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Functional Derivatives of Meta-Generalized Gradient Approximation (Meta-GGA) Type Exchange-Correlation Density Functionals

Federico Zahariev
_Iowa State University_, fzahari@iastate.edu

Sarom Sok Leang
_Iowa State University_, ssok1@iastate.edu

Mark S. Gordon
_Iowa State University_, mgordon@iastate.edu

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Functional Derivatives of Meta-Generalized Gradient Approximation (Meta-GGA) Type Exchange-Correlation Density Functionals

Abstract
Meta-generalized gradient approximation (meta-GGA) exchange-correlation density functionals depend on the Kohn-Sham (KS) orbitals through the kinetic energy density. The KS orbitals in turn depend functionally on the electron density. However, the functional dependence of the KS orbitals is indirect, i.e., not given by an explicit expression, and the computation of analytic functional derivatives of meta-GGA functionals with respect to the density imposes a challenge. The practical solution used in many computer implementations of meta-GGA density functionals for ground-state calculations is abstracted and generalized to a class of density functionals that is broader than meta-GGAs and to any order of functional differentiation. Importantly, the TDDFT working equations for meta-GGA density functionals are presented here for the first time, together with the technical details of their computer implementation. The analysis presented here also uncovers the implicit assumptions in the practical solution to computing functional derivatives of meta-GGA density functionals. The connection between the approximation that is invoked in taking functional derivatives of density functionals, the non-uniqueness with respect to the KS orbitals, and the non-locality of the resultant potential is also discussed.

Keywords
Density functional theory, Ground states, Exchange correlation functionals, Laser Doppler velocimetry, Excitation energies

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F. Zahariev, S. S. Leang, and Mark S. Gordon

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I. INTRODUCTION

In recent years, density functional theory (DFT)\(^1\)-\(^3\) and its time-dependent version (TDDFT)\(^4\)-\(^7\) that is commonly used to study electronic excited states have arguably been the most popular computational chemistry methods for the study of the ground- and excited-state properties of relatively large molecular systems that are practically inaccessible to well correlated wavefunction methods.

The rigorous foundation of DFT was established by the Hohenberg-Kohn theorems\(^8\) that were further simplified and extended by Levy’s “constrained search” method.\(^7\) Shortly after the Hohenberg-Kohn theorems were proved, Kohn and Sham developed a practical computational scheme\(^8\) using orbitals (now called Kohn-Sham (KS) orbitals) in the computation of the electron density and energy. There is an alternative orbital-free approach to DFT\(^9\) based on a generalization of the Thomas-Fermi model,\(^10\)-\(^12\) but at present the KS approach represents the mainstream of DFT, due to its superior description of the kinetic energy that is very difficult to approximate.

The KS approach to DFT converts a real interacting electronic system into an auxiliary non-interacting electronic system (independent particle model, analogous to Hartree-Fock) that is, in principle, capable of reproducing the exact ground-state density and energy of the real system.\(^8\) A crucial ingredient in constructing the KS non-interacting electronic system is the exchange-correlation energy \(E_{xc}(\rho)\), a functional of the electron density \(\rho(\vec{r})\). The theoretically exact exchange-correlation functional \(E_{xc}(\rho)\) is known to be universal, i.e., applicable to all possible many-electron systems covering the entire range from single atoms to potentially infinite solids and including all possible molecular systems. The explicit form of \(E_{xc}(\rho)\) is presently unknown and is approximated, in practice. The functional derivative of the exchange-correlation energy produces the exchange-correlation potential \(v_{xc}(\vec{r}) = \frac{\delta E_{xc}(\rho)}{\delta \rho(\vec{r})}\), which is the unknown component of the single-particle KS potential \(v_0(\vec{r})\). The single-particle potential \(v_0(\vec{r})\) determines the KS orbitals \(\psi_j(\vec{r})\).

Perdew described a “Jacob’s ladder” metaphor\(^13\) in which the “rungs” (levels of sophistication) of density functional approximations ultimately lead to the “Heaven” of chemical accuracy. The first few “rungs” are populated by density functionals that had already been invented at that time, and the rest are waiting to be populated in the future. The first “rung” consists of density functionals that are classified as local density approximations (LDAs).\(^14\)-\(^19\) The second “rung” consists of density functionals that depend explicitly on both the electron density and the density gradient \(\nabla \rho(\vec{r})\) and are referred to as generalized gradient approximations (GGAs).\(^20\)-\(^25\) The GGA density functionals increase the level of accuracy previously achieved by the LDA. The third “rung” consists of density functionals that in addition to \(\rho(\vec{r})\) and \(\nabla \rho(\vec{r})\) depend explicitly on the kinetic energy-density \(\tau(\vec{r})\), a quantity expressed in terms of the occupied KS orbitals \(\psi_j(\vec{r})\). Density functionals in the third “rung” are called meta-GGAs,\(^26\)-\(^47\) and they strive for wider applicability and better accuracy than LDA or GGA functionals. There are two main categories of meta-GGAs: empirical and non-empirical. The Minnesota set of meta-GGA density functionals MXX (M05, M06, M08, and M11),\(^30\)-\(^37\) for example, are based on empirically fitting the parameters of generalizations to the V598 meta-GGA density functional\(^29\) based on large molecular databases. On the other hand, the meta-GGA density functionals of Perdew and

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\(^3\)mgordon@iastate.edu
collaborators and others who have followed the Perdew approach (PKZB, TPSS, etc.) are based on first principles and utilize theoretical constraints. The fourth “rung” of “Jacob’s ladder” uses the exchange-energy density in addition to all of the previous ingredients and are termed hyper-GGAs. Hyper-GGAs include all of the global hybrid functionals, such as B3LYP, B3PW91, PBE0, as well as local hybrid density functionals. There is also an important family of range-separated hybrid density functionals in the fourth “rung,”. For an application of range-separated hybrid density functionals to solid-state physics, see Ref. 52. The fifth “rung” adds unoccupied KS orbitals and KS energies to the ingredients from the fourth “rung.” Examples include density functionals based on the random phase approximation and a KS version of the coupled-cluster and other ab initio methods.

The kinetic energy density \( \tau(\vec{r}) \) dependence of meta-GGA density functionals introduces an analytic difficulty in calculating the functional derivative with respect to the electron density \( \rho(\vec{r}) \). The optimized effective potential (OEP) method provides a solution to the problem, but the OEP formalism is complicated and computationally demanding. Consequently, most computer implementations of meta-GGA density functionals for ground-state calculations use the Neuman-Nobes-Handy (NNH) formula. An abstraction of the implicit approach used in the NNH formula is developed in the current study and termed the analytic “orbital-based density-functional derivative method” (ODDM). This terminology is intended to reflect the essential characteristics of the presented method. The NNH formula is identically recovered here within a systematic development starting from simple basic principles. Importantly, the present approach allows the ODDM to be extended to density functionals beyond the meta-GGA family and easily applied to any order of functional differentiation. An essential point is that the analysis presented in this work reveals the underlying assumptions that are used, but not widely recognized, in the computation of functional derivatives of meta-GGA density functionals. The underlying assumptions mentioned here make the ODDM, in general, and the NNH formula, in particular, approximate. It is emphasized that “exact” (or “approximate”) in this context means that the functional derivative of some density functional is reproduced exactly (or approximately). It is shown here that the xc-potential obtained by the NNH formula is not a local multiplicative potential; moreover, the xc potential is not unique with respect to the KS orbitals. This is in contrast to the expected behavior of an exact xc-potential \( v_{XC}(\rho(\vec{r})) = \frac{E_{XC}(\rho)}{\rho} \) that is based on the exact functional differentiation with respect to the density.

The explicit expressions for the second-order functional derivatives of meta-GGA density functionals that are needed for TDDFT calculations are presented here for the first time. In addition, technical aspects related to the implementation of multiple meta-GGA exchange-correlation density functionals for both DFT and TDDFT into the General Atomic Molecular Electronic Structure System (GAMESS) quantum chemistry package are discussed. For a benchmarking study on the performance of meta-GGA density functionals in TDDFT, the reader is referred to a previous paper by the authors that is based on the working equations that are presented in the Appendix.

The text is organized as follows. In Sec. II the fact that the KS orbitals are implicit density functionals is recalled, the difficulty of taking an analytic functional derivative of meta-GGA density functionals is demonstrated, and the OEP method is briefly reviewed. Section III formulates the ODDM. This approach is demonstrated by applying it to the first-order functional derivative of meta-GGA density functionals and subsequently generalized to higher-order functional derivatives. The explicit expressions for the second functional derivative of meta-GGA density functionals are provided in the Appendix. Section IV analyzes in detail the underlying assumptions in the ODDM that make this method approximate. Section V discusses the degree of non-locality of the resultant potentials. Section VI briefly discusses the technical aspects of the implementation of meta-GGA functional derivatives for DFT and TDDFT. Section VIII summarizes the results and outlines some future directions. Section VII gives sample numerical results based on the TDDFT working equations from the Appendix.

II. ANALYTIC FUNCTIONAL DERIVATIVES OF ORBITAL DEPENDENT EXCHANGE-CORRELATION FUNCTIONALS

The main topic of interest in this paper is the analysis of the challenges that are involved in taking the analytic functional derivatives of meta-GGA exchange-correlation (xc) density functionals. The general form of a meta-GGA functional is

\[
E_{XC}[\rho] = \int e_{XC}(\rho(\vec{r}), \nabla \rho(\vec{r}), \tau(\vec{r})) d\vec{r},
\]

where \( e_{XC} \) is a regular function, and the kinetic-energy density is given by

\[
\tau(\vec{r}) = \frac{1}{2} \sum_i [\nabla \psi_i(\vec{r})] \cdot [\nabla \psi_i(\vec{r})].
\]

Note that the kinetic energy density that follows directly from the KS system is a different, Laplacian-based expression:

\[
\tau^{\ell}(\vec{r}) = -\frac{1}{2} \sum_i \psi_i(\vec{r}) \nabla^2 \psi_i(\vec{r}).
\]

Since the two forms of the kinetic-energy density differ by a full differential \( \frac{1}{2} \nabla^2 \rho(\vec{r}) \) that integrates to zero, the integrals of both \( \tau(\vec{r}) \) and \( \tau^{\ell}(\vec{r}) \) have the same kinetic-energy value (see Ref. 69, for example). In general, there is an infinite variety of kinetic-energy density forms that differ from \( \tau(\vec{r}) \) by some full differential expression. Although all of these expressions upon integration give the same kinetic energy value, the use of different forms of the kinetic energy density in Eq. (1) would lead to different exchange-correlation energies. This is because the kinetic energy density is first transformed by some expression on the right-hand side of Eq. (1) before the integration is applied. Consequently, the additional full differential expression does not simply integrate away. Typically, the kinetic energy density in the form of Eq. (2) is preferred as it is non-negative and involves only gradients.
The first functional derivative of $E_{XC}[\rho]$ with respect to the density $\rho(\vec{r})$ involves the computation of $\frac{\delta E_{XC}[\rho]}{\delta \rho(\vec{r})}$ and $\frac{\delta \psi_i(\vec{r})}{\delta \rho(\vec{r})}$ since the kinetic energy density $\tau(\vec{r})$ is expressed in terms of the KS orbitals $\psi_i(\vec{r})$. The functional derivatives of $\frac{\delta E_{XC}[\rho]}{\delta \rho(\vec{r})}$ and $\frac{\delta \psi_i(\vec{r})}{\delta \rho(\vec{r})}$ are meaningful only if the KS orbitals $\psi_i[\rho(\vec{r})]$ and, consequently, the kinetic energy density $\tau[\rho(\vec{r})]$ are expressed as functions of the density $\rho(\vec{r})$.

In order to demonstrate that the KS orbitals $\psi_i(\vec{r})$ are themselves implicitly density functionals, recall the constrained search derivation of the KS system. At first, using real-valued KS orbitals $\psi_i(\vec{r})$, the kinetic energy universal functional is defined as

$$T_i[\rho] = \min_{\Phi \rightarrow \rho} \left( \Phi \right) 
= \min_{i = 1}^{N} \left[ \frac{1}{2} \sum_{i=1}^{N} \int \psi_i(\vec{r}) \nabla^2 \psi_i(\vec{r}) \right], \tag{4}$$

where $\Phi$ is a determinant composed of $N$ orthonormal single-particle orbitals $\{ \psi_i(\vec{r}) ; i = 1, 2, \ldots, N \}$ and $\Phi \rightarrow \rho$ means that the wavefunction $\Phi$ yields the density $\rho$:

$$\rho(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2. \tag{5}$$

Equation (4) is an example of a constrained search in which the search for a wavefunction $\Phi$ that minimizes the kinetic energy of a non-interacting system is subject to the constraint in Eq. (5). It is known that the minimum on the RHS of Eq. (4) exists, i.e., there is a set of orbitals $\{ \psi_{i_{min}}(\vec{r}) ; i = 1, 2, \ldots, N \}$ such that

$$T_i[\rho] = -\frac{1}{2} \sum_{i=1}^{N} \int \psi_{i_{min}}(\vec{r}) \nabla^2 \psi_{i_{min}}(\vec{r}), \tag{6}$$

while still yielding the density $\rho(\vec{r})$ as in Eq. (5). The set of orbitals $\{ \psi_{i_{min}}(\vec{r}) ; i = 1, 2, \ldots, N \}$ clearly depends on the density $\rho(\vec{r})$ through the constrained search; hence, the orbitals are implicitly functionals of this density: $\{ \psi_{i_{min}}[\rho(\vec{r})] ; i = 1, 2, \ldots, N \}$.

For example, consider a ground-state density $\rho(\vec{r})$ (for simplicity it is assumed there is no degeneracy). Then $\{ \psi_{i_{min}}[\rho(\vec{r})] ; i = 1, 2, \ldots, N \}$ are the KS orbitals that correspond to this ground-state density $\rho(\vec{r})$. The corresponding KS orbital energies $\{ \epsilon_i ; i = 1, 2, \ldots, N \}$ are also implicit functionals of the density $\rho(\vec{r})$, i.e., $\{ \epsilon_i[\rho] ; i = 1, 2, \ldots, N \}$.

The foregoing can also be understood from the perspective of the first Hohenberg-Kohn theorem as applied to a KS system. Given a ground-state density $\rho(\vec{r})$, one should, in principle, be able to recover the KS potential $v(\vec{r})$ that generates this density and, consequently, the KS orbitals and orbital energies $\{ \psi_i[\rho(\vec{r})], \epsilon_i[\rho] ; i = 1, 2, \ldots, N \}$.

In practice, one can achieve the above functional dependence by using the “Kohn-Sham inversion” (KSI) technique. In this numerical procedure one starts with a reasonable approximation of the ground-state density $\rho(\vec{r})$.

This starting density is reasonably obtained, for example, using coupled cluster with singles and doubles (CCSD), Quantum Monte Carlo (QMC), or another accurate computational method. One then iteratively solves a set of equations that ultimately lead to the KS orbitals and orbital energies $\{ \psi_i[\rho(\vec{r})], \epsilon_i[\rho] ; i = 1, 2, \ldots, N \}$ that correspond to the density $\rho(\vec{r})$. The KS inversion algorithm is, in principle, exact and does not involve any approximate density functionals.

The functional dependence of the KS orbitals and energies $\{ \psi_i[\rho(\vec{r}), \epsilon_i[\rho]] ; i = 1, 2, \ldots, N \}$ is not often discussed in the literature. In the present study this functional dependence plays a central role.

Once the density functional dependent set $\{ \psi_i[\rho(\vec{r}), \epsilon_i[\rho]] \}$ of KS orbitals and orbital energies is inserted back into an orbital dependent functional of the type $E_{XC}[\{ \psi_i, \epsilon_i \}]$ (for simplicity it is assumed there is no additional explicit functional dependence on $\rho(\vec{r})$, $\nabla \rho(\vec{r})$, etc.), the pure density-functional dependence of the exchange-correlation energy becomes evident:

$$E_{XC}[\{ \psi_i[\rho(\vec{r}), \epsilon_i[\rho]] \}] = E_{XC}[\rho]. \tag{7}$$

Thus, all orbital-dependent density functionals are true density functionals albeit in an implicit manner. The problem with orbital-dependent density functionals is the technical difficulty involved in computing the exchange-correlation potential:

$$v_{XC}(\vec{r}) = \frac{\delta E_{XC}[\{ \psi_i[\rho(\vec{r}), \epsilon_i[\rho]] \}]}{\delta \rho(\vec{r})} = \sum_i \int \frac{\delta E_{XC}[\{ \psi_i(\vec{r}), \epsilon_i \}]}{\delta \psi_i(\vec{r})} \frac{\delta \psi_i(\vec{r})}{\delta \rho(\vec{r})} + \frac{\delta E_{XC}[\{ \psi_i(\vec{r}), \epsilon_i \}]}{\delta \epsilon_i} \frac{\delta \epsilon_i}{\delta \rho(\vec{r})}. \tag{8}$$

In Eq. (8) the functional version of the chain rule for differentiation is applied. While the functional derivatives $\frac{\delta E_{XC}[\{ \psi_i(\vec{r}), \epsilon_i \}]}{\delta \psi_i(\vec{r})}$ and $\frac{\delta E_{XC}[\{ \psi_i(\vec{r}), \epsilon_i \}]}{\delta \epsilon_i}$ can be computed easily given the explicit form of $E_{XC}[\{ \psi_i(\vec{r}), \epsilon_i \}]$, the functional derivatives $\frac{\delta \psi_i(\vec{r})}{\delta \rho(\vec{r})}$ and $\frac{\delta \epsilon_i}{\delta \rho(\vec{r})}$ are much more difficult to obtain due to the implicit nature of the density functional dependence in $\{ \psi_i[\rho(\vec{r}), \epsilon_i[\rho]] \}$. The density dependence of the KS orbitals and orbital energies is mediated by the KS potential $v_i[\rho(\vec{r})]$. One method for computing the functional derivatives $\frac{\delta \psi_i(\vec{r})}{\delta \rho(\vec{r})}$ and $\frac{\delta \epsilon_i}{\delta \rho(\vec{r})}$ is to use the OEP method. The OEP method is based on response theory and is typically applied in combination with approximations. First, the functional chain-rule is used:

$$\frac{\delta \psi_i[\rho(\vec{r})]}{\delta \rho(\vec{r})} = \int \frac{\delta \psi_i(\vec{r})}{\delta \psi_i(\vec{r}')} \frac{\delta \psi_i(\vec{r}')}{\delta \rho(\vec{r})} + \frac{\delta \psi_i(\vec{r}')}{\delta \rho(\vec{r}')}, \tag{9}$$

and

$$\frac{\delta \epsilon_i[\rho]}{\delta \rho(\vec{r})} = \int \frac{\delta \epsilon_i}{\delta \psi_i(\vec{r}') \delta \rho(\vec{r}')}. \tag{10}$$

From response theory it can be shown that $59-64$

$$\frac{\delta \psi_i(\vec{r})}{\delta \psi_i(\vec{r}')} = -G_i(\vec{r}, \vec{r}') \psi_j(\vec{r}'), \tag{11}$$

where the Green’s function $G_i(\vec{r}, \vec{r}')$ is

$$G_i(\vec{r}, \vec{r}') = \sum_{j \neq i} \frac{\psi_j(\vec{r}) \psi_j(\vec{r}')}{\epsilon_i - \epsilon_j}. \tag{12}$$
and
\[ \frac{\delta E_i}{\delta v_{\psi i}(\vec{r}')} = |\psi_i(\vec{r}'')|^2. \] (13)

Last, \( \frac{\delta E}{\delta \rho(\vec{r}'')} \) is computed by inverting the density-response function
\[ \chi_s(\vec{r}', \vec{r}'') = \frac{\delta \rho(\vec{r}'')}{\delta v_{\psi i}(\vec{r}'')} = \sum_i \frac{\delta |\psi_i(\vec{r}'')|^2}{\delta v_{\psi i}(\vec{r}'')} = -2 \sum_i \psi_i(\vec{r}'') G_i(\vec{r}', \vec{r}'') \psi_i(\vec{r}''). \] (14)

Equation (11) was used to obtain the last equality in Eq. (14).

The inverse density-response function \( \chi_s^{-1}(\vec{r}', \vec{r}'') \) can be represented as
\[ \int \chi_s(\vec{r}', \vec{r}'') \chi_s^{-1}(\vec{r}', \vec{r}'') d\vec{r} = \delta(\vec{r} - \vec{r}''). \] (15)

It is difficult to evaluate the integral required to compute the inverse density response function. Therefore, approximation schemes have been devised within the OEP method. Nonetheless, the OEP method remains a challenge from a numerical point of view, as it extends the original KS system with additional equations that must be solved self-consistently. In Sec. III an alternative to the OEP method is developed for meta-GGA and other similar types of density functionals.

III. ANALYTIC FUNCTIONAL DERIVATIVES OF META-GGA TYPE EXCHANGE-CORRELATION ENERGY FUNCTIONALS

The ODDM that is presented here is based on the following observation. Although it is very difficult to compute \( v_{\psi i}(\vec{r}) = \frac{\delta E_{xc}[\psi_i(\vec{r})]}{\delta \rho(\vec{r})} \) for orbital-based density functionals, it is the product \( v_{\psi i}(\vec{r}) \psi_i(\vec{r}) \) that is used, in practice, not the bare exchange-correlation potential \( v_{\psi i}(\vec{r}) \). For example, it is in the form of the product \( v_{\psi i}(\vec{r}) \psi_i(\vec{r}) \) that the exchange-correlation potential \( v_{\psi i}(\vec{r}) \) appears in the KS method. Most importantly, computer programs commonly use the matrix elements \( \int \psi_i^*(\vec{r}) v_{\psi i}(\vec{r}) \psi_j(\vec{r}) d\vec{r} \) of the exchange-correlation potential \( v_{\psi i}(\vec{r}) \) itself. Also note that
\[ \frac{\delta E_{xc}[\rho]}{\delta \psi_i(\vec{r})} = \int \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \frac{\delta \rho(\vec{r})'}{\delta \psi_i(\vec{r})} d\vec{r}', \] (16)

where the functional version of the chain rule is used, and
\[ \frac{\delta \rho(\vec{r}')}{\delta \psi_i(\vec{r})} = 2 \psi_i(\vec{r}) \delta(\vec{r}' - \vec{r}). \] (17)

Equation (17) follows directly from Eq. (5). Here, it is assumed that the set of orthonormal orbitals \( \{\psi_i(\vec{r}); i = 1, 2, \ldots, N\} \) is constrained only by Eq. (5); i.e., these orbitals are not necessarily the ones that minimize the kinetic-energy expression in Eq. (4). Such orbitals are referred to here as “pre-KS orbitals” for convenience, because they are an intermediate set of orbitals, not the ones that one would obtain in at the convergence of a KS calculation. The KS orbitals themselves are orthonormal orbitals that satisfy Eq. (5) and achieve a minimum in Eq. (4). Consequently, the pre-KS orbitals are not required to minimize Eq. (4). Equation (17) cannot be interpreted in terms of KS orbitals. The functional derivative in Eq. (17) is not the inverse of the functional derivative in Eq. (9). Moreover, the functional derivative of the density with respect to a KS orbital cannot be consistently defined, because any variation of a KS orbital is due to a variation of the xc-potential, which in turn gives rise to a variation of all the other KS orbitals. Consequently, the original KS orbital variation cannot be an independent variation. The pre-KS orbitals are not functionals of the density, and therefore the functional derivatives of the density with respect to the pre-KS orbitals are well defined. In the remainder of this paper, in those places where the difference between the two sets of orbitals is important, the KS orbitals will be highlighted with the notation \( \{\psi_i^{KS}(\rho)(\vec{r}); i = 1, 2, \ldots, N\} \) or \( \{\psi_i^{KS}(\vec{r}); i = 1, 2, \ldots, N\} \). Combining Eqs. (16) and (17), in terms of pre-KS orbitals, results in
\[ \frac{\delta E_{xc}[\tau][\rho]}{\delta \psi_i(\vec{r})} = \frac{1}{2} \frac{\delta E_{xc}[\tau][\rho]}{\delta \psi_i^{KS}(\vec{r})}. \] (18)

The application of Eq. (18) to meta-GGA type density functionals reduces the computation of the exchange-correlation potential \( v_{\psi i}(\vec{r}) \) to the computation of
\[ \frac{\delta E_{xc}[\tau][\rho]}{\delta \psi_i(\vec{r})} = \frac{1}{2} \frac{\delta E_{xc}[\tau][\rho]}{\delta \psi_i^{KS}(\vec{r})}. \] (19)

For simplicity of presentation it is assumed in Eq. (19) that the exchange-correlation energy \( E_{xc}[\tau] \) depends only on the kinetic energy \( \tau(\vec{r}) \) as defined in Eq. (2), for example, as defined by a simplified form of Eq. (1): \( E_{xc}[\tau] = \int e_{xc}(\tau(\vec{r})) d\vec{r} \). Since the KS orbitals are implicit functionals of the density, i.e., \( \psi_i^{KS}(\rho)(\vec{r}) \), the kinetic energy \( \tau(\vec{r}) \) also becomes an implicit functional of the density and is denoted as \( \tau[\rho](\vec{r}) \). Depending on the context, the notation in the remainder of the paper will emphasize either the dependence of the kinetic energy on the orbitals or on the density or both. The computation of \( \frac{\delta E_{xc}[\tau][\rho]}{\delta \psi_i(\vec{r})} \) in Eq. (19) is often assumed to be a relatively straightforward task, since the kinetic energy \( \tau(\vec{r}) \) in Eq. (2) is expressed in terms of the KS orbitals \( \psi_i^{KS}(\vec{r}) \). The discussion so far has been mathematically exact. However, as discussed in Sec. IV and expressed explicitly in Eq. (20), the evaluation of \( \frac{\delta E_{xc}[\tau][\rho]}{\delta \psi_i(\vec{r})} \) within the ODDM employs a subtle approximation.

\[ \frac{\delta E_{xc}[\tau][\rho]}{\delta \psi_i(\vec{r})} \approx \frac{\delta E_{xc}[\tau]}{\delta \psi_i^{KS}(\vec{r})} = \int \frac{\delta E_{xc}[\tau]}{\delta \tau(\vec{r})} \frac{\delta \tau(\vec{r})}{\delta \psi_i^{KS}(\vec{r})} d\vec{r}'. \] (20)

The approximate nature of the above equality is due to the fact the functional derivatives with respect to the orbitals on the LHS and RHS differ in meaning. On the LHS, the variation of a pre-KS orbital \( \delta \psi_i(\vec{r}) \) leads to a variation \( \delta E_{xc}[\tau][\rho] \) through the intermediate role of the density variation \( \delta \rho(\vec{r}) \) as
in Eqs. (16)–(19). On the RHS, the variation of a KS orbital \( \delta \psi_i^{KS}(\vec{r}) \) leads directly to a change \( \delta E_{XC}[\tau] \) through the variation of the kinetic-energy density \( \delta \tau(\vec{r}) \) following the connection between the KS orbitals \( \{ \psi_i^{KS}(\vec{r}); i = 1, 2, ..., N \} \) and the kinetic-energy density \( \tau(\vec{r}) \) expressed in Eq. (2). Equivalently, the exchange-correlation energy \( E_{XC}[\tau_0] \) on the RHS of Eq. (20) is assumed to be a density functional, while the same exchange-correlation energy \( E_{XC}[\tau] \) on the RHS is assumed to be an orbital functional.

In summary, the root cause of Eq. (20) being approximate rather than exact is that the pre-KS orbitals appear on the RHS of Eq. (20), while the KS orbitals appear on the RHS of Eq. (20). 

\[
\frac{\delta E_{XC}[\tau]}{\delta \rho(\vec{r})} \quad \text{on the right-hand side of Eq. (20)} \quad \text{is relatively easy to compute especially when} \quad E_{XC}[\tau] = \int \epsilon_{XC}(\tau(\vec{r})) d\vec{r} \quad \text{in which case} \quad \frac{\delta E_{XC}[\tau]}{\delta \rho(\vec{r})} = \frac{\delta E_{XC}[\tau]}{\delta \psi_i^{KS}(\vec{r})} \quad \text{and the term}
\]

\[
\frac{\delta \tau(\vec{r}')}{\delta \psi_i^{KS}(\vec{r})} = 2\nabla \psi_i^{KS}(\vec{r}) \nabla \delta(\vec{r}' - \vec{r})
\]

follows directly from Eq. (2).

Equations (19) and (20), and a subsequent integration by parts, produces the ODDM approximation to (as a simple example) the first functional derivative of a pure meta-GGA density functional with respect to the density:

\[
\frac{\delta E_{XC}[\tau]}{\delta \rho(\vec{r})} \approx \frac{1}{2\psi_i^{KS}(\vec{r})} \frac{\delta E_{XC}[\tau]}{\delta \psi_i^{KS}(\vec{r})} = -\frac{1}{\psi_i^{KS}(\vec{r})} \nabla \left( \frac{\delta E_{XC}[\tau]}{\delta \psi_i^{KS}(\vec{r})} \right).
\]

On the LHS of the approximate sign in Eq. (22) the density is expressed as a sum of orbitals to be optimized, i.e., pre-KS orbitals constrained by Eq. (5) only. On the RHS of the approximate sign the orbitals are expressed as the proper KS- orbitals. It is stressed that the ODDM is approximate because of the interchange of pre-KS orbitals with KS orbitals in the middle equality of Eq. (22). While the functional derivative on the far LHS defines the exact xc-potential, \( v_{XC}(\vec{r}) = \frac{\delta E_{XC}[\tau]}{\delta \rho(\vec{r})} \), the xc-potential obtained by applying the ODDM approximation \( v_{ODDM}(\vec{r}) = \frac{1}{2\psi_i^{KS}(\vec{r})} \frac{\delta E_{XC}[\tau]}{\delta \psi_i^{KS}(\vec{r})} \) is non-unique with respect to the KS orbital \( \psi_i^{KS}(\vec{r}) \). Consequently, the ODDM approximation can also be expressed as

\[
v_{XC}(\vec{r}) = \frac{\delta E_{XC}[\tau]}{\delta \rho(\vec{r})} \approx \frac{1}{2\psi_i^{KS}(\vec{r})} \frac{\delta E_{XC}[\tau]}{\delta \psi_i^{KS}(\vec{r})} = v_{ODDM}(\vec{r}).
\]

Surprisingly, \( \frac{\delta E_{XC}[\tau]}{\delta \rho(\vec{r})} \approx \frac{1}{2\psi_i^{KS}(\vec{r})} \frac{\delta E_{XC}[\tau]}{\delta \psi_i^{KS}(\vec{r})} \) is an exact equality for any pre-KS index \( i \) based on Eq. (19).

Having already identified the crucial step in the derivation of ODDM that makes this method approximate in nature, for simplicity of notation, the KS orbitals are not explicitly highlighted for the remainder of this section.

In general, a meta-GGA density functional is given by Eq. (1) and its functional derivative with respect to the density is

\[
\frac{\delta E_{XC}[\rho]}{\delta \rho(\vec{r})} = e_{XC}^{\psi}(\rho(\vec{r}), \nabla \rho(\vec{r}), \tau(\vec{r})) - \nabla e_{XC}^{\psi}(\rho(\vec{r}), \nabla \rho(\vec{r}), \tau(\vec{r})) + \int e_{XC}^{\psi}(\rho(\vec{r}), \nabla \rho(\vec{r}), \tau(\vec{r}))(\frac{\delta \rho(\vec{r})}{\delta \rho(\vec{r})}) d\vec{r},
\]

where the following notation is used: \( e_{XC}^{\psi}(x_1, x_2, x_3) = \frac{\delta e_{XC}(x_1, x_2, x_3)}{\delta x_i}, \quad e_{XC}^{\psi}(x_1, x_2, x_3) = \frac{\delta e_{XC}(x_1, x_2, x_3)}{\delta x_2} \), an integration by parts is done to obtain the second term and the chain rules is used to obtain the third term. The third term in Eq. (24) is an analog of the LHS of Eq. (22), so the application of the ODDM approximation to Eq. (24) amounts to exchanging the RHS with the RHS of Eq. (22) resulting in

\[
\frac{\delta E_{XC}[\rho]}{\delta \rho(\vec{r})} \approx e_{XC}^{\psi}(\rho(\vec{r}), \nabla \rho(\vec{r}), \tau(\vec{r})) - \nabla e_{XC}^{\psi}(\rho(\vec{r}), \nabla \rho(\vec{r}), \tau(\vec{r})) - \frac{1}{\psi_i^{KS}(\vec{r})} \nabla \left[ e_{XC}^{\psi}(\rho(\vec{r}), \nabla \rho(\vec{r}), \tau(\vec{r})) \nabla \psi_i^{KS}(\vec{r}) \right].
\]

Based on Eq. (22), the matrix element of the pure meta-GGA exchange-correlation potential \( \int \psi_i(\vec{r}) \frac{\delta E_{XC}[\tau]}{\delta \rho(\vec{r})} \psi_j(\vec{r}) d\vec{r} \) becomes

\[
\int \psi_i(\vec{r}) \frac{\delta E_{XC}[\tau]}{\delta \rho(\vec{r})} \psi_j(\vec{r}) d\vec{r} \approx \int \frac{\delta E_{XC}[\tau]}{\delta \rho(\vec{r})} \psi_i(\vec{r}) \psi_j(\vec{r}) d\vec{r}. \]

By using Eq. (25) it is not difficult to derive the analog of Eq. (26) for a general meta-GGA density functional as given by Eq. (1). Equation (26) has already appeared in Ref. 65, but without a detailed derivation, without revealing the approximate nature of the above equality, and without pinpointing the actual source of the approximation.

Based on the analysis presented here, it is straightforward to generalize Eq. (26) to a broader class of orbital-based density functionals and to higher-order functional derivatives. The analysis presented in Sec. IV also provides a way to better understand the approximate nature of the analytic ODDM and its natural boundaries of applicability.

For example, consider the matrix element of the TDDFT exchange-correlation kernel \( f_{XC}(\vec{r}, \vec{r}') = \frac{\delta^2 E_{XC}[\tau]}{\delta \psi_i^{KS}(\vec{r}) \delta \psi_j^{KS}(\vec{r})} \):

\[
\int \psi_i(\vec{r}) \psi_j(\vec{r}') f_{XC}(\vec{r}, \vec{r}') \psi_i(\vec{r}) \psi_j(\vec{r}) d\vec{r} d\vec{r}' \approx \frac{1}{4} \int \psi_i(\vec{r}) \psi_j(\vec{r}') \delta^2 E_{XC}[\tau] \psi_i(\vec{r}) \psi_j(\vec{r}) d\vec{r} d\vec{r}'.
\]

Equation (20) is used twice to obtain Eq. (27). Using Eqs. (20) and (21) twice each, the double integral on the right-hand side
of Eq. (27) becomes
\[
\int \int \nabla \psi_p(\vec{r}) \nabla \psi_q(\vec{r}) \frac{\delta^2 E_{\text{XC}}[\rho]}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \nabla \psi_q(\vec{r}) \nabla \psi_p(\vec{r}') d\vec{r} d\vec{r}'.
\]
(28)

Similarly, the matrix elements of the third-order functional derivative of the exchange-correlation energy \(g_{\text{XC}}(\vec{r}, \vec{r}', \vec{r}'')\), which is used for the TD-DFT gradient and non-linear-response TD-DFT, are (using Eq. (20) three times)
\[
\int \int \int \psi_p(\vec{r}) \psi_q(\vec{r}) \psi_r(\vec{r}') \frac{\delta^3 E_{\text{XC}}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}) \delta \rho(\vec{r}'')} \psi_r(\vec{r}'') d\vec{r} d\vec{r}' d\vec{r}''.
\]
\[
\approx \frac{1}{8} \int \int \int \psi_p(\vec{r}) \psi_q(\vec{r}) \psi_r(\vec{r}') \frac{\delta^3 E_{\text{XC}}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}) \delta \rho(\vec{r}'')} \psi_r(\vec{r}'') d\vec{r} d\vec{r}' d\vec{r}''.
\]
(29)

Using Eqs. (20) and (21) three times each, the triple integral on the right-hand side of Eq. (29) becomes
\[
\int \int \int \nabla \psi_p(\vec{r}) \nabla \psi_q(\vec{r}) \nabla \psi_r(\vec{r}') \frac{\delta^3 E_{\text{XC}}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}) \delta \rho(\vec{r}'')} \nabla \psi_r(\vec{r}'') d\vec{r} d\vec{r}' d\vec{r}''.
\]
\[
\nabla \psi_q(\vec{r}) \nabla \psi_r(\vec{r}') d\vec{r} d\vec{r}' d\vec{r}'.
\]
(30)

The Appendix contains the detailed expression needed for the implementation of meta-GGA density functionals in TD-DFT computer programs.

IV. THE APPROXIMATE NATURE OF THE ANALYTIC ODDM

As noted above, Eq. (20) includes a subtle approximation. On the one hand, the functional derivative \(\frac{\delta E_{\text{XC}}[\rho]}{\delta \psi_i(\vec{r})}\) on the left-hand side of Eq. (20) could be interpreted as \(\frac{\delta E_{\text{XC}}[\rho]}{\delta \psi_i(\vec{r})}\). Recall that the kinetic energy \(\tau(\vec{r})\) is defined in Eq. (2) in terms of the Kohn-Sham orbitals \(\psi_i^{KS}(\vec{r})\) that are implicit functionals of the density \(\rho(\vec{r})\). Consequently, the kinetic energy \(\tau(\vec{r})\) is an implicit functional of the density. In addition, recall that the density \(\rho(\vec{r})\) has a functional dependence on the set of pre-KS orbitals \(\{\psi_i(\vec{r})\}_{j=1,2,...,n}\) as given by Eq. (5). \(\frac{\delta E_{\text{XC}}[\rho]}{\delta \psi_i(\vec{r})}\) can be expressed in more detail as \(\frac{\delta E_{\text{XC}}[\rho]}{\delta \psi_i(\vec{r})}_{|\{\psi_i^{KS}(\vec{r})\}_{j=1,2,...,n}}\); i.e., as a functional derivative with respect to a pre-KS orbital through the intermediacy of the density, in which case the chain rule in the form of Eq. (16) applies.

On the other hand, the RHS of Eq. (20) is the application of the chain rule based on a different intermediate form. The kinetic energy \(\tau(\vec{r})\), as defined by Eq. (2), can be thought of as a functional of the KS orbitals: \(\tau(\{\psi_i^{KS}(\vec{r})\}_{j=1,2,...,n})\). Indeed, the RHS of Eq. (20) is equivalent to \(\frac{\delta E_{\text{XC}}[\rho]}{\delta \psi_i(\vec{r})}_{|\{\psi_i^{KS}(\vec{r})\}_{j=1,2,...,n}}\) on the LHS of Eq. (20). More generally, for any orbital-dependent exchange-correlation functional \(E_{\text{XC}}[\{\psi_i^{KS}(\vec{r})\}_{j=1,2,...,n}]\), whether \(\frac{\delta E_{\text{XC}}[\{\psi_i^{KS}(\vec{r})\}_{j=1,2,...,n}]}{\delta \psi_i(\vec{r})}\) equals \(\frac{\delta E_{\text{XC}}[\{\rho(\vec{r})\}_{j=1,2,...,n}]}{\delta \psi_i(\vec{r})}\), the distinction between pre-KS and KS orbitals is suppressed until the end of the paragraph. Now, one might assume that \(\{\psi_i[\rho(\vec{r})]\}_{i=1,2,...,n}\) are the inverse of each other, in the sense that \(\{\psi_i[\rho(\vec{r})]\}_{i=1,2,...,n}\) are equivalent to \(\{\psi_i(\vec{r})\}_{i=1,2,...,n}\), similar to \(x(y(x)) = \tilde{x}\) meaning that \(y = \tilde{x}\) and \(x = \tilde{x}\) are inverse functions. Then, Eq. (20) would be an exact equality. However, in the case of \(\{\psi_i[\rho(\vec{r})]\}_{i=1,2,...,n}\) and \(\{\psi_i(\vec{r})\}_{i=1,2,...,n}\), this assumption can be disproved by considering \(\frac{\delta \psi_i(\vec{r})}{\delta \psi_i(\vec{r})}\) and showing that it is not equal to \(\delta_1(\vec{r} - \vec{r}')\) for the simplest case of the exchange-only LDA; the LDA functional is
\[
E_{\text{LDA}}[\rho] = -\frac{3}{4} \left(\frac{\pi}{3}\right)^{\frac{1}{3}} \int \rho(\vec{r})^{\frac{1}{3}} d\vec{r}.
\]
(31)

Now, apply the chain rule to \(\frac{\delta \psi_i(\vec{r})}{\delta \psi_i(\vec{r})}\) for the functional in Eq. (31):
\[
\frac{\delta \psi_i[\rho(\vec{r})]}{\delta \rho(\vec{r})} = \int \frac{\delta \psi_i[\rho(\vec{r})]}{\delta \rho(\vec{r})} \frac{\delta \rho(\vec{r})}{\delta \psi(\vec{r}') d\vec{r}'.
\]
(32)

Next, the RHS of Eq. (32) is further transformed. By using Eqs. (9), (11), (12), and (31), \(\frac{\delta \psi_i[\rho(\vec{r})]}{\delta \psi(\vec{r}') d\vec{r}'.}\) becomes
\[
\frac{\delta \psi_i[\rho(\vec{r})]}{\delta \rho(\vec{r})} = \frac{1}{3} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \sum_{j \neq i} \psi_j(\vec{r}') \psi_j(\vec{r}) \rho(\vec{r})^{-\frac{3}{2}},
\]
(33)

and \(\frac{\delta \psi_i[\rho(\vec{r})]}{\delta \psi(\vec{r}') d\vec{r}'.}\) is already given by Eq. (17). Ultimately Eq. (32) is transformed to
\[
\frac{\delta \psi_i[\rho(\vec{r})]}{\delta \psi(\vec{r}') d\vec{r}'.}
\]
\[
= -\frac{2}{3} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \sum_{j \neq i} \psi_k(\vec{r}') \psi_k(\vec{r}) \rho(\vec{r})^{-\frac{3}{2}},
\]
(34)

a result that cannot be equal to \(\delta_1(\vec{r} - \vec{r}')\).

The fact that \(\psi_i^{KS}[\rho(\vec{r})]_{i=1,2,...,n}\) (i.e., \(\rho(\vec{r}) \rightarrow \psi_i^{KS}(\vec{r})_{i=1,2,...,n}\)) and \(\rho(\{\psi_i\}_{i=1,2,...,n})\) (i.e., \(\{\psi_i(\vec{r})\}_{i=1,2,...,n} \rightarrow \rho(\vec{r})\)) are not inverse maps with respect to each other can also be understood as follows. \(\rho(\{\psi_i\}_{i=1,2,...,n})\) is a many-to-one mapping based on Eq. (4), i.e., there are many pre-KS orbital sets \(\{\psi_i(\vec{r})\}_{i=1,2,...,n}\) that yield a particular density \(\rho(\vec{r})\). On the other hand, \(\psi_i^{KS}[\rho(\vec{r})]_{i=1,2,...,n}\) is a one-to-one mapping based on Eq. (5), as there is a unique set of KS orbitals \(\{\psi_i^{KS}(\vec{r})\}_{i=1,2,...,n}\) among the many pre-KS sets of orbitals \(\{\psi_i(\vec{r})\}_{i=1,2,...,n}\) both yielding the density \(\rho(\vec{r})\) by Eq. (5) and minimizing the kinetic energy by Eq. (4). Consequently, \(\{\psi_i[\rho(\vec{r})]\}_{i=1,2,...,n}\) and \(\rho(\{\psi_i\}_{i=1,2,...,n})\) cannot be inverse maps of each other by construction.
As a result Eq. (20) and its generalization, the relation
\[ \delta E_{\text{XC}}[\{\psi_k^{\text{KS}}[\rho[(\psi_j)]_{j=1,2,...,n}]\}_{k=1,2,...,n}] \]
\[ \approx \frac{\delta E_{\text{XC}}[\{\psi_j^{\text{KS}}\}]_{j=1,2,...,n]}{\delta \psi_i^{\text{KS}}(\hat{r})}, \] (35)
must be considered approximate.

As observed in Ref. 62, the application of the OEP method to the Perdew-Kurth-Zupan-Blaha (PKZB) meta-GGA density functional^63^ obtains ground-state magnetic properties that are noticeably different from the ones obtained by the application of the ODDM to PKZB. The difference between the two methods for computing functional derivatives is less pronounced, but still noticeable for the HOMO (highest occupied molecular orbital)-LUMO (lowest unoccupied molecular orbital) gap (around 0.2 eV), a result suggesting that a comparable difference between the two methods might be expected for TDDFT excitation energies. The OEP-like approaches from Refs. 73–75 could be used for the computation of TDDFT excitations by meta-GGA density functionals.

The OEP method has also been applied to the computation of ground-state properties by the hyper-GGA density functional B05, i.e., a GGA that has an additional dependence on the kinetic-energy density and the KS-orbital-dependent exact-exchange-energy density.65 The above observation on the HOMO-LUMO gap and excitation energies, respectively, of the meta-GGA density functional PKZB suggests that a similar analysis for hyper-GGA density functionals is warranted.

A further generalization to the fifth “rung” of density functionals is obtained by appropriately generalizing the analysis leading to Eq. (35) with terms due to the orbital energy dependence of the exchange-correlation energy in Eq. (7).

V. NON-LOCALITY OF THE RESULTANT EXCHANGE-CORRELATION POTENTIALS

In this section it is analytically proven that the ODDM produces a non-local exchange-correlation potential, whereas the exact functional derivative of any exchange-correlation density functional has to produce a strictly local exchange-correlation potential. The examples considered in this section are a pure meta-GGA density functional and the Hartree-Fock energy expression viewed as an orbital-dependent pure-exchange density functional.

Consider the exchange-correlation potential \( \frac{\delta E_{\text{XC}}[\tau]}{\delta \rho(\hat{r})} \) produced by applying Eqs. (20) and (21) to a pure meta-GGA functional \( E_{\text{XC}}[\tau] \). After performing an integration by parts on the RHS of Eq. (20) one obtains
\[ v_{\text{XC}}(\hat{r}, \hat{r}') = -\nabla \left[ \frac{\delta E_{\text{XC}}[\tau]}{\delta \tau(\hat{r})} \right] \cdot \nabla \delta(\hat{r} - \hat{r}') - \frac{\delta E_{\text{XC}}[\tau]}{\delta \tau(\hat{r})} \nabla^2 \delta(\hat{r} - \hat{r}'). \] (36)
This is not the local form of the exchange-correlation potential \( v_{\text{XC}}(\hat{r}) = \frac{\delta E_{\text{XC}}[\tau]}{\delta \rho(\hat{r})} \) one would expect to see in DFT.

In general, the action of any operator \( \hat{v}_{\text{XC}} \) on a KS orbital may be expressed as
\[ \int v_{\text{XC}}(\hat{r}, \hat{r}') \psi_i(\hat{r}') d\hat{r}', \] (37)
where \( v_{\text{XC}}(\hat{r}, \hat{r}') \) is the integral kernel of the operator \( \hat{v}_{\text{XC}} \) that may be termed a non-local potential. For a hybrid density functional, the Hartree-Fock admixture results in a truly non-local potential due to the truly non-local character of the Fock exchange potential, i.e., the Fock exchange potential cannot be written as a multiplicative potential. \( v_{\text{XC}}(\hat{r}, \hat{r}') \) could be a generalized function, so it could be composed of Dirac delta functions and their derivatives. For a pure density functional, the exchange-correlation potential is restricted by the locality condition:^3
\[ v_{\text{XC}}(\hat{r}, \hat{r}') = \delta(\hat{r} - \hat{r}') v_{\text{XC}}(\hat{r}). \] (38)
The insertion of Eq. (38) into Eq. (37) produces the multiplicative action of a local exchange-correlation potential \( v_{\text{XC}}[\rho(\hat{r})] \psi_i(\hat{r}) \). The locality of every pure DFT potential \( v_{\text{XC}}[\rho(\hat{r})] \) is a simple consequence of the locality of the functional differentiation: \( v_{\text{XC}}[\rho(\hat{r})] = \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\hat{r})} \). In particular, any orbital-based exchange-correlation density functional is expected to produce a multiplicative local potential. The main characteristic of locality in Eq. (38) is given by the delta function \( \delta(\hat{r} - \hat{r}') \) multiplying a regular single-variable function.

To the contrary, in Eq. (36) there is a sum of terms, each of which is a delta function derivative multiplying a regular single-variable function. One might call a potential like that in Eq. (36) a semi-local potential. The terminology “semi-locality” can be used in different contexts and will consequently have a context dependent meaning. For example, the GGA density functionals are often termed “semi-local density functionals” because a GGA potential \( v_{\text{XC}}^\text{GGA}[\rho(\hat{r})] \) depends functionally not only on the density \( \rho(\hat{r}) \) at the point \( \hat{r} \) but also on the gradient of the density \( \nabla \rho(\hat{r}) \) at the same point \( \hat{r} \), i.e., on the density \( \rho(\hat{r}) \) in an entire infinitesimal neighborhood of \( \hat{r} \). The semi-local density functionals as well as all the density functionals have to produce strictly local potentials \( v_{\text{XC}}[\rho(\hat{r})] \).

In contrast with the approximate ODDM, the OEP procedure is constructed so as to produce the correct local potential for any orbital-dependent exchange-correlation functional. In particular, the application of the OEP approach to a pure meta-GGA exchange-correlation functional \( E_{\text{XC}}[\tau[\rho]] \) must formally produce the correct local potential \( v_{\text{XC}}(\hat{r}) = \frac{\delta E_{\text{XC}}[\tau]}{\delta \rho(\hat{r})} \).

Consider the consequences that could arise if the approximate nature of Eq. (20) and of its generalization in Eq. (35) are not recognized.

For example, the total Hartree-Fock energy expression \( E_{\text{HF}}[\{\psi_{\text{KS}}^i[\rho]\}_{i=1,2,...,n}] \) and, in particular, its exchange part \( E_{\text{HF}}^{\text{ex}}[\{\psi_{\text{KS}}^i[\rho]\}_{i=1,2,...,n}] \) can be thought of as KS-orbital-based density functionals. The optimization of the density would...
then lead to
\[ \delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right] = 0 \] (39)
together with a constraint on the normalization of the density. Consider the application of the ODDM approximation to the functional derivative with respect to the density in Eq. (39). In this case, the LHS of Eq. (35) after applying the appropriately generalized form of Eq. (19) becomes
\[ \delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right] \frac{\delta \rho(\vec{r})}{\delta \rho(\vec{r})} = 2 \frac{\delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right]}{\delta \rho(\vec{r})} \psi_i(\vec{r}), \] (40)
and consequently Eq. (35), i.e., the ODDM approximation, becomes
\[ \delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right] \frac{\delta \rho(\vec{r})}{\delta \rho(\vec{r})} \psi_i(\vec{r}) \approx \frac{\delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right]}{\delta \rho(\vec{r})} \psi_i(\vec{r}). \] (41)
As a result of the ODDM approximation Eq. (39) becomes
\[ \delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right] = 0. \] (42)
Equation (42) together with the constraint on the normalization of the KS-orbitals give rise to the standard Hartree-Fock equations and are obtained by optimizing the KS-orbitals in the total Hartree-Fock energy expression \( E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right] \). One can view the use of Hartree-Fock exchange in hybrid density functional approximations as the application of ODDM to \( E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right] \).

Consider further the application of the ODDM approximation to the functional derivative of the exchange part \( \frac{\delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right]}{\delta \rho(\vec{r})} \) only and the resulting potential. In this case too, the LHS of Eq. (35) after applying the appropriately generalized form of Eq. (19) becomes
\[ \delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right] \frac{\delta \rho(\vec{r})}{\delta \rho(\vec{r})} \psi_i(\vec{r}) \approx 2 \frac{\delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right]}{\delta \rho(\vec{r})} \psi_i(\vec{r}). \] (43)
Since \( \frac{\delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right]}{\delta \rho(\vec{r})} \) can be formally obtained by the OEP method as noted above, the LHS of Eq. (35) can be written (using Eq. (43)) as
\[ \delta E^{\text{HF}} \left[ \left\{ \psi_i^{\text{KS}} [\rho] \right\}_{k=1,2,...,n} \right] \psi_i(\vec{r}) = 2 \left( \psi_i^{\text{OEP}}(\vec{r}) \right) \psi_i(\vec{r}). \] (44)
In this case, the RHS of Eq. (35) is the action of a non-local potential formally equivalent to the Fock operator built from KS orbitals acting on a KS orbital \( \psi_i(\vec{r}) \).

Using the analytic ODDM approximation on the RHS of Eq. (45) would effectively result in the use of the standard Hartree-Fock theory with its substantially non-local potential, while the exchange-only OEP procedure on the LHS of Eq. (45) is the best local-potential approximation. Consequently, reliance on Eq. (35) leads to a significant deviation from locality and from the correct answer.

The deviation from locality of the exchange-correlation potential that is produced as discussed in the preceding paragraph can be taken as a guide with regard to how good (or bad) the analytic ODDM approximation is. For meta-GGA functionals the deviation of the “semi-local” potential is relatively small. For Hartree-Fock exchange, the non-locality of the produced potential is substantial.

The analysis of this section suggests that the analytic ODDM approximation could be successfully used on a broader class of exchange-correlation functionals, especially on the ones producing semi-local potentials. Nonetheless, in general, it is important that users of the ODDM are aware of the limitations described in this section.

As an example consider the CO molecule. The CO HOMO-LUMO gap predicted by ODDM with the PKZB meta-GGA density functional is 7.36 eV.62 This can be compared with 7.12 eV using OEP and the same PKZB density functional.62 The Hartree-Fock CO HOMO-LUMO gap of CO is 15.71-18.59 eV depending on the basis set used and 7.16-7.29 eV using the OEP pure-exchange density functional (localized Hartree-Fock) depending on the basis set and the particular flavor of OEP used.64 The basis sets in both studies,62,64 although different, are of high quality. Clearly, the deviation from locality has a milder effect on the HOMO-LUMO gap (and presumably on the excitation) of CO by the PKZB meta-GGA density functional than by the Hartree-Fock energy expression viewed as a pure-exchange density functional. Of course, no decisive conclusion can be drawn based on calculations on one system. Therefore, more extensive numerical benchmarks would be very useful.

VI. IMPLEMENTATION DETAILS

The approach described in Secs. II and III, specifically Eq. (26) for the ground-state and Eq. (28) for the excited state, was used to implement meta-GGA exchange-correlation density functionals for use in both the DFT and TDDFT modules of GAMESS. A more detailed working expression based on Eq. (28) can be found in the Appendix. The present implementation requires numerous partial derivatives of the
TABLE I. TDDFT excitations (in eV) of CO computed by different density functionals and the 6-311G(3df, 3pd) basis set compared with the experimental values. The leftmost column identifies the excitations by their symmetry labels.

<table>
<thead>
<tr>
<th></th>
<th>SVWN</th>
<th>PBE</th>
<th>PBE0</th>
<th>B3LYP</th>
<th>TPSS</th>
<th>TPSSh</th>
<th>revTPSS</th>
<th>M08-SO</th>
<th>M08-HX</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Pi$</td>
<td>5.98</td>
<td>5.68</td>
<td>5.77</td>
<td>5.89</td>
<td>5.74</td>
<td>5.77</td>
<td>5.76</td>
<td>6.25</td>
<td>6.38</td>
<td>6.32</td>
</tr>
<tr>
<td>$^3\Sigma^+$</td>
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function $e_{xc}$ in Eq. (1) for each meta-GGA density functional to be computed analytically. When the function $e_{xc}$ is relatively complex, these tasks become very complicated, especially for higher-order functional derivatives. Manual implementation of higher-order functional derivatives is tedious and error prone, while numerical differentiation reduces the quality of the calculated results. To facilitate the implementation of the numerous exact partial derivatives of $e_{xc}$ the open source MAXIMA automatic code generator\textsuperscript{77} was used in conjunction with Python scripts.

The analytic form of the function $e_{xc}$ for a given meta-GGA density functional together with the request to compute specific partial derivatives was encoded in a MAXIMA input file using the MAXIMA syntax. The processing of this input file with the MAXIMA system produces the requested partial derivatives of $e_{xc}$ in a MAXIMA output file. Then, the MAXIMA output file is further converted to a FORTRAN code using a Python script.

VII. SAMPLE NUMERICAL RESULTS

As mentioned above, the TDDFT/meta GGA method described here was employed in a previous work by the authors.\textsuperscript{68} In addition, Table I shows sample TDDFT/6-311G(3df, 3pd) calculations comparing the experimental values of CO excitations with the computed ones by several commonly used density functionals: LDA (SVWN\textsuperscript{16}), GGA (PBE\textsuperscript{25}), hybrid GGA (PBE0)\textsuperscript{49}, B3LYP\textsuperscript{24,48}, pure meta-GGA (TPSS\textsuperscript{39,40}, revTPSS\textsuperscript{43}), and hybrid meta GGA (TPSSH\textsuperscript{42}, M08-SO\textsuperscript{36}, M08-HX\textsuperscript{36}). The results are very similar to those obtained previously.\textsuperscript{78} For a more extensive benchmarking using these meta-GGA density functionals see Ref. 68.

VIII. CONCLUSIONS

In this paper a careful analysis of the analytic subtleties involved in taking functional derivatives of meta-GGA density functionals has been presented. Although the basic idea of the ODDM was previously published\textsuperscript{65} and is a basis for the implementations of meta-GGA density functionals in electronic structure codes (see Ref. 79 for such an example), the detailed derivation of this method has not previously been presented in the literature. Importantly, the detailed working expressions for time-dependent DFT (used by many groups to explore excited electronic state phenomena) are presented here for the first time for meta-GGA functionals. The practical aspects of the implementation of the TDDFT working equations have been discussed and a sample TDDFT calculation using some of the implemented meta-GGA density functionals is shown. Previous work by the authors\textsuperscript{68} in which TDDFT excitation energies were benchmarked was based on the TDDFT working equations presented here.

The approximate nature of the ODDM is one of the main results of this paper. The analysis presented here, which is relevant to any orbital-dependent density functional, reveals that the ODDM produces non-unique derivatives with respect to the KS orbitals and non-local exchange-correlation potentials, whereas the potential of any non-hybrid exchange-correlation density functional is expected to be local.

A detailed analytical and numerical comparison of the presented approach with the exact OEP method as applied to meta-GGA density functionals will be presented in a future work.

ACKNOWLEDGMENTS

The authors thank Professors Mel Levy and Peter Gill for very helpful discussions. This work was supported in part by the National Science Foundation SI2 and Petascale Applications grants, by a grant (FA9550-08-1-003) from the Air Force Office of Scientific Research, and by funds provided by the Iowa State University through the Frances M. Craig endowment.

APPENDIX: TDDFT WORKING EQUATIONS FOR META-GGA DENSITY FUNCTIONALS

The additional $\tau$-dependent terms to the singlet ($A1$) and triplet ($A2$) exchange-correlation kernel of TDDFT are given below. The standard non-$\tau$-dependent terms can be found in Ref. 80:
\[ M'_{ia,jb} = \sum \frac{1}{4} \int [\nabla \psi_i(\vec{r})] \cdot [\nabla \psi_a(\vec{r})] \left( \frac{\partial^2 e_{XC}}{\partial \tau_a^2(\vec{r})} + \frac{\partial^2 e_{XC}}{\partial \tau_a \partial \tau_b(\vec{r})} \right) [\nabla \psi_j(\vec{r})] \cdot [\nabla \psi_b(\vec{r})] d\vec{r} \]

\[ + \frac{1}{2} \int \left( \psi_i(\vec{r}) \psi_a(\vec{r}) [\nabla \psi_j(\vec{r})] \cdot [\nabla \psi_b(\vec{r})] + [\nabla \psi_i(\vec{r})] \cdot [\nabla \psi_a(\vec{r})] \psi_j(\vec{r}) \psi_b(\vec{r}) \right) \left( \frac{\partial^2 e_{XC}}{\partial \rho_a(\vec{r}) \partial \tau_b(\vec{r})} + \frac{\partial^2 e_{XC}}{\partial \rho_b(\vec{r}) \partial \tau_a(\vec{r})} \right) d\vec{r} \]

\[ + \int \left( [\nabla \rho(\vec{r})] \cdot [\nabla \psi_i(\vec{r})] \psi_a(\vec{r}) [\nabla \psi_j(\vec{r})] \cdot [\nabla \psi_b(\vec{r})] + [\nabla \psi_i(\vec{r})] \cdot [\nabla \psi_a(\vec{r})] \nabla \rho(\vec{r}) \cdot [\psi_j(\vec{r}) \psi_b(\vec{r})] \right) \left( \frac{\partial^2 e_{XC}}{\partial \gamma_{\alpha\alpha}(\vec{r}) \partial \tau_j(\vec{r})} + \frac{\partial^2 e_{XC}}{\partial \gamma_{\beta\beta}(\vec{r}) \partial \tau_a(\vec{r})} + \frac{\partial^2 e_{XC}}{\partial \gamma_{\beta\alpha}(\vec{r}) \partial \tau_a(\vec{r})} \right) d\vec{r}. \]


