Violations of the v-representability condition underlying Kohn-Sham density-functional theory

Egor Trushin^{1,2} Jannis Erhard¹, and Andreas Görling^{1,2,*}

¹Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany ²Erlangen National High Performance Computing Center (NHR@FAU), Martensstraße 1, D-91058 Erlangen, Germany

(Received 15 February 2024; accepted 19 July 2024; published 7 August 2024)

Electronic structure methods based on the Kohn-Sham (KS) formalism of density-functional theory are ubiquitously and highly successfully used in physics, chemistry, and materials science. Whether the KS formalism is universally applicable is, however, an open question because it is not known whether a KS model system exists for all physical electron systems. This is the question of whether electron densities of real physical systems are always noninteracting *v*-representable. Here we give indications that this is not always the case. To that end, we calculated highly accurate electron densities of first and second row atoms with a partially filled pshell by high-level quantum chemistry methods and by full configuration interaction and then tried to determine the effective KS potential by KS inversion. Except for nitrogen and phosphorus this was only possible for an occupation pattern violating the Aufbau principle. This means that the resulting wave function is not a ground state of the KS Hamiltonian operator and therefore not a valid KS wave function, which indicates that the KS formalism is not always applicable. Strategies to avoid the presented *v*-representability problem are discussed.

DOI: 10.1103/PhysRevA.110.L020802

Methods based on the Kohn-Sham (KS) formalism of density-functional theory (DFT) [1-3] are the most widely used approaches to treat electronic structures in chemistry, physics, and materials science. While KS-DFT is ubiquitously and highly successfully employed in practice, a question concerning its formal basis is still open. This is the question of whether or not there exists a KS model system for each physical electron system. In the KS formalism a model system of noninteracting "electrons," the KS model system, is associated with a given physical electron system. The KS model system consists of hypothetical particles that are identical to electrons except that they do not carry a charge and therefore do not interact with each other. The electrons of the KS model system move in an effective potential, the KS potential, which is determined by the requirement that the density of the ground state of the KS system equals the ground state electron density of the physical electron system. According to the Hohenberg-Kohn theorem this uniquely defines the effective KS potential up to an additive constant. The Hohenberg-Kohn theorem holds true for local multiplicative potentials and only those potentials are considered in this work. In nonrelativistic electronic structure theory all potentials are local multiplicative if no magnetic fields are present, which is assumed here. While the Hohenberg-Kohn theorem guarantees the uniqueness of the KS potential, it does not guarantee its existence. For the KS formalism to be generally applicable, a KS potential and thus a KS model system must exist for all physical electron systems. The results presented in this Letter, however, indicate that this is not the case.

If a given electron density is the ground state electron density of a physical electron system then it is called interacting v-representable. Similarly, if a density is the ground state density of a system of noninteracting model "electrons," i.e., of KS electrons, then it is called noninteracting *v*-representable. In this work the term *v*-representable always means pure-state v-representable, which means that a density is the density of a single ground state wave function. Note that this does not imply that the KS wave function has to be a single Slater determinant; it can also be a linear combination of Slater determinants. Whether a density results from a density matrix corresponding to an ensemble of wave functions is the question of ensemble v-representability and is not the subject of this work. In applications of the KS formalism the starting point is a given physical electronic system defined by its Hamiltonian operator. The electron density of the ground state of this physical system, by construction, is interacting v-representable. The crucial question is whether there exists a Hamiltonian operator of a system of noninteracting model electrons with a ground state density that is identical to that of the considered physical system. This means there needs to be an effective KS potential such that the Hamiltonian operator of a system of noninteracting model electrons with this effective potential has a ground state with an electron density identical to the one of the physical system. In this case the interacting v-representable ground state density of the physical electron system is also noninteracting v-representable, which is a necessary condition for the KS formalism to be applicable. Examples of mathematically well-behaved densities that are not noninteracting v-representable are known [4,5]. However, the existence of such non-*v*-representable densities does not yet pose a problem with respect to the applicability of the KS formalism, because only a conditional v-representability condition is required, namely that each interacting *v*-representable density is also noninteracting v-representable. Here we present examples that violate this

^{*}Contact author: andreas.goerling@fau.de

conditional v-representability condition. These examples are not exotic but include all first and second row atoms with partially filled p shells except nitrogen and phosphorus. In Ref. [6] arguments are put forward that for closed-shell systems the KS v-representability condition is always obeyed. Our examples of violations of the *v*-representability condition comprise exclusively open-shell systems and therefore match with the findings of Ref. [6]. In Refs. [7-10] examples of atoms and molecules were presented, for which no KS state given by a single Slater determinant could be found and resorting to an ensemble KS formalism was advocated. However, in all these cases, the electron density can be obtained by a KS wave function consisting of several Slater determinants (exactly those Slater determinants used in the ensemble treatment) and therefore the systems considered in Refs. [7-10]do not violate the KS v-representability condition; see Supplemental Material (SM) [11] for further discussion.

In this Letter, we consider the original spin-restricted KS formalism, using exclusively the electron density as the basic quantity in all cases, including open-shell atoms or molecules. In the original papers underlying the KS formalism [1,2] closed-shell systems are considered but the original work is equally valid for open-shell systems; see SM for details [11]. The KS v-representability condition is required both for open- and closed-shell systems. By presenting examples of violations of this condition we demonstrate that the basic KS formalism is not generally applicable and affirmatively answer the long-standing fundamental question of whether such violations exist for physically relevant systems. In practice, open-shell systems are usually treated within a spin-unrestricted KS formalism, which relies on the α and β spin densities as basic variables. This leads to different KS potentials for α and β electrons, resulting in spin contamination; i.e., the corresponding KS determinants do not correspond to a state with a definite value of the total spin. In the original spin-restricted KS formalism relying exclusively on the electron density, there is only one effective KS potential for both α and β electrons, and the problem of spin contamination does not arise. This means there is only one set of spatial orbitals used for spin orbitals of α as well as β spin even for open-shell systems. In open-shell systems, however, the occupation numbers of the two spin channels are different. The effective KS potential v_s determining the spatial orbitals is given by

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$
(1)

as the sum of the external potential v_{ext} of the corresponding physical electron system, usually the electrostatic potential of the nuclei of the atoms, the Hartree potential v_H , the electrostatic potential of the electron density, and the exchange-correlation potential v_{xc} , the functional derivative $\delta E_{xc}/\rho(\mathbf{r})$ of the exchange-correlation energy E_{xc} with respect to the electron density ρ .

We carried out full configuration interaction calculations for the atoms boron and carbon and high-level post-Hartree-Fock (post-HF) quantum chemistry calculations, second-order Rayleigh-Schrödinger perturbation theory (RS2) [12], configuration interaction with singles and doubles (CISD) [13], and averaged quadratic coupled cluster (AQCC) [14] with three different basis sets of increasing quality, aug-cc-pwCVXZ



FIG. 1. Schematic representation of possible eigenvalue spectra of the partially filled p shells of B, C, O, F, Al, Si, S, and Cl. Upper row corresponds to orbital occupations according to the Aufbau principle. Bottom row shows occupation patterns with a negative HOMO-LUMO gap, i.e., occupation patterns not obeying the Aufbau principle, in the α spin channel for B, C, Al, and Si, and in the β spin channel for O, F, S, and Cl.

[15] (X = T, Q, 5), for first and second row atoms with partially filled p shells with the Molpro quantum chemistry package [16,17] to obtain highly accurate reference electron densities. We used two different starting points for the post-HF calculations, restricted open-shell Hartree-Fock (ROHF) and configuration-averaged Hartree-Fock (CAHF). In the latter case, the full spatial symmetry of the orbitals is retained. We discuss here results based on CAHF and the best basis set aug-cc-pwCV5Z. The results for the other basis sets and for the ROHF starting point are qualitatively equal and can be found in the SM [11]. In addition, we performed exactexchange-only KS calculations for the considered atoms using the optimized effective potential (OEP) method [18-21] in the implementation presented in Ref. [22]. For the auxiliary basis sets required to represent the exchange potential in the OEP method we used aug-cc-pVDZ/mp2fit and aug-ccpVTZ/mp2fit basis sets [23] for the atoms Li to Ne and Na to Ar, respectively. For technical details, see Refs. [22,24] and SM [11]. In the SM we also show results for larger auxiliary basis sets, which, however, do not show any significant differences from the results discussed here.

For all open-shell atoms we considered in the post-HF calculations the state of the ground state multiplet that exhibits the highest magnetic spin quantum number M_S (for B, F, Al, and Cl $M_s = +1/2$; for C, O, Si, and S $M_s = +1$; for N and $P M_s = +3/2$) and a magnetic angular momentum quantum number $M_L = 0$. This leads to real-valued wave functions that can be constructed from real-valued orbitals. All KS states corresponding to the states considered in the post-HF calculations are single Slater determinants. This choice of magnetic spin and angular momentum quantum numbers leading to real-valued single KS determinants is common in KS DFT. In Fig. 1 eigenvalue spectra of the open p shell and possible occupation patterns are displayed for the atoms B, C, O, F, Al, Si, S, and Cl. Note that the α and β orbitals are identical, even though they have different occupation numbers. Moreover, the p orbitals do not exhibit a threefold degeneracy but split into a nondegenerate and a doubly degenerate level, reflecting a cylindrical spatial symmetry. This is in agreement with basic formalism. The KS Hamiltonian operator has to exhibit only the symmetry of the electron density but not the full symmetry of the physical Hamiltonian operator [25]. In the open-shell atoms investigated in Fig. 1, the exact densities of the physical

TABLE I. The HOMO-LUMO gap in the α spin channel for the atoms B, C, Al, Si and in the β spin channel for the atoms O, F, S, Cl from
EXX and from KS inversion calculations using RS2, CISD, and AQCC reference densities. Negative HOMO-LUMO gaps indicate a violation
of the Aufbau principle. Total energies (Etot) are provided for the EXX calculations and post-Hartree-Fock calculations at the RS2, CISD, and
AQCC levels from which the reference density is obtained. All values are given in atomic units.

	В		С		0		F	
Method	α gap	$E_{\rm tot}$	α gap	$E_{\rm tot}$	β gap	$E_{\rm tot}$	β gap	$E_{\rm tot}$
EXX	0.00594	-24.52759	0.00868	-37.68655	-0.02843	-74.80866	-0.02877	-99.40828
RS2	-0.01871	-24.64566	0.00251	-37.82847	-0.02681	-75.05395	-0.02853	-99.71810
CISD	-0.01682	-24.65032	-0.01747	-37.83619	-0.03156	-75.05124	-0.03456	-99.71304
AQCC	-0.01701	-24.65116	-0.01823	-37.83835	-0.03569	-75.05666	-0.03870	-99.71990
	Al		Si		S		Cl	
Method	α gap	$E_{\rm tot}$	α gap	E _{tot}	β gap	E _{tot}	β gap	E _{tot}
EXX	0.00286	-241.87346	0.00308	-288.84969	-0.01227	-397.49984	-0.01223	-459.47670
RS2	-0.00729	-242.31034		-289.31684	-0.01376	-398.06517	-0.01477	-460.09718
CISD	-0.00531	-242.30016	-0.00397	-289.30120	-0.01351	-398.03897	-0.01623	-460.07070
AQCC	-0.00609	-242.31268	-0.00678	-289.31887	-0.02026	-398.06667	-0.02397	-460.10289

ground states exhibit only a cylindrical symmetry and not the full spherical symmetry of the atomic Hamiltonian operator. Eigenstates of a Hamiltonian operator generally do not have to exhibit the full symmetry of the Hamiltonian operator but are only required to transform according to an irreducible representation of the full symmetry group if subject to a symmetry operation of this group.

The exact-exchange (EXX) calculations for all atoms except O, F, S, and Cl converged without problems for the occupation pattern obeying the Aufbau principle; see Fig. 1 here and Fig. 1 in the SM [11]. For the atoms O, F, S, and Cl, however, convergence could not be achieved for any of the basis sets considered, even when the convergence accelerators were switched off and the mixing of KS Hamiltonian operators during the SCF (self-consistent field) process was carried out with small fixed mixing parameters. The reason was the same in all cases. Right at the beginning, the SCF process completely destroyed the symmetry of the *p* orbitals; i.e., all three p orbitals became different in energy. Then, during the SCF process, the HOMO-LUMO gap (energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital) approached zero, and the HOMO and LUMO changed position energetically, leading to an occupation of the LUMO in the next SCF cycle. Due to such occupation changes convergence was not possible. Such a behavior indicates that the occupation pattern underlying the SCF calculation is not suitable. Indeed, changing the occupation pattern of the open p shell such that the occupied p orbitals were those with the higher energy, see Fig. 1, led in all four cases to convergence without problems and to a result with the required cylindrical symmetry, resulting in two degenerate p orbitals and a third one with a different energy.

The EXX calculations for O, F, S, and Cl, thus, require an occupation inversion leading to a violation of the Aufbau principle in order to converge. This situation can be characterized by a negative HOMO-LUMO gap for the β spin channel; see Table I. This means that it is possible to assign an eigenstate of a model system of noninteracting electrons to the physical ground state of the atoms O, F, S, and Cl at the exact-exchange-only level, but this eigenstate is not a ground state and thus not a valid KS state. Note that in the KS model system the total energy is given simply by the sum of the eigenvalues of the occupied KS orbitals. This total energy of the KS model system has no physical meaning but it has to be the lowest energy of all eigenstates of the many-electron KS Hamiltonian operator in order to obey the requirement that the KS state corresponding to the physical system is the ground state of the KS Hamiltonian operator. That EXX calculations for O, F, S, and Cl can only be converged when violating the Aufbau principle is an indication of a violation of the KS v-representability condition. Similarly, EXX calculation for the LiF molecule at large bonding distances [26] required a violation of the Aufbau principle. However, because correlation is neglected at the exchange-only level it cannot be excluded that violations of the KS v-representability condition in EXX calculations are an artifact due to the neglect of correlation. Indeed, for approximate exchange-correlation potentials, indications for violations of the v-representability condition were found long ago [27,28]. From a fundamental point of view, the crucial question is whether such violations of the v-representability condition occur also for the exact-exchange-correlation potential. We therefore carried out KS inversions [29] for the highly accurate densities of the post-Hartree-Fock quantum chemistry calculations for the considered atoms (and from full configuration interaction for B and C) with the approach of Ref. [30] using the same auxiliary basis sets and computational settings as in the EXX calculations; for details see the Supplemental Material [11]. That is, we tried for each of the atoms to determine the effective KS potentials such that the resulting KS systems have electron densities equal to those of the reference calculations.

The results of the KS inversions for the atoms with open p shells are shown in Table I. For the atoms O, F, S, and Cl, the KS inversions did not converge for any of the electron densities of the correlated calculations if the occupation pattern required by the KS formalism was used. On the other hand, with an occupation inversion, convergence was possible in all cases. In Table I this is reflected by negative HOMO-



FIG. 2. The KS densities of the atoms O [(a), (b)] and N (c) resulting from KS inversion, the corresponding reference AQCC densities, and their differences multiplied by 10³. The KS density of the O atom exhibits cylindrical symmetry leading to equal densities $\rho_{KS}^{x,y}$ and $\rho_{Ref}^{x,y}$ along the *x* and *y* axes differing from the densities ρ_{KS}^{z} and ρ_{Ref}^{z} along the *z* axis. The KS density of the N atom is spherical and therefore the same along any axis.

LUMO gaps for the β spin channel for the atoms O, F, S, and Cl. In Table I the total energies of the EXX and the RS2, CISD, and AQCC calculations are listed in addition to the HOMO-LUMO gap. For the EXX case, by definition, the correlation energy is zero and consequently the EXX total energy is always the highest. The AQCC total energy is always the lowest. The RS2 and CISD total energies lie between those of the EXX and AQCC. Table I shows that by taking into account correlation the HOMO-LUMO gap of O, F, S, and Cl stays negative and has the largest magnitude in the case of KS inversion from AQCC densities. This means that if the ground state electron density of the exact physical wave functions is approached then the violation of the KS v-representability condition becomes more pronounced. That is, taking into account correlation does not prevent the violation of *v*-representability but leads to an even stronger manifestation of it. The violation of the KS v-representability conditions also shows up for the other basis sets and computational setups, see SM [11], indicating that the findings of this work are not due to technical inaccuracies. Indeed, in Ref. [31] it was also found that KS inversions for the atoms O, F, S, and Cl did not converge but the reason for the convergence problems was not investigated further.

In Fig. 2, the KS densities resulting from the KS inversion for the atoms N and O is compared to the reference AOCC densities. In both cases the deviations between the KS and the reference densities are of similar magnitude. For nitrogen with its completely occupied (unoccupied) p shell in the α (β) channel with the resulting spherical symmetry of the electron density, there is no v-representability problem. The deviations between KS and reference densities are a measure of the technical accuracy in our KS inversion. The case violating the KS v-representability condition, oxygen, exhibits even somewhat smaller deviations between the involved densities than the case not violating the *v*-representability condition, nitrogen, which again suggests that our findings are not affected by technical inaccuracies. In the SM [11] we also provide integrated density errors $\left[\frac{1}{N_e}\int |\rho_{\text{KS}}(\mathbf{r}) - \rho_{\text{Ref}}(\mathbf{r})|d\mathbf{r}\right]$, where N_e is the number of electrons] for all considered atoms. The errors are comparable for systems that require occupation inversion and those that do not.

Next we discuss the atoms with open p shells for which the EXX calculations converge. For B, C, Al, and Si the KS inversion again requires occupation patterns violating the Aufbau principle. The only exception is KS inversion for the C atom with the RS2 density. KS inversion for the Si atom from the RS2 density does not converge with or without occupation inversion. The reason is most likely that this case is close to the point where the occupation pattern changes and therefore is characterized by an almost vanishing HOMO-LUMO gap which generally hampers convergence in SCF or KS inversion processes. The results for B, C, Al, and Si are in line with those of O, F, S, and Cl. In all cases, the KS v-representability condition is violated if correlation is taken into account to a sufficient amount; indeed the violation becomes systematically more pronounced when going from CISD to AQCC, i.e., when taking into account correlation more completely. This finding is corroborated for the atoms B and C by KS inversions from ground state densities from full configuration interaction that lead to negative HOMO-LUMO gaps as well; see SM [11]. The only considered atoms with open p shell that do not exhibit a violation of the KS v-representability condition are N and P, which have a fully occupied p shell in the α channel and a completely empty p shell in the β channel and are, therefore, spherically symmetric. This indicates that the violation of the KS v-representability condition occurs if the ground state electron density has a lower symmetry than the underlying physical Hamiltonian operator.

To test the the robustness of our findings we considered for the atoms B, C, O, and F in addition to the states with magnetic angular momentum quantum numbers $M_L = 0$ also the states with $M_L = \pm 1$; the magnetic spin quantum numbers remained unchanged, i.e., $M_S = +1/2$ for B and F and $M_S = +1$ for C and O. In this case, the KS state is a linear combination of two Slater determinants with coefficients determined by symmetry, i.e., a configuration state function, or alternatively a single Slater determinant with complex-valued orbitals. This leads to fractional occupation numbers although we remain within the pure-state KS formalism and do not resort to an ensemble KS formalism; see SM [11]. The electron density of the states with $M_L = \pm 1$ is different from that of the state with $M_L = 0$ which leads to different KS orbitals. EXX calculations for the states with $M_L = \pm 0$ showed the same behavior as those for the states with $M_L = 0$: the calculations for B and C converged without occupation inversion, and the calculations for O and F only converged with occupation inversion. This demonstrates that the presented violations of the KS *v*-representability condition do not result from a specific choice for the considered state of a multiplet. Interestingly, our findings for the ground states of B, C, O, and F with $M_L = \pm 1$ can be interpreted alternatively from an ensemble KS perspective and then show that for these systems the KS *v*-representability condition is violated even in an ensemble KS formalism; see SM [11] for details.

The finding that the v-representability condition underlying the KS formalism seems to be violated in open-shell atoms indicates that one of the most successful and widely used electronic structure methods is not generally applicable. This suggests that generalizations of the KS formalism that do not require the reference state of noninteracting model electrons to be a ground state should be explored further. In Ref. [32] such a generalization was presented. Its advantage is that it applies to ground as well as to excited states. The price of not requiring the reference state to be a ground state is that the Hohenberg-Kohn theorem can no longer be used in assigning reference states to physical electron states.

The presented violations of the *v*-representability condition occurred for open-shell systems. In Ref. [25] a fully symmetrized KS formalism was presented that relies on the totally symmetric contribution to the ground state electron density instead of the ground state density itself. This formalism does not break symmetries in spin and real space and therefore solves a fundamental shortcoming not only of KS methods but generally of methods generating orbitals in a mean field procedure. With the development of numerically stable Gaussian-basis-set OEP methods [22] the formalism of Ref. [25] could be applied, at the EXX level, to a wide range of atoms and molecules and it showed that the atoms O, F, S, and Cl do not exhibit the *v*-representability problem encountered in the standard KS formalism [24]. To investigate this further we developed a fully symmetrized KS inversion approach and found that the symmetrized KS formalism does not exhibit v-representability problems in any of the cases shown here to violate the *v*-representability condition in the standard formalism; results will be published elsewhere [33]. That the fully symmetrized KS formalism of Ref. [25], in contrast to the standard KS formalism, does not suffer from v-representability problems for open-shell systems is a further strong argument to develop on its basis KS methods that can be applied in practical applications. (The EXX approach of Ref. [24], which completely neglects correlation, is not accurate enough for this purpose.)

The data supporting the results of this study are openly available in the Zenodo repository [34].

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), Project-ID Grant No. 431791331, SFB 1452.

- P. Hohenberg and W. Kohn, Inhomogeneous electron gas, Phys. Rev. 136, B864 (1964).
- [2] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140, A1133 (1965).
- [3] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).
- [4] M. Levy, Electron densities in search of Hamiltonians, Phys. Rev. A 26, 1200 (1982).
- [5] E. H. Lieb, Density functionals for Coulomb systems, Int. J. Quantum Chem. 24, 243 (1983).
- [6] A. Gonis, Is an interacting ground state (pure state) v-representable density also non-interacting ground state v-representable by a Slater determinant? In the absence of degeneracy, yes! Phys. Lett. A 383, 2772 (2019).
- [7] P. R. T. Schipper, O. V. Gritsenko, and E. J. Baerends, Onedeterminantal pure state versus ensemble Kohn-Sham solutions in the case of strong electron correlation: CH₂ and C₂, Theor. Chem. Acc. **99**, 329 (1998).
- [8] P. R. T. Schipper, O. V. Gritsenko, and E. J. Baerends, Benchmark calculations of chemical reactions in density functional theory: Comparison of the accurate Kohn-Sham solution with generalized gradient approximations for the H₂+H and H₂+H₂ reactions, J. Chem. Phys. **111**, 4056 (1999).
- [9] C. A. Ullrich and W. Kohn, Kohn-Sham theory for ground-state ensembles, Phys. Rev. Lett. 87, 093001 (2001).

- [10] R. C. Morrison, Electron correlation and noninteracting vrepresentability in density functional theory: The Be isoelectronic series, J. Chem. Phys. 117, 10506 (2002).
- [11] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevA.110.L020802 for a discussion of the Hohenberg-Kohn theorem in the case of degeneracies, a discussion of multideterminantal KS states, technical details, and results of additional calculations.
- [12] H.-J. Werner, Third-order multireference perturbation theory: The CASPT3 method, Mol. Phys. 89, 645 (1996).
- [13] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (Dover Press, New York, 1996).
- [14] P. G. Szalay and R. J. Bartlett, Approximately extensive modifications of the multireference configuration interaction method: A theoretical and practical analysis, J. Chem. Phys. 103, 3600 (1995).
- [15] K. A. Peterson and T. H. Dunning Jr., Accurate correlation consistent basis sets for molecular core-valence correlation effects: The second row atoms A–Ar, and the first row atoms B–Ne revisited, J. Chem. Phys. **117**, 10548 (2002).
- [16] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, Molpro: A general-purpose quantum chemistry program package, WIREs Comput. Mol. Sci. 2, 242 (2012).
- [17] H.-J. Werner, P. J. Knowles, F. R. Manby, J. A. Black, K. Doll, A. Heßelmann, D. Kats, A. Köhn, T. Korona, D. A. Kreplin, Q. Ma, I. Miller III, A. Mitrushchenkov, K. A. Peterson, I. Polyak,

- [18] R. T. Sharp and G. K. Horton, A variational approach to the unipotential many-electron problem, Phys. Rev. 90, 317 (1953).
- [19] J. D. Talman and W. F. Shadwick, Optimized effective atomic central potential, Phys. Rev. A 14, 36 (1976).
- [20] A. Görling, Orbital- and state-dependent functionals in densityfunctional theory, J. Chem. Phys. 123, 062203 (2005).
- [21] S. Kümmel and L. Kronik, Orbital-dependent density functionals: Theory and applications, Rev. Mod. Phys. 80, 3 (2008).
- [22] E. Trushin and A. Görling, Numerically stable optimized effective potential method with standard Gaussian basis sets, J. Chem. Phys. 155, 054109 (2021).
- [23] F. Weigend, A. Köhn, and C. Hättig, Efficient use of the correlation consistent basis sets in resolution of the identity MP2 calculations, J. Chem. Phys. **116**, 3175 (2002).
- [24] E. Trushin and A. Görling, Avoiding spin contamination and spatial symmetry breaking by exact-exchange-only optimizedeffective-potential methods within the symmetrized Kohn-Sham framework, J. Chem. Phys. 159, 244109 (2023).
- [25] A. Görling, Symmetry in density-functional theory, Phys. Rev. A 47, 2783 (1993).

- [26] A. Makmal, S. Kümmel, and L. Kronik, Dissociation of diatomic molecules and the exact-exchange Kohn-Sham potential: The case of LiF, Phys. Rev. A 83, 062512 (2011).
- [27] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).
- [28] J. F. Janak, Proof that $\frac{\partial e}{\partial n_i} = \epsilon$ in density-functional theory, Phys. Rev. B **18**, 7165 (1978).
- [29] Y. Shi and A. Wasserman, Inverse Kohn-Sham density functional theory: Progress and challenges, J. Phys. Chem. Lett. 12, 5308 (2021).
- [30] J. Erhard, E. Trushin, and A. Görling, Numerically stable inversion approach to construct Kohn-Sham potentials for given electron densities within a Gaussian basis set framework, J. Chem. Phys. 156, 204124 (2022).
- [31] T. Gould, Toward routine Kohn-Sham inversion using the "Lieb-response" approach, J. Chem. Phys. 158, 064102 (2023).
- [32] A. Görling, Density-functional theory beyond the Hohenberg-Kohn theorem, Phys. Rev. A 59, 3359 (1999).
- [33] J. Erhard, E. Trushin, and A. Görling, Kohn-Sham inversion for open-shell systems (unpublished).
- [34] E. Trushin, Violations of the v-representability condition underlying Kohn-Sham density-functional theory, http://doi.org/ 10.5281/zenodo.12772192 (2024).