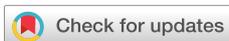


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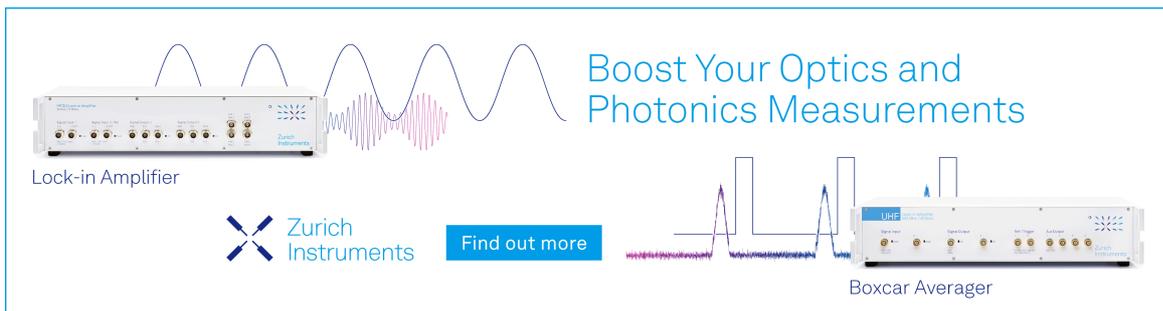


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ABSTRACT

A way to improve the accuracy of the spectral properties in density functional theory (DFT) is to impose constraints on the effective, Kohn–Sham (KS), local potential [J. Chem. Phys. **136**, 224109 (2012)]. As illustrated, a convenient variational quantity in that approach is the “screening” or “electron repulsion” density, ρ_{rep} , corresponding to the local, KS Hartree, exchange and correlation potential through Poisson’s equation. Two constraints, applied to this minimization, largely remove self-interaction errors from the effective potential: (i) ρ_{rep} integrates to $N - 1$, where N is the number of electrons, and (ii) $\rho_{\text{rep}} \geq 0$ everywhere. In this work, we introduce an effective “screening” amplitude, f , as the variational quantity, with the screening density being $\rho_{\text{rep}} = f^2$. In this way, the positivity condition for ρ_{rep} is automatically satisfied, and the minimization problem becomes more efficient and robust. We apply this technique to molecular calculations, employing several approximations in DFT and in reduced density matrix functional theory. We find that the proposed development is an accurate, yet robust, variant of the constrained effective potential method.

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I. INTRODUCTION

Replacing the Kohn–Sham (KS) potential¹ for approximate functionals in Density Functional Theory (DFT) with a variational, constrained potential that fulfills exact properties is one of the proposed ways to improve spectral properties² and more specifically the interpretation of KS orbital energies as a meaningful electronic spectrum of the system. One can minimize the total energy of any Density Functional Approximation (DFA) under the constraint that the optimal effective local potential exhibits the correct asymptotic behavior. It was argued that, in this way, the effect of self-interactions (SI) on the local potential is suppressed, and the ionization energies obtained by the orbital energies of the highest occupied molecular orbital (HOMO) are significantly closer to the experiment than those obtained from the unconstrained, approximate KS potential.^{2–5}

In single particle theories, like KS, SIs can appear when the exact exchange energy functional is replaced with approximations that violate the complete cancellation of the Hartree SI terms. Characteristic examples are local/semi-local approximations like LDA^{1,6–8} or GGAs.^{9–12} The seminal work of Perdew and Zunger⁶ aimed at correcting this problem. Several other attempts were made to address the same problem.^{2,3,13–21} All these attempts aim at correcting the total energy. Contrarily, the main concept of Ref. 2 is to correct the effective potential instead through additional constraints. A typical manifestation of SIs is the wrong asymptotic behavior of the KS potential. On the other hand, the correct behavior of the potential at large distances plays a crucial role in the determination of several molecular properties. The Coulomb potential, V_H , behaves like N/r at large distances. In order to obtain the correct overall behavior, the exchange and correlation (xc) potential V_{xc} should behave as $-1/r$, which does not hold for many

approximations. Indeed, in most semilocal DFAs, the xc potential decays exponentially fast. In Ref. 2, the aim was to replace the Hartree-exchange and correlation (HXC) part of the KS potential with the energetically optimal effective potential V_{rep} (that minimizes the total energy functional) but that also satisfies two subsidiary conditions. These conditions or constraints are expressed in terms of the screening (or electron repulsion) density,²² ρ_{rep} ; this density corresponds to V_{rep} through Poisson's equation. The first is that ρ_{rep} integrates to $N - 1$ electrons, and the second is that it is everywhere non-negative [$\rho_{\text{rep}}(\mathbf{r}) \geq 0$]. With this approach, the effect of SIs on the effective potential V_{rep} was largely corrected, and molecular properties were improved.²⁻⁵

A recent publication⁵ explored the relaxation of the positivity constraint, $\rho_{\text{rep}}(\mathbf{r}) \geq 0$; this leads to a mathematical optimization problem that is strictly not well-posed. Nevertheless, in practice, the mathematical problems became evident only with large auxiliary basis sets or for systems with few electrons. In addition, a density inversion method, yielding the corresponding KS potential that satisfies the correct asymptotic behavior, was introduced recently.^{23,24} Finally, a hybrid scheme was proposed,²⁵ where the local part of the KS potential is optimized under the aforementioned subsidiary conditions, yielding single-particle energies in excellent agreement with experimental ionization energies, even for the core electrons. The hybrid potential scheme in Ref. 5 is applicable to any semilocal DFA.

The idea of optimizing the energy functional with respect to a constrained local potential has also been applied to approximations within the framework of the reduced, density-matrix functional theory (RDMFT),^{26,27} leading to an approach that was called local RDMFT (LRDMFT). In RDMFT, functionals are usually explicitly expressed in terms of the natural orbitals and their corresponding occupation numbers, i.e., the eigenfunctions and eigenvalues of the one-body, reduced, density-matrix (1RDM). Although the foundations of RDMFT were laid a long time ago,²⁸⁻³⁰ it has received significant attention in the last couple of decades.^{15,31-39} One of its main advantages is that the kinetic energy can be written as an explicit functional of the 1-RDM, so the exchange-correlation term is not "contaminated" by kinetic energy contributions. Fractional occupation numbers are introduced through Coleman's N -representability conditions.⁴⁰ RDMFT provides the opportunity to express energy terms exactly as functionals of 1-RDM except for the electron-electron interaction energy. For this term, many approximate functionals have been proposed,^{31-35,41-47} offering a good description of electronic correlations. In these approaches, energy minimization is performed iteratively in two steps: (1) Minimization with respect to natural occupation numbers and (2) minimization with respect to natural orbitals. The first of these steps is relatively inexpensive computationally, but the second is very demanding. Although significant progress has been achieved in improving its efficiency,³⁶ this minimization still remains a considerable bottleneck.

In LRDMFT,^{26,27} functionals of the 1RDM are employed, but the minimization with respect to the orbitals is replaced with a constrained minimization that restricts the domain of orbital variation to those that are obtained from a single particle Schrödinger equation with local potential. Thus, it becomes a direct application of the constrained potential optimization of Refs. 2-5 to

1RDM functionals. One important attribute of this approach is, of course, the relative efficiency in orbital optimization compared to full RDMFT minimization. A second one is that single-particle properties are offered through the spectrum of the single-particle Hamiltonian. It was found that energy eigenvalues of the highest occupied orbitals (HOMO) obtained in that way reproduce accurately the ionization potentials (IPs).^{26,27} LRDMFT should not be considered as an approximation of RDMFT because the true natural orbitals cannot be obtained (even approximately) by a local potential, and the optimal orbitals from LRDMFT are KS-like orbitals.⁴⁸ It can be considered as a DFA with fractional occupation numbers introduced through the minimization of the energy. LRDMFT incorporates good aspects of both RDMFT and DFT, combining the low computational cost of DFT and the description of the static correlation of RDMFT through the introduction of fractional occupation numbers.

A hurdle in the application of the constrained minimization method is the enforcement of the positivity condition for the effective density, $\rho_{\text{rep}}(\mathbf{r})$. The fact that this condition has to be satisfied at each point in space, e.g., by a penalty term, has been proven computationally inefficient. In this work, we present a variant of the constrained minimization method with the positivity condition enforced by expressing the screening density as the square of an orbital-like "screening-density amplitude," $\rho_{\text{rep}}(\mathbf{r}) = f(\mathbf{r})^2$, and using this amplitude, $f(\mathbf{r})$, as the minimization variable. In that way, the positivity condition is automatically satisfied; however, there is a price to pay, since the variation with respect to $f(\mathbf{r})$ does not lead to linear equations. Hence, in this work, we determine f through a minimization procedure instead of solving any variational equations. In this first application, for simplicity, we assume that f is expanded on the same orbital basis as the molecular orbitals. We apply the new method to the LDA functional in DFT as well as several approximations in LRDMFT.

This paper is organized as follows: In Sec. II, we present the methodology to determine the screening-density amplitude. Section III is devoted to applications. In Sec. III A, we include the results of the application of the present method in optimizing total energies for a few local, semi-local, and hybrid DFAs and focus on the agreement of the obtained IPs with the experiment. Finally, in Sec. III B, we show the results of applying the present method to RDMFT functionals, i.e., as a variant of the LRDMFT methodology.

II. THEORY

In KS theory,¹ the local potential V_{KS} is the sum $V_{\text{KS}} = V_{\text{ext}} + V_{\text{Hxc}}$ of the external potential, V_{ext} , and the Hartree, exchange, and correlation term, V_{Hxc} . It is obtained from the functional derivative of the total electronic energy with respect to the electron density. This potential is inserted in the single particle Kohn-Sham equations,

$$\left[-\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + V_{\text{Hxc}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad (1)$$

yielding the KS orbitals, hence the density, in a self-consistent cycle.

Following Refs. 2 and 3, V_{Hxc} , in Eq. (1), is replaced by a variational effective repulsive potential V_{rep} . The total energy, E ,

depending explicitly on the orbitals, $\{\phi_i\}$, can be considered a functional of V_{rep} if we assume that the orbitals are obtained from the solution of an equation like Eq. (1), but with the variational potential, V_{rep} replacing V_{Hxc} . For any DFA, this energy functional can be minimized with respect to V_{rep} , under additional constraints (subsidiary conditions), e.g., in order to enforce exact properties for the potential. Without any such constraint, it is easy to see that the optimal V_{rep} will be equal to V_{Hxc} . Since the considered additional constraints concern the “screening” or “electron repulsion” density, ρ_{rep} , associated with V_{rep} through Poisson’s equation, it is convenient to express V_{rep} in terms of ρ_{rep} as^{2,3,22,26}

$$V_{\text{rep}}(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho_{\text{rep}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2)$$

An exact property of the KS potential is that the asymptotic behavior of the electron–electron repulsion part, V_{Hxc} , is

$$\lim_{r \rightarrow \infty} V_{\text{Hxc}}(\mathbf{r}) = \frac{N - \alpha}{r}, \text{ with } \alpha = 1, \quad (3)$$

i.e., an electron at infinity “feels” the repulsion of the remaining $N - 1$ electrons. One of the manifestations of SIs, which are

present in most DFAs, is that this property is not satisfied by the approximate V_{Hxc} , typically with $0 \leq \alpha < 1$. In Ref. 2, it was proposed that properties of the exact KS potential, like Eq. (3), can be enforced in the minimization with respect to V_{rep} , thus the optimal V_{rep} differs from V_{Hxc} , i.e., it is no longer the functional derivative of the total energy with respect to the density. For such an optimization, it is convenient to express V_{rep} in the form^{2,22} of Eq. (2).

Assuming the form of Eq. (2), one can minimize the total DFA energy with respect to ρ_{rep} , instead of the effective potential. ρ_{rep} can be expanded in an auxiliary basis set, in principle different than the basis used for the expansion of the KS orbitals. In terms of ρ_{rep} , condition (3) concerns the total repulsive charge, Q_{rep} ,

$$Q_{\text{rep}} = \int d\mathbf{r} \rho_{\text{rep}}(\mathbf{r}) = N - 1. \quad (4)$$

In Refs. 2 and 3, it was argued that this condition alone does not lead to a mathematically well-posed optimization problem and is not sufficient to obtain well-behaved solutions in general. The reason is that with this condition alone, the constrained minimization of the total energy of a DFA that is contaminated with SIs (i.e., whose unconstrained screening density corresponds to $Q_{\text{rep}}^{\text{DFA}} = N$) would not lead to a well-converged solution. It would be

TABLE I. Ionization potentials, in eV, using cc-pVTZ basis sets for various molecules obtained with different DFAs (a) with the standard KS scheme and (b) using the optimization of the screening-density amplitude proposed here, compared with vertical experimental (Exp) ionization potentials.⁴⁹ Hartree–Fock (HF) Koopmans’ results are also shown. For each DFA, the average absolute percentage error, $\Delta = (100/N) \sum_i |(\chi_i - \chi_i^{(\text{Exp})}) / \chi_i^{(\text{Exp})}|$, is also included.

System	LDA		PBE		B3LYP		HF	Exp.
	(a)	(b)	(a)	(b)	(a)	(b)		
He	15.30	23.13	15.63	23.65	17.91	23.77	24.97	24.59
Ne	13.01	18.96	12.79	19.15	15.18	19.66	23.01	21.60
Be	5.62	8.54	5.65	8.74	6.36	8.62	8.42	9.32
H ₂	10.21	15.50	10.38	15.83	11.84	15.79	16.21	15.43
H ₂ O	6.85	11.28	6.72	10.93	8.39	11.26	13.73	12.78
NH ₃	5.9	9.82	5.84	9.52	7.23	9.82	11.64	10.80
CH ₄	9.36	12.90	9.38	12.60	10.72	12.83	14.82	13.60
O ₃	8.03	10.86	7.83	11.00	9.60	11.46	13.18	12.73
C ₂ H ₂	7.26	10.53	7.10	10.24	8.09	10.51	11.07	11.49
C ₂ H ₄	6.86	9.85	6.69	9.60	7.58	9.61	10.24	10.68
C ₂ H ₅	5.75	8.61	5.69	8.31	6.92	8.67	10.73	9.85
SiH ₄	8.47	11.28	8.51	11.39	9.68	11.35	13.23	11.00
H ₂ O ₂	6.10	9.78	5.97	9.31	7.68	9.82	13.08	11.70
O ₂	5.95	9.63	5.70	9.63	7.04	9.95	12.78	12.30
CO ₂	9.19	12.37	8.97	12.25	10.35	12.41	14.74	13.78
CO	9.09	12.56	9.03	12.6	10.56	12.96	15.14	14.01
Li ₂	3.23	5.14	3.22	5.16	3.65	5.10	4.89	5.11
CH ₃ OH	6.07	9.42	5.99	9.13	7.50	9.31	12.22	10.96
C ₂ H ₆	8.01	11.01	8.07	10.80	9.36	11.3	13.22	11.99
CH ₃ NH ₂	5.24	8.43	5.20	7.99	6.52	8.27	10.66	9.65
C ₂ H ₅ OH	6.03	8.85	5.95	8.39	7.43	8.84	11.99	10.00
Δ	38.87	9.74	39.4	11.21	28.21	9.14	8.31	

TABLE II. Same as in Table I, but for cc-pVQZ basis sets.

System	LDA		PBE		B3LYP		HF	Exp.
	(a)	(b)	(a)	(b)	(a)	(b)		
He	15.32	23.13	15.66	23.59	17.93	23.73	24.98	24.59
Ne	13.23	19.06	13.03	18.77	15.38	19.34	23.10	21.60
Be	5.62	8.52	5.65	8.77	6.36	8.62	8.42	9.32
H ₂	10.22	15.48	10.39	15.81	11.84	15.80	16.21	15.43
H ₂ O	7.07	11.33	6.94	11.11	8.57	11.49	13.82	12.78
NH ₃	6.06	9.88	5.99	9.66	7.36	9.96	11.69	10.80
CH ₄	9.37	12.98	9.40	12.67	10.73	13.01	14.83	13.60
O ₃	8.12	11.41	7.93	11.36	9.68	11.73	13.22	12.73
C ₂ H ₂	7.29	10.54	7.14	10.13	8.12	10.52	11.10	11.49
CO ₂	9.24	12.86	9.03	12.23	10.41	12.84	14.79	13.78
Li ₂	3.23	5.13	3.22	5.17	3.65	5.12	4.90	5.11
N ₂	10.34	14.10	10.22	13.77	11.94	14.16	16.33	15.58
Δ	37.15	7.19	37.54	8.55	27.21	6.54	6.02	

energetically favorable for the constrained minimization to converge to a screening density that locally, near the system, matches the unconstrained screening density, integrating locally to screening charge N ; the constraint $Q_{\text{rep}} = N - 1$ would then be satisfied by distributing negative screening charge of -1 away from the system, depending on the size of the auxiliary basis. In Ref. 5, an investigation of constrained minimization is shown, imposing the constraint just on the norm of the screening charge (4). A proposed successful solution in Refs. 2–4 is to supplement this condition with the positivity of ρ_{rep} at all points in space:

$$\rho_{\text{rep}}(\mathbf{r}) \geq 0, \quad \forall \mathbf{r}. \quad (5)$$

This condition is sufficient to yield well-behaved solutions, although it is not necessarily satisfied by the exact KS potential. It concerns the whole Hxc screening density, which is mostly positive because the Hartree repulsion dominates. So, according to this condition, the xc part of the screening density cannot exceed, in absolute

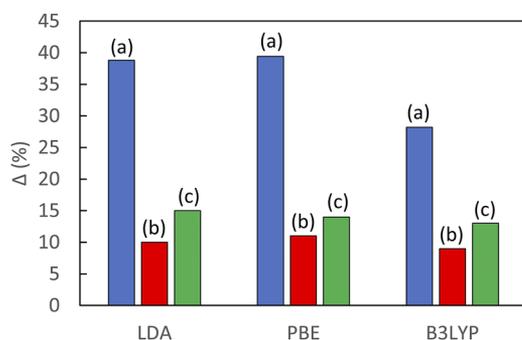


FIG. 1. Average absolute percentage error, Δ , defined in the caption of Table I, in the IPs for various DFAs calculated with (a) the standard KS scheme, (b) the present method, and (c) results from Refs. 2 and 3.

TABLE III. Calculated ionization potentials, in eV, for cc-pVTZ basis sets for various molecules using the present variant of LRDMFT of optimizing the screening-density amplitude and different functionals of the 1RDM, compared with vertical experimental ionization potentials.⁴⁹ Hartree–Fock Koopmans’ results are also shown. The average absolute percentage errors, defined in the caption of Table I, are also included.

System	Müller	BBC3	POW	ML	PNOF5	HF	Exp.
He	24.67	24.62	24.78	25.05	24.35	24.97	24.59
Ne	21.76	22.34	22.22	22.76	22.58	23.01	21.6
Be	9.41	8.93	8.80	8.74	8.72	8.42	9.32
H ₂	16.27	16.18	16.16	16.23	16.14	16.21	15.43
H ₂ O	13.19	12.9	12.89	13.39	13.39	13.73	12.78
NH ₃	11.62	11.12	11.13	11.36	11.31	11.64	10.80
CH ₄	14.11	14.10	13.91	14.23	14.12	14.82	13.60
O ₃	14.02	12.87	14.10	13.19	12.42	13.18	12.73
C ₂ H ₂	12.20	11.26	11.47	11.62	11.50	11.07	11.49
C ₂ H ₄	10.98	10.59	10.73	10.92	10.74	10.24	10.68
C ₂ H ₅ N	11.33	10.40	10.53	10.37	10.37	10.73	9.85
SiH ₄	11.33	11.72	10.39	10.38	11.07	13.24	11.00
H ₂ O ₂	11.31	11.70	11.18	12.25	11.53	13.08	11.70
O ₂	13.04	11.9	12.98	11.90	12.24	12.78	12.30
CO ₂	14.29	14.82	14.61	15.23	14.86	14.74	13.78
CO	14.44	14.57	14.79	13.73	14.37	15.14	14.01
Li ₂	5.96	4.99	5.06	4.91	4.87	4.89	5.11
CH ₃ OH	11.00	10.93	11.00	11.20	11.07	12.22	10.96
C ₂ H ₆	12.01	12.29	12.11	12.53	12.24	13.22	11.99
CH ₃ NH ₂	10.24	9.69	9.88	10.00	9.81	10.66	9.65
C ₂ H ₅ OH	10.35	9.78	10.80	10.61	10.00	11.97	10.00
Δ	5.04	2.98	4.17	4.70	3.30	8.5	

size, the electronic density at any point in space. Unfortunately, this supplementary condition results in an additional computational cost since it has to be verified and enforced for all points in space.

A choice that renders the positivity condition redundant is to introduce a new variational parameter, namely an effective screening-density amplitude, f , such that

$$\rho_{\text{rep}}(\mathbf{r}) = f(\mathbf{r})^2. \quad (6)$$

In order to get the derivative of the total energy, E , with respect to f , we apply a chain rule and obtain

$$\frac{\delta E[f]}{\delta f(\mathbf{x})} = 2f(\mathbf{x}) \left[\tilde{b}(\mathbf{x}) - \int d\mathbf{y} \tilde{\chi}(\mathbf{x}, \mathbf{y}) f^2(\mathbf{y}) \right], \quad (7)$$

where

$$\tilde{b}(\mathbf{x}) = \int d\mathbf{r} \frac{1}{|\mathbf{r} - \mathbf{x}|} \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') V_{\text{Hxc}}(\mathbf{r}'), \quad (8)$$

and

$$\tilde{\chi}(\mathbf{x}, \mathbf{y}) = \iint d\mathbf{r} d\mathbf{r}' \frac{\chi(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{x}| |\mathbf{r}' - \mathbf{y}|}. \quad (9)$$

The quantity $\chi(\mathbf{r}, \mathbf{r}')$ is the KS density–density response function given by

$$\chi(\mathbf{r}, \mathbf{r}') = 2 \sum_i \sum_{\alpha} \frac{\phi_i(\mathbf{r}) \phi_i(\mathbf{r}') \phi_{\alpha}(\mathbf{r}) \phi_{\alpha}(\mathbf{r}')}{\epsilon_i - \epsilon_{\alpha}}. \quad (10)$$

Due to its similarity with an orbital, we can expand the amplitude f in the same local basis set employed to expand the molecular orbitals, $f(\mathbf{r}) = \sum_k f_k \xi_k(\mathbf{r})$ and we obtain

$$\frac{\partial E}{\partial f_n} = 2 \sum_k B_{nk} f_k - 2 \sum_{kml} f_k A_{nkml} f_m f_l, \quad (11)$$

where

$$A_{nkml} = \iint d\mathbf{x} d\mathbf{y} \xi_n(\mathbf{x}) \xi_k(\mathbf{x}) \tilde{\chi}(\mathbf{x}, \mathbf{y}) \xi_m(\mathbf{y}) \xi_l(\mathbf{y}), \quad (12)$$

$$B_{nk} = \int d\mathbf{x} \xi_n(\mathbf{x}) \tilde{b}(\mathbf{x}) \xi_k(\mathbf{x}). \quad (13)$$

TABLE IV. Same as in Table III, for cc-pVQZ basis sets.

System	Müller	BBC3	POW	PNOF5	HF	Exp.
He	24.67	24.61	24.78	24.41	24.98	24.59
Ne	21.59	22.3	22.24	22.72	23.10	21.60
Be	9.24	8.80	8.59	8.49	8.42	9.32
H ₂	16.13	16.11	16.11	16.13	16.21	15.43
H ₂ O	12.90	13.15	12.60	13.09	13.82	12.78
NH ₃	11.60	11.15	10.97	11.60	11.69	10.80
CH ₄	13.68	13.92	13.83	14.14	14.83	13.60
O ₃	13.54	12.42	13.58	12.53	13.22	12.73
C ₂ H ₂	11.94	10.72	10.73	10.43	11.10	10.68
CO ₂	14.15	14.47	14.13	13.90	14.79	13.78
Li ₂	5.98	5.00	5.04	4.88	4.90	5.11
N ₂	15.91	15.99	16.36	15.60	16.33	15.58
Δ	4.56	2.87	3.06	3.55	6.10	

Equation (11) no longer leads to a linear equation unlike the equation derived in our previous work.² Here, we solve directly the minimization problem of E using standard minimization techniques,⁵⁰ which require the gradient with respect to f_n of Eq. (11).

The optimization with respect to f has to be carried out in the domain of amplitudes normalized to $N - 1$ according to the constraint of Eq. (4). This requirement can be incorporated by the Lagrange multipliers technique. However, in this work, we chose an alternative equivalent way by introducing an auxiliary amplitude, $f'(\mathbf{r})$, as our variational quantity that is not normalized, i.e.,

$$f_n = s f'_n, \quad s = \frac{\sqrt{N-1}}{\|f'\|}, \quad (14)$$

where $\|f'\|^2 = \int d\mathbf{x} (f'(\mathbf{x}))^2 = \sum_{kl} f'_k S_{kl} f'_l$ and $S_{kl} = \int d\mathbf{r} \xi_k(\mathbf{r}) \xi_l(\mathbf{r})$. Then, the gradient with respect to f' is

$$\frac{\partial E}{\partial f'_n} = s \frac{\partial E}{\partial f_n} - \frac{s}{\|f'\|^2} \sum_m \frac{\partial E}{\partial f'_m} f'_m \sum_{\lambda} S_{n\lambda} f'_{\lambda}. \quad (15)$$

Through Eq. (14), E becomes as functional of f' , $E = E[f] = E[s f']$, and can be minimized through an unconstrained variation with respect to f' , using the gradient with respect to f' given in Eq. (15).

In principle, one can expand the auxiliary amplitude f' (or equivalently f) in any set of basis functions, different from that of the orbitals. In this first implementation, however, we chose to expand it in the same basis set as the orbitals. This is a restriction compared to our previous work, where ρ_{rep} was expanded in a different (auxiliary) basis set. However, due to the similarity of the screening-density amplitude to an orbital, as we will demonstrate, this choice does not affect the accuracy of our results. We implemented the present method in the HIPPO computer code.⁵¹

III. APPLICATIONS

A. Application to DFAs

As a first application, we use the effective screening density amplitude method for the constrained optimization of DFAs for

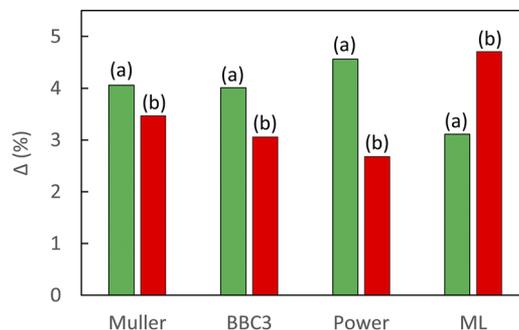


FIG. 2. Average absolute percentage error Δ , defined in the caption of Table I, in the IPs calculated with LRDMFT for various functionals with (a) the method of Ref. 26 and (b) the present method.

TABLE V. Ionization potentials, in eV, calculated with LRDMFT for various 1-RDM functionals and cc-pVTZ basis sets using (a) the method of Ref. 26 and (b) the present method.

	Müller (a)	Müller (b)	BBC3 (a)	BBC3 (b)	Power (a)	Power (b)	ML (a)	ML (b)	Exp.
He	24.69	24.67	24.57	24.62	24.84	24.78	25.15	25.05	24.59
Be	9.51	9.41	8.73	8.93	8.58	8.80	8.55	8.74	9.32
Ne	22.9	21.76	20.92	22.34	21.65	22.22	21.32	22.76	21.6
H ₂	16.24	16.27	16.15	16.18	16.15	16.16	16.28	16.23	15.43
H ₂ O	12.59	13.19	12.03	12.9	12.1	12.89	12.64	13.39	12.78
NH ₃	11.03	11.62	10.65	11.12	10.74	11.13	10.95	11.36	10.8
CH ₄	13.55	14.11	13.72	14.1	13.43	13.91	13.84	14.23	13.6
C ₂ H ₂	11.67	12.2	11.12	11.26	11.46	11.47	11.59	11.62	11.49
C ₂ H ₄	10.68	10.98	10.45	10.59	10.47	10.73	10.9	10.92	10.68
CO ₂	13.81	14.29	13.67	14.82	13.3	14.61	14.42	15.23	13.78

molecular systems. The effect of applying this method to common DFAs is to improve the values of the ionization potentials as calculated from the highest occupied molecular orbital (HOMO) energies in the same manner as in Refs. 2 and 3.

Our results for several molecules and different DFAs are presented in Tables I and II using the cc-pVTZ and cc-pVQZ basis sets, respectively, compared with results from plain DFAs and the experiment values of (vertical) IPs obtained from the NIST WebBook.⁴⁹ As we see, the corrected DFAs have an error of roughly half that of the uncorrected functionals. These corrected IPs have a similar error to those from Hartree–Fock without needing to perform a non-local calculation. As mentioned, the screening-density amplitude is expanded on the same basis as the orbitals and that introduces an additional basis set dependence of the IPs. Reasonably, the results of the larger cc-pVQZ basis sets are superior.

The present results are in line with those of our previous work^{2,3} where the ρ_{rep} was the variational parameter and the positivity had to be enforced additionally. This is shown in Fig. 1 where we compare the average absolute percentage errors for the present method with those of Ref. 3. However, we should note that the results of Ref. 3 are obtained with cc-pVDZ orbital basis and an auxiliary uncontracted cc-pVDZ basis for the screening density. The present method has enhanced convergence compared to that of Ref. 2 in the objective functional minimization and provides a more robust framework.

B. Application to local-RDMFT

As a second application of the present constrained minimization, we considered LRDMFT, i.e., we minimized functionals of the 1RDM under the subsidiary condition that the orbitals are eigenfunctions of a single particle Hamiltonian with local potential. The repulsion part of this potential is assumed to be of the form of Eq. (2) where ρ_{rep} is given by the quadratic form of Eq. (6). The occupation numbers are minimized directly as in standard RDMFT calculations.

For the calculations, we employed five popular approximate RDMFT functionals, namely Müller,⁴⁵ BBC3,³³ Power,⁴⁴ ML,³⁵ and PNOF5.⁴⁶ As far as the basis sets are concerned, the cc-pVTZ and

cc-pVQZ were employed for expanding both the orbitals and the screening-density amplitude for selected systems. However, due to limitations of the HIPPO code, *g*-functions were removed from the cc-pVQZ basis set, a modification that is not expected to affect our results.

We compare energy eigenvalues of the HOMOs with the values of (vertical) experimental IPs (from NIST WebBook⁴⁹), in Tables III and IV for the two different basis sets, respectively. For comparison, we also calculated IPs from standard Hartree–Fock through Koopman’s theorem. As we see, there is a general trend of improvement of the results with the size of the basis set, i.e., the results of the cc-pVQZ basis set are better than those of cc-pVTZ. Nevertheless, our results are of similar quality to those of Refs. 26 and 27, as seen in Fig. 2 and Table V. As we see, BBC3, Power, and PNOF5 functionals are yielding very good results compared with the experiment.

IV. CONCLUSION

In conclusion, we present a variant of the constrained local potential optimization method,² where an effective screening-density amplitude is introduced, replacing the screening density as the variational parameter. With this choice, the positivity condition of the screening density is automatically satisfied, and thus, it does not need to be imposed. This condition was proven necessary in many cases to obtain reasonable effective local potentials without certain pathologies in the asymptotic region. However, its explicit imposition is a formidable task, and in this work, we circumvent this problem by assuming a quadratic form for the screening density. The price to pay is that the optimization with respect to the effective amplitude is no longer equivalent to the solution of a set of linear equations. Although linearization schemes can be applied to solve these equations, we chose, in this first application, to solve the problem by a direct minimization algorithm. In addition, for simplicity, we expanded the effective amplitude in the same basis set as the orbitals.

We demonstrate that, with the present method, accurate local potentials are obtained, as evidenced by the agreement of the obtained IPs (for several DFAs) with those of our previous work and the experiment. Thus, the choice of expanding the effective

amplitude in the same basis set as the orbitals is not affecting the method's accuracy. This accuracy, as expected, improves with the size of the basis set. In addition, similarly, we applied the effective amplitude method to local RDMFT, i.e., we minimized functionals of the 1RDM in terms of the effective amplitude. We found that the obtained IPs are of similar quality to those of Refs. 26 and 27, i.e., the present minimization technique offers a more efficient and robust method in LRDMFT.

The pursuit of high-quality spectral properties coming from single particle Kohn–Sham theoretical models is of central importance, and there exist numerous efforts addressing this issue.^{52–57} The methodology of applying additional constraints to the potential and in that way enforcing exact properties is an elegant and promising solution that is applicable to any DFA by modifying the potential but not the energy functional.^{2–5} As such, it is fairly easy to implement in existing computer codes. If tuned, we obtain very accurate ionization potentials compared to other theoretical models and experiments.²⁵ With the present proposition, this methodology becomes simpler, more robust, and more efficient than previous implementations yet equally accurate.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Thomas C. Pitts: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Writing – review & editing (equal). **Sofia Bousiadi:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Nikitas I. Gidopoulos:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal). **Nektarios N. Lathiotakis:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Software (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

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

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