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Within a basis set of one-electron functions that form linearly independent products (LIPs) it is always possible to construct a unique local (multiplicative) real-space potential that is precisely equivalent to an arbitrary given operator. Although standard basis sets of quantum chemistry rarely form LIPs in a numerical sense, occupied and low-lying virtual canonical Kohn–Sham orbitals often do so, at least for small atoms and molecules. Using these principles, we construct atomic and molecular exchange-correlation potentials from their matrix representations in LIP basis sets of occupied canonical Kohn–Sham orbitals. The reconstructions are found to imitate the original potentials in a consistent but exaggerated way. Since the original and reconstructed potentials produce the same ground-state electron density and energy within the associated LIP basis set, the procedure may be regarded as a rigorous solution to the Kohn–Sham inversion problem within the subspace spanned by the occupied Kohn–Sham orbitals.

1. Introduction

Much of nonrelativistic quantum mechanics is concerned with eigenvalue problems for Hermitian operators whose domain is an infinite-dimensional Hilbert space. In particular, the Kohn–Sham density-functional theory[1] of spin-compensated many-electron systems is centered on the one-electron Schrödinger equation

$$\hat{h}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \tag{1}$$

where (using atomic units)

$$\hat{h} = -\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \tag{2}$$

is the Kohn–Sham Hamiltonian consisting of the kinetic energy operator and a multiplicative operator $v_{\text{eff}}(\mathbf{r})$ known as the Kohn–Sham effective potential.

In actual implementations of eq 1, one usually replaces operators with their finite-dimensional matrix representations in terms of some fixed one-electron basis functions $f_k(\mathbf{r})$ $(k = 1, 2, \ldots, K)$.[2] Within this basis set, the Hamiltonian of eq 1 becomes a $K \times K$ matrix with elements

$$H_{kl} = \langle f_k|\hat{h}|f_l\rangle \tag{3}$$

and eq 1 turns into the matrix equation

$$\mathbf{H}\mathbf{c}_i = \epsilon_i\mathbf{S}\mathbf{c}_i \tag{4}$$

Here $\mathbf{c}_i$ are column vectors of expansion coefficients of the corresponding eigenfunctions

$$\phi_i(\mathbf{r}) = \sum_{k=1}^{K} c_{ki}f_k(\mathbf{r}) \tag{5}$$

and $\mathbf{S}$ is the overlap matrix of the basis functions

$$S_{kl} = \langle f_k|f_l\rangle \tag{6}$$

The transition from operators to finite-dimensional matrices involves partial loss of information about $\hat{h}$, so the eigenfunctions $\phi_i(\mathbf{r})$ and their eigenvalues ϵ_i obtained by solving eq 4 are only approximations to the solutions of eq 1, as is also true in the Hartree–Fock theory.[3] Consistency between eqs 1 and 4 can be achieved only if one uses a complete (in practice, sufficiently large) basis set or a small finite basis set consisting of exact eigenfunctions of $\hat{h}$.

For a given potential $v(\mathbf{r})$, it is straightforward to construct its matrix representation $\mathbf{V}$ in any finite basis. Can one also go backwards, that is, recover $v(\mathbf{r})$ from the Fock matrix $\mathbf{V}$, provided that the basis set is known? This question is relevant to the Kohn–Sham inversion problem, where one attempts to find the $v_{\text{eff}}(\mathbf{r})$ that reproduces a given ground-state electron density $\rho(\mathbf{r})$ within a complete or finite basis set.[4–6] An analogous problem arises in optimized effective potential (OEP) methods, where one needs to extract a multiplicative operator from the OEP integral equation written in matrix form.[7–17]

The strict answer to the above question is negative because restriction of operators to finite-dimensional subspaces amounts to projection, and projections are not invertible. On the other hand, it is not difficult to find a potential $\tilde{v}(\mathbf{r})$ that is distinct from $v(\mathbf{r})$ but has the same matrix representation $\mathbf{V}$. This can be done by expanding $\tilde{v}(\mathbf{r})$ in some auxiliary basis set and determining the expansion coefficients by solving a system of simultaneous linear equations.[7–12] The trouble with such expansions is that different basis sets for $\tilde{v}(\mathbf{r})$ give different potentials and it is unclear what, if any, constraints on $\tilde{v}(\mathbf{r})$ should be imposed.[8–11] Conventional metrics of smoothness of $\tilde{v}(\mathbf{r})$ or its similarity to the original $v(\mathbf{r})$ are inherently arbitrary and subjective. It is desirable to have a procedure that is mathematically rigorous and leaves no room for ambiguity.

In this work, we describe a method for recovering multiplicative operators from their matrix representations that is rigorous and practical, at least for small atoms and molecules. This method is based on Harriman's theory of operators in finite basis sets.[18–25] The proposed approach may be interpreted as a way of solving the Kohn–Sham inversion problem under the condition that the matrix representation of the potential is known.

2. Methodology

For simplicity, we will restrict our discussion to vector spaces of real-valued functions over the real numbers.

Consider an arbitrary multiplicative potential $v(\mathbf{r})$ and a finite set of real basis functions $f_k(\mathbf{r})$ $(k = 1, 2, \ldots, K)$, not necessarily orthogonal or normalized. Within this basis set, the operator $v(\mathbf{r})$ is represented by a $K \times K$ matrix $\mathbf{V}$ with elements

$$V_{kl} = \langle f_k | v | f_l \rangle \tag{7}$$

Matrix $\mathbf{V}$ is symmetric and contains

$$M = \frac{K(K+1)}{2} \tag{8}$$

independent elements. There are infinitely many other potentials $\tilde{v}(\mathbf{r})$ represented by the same $\mathbf{V}$, i.e.,

$$\langle f_k | \tilde{v} | f_l \rangle = V_{kl} \tag{9}$$

for all k and l. All such potentials are equivalent to $v(\mathbf{r})$ within the basis $\{f_k\}$. To construct a particular $\tilde{v}(\mathbf{r})$, expand it in suitably chosen M basis functions $g_{ij}(\mathbf{r})$ as

$$\tilde{v}(\mathbf{r}) = \sum_{ij=1}^{M} a_{ij} g_{ij}(\mathbf{r}) \qquad (1 \leq i \leq j \leq K) \tag{10}$$

where ij is treated as a collective index. To determine the coefficients a_{ij}, substitute eq 10 into eq 9 and write the result as

$$\sum_{ij=1}^{M} W_{kl,ij} a_{ij} = V_{kl} \qquad (1 \leq k \leq l \leq K) \tag{11}$$

where kl is also a collective index and

$$W_{kl,ij} = \langle f_k | g_{ij} | f_l \rangle \tag{12}$$

are elements of an $M \times M$ matrix $\mathbf{W}$. If matrix $\mathbf{W}$ happens to be nonsingular, then eq 11 has a unique solution: a column vector of coefficients a_{ij}. Different sets of functions $g_{ij}(\mathbf{r})$ produce different unique potentials $\tilde{v}(\mathbf{r})$.

If $\mathbf{W}$ is singular, the above recipe will not work, but that does not alter the fact that $\mathbf{V}$ can be reproduced by infinitely many different potentials. To see this, consider the homogeneous equation $\sum_{ij=1}^{M} W_{kl,ij} a_{ij} = 0$. For a singular $\mathbf{W}$, this equation has a nontrivial solution, call it $\Delta \tilde{v}(\mathbf{r}) = \sum_{ij=1}^{M} a_{ij} g_{ij}(\mathbf{r})$. Then the potential $v(\mathbf{r}) + \Delta \tilde{v}(\mathbf{r})$ is distinct from $v(\mathbf{r})$ but has the same matrix elements as $v(\mathbf{r})$ in the basis $\{f_k\}$.

The essential idea represented by eq 11 is well known[7-17] but there are varied opinions on how to choose the basis functions $g_{ij}(\mathbf{r})$. Most choices are guided by expectations or experience and therefore remain subjective. We argue here that, for the purpose of constructing $\tilde{v}(\mathbf{r})$ from $\mathbf{V}$, the proper method was given by Harriman.[18] Let us recapitulate Harriman's approach.

The multiplicative operator $\tilde{v}(\mathbf{r})$ is in fact a part of the symmetric integral-operator kernel

$$\tilde{V}(\mathbf{r}, \mathbf{r}') = \tilde{v}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') \tag{13}$$

Within a finite basis set, this kernel has finite rank and is given by

$$\tilde{V}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{K} \sum_{j=1}^{K} (\mathbf{S}^{-1} \mathbf{V} \mathbf{S}^{-1})_{ij} f_i(\mathbf{r}) f_j(\mathbf{r}') \tag{14}$$

where $\mathbf{S}$ is the overlap matrix of eq 6. Note that the matrix representation of $\tilde{V}(\mathbf{r}, \mathbf{r}')$ in the basis $\{f_k\}$ is again $\mathbf{V}$. Equation 14 looks like an expansion in K^2 linearly independent products $f_i(\mathbf{r}) f_j(\mathbf{r}')$ but the symmetry of $V(\mathbf{r}, \mathbf{r}')$ implies that only M symmetric combinations

$$\Phi_{ij}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \left[f_i(\mathbf{r}) f_j(\mathbf{r}') + f_j(\mathbf{r}) f_i(\mathbf{r}') \right] \quad (i \leq j) \tag{15}$$

actually contribute. This can be made explicit by writing

$$\tilde{V}(\mathbf{r}, \mathbf{r}') = \sum_{ij=1}^{M} (\mathbf{S}^{-1} \mathbf{V} \mathbf{S}^{-1})_{ij} (2 - \delta_{ij}) \Phi_{ij}(\mathbf{r}, \mathbf{r}') \quad (i \leq j) \tag{16}$$

Now if $\tilde{V}(\mathbf{r}, \mathbf{r}')$ is treated as an element of an M-dimensional vector space $\mathcal{E}_r$ of integral-operator kernels, then $\tilde{v}(\mathbf{r})$ can be regarded as an element of the vector space $\mathcal{F}_r$ of the associated potentials.[18-20] The space $\mathcal{E}_r$ is a linear manifold of functions $\Phi_{ij}(\mathbf{r}, \mathbf{r}')$, whereas $\mathcal{F}_r$ is a linear manifold of functions

$$g_{ij}(\mathbf{r}) = f_i(\mathbf{r}) f_j(\mathbf{r}) \qquad (1 \leq i \leq j \leq K) \tag{17}$$

which are related to $\Phi_{ij}(\mathbf{r}, \mathbf{r}')$ through the linear "collapse operator" defined by

$$g_{ij}(\mathbf{r}) \equiv \Phi_{ij}(\mathbf{r}, \mathbf{r}) = \hat{\delta}\Phi_{ij}(\mathbf{r}, \mathbf{r}') \tag{18}$$

The M functions $\Phi_{ij}(\mathbf{r}, \mathbf{r}')$ form a basis for $\mathcal{E}_r$ but the M functions $g_{ij}(\mathbf{r})$ are generally not a basis for $\mathcal{F}_r$ because they may be linearly dependent. However, if the functions $g_{ij}(\mathbf{r})$ happen to be linearly independent, then there is one-to-one correspondence between every $\tilde{V}(\mathbf{r}, \mathbf{r}') \in \mathcal{E}_r$ and $\tilde{v}(\mathbf{r}) \in \mathcal{F}_r$.[19] Thus, within a LIP basis set, it is possible to construct $\tilde{v}(\mathbf{r})$ rigorously and unambiguously by using eqs 10–12 and the functions of eq 17.

Given that the LIP basis set method is the answer, one should wonder why it is not widely used. The reason is the scarcity of LIP basis sets. If the functions $f_k(\mathbf{r})$ form a complete (infinite) basis set, their products are necessarily linearly dependent.[12,19] This is especially easy to see for complete basis sets of plane waves and monomials such as $f_k = x^k$. Standard basis sets of quantum chemistry are finite, but this is of little help. Only the smallest Gaussian basis sets such as 6-31G and only for the lightest atoms form LIPs, at least in a numerical sense.[23,25–27] The situation does not improve much by extending basis

functions to momentum space.[28] This seems to put an end to the whole proposal, but there is a way out.

Every many-electron system has a natural minimal one-electron basis set: the set of occupied Kohn–Sham orbitals. Solving the Kohn–Sham equations in this basis set yields the same ground-state electron density and energy as the original basis set, no matter how large. Using standard terminology, we will refer to a non-orthogonal basis of K nucleus-centered functions $f_k(\mathbf{r})$ as the atomic orbital (AO) basis set, and to the corresponding set of K orthonormal Kohn–Sham orbitals as the molecular orbital (MO) basis.

One can show that any nonsingular linear transformation of basis functions preserves the linear independence of their products.[29] This means that if an AO basis set is not of the LIP type, no full set of MOs (occupied and virtual) will be. Often, however, only a subset of all MOs is needed. Hoch and Harriman observed[23] that the occupied Hartree–Fock self-consistent-field (SCF) orbitals of small molecules commonly form LIPs; Morrison[30] constructed LIPs of selected atomic natural orbitals of the Be atom. We add to these reports that the occupied Kohn–Sham SCF orbitals often form LIPs as well. This remains true even for very large underlying AO basis sets. The minimal LIP basis set of occupied Kohn–Sham orbitals can be sometimes extended by including several virtual orbitals (see below).

The ability of low-lying Kohn–Sham MOs to serve as LIP basis sets allows us to achieve our objectives as follows. Consider an N-electron closed-shell system and let n ($N/2 \leq n \leq K$) be the number of real canonical Kohn–Sham MOs, $\phi_i(\mathbf{r})$. Form the product basis functions

$$g_{ij}^{\mathrm{MO}}(\mathbf{r}) = \phi_i(\mathbf{r})\phi_j(\mathbf{r}) \qquad (1 \leq i \leq j \leq n) \qquad (19)$$

calculate the overlap matrix elements

$$W_{kl,ij} = \langle g_{kl}^{\mathrm{MO}}|g_{ij}^{\mathrm{MO}}\rangle = \int \phi_k(\mathbf{r})\phi_l(\mathbf{r})\phi_i(\mathbf{r})\phi_j(\mathbf{r})\, d\mathbf{r} \quad (20)$$

and diagonalize $\mathbf{W}$ to check whether the functions $g_{ij}^{\mathrm{MO}}(\mathbf{r})$ are linearly independent. If so, set up the right-hand side of eq 11 by starting with a matrix $\mathbf{V}$ of the original potential $v(\mathbf{r})$ in the AO basis, transforming it to the MO basis, and picking out the elements

$$V_{kl} = \langle \phi_k|v|\phi_l\rangle \qquad (1 \leq k \leq l \leq n) \qquad (21)$$

of the occupied block. Finally, solve eq 11 for the expansion coefficient a_{ij} of the reconstructed potential $\tilde{v}(\mathbf{r})$.

Within a basis set of n occupied MOs, the potential $\tilde{v}(\mathbf{r})$ reproduces the $n \times n$ matrix $\mathbf{V}$ by construction and therefore yields the same ground-state electron density and hence energy as the original potential $v(\mathbf{r})$ in the full AO basis set. The matrix of $\tilde{v}(\mathbf{r})$ in the AO basis, however, will not reproduce the density. This is because the occupied-virtual block of the matrix of $\tilde{v}(\mathbf{r})$ in the basis of all MOs (occupied and virtual) is no longer zero.

In essence, the proposed method consists in replacing the full AO basis set with a smaller system-specific LIP basis set which gives the same $\rho(\mathbf{r})$ as the AO basis set and makes the recovery of $\tilde{v}(\mathbf{r})$ possible. There is no reason why the potential $\tilde{v}(\mathbf{r})$ extracted from its matrix in the smaller basis set should be identical or even close to the original $v(\mathbf{r})$. We will see, however, that the outputs of this procedure are consistent and reasonable.

3. Results and Discussion

We implemented the procedure of Sec. 2 as a MATLAB code processing the output of Kohn–Sham SCF calculations. Two types of multiplicative reference potentials $v_{\mathrm{XC}}(\mathbf{r})$ were used: the local density approximation (LDA) for exchange and correlation in the Perdew–Wang parametrization[31] and accurate exchange-correlation potentials derived from full configuration interaction (FCI) wavefunctions using the method of refs 32–35. The LDA matrices were generated with the Psi4NumPy program;[36] Kohn–Sham orbitals and matrices of accurate potentials were obtained using the method of ref 34. The LDA rather than some generalized gradient approximation (GGA) was chosen because GGA exchange-correlation potentials have irrelevant artifacts (divergences at atomic nuclei[37] and small unphysical bumps) which pose no problems but would be distracting when comparing $v_{\mathrm{XC}}(\mathbf{r})$ and $\tilde{v}_{\mathrm{XC}}(\mathbf{r})$. Matrix elements of eq 20 were computed by expanding them in terms of four-center AO overlap integrals and evaluating the latter analytically

Table 1. Size (M) of Various LIP Basis Sets Formed by Canonical SCF LDA MOs and the Smallest Eigenvalue ($\lambda_{\min}$) of the Overlap Matrix of Normalized MO Products $g_{ij}(\mathbf{r})$

system	MOs	M^{a}	basis set	$\lambda_{\min}$
Be	$[1s, 2s]$	3	def2-SVP	3.36×10^{-2}
		3	def2-TZVP	2.59×10^{-2}
		3	def2-QZVP	2.59×10^{-2}
Be	$[1s, 2s, 2p]$	15	def2-SVP	3.21×10^{-3}
		15	def2-TZVP	5.46×10^{-3}
		15	def2-QZVP	4.12×10^{-3}
Be	$[1s, 2s, 2p, 3s]$	21	def2-SVP	9.12×10^{-6}
		21	def2-TZVP	1.80×10^{-5}
		21	def2-QZVP	8.08×10^{-6}
Ne	all occupied	15	def2-SVP	6.48×10^{-4}
HF	all occupied	15	def2-SVP	2.17×10^{-3}
H_2O	all occupied	15	def2-SVP	5.19×10^{-3}
NH_3	all occupied	15	def2-SVP	9.00×10^{-3}
CH_4	all occupied	15	def2-SVP	1.37×10^{-2}
LiH	all occupied	3	def2-SVP	9.83×10^{-1}
HCN	all occupied	28	def2-SVP	2.47×10^{-6}
N_2	all occupied	28	def2-SVP	1.65×10^{-8}
C_2H_4	all occupied	36	def2-SVP	1.84×10^{-8}
HCOOH	all occupied	78	def2-SVP	2.00×10^{-8}
CH_3COOH^{b}	all occupied	136	def2-SVP	9.05×10^{-9}

$^{\mathrm{a}}$ Some of products may not contribute by symmetry
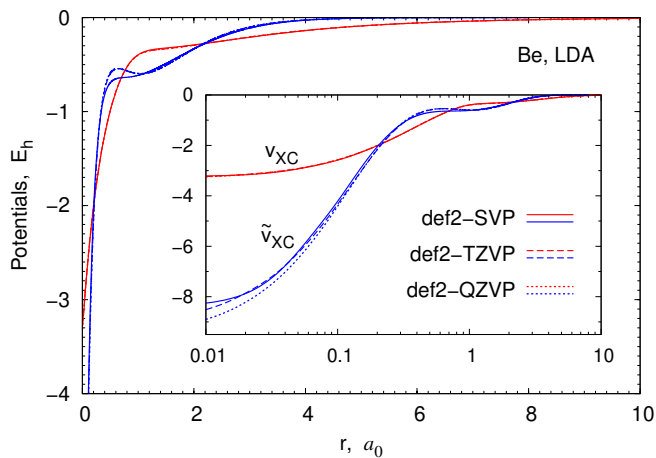$^{\mathrm{b}}$ PBE1PBE/def2-SVP geometry

Figure 1. Self-consistent LDA exchange-correlation potentials (v_{XC}, red) of Be and their reconstructions ($\tilde{v}_{XC}$, blue) from the corresponding matrix representations of v_{XC} in the basis of the occupied Kohn–Sham orbitals. The inset shows the same data on the logarithmic r-scale.

Figure 2. Accurate exchange-correlation potentials (v_{XC}, red) derived from FCI wavefunctions of Be and their reconstructions ($\tilde{v}_{XC}$, blue) from matrix representations of v_{XC} in the basis of the occupied Kohn–Sham orbitals. The inset shows the same data on the logarithmic r-scale.

using the method of refs 38 and 39. All calculations on molecules were performed for the experimental geometries from ref 40, except where noted otherwise.

To investigate how the original and reconstructed exchange-correlation potentials for atoms and molecules vary with respect to the AO basis set, we used standard Gaussian basis sets of the same family: def2-SVP (small), def2-TZVP (medium), def2-QZVP (large).[41] As a measure of linear independence of MO products we used the smallest positive eigenvalue λ_{min} of the four-center overlap matrix $\mathbf{W}$. All canonical Kohn–Sham MOs used as basis functions were confirmed to form LIPs for the atoms and molecules studied, with λ_{min} values ranging between about 1 and $\sim 10^{-8}$ (see Table 1). For comparison, Hoch and Harriman[24,25] considered a set of normalized orbitals to be a LIP basis set if λ_{min} was below a threshold of 10^{-8} or 10^{-9} or 10^{-10}. We have also verified that, in each case, the original $v_{XC}(\mathbf{r})$ and the corresponding reconstruction $\tilde{v}_{XC}(\mathbf{r})$ produce the same Fock matrix in the LIP basis set and hence the same electron density.

Figure 1 shows that exchange-correlation potentials for Be reconstructed from matrix representations of conventional LDA potentials using products of occupied Kohn–Sham orbitals have a weak dependence on the underlying AO basis set. This suggests that there exists a unique, well-defined AO basis-set limit of $\tilde{v}_{XC}(\mathbf{r})$. Similar results were obtained for nearly exact exchange-correlation potentials and the corresponding Kohn–Sham orbitals derived from FCI wavefunctions of the Be atom (Figure 2).

The original and reconstructed potentials of Figures 1 and 2 are similar in some respects: both $v_{XC}(\mathbf{r})$ and $\tilde{v}_{XC}(\mathbf{r})$ are finite at the nucleus, approach zero as $r \to \infty$, and have a single bump. The differences are also considerable: the reconstructed potentials are much more negative near the nucleus, have a bump closer to $r = 0$, and
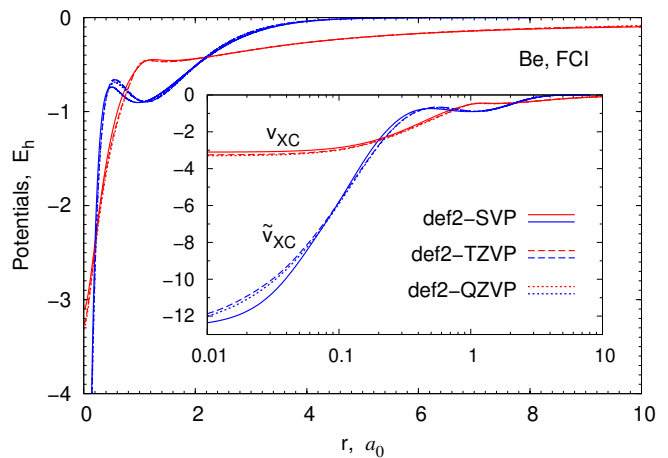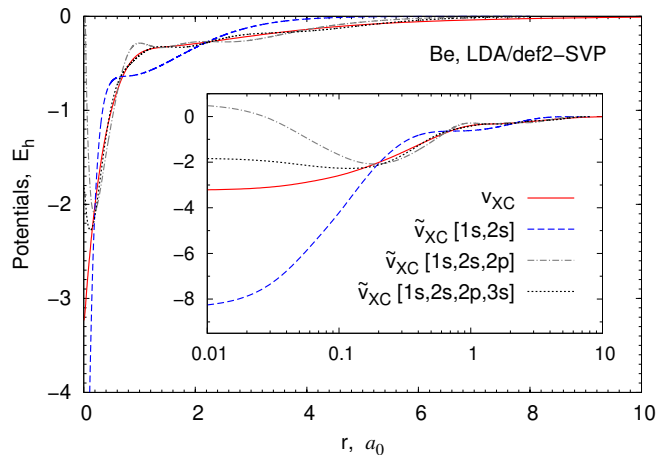

Figure 3. Self-consistent LDA/def2-SVP exchange-correlation potential (v_{XC}) of Be and its reconstructions ($\tilde{v}_{XC}$) from the corresponding matrix representations of v_{XC} in three different LIP Kohn–Sham orbital basis sets. The inset shows the same data on the logarithmic r-scale.

decay with r significantly faster than does $v_{XC}(\mathbf{r})$.

The occupied Kohn–Sham orbitals form the natural minimal LIP basis set for reproducing the ground-state $\rho(\mathbf{r})$, but this choice is not the only possibility. Inclusion of a few low-lying virtual Kohn–Sham orbitals produces other LIP basis sets suitable for reproducing the density (Table 1). To find out this affects the shape of $\tilde{v}_{XC}(\mathbf{r})$ for the Be atom, we compared potentials reconstructed using three different LIP basis sets of Kohn–Sham orbitals: $[1s, 2s]$ (occupied orbitals only), $[1s, 2s, 2p]$, and $[1s, 2s, 2p, 3s]$, where $2p$ stands for the entire $(2p_x, 2p_y, 2p_z)$ subshell. Inclusion of virtual orbitals generally improves the agreement between $\tilde{v}_{XC}(\mathbf{r})$ and $v_{XC}(\mathbf{r})$, although near the nucleus the
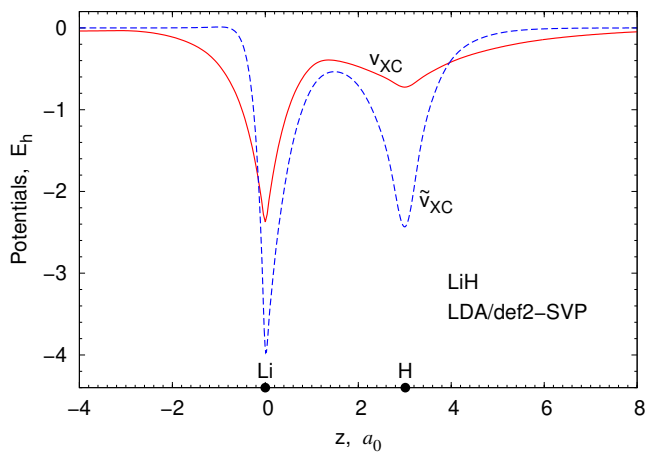
Figure 4. Self-consistent LDA/def2-SVP potentials for the ground state of LiH ($R_e = 3.014a_0$): conventional (v_{XC}) and reconstructed ($\tilde{v}_{XC}$) from the matrix representation of v_{XC} in the occupied MO basis.
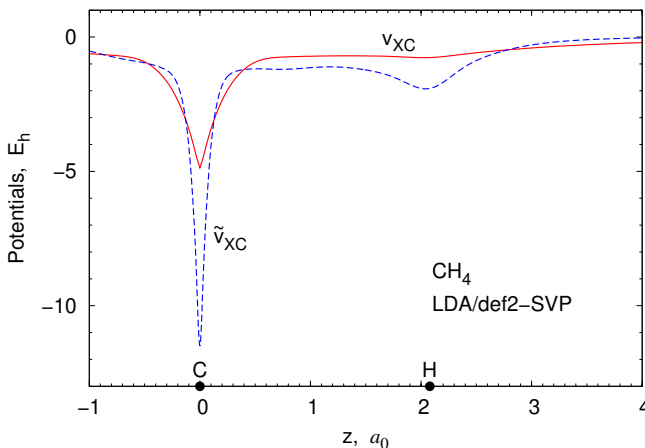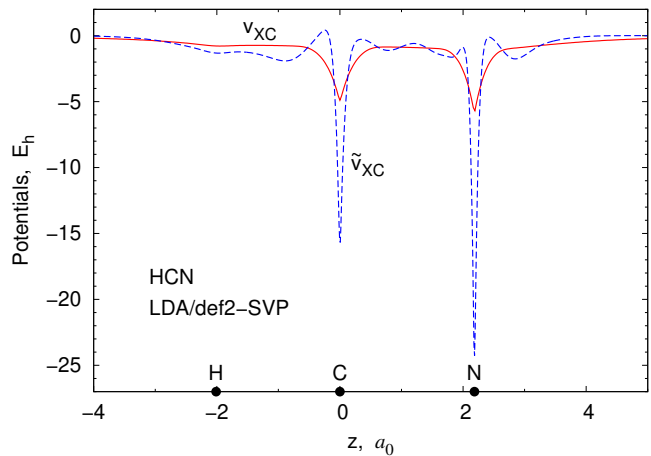

Figure 6. Self-consistent LDA/def2-SVP potentials for the ground state of HCN ($R_{HC} = 2.011a_0$, $R_{CN} = 2.185a_0$): conventional (v_{XC}) and reconstructed ($\tilde{v}_{XC}$) from the matrix representation of v_{XC} in the occupied MO basis. Both potentials are shown along the internuclear axis.

Examples of molecular exchange-correlation potentials reconstructed from LDA Fock matrices in the occupied MO basis set are shown in Figures 4–6. For hydrides such as LiH and CH_4, $\tilde{v}_{XC}(\mathbf{r})$ has the same structure as the original $v_{XC}(\mathbf{r})$ (Figures 4 and 5). For molecules involving multiple bonds between heavier atoms (HCN, N_2, CO, etc.), the reconstructed LDA potentials have strongly pronounced shell-boundary bumps and mid-bond undulations that are not seen in the original potentials (Figure 6). Observe that, in all cases, the depth of $\tilde{v}_{XC}(\mathbf{r})$ near the nucleus increases with nuclear charge Z much more rapidly than the depth of $v_{XC}(\mathbf{r})$. The low values of $\tilde{v}_{XC}(\mathbf{r})$ near atomic nuclei are not a concern from numerical point of view because GGA potentials diverge as $r \to 0$ and are even more negative.[37]

It is interesting that the exaggerated bumps and mid-bond maxima seen in the reconstructed LDA potential of Figure 6 are reminiscent of the similarly exaggerated features of accurate exchange-correlation potentials in stretched molecules.[32,33] The greater prominence of bumps in the reconstructed LDA potentials suggests that matrix representations of an approximate $v_{XC}(\mathbf{r})$ may effectively incorporate the atomic shell structure of the corresponding exact potential even when the approximation $v_{XC}(\mathbf{r})$ itself is relatively featureless.

Figure 5. Self-consistent LDA/def2-SVP potentials for the ground state of CH_4 ($R_e = 2.079a_0$): conventional (v_{XC}) and reconstructed ($\tilde{v}_{XC}$) from the matrix representation of v_{XC} in the occupied MO basis. Both potentials are shown along the C–H axis.

changes are somewhat erratic (Figure 3). It is significant that the $[1s, 2s, 2p]$ reconstruction decays more slowly than $[1s, 2s]$, and the $[1s, 2s, 2p, 3s]$ reconstruction decays more slowly still. Overall, the $[1s, 2s, 2p, 3s]$ reconstruction becomes very close to the reference $v_{XC}(\mathbf{r})$ everywhere except $r < 0.1a_0$. This is consistent with the basic premise that if we had a large enough LIP basis set, we would be able to recover $v_{XC}(\mathbf{r})$ from its matrix faithfully.

The LIP basis set method is even more robust for molecules than for atoms of comparable size because linear independence of MO products is enhanced by MO delocalization over multiple nuclei. For example, in the 10-electron series (Ne, HF, H_2O, NH_3, CH_4), the smallest eigenvalue $\lambda_{\min}$ increases by two orders of magnitude from Ne to CH_4 (Table 1).

4. Conclusion

Within LIP basis sets, the mapping between Kohn–Sham potentials and ground-state electron densities is bijective and invertible in practice.[19] Although this result has been known for some time, it did not appear to have much practical significance because standard LIP basis sets are virtually non-existent. We have shown here

that the LIP basis-set machinery can be practical if one uses occupied and low-lying Kohn–Sham orbitals as basis functions. The potential $\tilde{v}_{\mathrm{XC}}(\mathbf{r})$ constructed using the natural minimal LIP basis set of the occupied Kohn–Sham orbitals is well-defined, reproduces the ground-state electron density and energy of $v_{\mathrm{XC}}(\mathbf{r})$ exactly, and shows weak dependence on the underlying AO basis.

Within a the LIP basis set, one can go back and forth between $\tilde{v}_{\mathrm{XC}}(\mathbf{r})$, its matrix representation, and the corresponding $\rho(\mathbf{r})$ without any loss of information. Exchange-correlation potentials recovered in this manner from Fock matrices resemble the originals in an exaggerated way and decay faster than even the conventional LDA potentials. The similarity between the original and reconstructed potentials can be improved by including unoccupied orbitals in the MO basis set, as long as the enlarged basis set still forms LIPs.

The fact that exchange-correlation potentials extracted from their Fock matrices are not very close to the complete-basis-set originals is instructive. It suggests that accurate representation of the size and position of the bumps, the rate of asymptotic decay, and other such features of exact $v_{\mathrm{XC}}(\mathbf{r})$ may not be as important for computing ground-state properties within finite basis sets as is often assumed. This finding offers another perspective on why local and semilocal density functionals perform much better than the shapes of their Kohn–Sham potentials might indicate.

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