kinetic potentials recovered from the LDAx, HF, and HF-mRKS matrices, however, are similar to one another (Fig. 8), as expected.

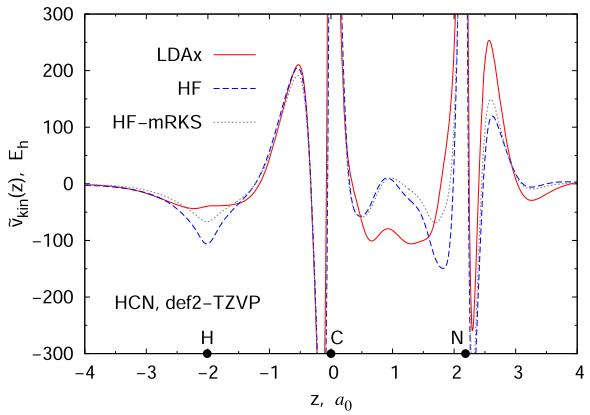


FIG. 8. Analog of Fig. 7 for multiplicative kinetic potentials. In contrast to Fig. 7, the three reconstructions are somewhat similar.

V. CONCLUSION

The takeaways from this work are as follows: First, the effect of any nonlocal operator $\hat{G}$ within a LIP basis set can be reproduced exactly by an associated basis-set-specific local potential $\tilde{v}(\mathbf{r})$. Construction of $\tilde{v}(\mathbf{r})$ requires solving Eq. (25) using the matrix $\mathbf{G}$ of $\hat{G}$ as input and delivers the result in the form of Eq. (22).

Second, occupied SCF orbitals form natural minimal LIP basis sets for many atoms and molecules. Such basis sets are sufficient to reproduce the ground-state density and energy within the HF and KS schemes for any underlying AO basis set. This technology can be practically useful for Kohn–Sham inversions and similar purposes.

Third, local potentials reproducing matrices of conventional local operators within basis sets of occupied SCF orbitals differ from the originals substantially but not beyond recognition. By contrast, local potentials reproducing matrices of nonlocal operators such as $\hat{K}$ and $\hat{t}$ tend to have intricate shapes. Potentials $\tilde{v}(\mathbf{r})$ associated with such operators are relatively insensitive to the underlying AO basis set or to the SCF method (HF, HF-mRKS, LDA, or some other density-functional approximation). This suggests a possibility of modeling the kinetic and exchange energy functionals by local density-functional approximations for basis sets of occupied SCF orbitals. The same principle may be useful for developing kinetic energy functionals (see Ref. 29 and references therein). It is also possible to construct noninteracting many-electron Hamiltonians with local potentials whose eigenfunctions are finite-basis-set configuration interaction wavefunctions,[30] but such potentials have no clear physical meaning and transcend Harriman's theory.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yan Oueis: Conceptualization (supporting); Methodology (lead); Software (lead); Writing – original draft (supporting); Writing – review & editing (supporting). **Viktor N. Staroverov**: Conceptualization (lead); Funding acquisition (lead); Methodology (supporting); Writing – original draft (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

APPENDIX: PRESERVATION OF LINEAR INDEPENDENCE

The following important properties of LIP basis sets complement Theorem 1 of Harriman.[4]

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Lemma 1. Let $f_i(\mathbf{r})$ be K complex-valued functions and $q_i(\mathbf{r})$ their linear transformations given by

$$q_i(\mathbf{r}) = \sum_{k=1}^{K} A_{ik} f_k(\mathbf{r}). \tag{A1}$$

If the K^2 products $f_i(\mathbf{r})f_j^*(\mathbf{r})$ are linearly independent and the transformation matrix $\mathbf{A}$ is nonsingular, then the products $q_i(\mathbf{r})q_j^*(\mathbf{r})$ are also linearly independent.

Proof. Let $\mathbf{f}$ be a column vector of K original basis functions

$$\mathbf{f} = \begin{pmatrix} f_1 \\ f_2 \\ \vdots \\ f_K \end{pmatrix}, \tag{A2}$$

with a similar definition for $\mathbf{q}$. Then $\mathbf{q} = \mathbf{A}\mathbf{f}$. The original product basis may be written in vector form as

$$\mathrm{vec}(\mathbf{f}\mathbf{f}^\dagger) = \begin{pmatrix} f_1 f_1^* \\ f_1 f_2^* \\ \vdots \\ f_1 f_K^* \\ f_2 f_1^* \\ f_2 f_2^* \\ \vdots \\ f_2 f_K^* \\ \vdots \\ f_K f_K^* \end{pmatrix}, \tag{A3}$$

where the dagger (†) means Hermitian conjugation and the operation vec(), defined to be row-major here, takes a matrix and stacks its transposed rows into a single column vector. The transformed products are given by

$$\mathrm{vec}(\mathbf{q}\mathbf{q}^\dagger) = \mathrm{vec}\Big[(\mathbf{A}\mathbf{f})(\mathbf{A}\mathbf{f})^\dagger\Big] = \mathrm{vec}\Big[\mathbf{A}(\mathbf{f}\mathbf{f}^\dagger)\mathbf{A}^\dagger\Big]. \tag{A4}$$

The transformation from the old products to the new ones may be written as

$$\mathrm{vec}(\mathbf{q}\mathbf{q}^\dagger) = \mathbf{U}\ \mathrm{vec}(\mathbf{f}\mathbf{f}^\dagger), \tag{A5}$$

where

$$\mathbf{U} = \mathbf{A} \otimes \mathbf{A}^\dagger \tag{A6}$$

is the direct (Kronecker) product, a $K^2 \times K^2$ matrix with elements $U_{ij,kl} = A_{ik}A_{jl}^*$. One of the basic properties of the Kronecker product[31] applied to Eq. (A6) gives

$$(\mathbf{A} \otimes \mathbf{A}^\dagger)^{-1} = \mathbf{A}^{-1} \otimes (\mathbf{A}^\dagger)^{-1}. \tag{A7}$$

Another property of Kronecker products[31] ensures that

$$\det(\mathbf{A} \otimes \mathbf{A}^\dagger) = [\det(\mathbf{A})]^K [\det(\mathbf{A}^\dagger)]^K = |\det(\mathbf{A})|^{2K}. \tag{A8}$$

Either of Eqs. (A7) and (A8) implies that $\mathbf{U}$ is nonsingular if and only if $\mathbf{A}$ is nonsingular. This concludes the proof.

Lemma 2. Let $f_i(\mathbf{r})$ be K real-valued functions and $q_i(\mathbf{r})$ their linear transformations by a nonsingular real matrix $\mathbf{A}$. If the $M = K(K+1)/2$ products $f_i(\mathbf{r})f_j(\mathbf{r})$ $(i \le j)$ are linearly independent, then the products $q_i(\mathbf{r})q_j(\mathbf{r})$ are also linearly independent.

Proof. Using the symbol $\mathbf{f}$ as defined in Lemma 1, we write the original product basis as

$$\mathrm{vech}(\mathbf{f}\mathbf{f}^T) = \begin{pmatrix} f_1 f_1 \\ f_1 f_2 \\ \vdots \\ f_1 f_K \\ f_2 f_2 \\ \vdots \\ f_2 f_K \\ \vdots \\ f_K f_K \end{pmatrix}, \tag{A9}$$

where the operation vech(), defined to be row-major here, takes a symmetric matrix and stacks the transposed rows of its upper triangular part into a single column vector. The transformed products are

$$\mathrm{vech}(\mathbf{q}\mathbf{q}^T) = \mathrm{vech}\Big[(\mathbf{A}\mathbf{f})(\mathbf{A}\mathbf{f})^T\Big] = \mathrm{vech}\Big[\mathbf{A}(\mathbf{f}\mathbf{f}^T)\mathbf{A}^T\Big]. \tag{A10}$$

The transformation from the old products to the new ones may be written as

$$\mathrm{vech}(\mathbf{q}\mathbf{q}^T) = \mathbf{U}_s\ \mathrm{vech}(\mathbf{f}\mathbf{f}^T), \tag{A11}$$

where

$$\mathbf{U}_s = \mathbf{A} \otimes_s \mathbf{A} \tag{A12}$$

is the symmetric Kronecker product, an $M \times M$ matrix which we define implicitly by its action on the upper triangular part of an arbitrary symmetric $K \times K$ matrix $\mathbf{S}$,

$$(\mathbf{A} \otimes_s \mathbf{A})\,\mathrm{vech}(\mathbf{S}) = \mathrm{vech}(\mathbf{A}\mathbf{S}\mathbf{A}^T). \tag{A13}$$

Note that our definition of the operation $\otimes_s$ differs of necessity in details from the one found in the literature.[32–34]

Observe that by virtue of Eq. (A13),

$$\begin{aligned}(\mathbf{A} \otimes_s \mathbf{A})(\mathbf{B} \otimes_s \mathbf{B})\,\mathrm{vech}(\mathbf{S}) &= (\mathbf{A} \otimes_s \mathbf{A})\,\mathrm{vech}(\mathbf{B}\mathbf{S}\mathbf{B}^T) \\ &= \mathrm{vech}(\mathbf{A}\mathbf{B}\mathbf{S}\mathbf{B}^T\mathbf{A}^T) \\ &= (\mathbf{A}\mathbf{B} \otimes_s \mathbf{A}\mathbf{B})\,\mathrm{vech}(\mathbf{S}).\end{aligned} \tag{A14}$$

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Therefore,

$$(\mathbf{A} \otimes_s \mathbf{A})(\mathbf{B} \otimes_s \mathbf{B}) = \mathbf{AB} \otimes_s \mathbf{AB}. \tag{A15}$$

Setting $\mathbf{B} = \mathbf{A}^{-1}$ or $\mathbf{A} = \mathbf{B}^{-1}$ in Eq. (A15), we find that

$$(\mathbf{A} \otimes_s \mathbf{A})^{-1} = \mathbf{A}^{-1} \otimes_s \mathbf{A}^{-1}. \tag{A16}$$

This means that the transformation matrix $\mathbf{U}_s$ is nonsingular if and only if $\mathbf{A}$ is nonsingular and concludes the proof.

Another demonstration that $\mathbf{U}_s$ is nonsingular can be given in terms of the eigenvalues of $\mathbf{A}$. If $\mathbf{v}_i$ is an eigenvector of $\mathbf{A}$ and λ_i is the associated eigenvalue, then

$$\begin{aligned}(\mathbf{A} \otimes_s \mathbf{A})\,\mathrm{vech}(\mathbf{v}_i\mathbf{v}_j^T) &= \mathrm{vech}\left[(\mathbf{A}\mathbf{v}_i)(\mathbf{A}\mathbf{v}_j)^T\right] \\ &= \lambda_i\lambda_j\,\mathrm{vech}(\mathbf{v}_i\mathbf{v}_j^T) \quad (i \le j).\end{aligned} \tag{A17}$$

This implies that

$$\det(\mathbf{A} \otimes_s \mathbf{A}) = \prod_{i \le j}^{K} \lambda_i\lambda_j = \left(\prod_{i=1}^{K} \lambda_i\right)^{K+1} = [\det(\mathbf{A})]^{K+1}. \tag{A18}$$

The last result means that $\mathbf{U}_s$ is nonsingular if and only if $\mathbf{A}$ is nonsingular.

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