

Orbital-free embedding applied to the calculation of induced dipole moments in $\text{CO}_2 \cdots X$ ($X = \text{He, Ne, Ar, Kr, Xe, Hg}$) van der Waals complexes

Christoph R. Jacob^{a)}

Department of Theoretical Chemistry, Faculty of Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Tomasz A. Wesolowski^{b)}

Département de Chimie Physique, Université de Genève, 30, quai Ernest-Ansermet, CH-1211 Genève, Switzerland

Lucas Visscher^{c)}

Department of Theoretical Chemistry, Faculty of Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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The orbital-free frozen-density embedding scheme within density-functional theory [T. A. Wesolowski and A. Warshel, *J. Phys. Chem.* **97**, 8050 (1993)] is applied to the calculation of induced dipole moments of the van der Waals complexes $\text{CO}_2 \cdots X$ ($X = \text{He, Ne, Ar, Kr, Xe, Hg}$). The accuracy of the embedding scheme is investigated by comparing to the results of supermolecule Kohn-Sham density-functional theory calculations. The influence of the basis set and the consequences of using orbital-dependent approximations to the exchange-correlation potential in embedding calculations are examined. It is found that in supermolecular Kohn-Sham density-functional calculations, different common approximations to the exchange-correlation potential are not able to describe the induced dipole moments correctly and the reasons for this failure are analyzed. It is shown that the orbital-free embedding scheme is a useful tool for applying different approximations to the exchange-correlation potential in different subsystems and that a physically guided choice of approximations for the different subsystems improves the calculated dipole moments significantly. © 2005 American Institute of Physics. [DOI: 10.1063/1.2107567]

I. INTRODUCTION

Orbital-free embedding is a promising approach to the efficient calculation of large scale molecular systems because it allows to split up the calculation using a “divide-and-conquer” strategy.

In the subsystem formulation of density-functional theory (DFT) proposed by Cortona¹ the total electron density $\rho_{\text{tot}}(\mathbf{r})$ is (in the case of two subsystems) represented as the sum of two components $\rho_{\text{I}}(\mathbf{r})$ and $\rho_{\text{II}}(\mathbf{r})$, which are determined separately from a set of one-electron equations. Usually $\rho_{\text{I}}(\mathbf{r})$ and $\rho_{\text{II}}(\mathbf{r})$ are chosen to be either the electron densities of two interacting fragments of the considered system or as the electron densities of a system under investigation and an environment. Since both subsystems are described using DFT, the formalism described here can be viewed as a “DFT in DFT” embedding scheme.

Given this partitioning of the electron density, the DFT total energy can be expressed as a bifunctional of ρ_{I} and ρ_{II} ,

$$E[\rho_{\text{I}}, \rho_{\text{II}}] = E_{\text{NN}} + \int (\rho_{\text{I}}(\mathbf{r}) + \rho_{\text{II}}(\mathbf{r})) (V_{\text{I}}^{\text{nuc}}(\mathbf{r}) + V_{\text{II}}^{\text{nuc}}(\mathbf{r})) d\mathbf{r} + \int \frac{(\rho_{\text{I}}(\mathbf{r}) + \rho_{\text{II}}(\mathbf{r}))(\rho_{\text{I}}(\mathbf{r}') + \rho_{\text{II}}(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[\rho_{\text{I}} + \rho_{\text{II}}] + T_{\text{s}}[\rho_{\text{I}}] + T_{\text{s}}[\rho_{\text{II}}] + T_{\text{s}}^{\text{naddr}}[\rho_{\text{I}}, \rho_{\text{II}}], \quad (1)$$

where E_{NN} is the nuclear repulsion energy, $V_{\text{I}}^{\text{nuc}}$ and $V_{\text{II}}^{\text{nuc}}$ are the electrostatic potentials of the nuclei in subsystems I and II, E_{xc} is the exchange-correlation functional, $T_{\text{s}}[\rho]$ is the kinetic energy of the noninteracting reference system, and $T_{\text{s}}^{\text{naddr}}[\rho_{\text{I}}, \rho_{\text{II}}]$ is the nonadditive kinetic energy, which is defined as

$$T_{\text{s}}^{\text{naddr}}[\rho_{\text{I}}, \rho_{\text{II}}] = T_{\text{s}}[\rho_{\text{I}} + \rho_{\text{II}}] - T_{\text{s}}[\rho_{\text{I}}] - T_{\text{s}}[\rho_{\text{II}}]. \quad (2)$$

If the densities $\rho_{\text{I}}(\mathbf{r})$ and $\rho_{\text{II}}(\mathbf{r})$ are represented using the canonical Kohn-Sham (KS) orbitals for the individual subsystems $\phi_i^{(n)}$ with $\rho_n(\mathbf{r}) = \sum_{i=1}^{N_n} \phi_i^{(n)}(\mathbf{r})^* \phi_i^{(n)}(\mathbf{r})$ ($n = \text{I, II}$), it is possible to calculate the kinetic energy of the corresponding noninteracting reference system as

$$T_{\text{s}}[\rho_n] = \sum_{i=1}^{N_n} \left\langle \phi_i^{(n)} \left| -\frac{\nabla^2}{2} \right| \phi_i^{(n)} \right\rangle. \quad (3)$$

With the partitioning of the total electron density into $\rho_{\text{I}}(\mathbf{r})$ and $\rho_{\text{II}}(\mathbf{r})$ there is in general no representation of $\rho_{\text{tot}}(\mathbf{r})$ in the canonical KS orbitals available, so that $T_{\text{s}}[\rho_{\text{I}} + \rho_{\text{II}}]$ cannot be

^{a)}Electronic mail: jacob@few.vu.nl

^{b)}Electronic mail: Tomasz.Wesolowski@chiphys.unige.ch

^{c)}Electronic mail: visscher@chem.vu.nl

calculated in this way. Because of this $T_s^{\text{nadd}}[\rho_I, \rho_{II}]$ is calculated using an approximated kinetic-energy functional in practical implementations.

The exchange-correlation energy in Eq. (1) can be split up in a similar way as the kinetic energy into

$$E_{\text{xc}}[\rho_I + \rho_{II}] = E_{\text{xc}}[\rho_I] + E_{\text{xc}}[\rho_{II}] + E_{\text{xc}}^{\text{nadd}}[\rho_I, \rho_{II}], \quad (4)$$

where the nonadditive part of the exchange-correlation energy is defined as

$$E_{\text{xc}}^{\text{nadd}}[\rho_I, \rho_{II}] = E_{\text{xc}}[\rho_I + \rho_{II}] - E_{\text{xc}}[\rho_I] - E_{\text{xc}}[\rho_{II}]. \quad (5)$$

This partitioning of the exchange-correlation energy functional is introduced here to make it possible to use different approximations for the exchange-correlation functionals in the two subsystems, which will be exploited in this work.

For a given frozen electron density $\rho_{II}(\mathbf{r})$ in one of the subsystems (fragment II) one can derive² the one-electron equations for the calculation of the electron density $\rho_I(\mathbf{r})$ in the other subsystem (fragment I). The effective potential in these equations can be derived from the requirement that the total density $\rho_{\text{tot}}(\mathbf{r}) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r})$ of the system is obtained, in an optimization process in which the electron density $\rho_{II}(\mathbf{r})$ of fragment II is kept frozen. On the assumption that the complementary $\rho_I(\mathbf{r})$ is positive definite and is noninteracting pure-state ν -representable,³ one obtains KS-type equations in which the effect of $\rho_{II}(\mathbf{r})$ is represented by an embedding term in the effective potential for the $\rho_I(\mathbf{r})$ system,²

$$\left[-\frac{\nabla^2}{2} + V_{\text{eff}}^{\text{KS}}[\mathbf{r}; \rho_I] + V_{\text{eff}}^{\text{emb}}[\mathbf{r}; \rho_I, \rho_{II}] \right] \phi_i^{(I)}(\mathbf{r}) = \epsilon_i \phi_i^{(I)}(\mathbf{r}), \quad (6)$$

$$i = 1, \dots, N_I.$$

These equations and the corresponding formalism, which are applied in this work, will be referred to as the Kohn-Sham equations with constrained electron density (KSCED). In these equations, $V_{\text{eff}}^{\text{KS}}[\mathbf{r}; \rho_I]$ is the KS effective potential of the isolated subsystem I and $V_{\text{eff}}^{\text{emb}}[\mathbf{r}; \rho_I, \rho_{II}]$ is the KSCED embedding potential which reads

$$V_{\text{eff}}^{\text{emb}}[\mathbf{r}; \rho_I, \rho_{II}] = V_{\text{II}}^{\text{nuc}}(\mathbf{r}) + \int \frac{\rho_{II}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta T_s^{\text{nadd}}[\rho_I, \rho_{II}]}{\delta \rho_I} + \frac{\delta E_{\text{xc}}^{\text{nadd}}[\rho_I, \rho_{II}]}{\delta \rho_I}. \quad (7)$$

In this KSCED effective embedding potential one recognizes the kinetic and exchange-correlation parts of the potential, given as functional derivative of the corresponding nonadditive (kinetic and exchange-correlation) energy functionals. These derivatives can also be written as

$$\frac{\delta T_s^{\text{nadd}}[\rho_I, \rho_{II}]}{\delta \rho_I} = \left. \frac{\delta T_s[\rho]}{\delta \rho} \right|_{\rho=\rho_I+\rho_{II}} - \left. \frac{\delta T_s[\rho]}{\delta \rho} \right|_{\rho=\rho_I}, \quad (8)$$

and

$$\frac{\delta E_{\text{xc}}^{\text{nadd}}[\rho_I, \rho_{II}]}{\delta \rho_I} = \left. \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \right|_{\rho=\rho_I+\rho_{II}} - \left. \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \right|_{\rho=\rho_I}. \quad (9)$$

In the case that $\rho_{II}(\mathbf{r})$ is chosen in such a way that the difference between the exact ground-state density of the entire system and $\rho_{II}(\mathbf{r})$ is positive definite and noninteraction pure-state ν -representable, the solution of Eq. (6) will yield the exact ground-state electron density.⁴ This makes the KSCED scheme an exact approach in the exact functional limit, in contrast to most other embedding methods commonly used in practical computer simulations.

Since Eq. (6) can be solved for any postulated electron density, $\rho_{II}(\mathbf{r})$ may also be obtained from simpler considerations.² For instance, a solvent can be modeled by just using a sum of electron densities of the individual solvent molecules.⁵⁻⁸ This type of applications underlines the “orbital-free” nature of the KSCED embedding scheme, since all the information concerning the environment of an embedded system is contained in the electron density $\rho_{II}(\mathbf{r})$.

While this strategy can be applied when the electron density of an environment has to be approximated, the KSCED embedding formalism can also be applied in so-called “freeze-and-thaw” iterations to determine the electron densities of both subsystems.⁹ This is done by starting with the calculation of one isolated fragment, freezing its density and calculating the density of the other fragment, taking the frozen density of the first fragment into account. Then the role of the frozen and the nonfrozen subsystem is iteratively interchanged until convergence is reached.

This procedure corresponds to minimizing the total energy bifunctional given in Eq. (1) by solving a set of two coupled KSCED equations,

$$\left[-\frac{\nabla^2}{2} + V_{\text{eff}}^{\text{KS}}[\mathbf{r}; \rho_I] + V_{\text{eff}}^{\text{emb}}[\mathbf{r}; \rho_I, \rho_{II}] \right] \phi_i^{(I)}(\mathbf{r}) = \epsilon_i^{(I)} \phi_i^{(I)}(\mathbf{r}), \quad (10)$$

$$i = 1, \dots, N_I,$$

$$\left[-\frac{\nabla^2}{2} + V_{\text{eff}}^{\text{KS}}[\mathbf{r}; \rho_{II}] + V_{\text{eff}}^{\text{emb}}[\mathbf{r}; \rho_{II}, \rho_I] \right] \phi_i^{(II)}(\mathbf{r}) = \epsilon_i^{(II)} \phi_i^{(II)}(\mathbf{r}), \quad (11)$$

$$i = 1, \dots, N_{II},$$

where $V_{\text{eff}}^{\text{KS}}[\mathbf{r}; \rho_I]$ and $V_{\text{eff}}^{\text{KS}}[\mathbf{r}; \rho_{II}]$ are the KS potentials of the isolated subsystem I or II, respectively, and $V_{\text{eff}}^{\text{emb}}$ is the KSCED effective embedding potential as defined in Eq. (7). The electron densities $\rho_I(\mathbf{r})$ and $\rho_{II}(\mathbf{r})$ are defined by the sets of KSCED orbitals $\phi_i^{(I)}(\mathbf{r})$ and $\phi_i^{(II)}(\mathbf{r})$ which are obtained as the solutions of the above equations.

In practical applications of the above equations, not only the nonadditive kinetic-energy component of the KSCED embedding potential [cf. Eq. (8)] has to be approximated, but also the exchange-correlation potential, which enters these equations at different points. First, it appears as part of the KS potentials $V_{\text{eff}}^{\text{KS}}$ of subsystems I and II. Since the electron densities of the two subsystems are determined separately from Eqs. (10) and (11), it is possible to use different approximations for the different subsystems. Furthermore, it is also possible to use orbital-dependent approximations to the

exchange-correlation potential of the isolated subsystems I and II. The benefits of these possibilities, not investigated in detail so far, will be demonstrated in this work. Second, an approximation to the exchange-correlation potential is also needed in the KSCED effective embedding potential, where the nonadditive exchange-correlation component of Eq. (9) appears. For this component it is in general not possible to use orbital-dependent approximations because there is no representation of $\rho_{\text{tot}}(\mathbf{r})$ in the canonical KS orbitals available. Details about the different approximations which have been used in this work are given in Sec. II.

The KSCED orbital-free embedding scheme has been used in a number of different applications such as the calculation of interaction energies in van der Waals complexes^{10–12} and in hydrogen-bound complexes,^{6,13} the description of the absorption of CO in zeolites¹⁴ or the calculation of crystal-field splittings of lanthanide cations.¹⁵ Recently, the extension of the KSCED scheme to time-dependent density-functional theory¹⁶ (TDDFT) has been used to model hydrogen-bonding-induced shifts of excitation energies in nucleic acid base pairs¹⁷ and for the calculation of solvatochromic shifts.^{7,8}

The KSCED embedding potential of Eq. (7) was also used by Carter and co-workers in a hybrid approach (“*ab initio* in DFT” embedding) combining a wave-function-based *ab initio* treatment of the system under investigation, a molecule absorbed on a surface, with a periodic DFT description of the surface. Using this approach they studied the absorption of CO on a Cu(111) surface^{18,19} and localized electronic excitations in a CO molecule absorbed on a Pd(111) surface.^{20,21}

Even though the KSCED scheme has been applied successfully to a number of different systems, there remain a number of open questions related to the quality of the approximations to the nonadditive kinetic-energy functional. For the development of improved approximations it is of great importance to identify and analyze the possible problems of the currently used approximations.

Furthermore, the ability to apply different approximations for the exchange-correlation potential for different subsystems in a straightforward way is another application of the KSCED scheme not exploited previously which will be examined in this work. This is particularly useful since the approximate exchange-correlation potentials which are applied in practical calculations do not lead to exact results. In this work, we show that a physically guided choice of approximations to the exchange-correlation potential for different subsystems can lead to results which are superior to those obtained from using a single KS-DFT calculation. This approach follows ideas similar to those of Carter and co-workers,^{18,20} in which instead of selecting the most appropriate approximation to the exchange-correlation potential for a given subsystem, as we do in the current work, they replaced the DFT description for one of the subsystems by a wave-function-based *ab initio* one.

The induced dipole moments in the weakly interacting $\text{CO}_2 \cdots X$ ($X = \text{He, Ne, Ar, Kr, Xe, Hg}$) van der Waals complexes are ideally suited to investigate the performance of the KSCED scheme and the quality of the approximation to the

nonadditive kinetic-energy functional in detail. The interaction in these van der Waals complexes is weak and the overlap between the densities of the CO_2 molecule and the rare-gas or mercury atom is small. The KSCED scheme has been applied to other van der Waals complexes before^{10–12} and the approximated nonadditive kinetic-energy functional used there has been shown to be the most accurate, both for the energy and for the potential, among a large family of gradient-dependent approximations. In particular, it gives accurate interaction energies for weakly overlapping densities. We note that in the KSCED scheme an approximated nonadditive kinetic-energy functional is used for two different purposes: First, its functional derivative is used in the construction of the embedding potential [Eqs. (7) and (8)] which is used to calculate the electron density and second, the functional itself is needed to calculate the total energy [Eqs. (1) and (2)]. Since the induced dipole moments depend directly on the density we only need to consider the functional derivative of the approximate nonadditive kinetic-energy functional and not the nonadditive kinetic-energy functional itself. This reduces the chances of encountering error cancellations which could mask possible problems with the method.

The induced dipole moments in these complexes should be mainly determined by the electrostatic interaction and the Pauli repulsion between the CO_2 molecule and the rare-gas or mercury atom. KS-DFT and the KSCED scheme are believed to be able to describe both effects accurately. Dispersion interactions, which cannot be described correctly within KS-DFT, would be important for the calculations of interaction energies and of geometries, but they should only have a small influence on the induced dipole moment. However, the accurate calculation of the small induced dipole moments in the van der Waals complexes investigated here is still a challenging task. The calculated dipole moments will be very sensitive to small changes in the electron density and can, therefore, be used as a good measure for the quality of the electron density which results from KSCED calculations.

van der Waals complexes of CO_2 and a rare-gas atom have been subject to a number of experimental and theoretical studies because they are a prototype system for the weak interaction of nonpolar constituents. For all CO_2 -rare-gas complexes, infrared^{22,23} and microwave spectra^{24–26} have been measured. All experiments have found that the complexes have a T-shaped geometry. Except for $\text{CO}_2 \cdots \text{He}$, the dipole moments of the complexes have been determined from measurements of the Stark effect on the rotational transitions. In our study, we also include the $\text{CO}_2 \cdots \text{Hg}$ complex, which can be viewed as an analog of the CO_2 -rare-gas complexes. This complex has also been investigated experimentally by microwave spectroscopy where a T-shaped structure has been found from the rotational spectrum and the dipole moment has been determined from the Stark effect splitting.²⁷

A number of theoretical works deal with CO_2 -rare-gas complexes. For $\text{CO}_2 \cdots \text{He}$, $\text{CO}_2 \cdots \text{Ne}$, and $\text{CO}_2 \cdots \text{Ar}$, the potential-energy surfaces have been calculated using Møller-Plesset perturbation theory.^{28–31} All these calculations confirm that the T-shaped structure is the global minimum on the

potential-energy surface and that the linear structure is a local minimum at significantly higher energy. Maroulis and Haskopoulos³² have studied the induced dipole moments and polarizabilities in the CO₂-rare-gas complexes using second-order Møller-Plesset perturbation theory (MP2). For the He and Ne complexes, they also performed CCSD(T) calculations, which are in good agreement with the MP2 results.

This work is organized as follows: After a brief outline of the computational details in Sec. II, the results of the calculations are discussed in Sec. III. In Sec. III A, a simple electrostatic interaction model for the description of the induced dipole moments in the considered complexes is presented. In Sec. III B, we present the results of supermolecular KS-DFT calculations of CO₂ ··· X. These calculations show that different exchange-correlation potentials fail to reproduce the experimentally observed induced dipole moments and we investigate the reasons for this failure. In Sec. III C, we investigate the performance of the KSCED embedding scheme by comparing the results of embedding calculations to the supermolecular KS-DFT results and it is demonstrated how the KSCED scheme can be used to get around the problems we have found when comparing the supermolecular KS-DFT calculations to experiment in Sec. III D. Concluding remarks are collected in Sec. IV.

II. COMPUTATIONAL DETAILS

For the performance of the KSCED scheme [Eqs. (1), (3), (10), and (11)], the choice of the approximation which is used for the nonadditive kinetic-energy component of the KSCED effective embedding potential is of great impor-

tance. The simplest approximation for the kinetic-energy functional, corresponding to the local-density approximation in KS-DFT, is the Thomas-Fermi functional,

$$T_s^{\text{TF}}[\rho] = C_{\text{TF}} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}. \quad (12)$$

An analysis of different approximations for the kinetic-energy functional is given in Refs. 10, 13, and 33. For the construction of these approximated functionals, the suggestion of Lee *et al.*³⁴ to use similar analytical forms for approximated kinetic-energy and exchange energy functionals is applied there,

$$\begin{aligned} E_x[\rho] &\approx E_x^{\text{GGA}}[\rho] = \int f(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|) d\mathbf{r} \\ &= -C_x \int \rho^{4/3}(\mathbf{r}) F(s(\mathbf{r})) d\mathbf{r}, \end{aligned} \quad (13)$$

and

$$T_s^{\text{GGA}}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) F(s(\mathbf{r})) d\mathbf{r}, \quad (14)$$

where $C_x = (3/4)(3/\pi)^{1/3}$, $C_F = (3/10)(3\pi^2)^{(2/3)}$, and $s = |\nabla\rho|/(2\rho k_F)$, with $k_F = (3\pi^2\rho)^{1/3}$.

Studies^{6,10,13} of the accuracy of various approximations to $T_s^{\text{nadd}}[\rho_I, \rho_{II}]$, approximated as $T_s^{\text{nadd}}[\rho_I, \rho_{II}] \approx T_s^{\text{approx}}[\rho_I + \rho_{II}] - T_s^{\text{approx}}[\rho_I] - T_s^{\text{approx}}[\rho_{II}]$, in the case of weakly overlapping pairs of electron densities showed that the most accurate nonadditive kinetic-energy functional (and the associated functional derivative) has the same analytic form of the enhancement factor $F(s)$ as the exchange functional of Perdew and Wang³⁵ but should be reparametrized for the kinetic energy as described by Lembarki and Chermette.³⁶ Its complete form reads,

$$F_{\text{LC94}}(s) = \frac{1 + 0.093\,907s \operatorname{arcsinh}(76.32s) + (0.266\,08 - 0.080\,961\,5e^{-100s^2})s^2}{1 + 0.093\,907s \operatorname{arcsinh}(76.32s) + 0.577\,67 \times 10^{-4}s^4}. \quad (15)$$

Equations (2), (14), and (15) lead to the nonadditive kinetic-energy functional (dubbed PW91k in the following) used in this work. In the current application, the calculation of the electron density using the KSCED equations, not this nonadditive kinetic-energy functional itself but only its functional derivative [Eq. (8)] is needed in the construction of the embedding potential.

In the supermolecular KS-DFT calculations two different approximations were employed for the exchange-correlation potential: The Perdew-Wang 91 functional, dubbed PW91,^{35,37} which is a typical example of the generalized gradient approximation (GGA), and the “statistical averaging of (model) orbital potentials” (SAOP),³⁸⁻⁴⁰ which is a more advanced approximation to the KS potential and shows the correct Coulombic decay of the potential at long distances.

In the KSCED embedding calculations, i.e., when Eqs.

(10) and (11) were solved using freeze-and-thaw iterations, approximations to the exchange-correlation potential are needed in different places, as explained in Sec. I. Different combinations of the two approximations PW91 and SAOP were used in these calculation. First, calculations were performed using PW91 both in the KS potential of the isolated subsystems and in the KSCED embedding potential. These calculations will be referred to as KSCED/PW91.

Second, the SAOP potential was used to approximate the exchange-correlation potential in the KS potentials of the isolated subsystems $\{V_{\text{eff}}^{\text{KS}}[\mathbf{r}; \rho_{I,II}]\}$ in Eqs. (10) and (11). Because the SAOP potential is orbital dependent it does not provide an expression for the nonadditive exchange-correlation potential [see Eqs. (5) and (9)] and therefore, cannot be used in the KSCED embedding potential. We chose to use the PW91 functional for the nonadditive exchange-

correlation contributions to the KSCED embedding potential [$V_{\text{eff}}^{\text{emb}}$ in Eqs. (10) and (11)] in these calculations, which introduces an inconsistency compared to the supermolecular KS-DFT calculations using SAOP. This inconsistency relative to supermolecular calculations will be further discussed in Sec. III C. Calculations using this combination of approximations to the exchange-correlation potential will be labeled KSCED/SAOP.

Finally, we will present KSCED calculations where different approximations to the exchange-correlation potential in the KS potential of the isolated subsystems I and II were chosen based on the physical knowledge about the investigated system and the available approximations. In these calculations, which will be referred to as KSCED/combi, PW91 was used to approximate the exchange-correlation potential in the KS potential of the isolated subsystem I [$V_{\text{eff}}^{\text{KSr}}[\mathbf{r}; \rho_{\text{I}}]$ in Eq. (10)] and SAOP was used in the KS potential of the isolated subsystem II [$V_{\text{eff}}^{\text{KSr}}[\mathbf{r}; \rho_{\text{II}}]$ in Eq. (11)]. For the complexes investigated in this work fragment I was chosen to be the CO_2 molecule and fragment II was chosen to be the attached rare-gas or mercury atom. For the nonadditive exchange-correlation contribution to the KSCED embedding potential [$V_{\text{eff}}^{\text{emb}}$ in Eqs. (10) and (11)], PW91 was used.

All calculations were performed using the Amsterdam density-functional (ADF) package.^{41,42} The KSCED scheme [Eqs. (10) and (11)] is implemented in a development version of ADF. To include the effects of relativity for the complexes containing the heavier elements Xe or Hg, the scalar zeroth-order regular approximation (ZORA)^{43–45} was used. The calculations of dipole polarizabilities were done using TDDFT as implemented in ADF.^{46,47} For numerical integration we used a grid that was denser than the default settings of ADF to get the dipole moments with the required accuracy. In the KSCED calculations, the same integration grid as in the corresponding supermolecular KS-DFT calculations was used. The use of a grid which is larger than the one in KS-DFT calculations for the isolated subsystems is needed because of the embedding potential of Eq. (7) extends over the environment.

By default, the ADF package uses the fitted electron density for the evaluation of the exchange-correlation potential. We found that for the evaluation of the nonadditive kinetic-energy and exchange-correlation contributions to the embedding potential in weakly interacting systems this fitted density is not accurate enough, especially when gradient-dependent functionals are used. This can be related to the differences between the fitted and the exact electron density in the outer regions, that are usually not important for the evaluation of the exchange-correlation potential, but that are significant for the contributions of the nonadditive kinetic energy to the embedding potential in KSCED calculations. Therefore, we modified the ADF implementation of the KSCED scheme⁴⁸ to use the exact electron density of both subsystems (ρ_{I} and ρ_{II}) in the evaluation of the nonadditive kinetic-energy and exchange-correlation contributions [Eqs. (8) and (9)] to the embedding potential.

For the accurate calculation of the induced dipole moments in the $\text{CO}_2 \cdots X$ complexes, large basis sets with a sufficient number of diffuse functions are needed.³² We used a

TABLE I. Intermolecular distances R used in this work (in a.u.). R denotes the distance between the carbon atom and the rare-gas or mercury atom in the T-shaped geometry of $\text{CO}_2 \cdots X$.

X	R
He	6.019
Ne	6.206
Ar	6.605
Kr	6.846
Xe	7.332
Hg	6.983

series of basis sets of increasing size to examine the influence of the basis set on the calculated dipole moments. First, we used the quadruple- ζ basis set with four sets of polarization functions (QZ4P) from the ADF basis set library.⁴¹ In addition, we used the even-tempered ET-pVQZ basis set,⁴⁹ which was augmented with field-induced polarization functions (aug-ET-pVQZ).^{50,51} This augmented basis set is smaller than the QZ4P basis set, but it was shown to be of similar quality for the calculation of various molecular properties.⁴⁹ Finally, we used the largest basis set available in the ADF basis set library, the even-tempered ET-QZ3P-3DIFFUSE basis set, which is of quadruple- ζ quality and contains three sets of diffuse functions. Unfortunately, the large even-tempered basis sets ET-pVQZ and ET-QZ3P-3DIFFUSE are only available for the elements up to Kr. Therefore, we have extended the standard QZ4P basis sets for Xe and Hg with additional diffuse functions, using the scheme described in Refs. 50 and 51, yielding the basis set labeled aug-QZ4P in this work. The convergence of the induced dipole moments with the size of the basis set will be discussed in the following section.

All calculations were performed for the same T-shaped geometries, which were used in Ref. 32, at which the C–O bond length in the CO_2 molecule is kept fixed at the experimental value of 2.192 a.u.⁵² The C—Rg (Rg=He, Ne, Ar, Kr, Xe) distances obtained from MP2 calculations taken from Ref. 32 were used. These values are in excellent agreement with the experimental geometries. For $\text{CO}_2 \cdots \text{Hg}$, the experimental C—Hg distance²⁷ was used. Table I collects the used distances.

III. RESULTS AND DISCUSSION

A. Simple electrostatic interaction model

In a simple electrostatic model, the interaction of the CO_2 molecule and the attached rare-gas or mercury atom can be described in the following picture: The electric field of the CO_2 molecule, which can be approximated by the electric field of a quadrupole, distorts the charge distribution around the rare-gas or mercury atom and induces a dipole moment which is given by

$$\mu_{\text{ind}} = \frac{3 Q_{xx} \alpha_X}{R^4}, \quad (16)$$

where Q_{xx} is the xx component of the traceless quadrupole moment of CO_2 (the z axis being along the CO_2 molecule),

TABLE II. Induced dipole moments (in debye) of $\text{CO}_2 \cdots X$ complexes, calculated from the simple electrostatic interaction model as described in the text.

	He	Ne	Ar	Kr	Xe	Hg
Electrostatic model	0.0128	0.0219	0.0708	0.0928	0.1148	0.1734
Experiment ^a		0.0244	0.0679	0.0829	0.1029	0.1070

^aReferences 26 and 27.

α_X is the static dipole polarizability of the attached atom X , and R is the $\text{C}-X$ distance.

In Table II, the induced dipole moments calculated using the model of Eq. (16) are given. The experimental values for the polarizabilities of the rare-gas atoms⁵³ and mercury,⁵⁴ which are also given in Table IV, were used. For the quadrupole moment of CO_2 the experimental value of $Q_{xx} = 1.595$ a.u. (Ref. 55) was used.

The results obtained within this simple model already account for the largest part of the experimentally observed induced dipole moments. It is—if experimental values are used as an input—able to reproduce the increase in the induced dipole moments along this series of complexes qualitatively and is able to give numerical values which are in reasonable agreement with the experimental dipole moments.

This simple electrostatic interaction model neglects the effects of higher multipole moments of the CO_2 molecule and of the finite size of the attached atom, which are expected to become more important if the size of the attached atom increases. The electrostatic interaction model could be further refined to take these effects into account, but it would still neglect the effects of Pauli repulsion and orbital interactions, which can only be described using quantum chemical methods.

Comparing the results which are obtained from the electrostatic interaction model with the experimental induced dipole moments shows that the effects which are neglected in the simple model become more important when going to the heavier attached atoms. Especially for the mercury complex the electrostatic interaction model overestimates the induced dipole moment significantly.

Still, the fact that the main part of the induced dipole moment originates from the interaction of the quadrupole moment of the CO_2 molecule with the polarizable electron

cloud of the attached atom shows that it is important to ensure that the methods used in more advanced calculations are capable of describing the CO_2 quadrupole moment and the polarizability of the attached atom accurately.

B. Supermolecular KS-DFT calculations

To provide a reference for the discussion of the results of the KSCED embedding calculations, we first performed supermolecular KS-DFT calculations. These calculations will also be used to investigate the influence of the basis set and the approximated exchange-correlation potential on the induced dipole moments. Table III shows the results for the supermolecular KS-DFT calculations using PW91 and different basis sets. They are compared to the experimentally observed dipole moments and the results of the CCSD(T) and MP2 calculations.³² The calculated dipole moments are—unlike the values given by Maroulis and Haskopoulos in Ref. 32—not corrected for basis set superposition errors (BSSE) to make comparisons with the results of the KSCED calculations in the next sections easier.

Nevertheless, we calculated the effect of the BSSE on the dipole moments using the counterpoise correction method and found these corrections to be small in all cases. In the calculations using the largest basis set the BSSE correction is smaller than 0.001 D for all complexes.

The results with different basis sets show that inclusion of diffuse functions is of great importance for the calculation of the induced dipole moments. The inclusion of diffuse functions when going from ET-pVQZ to aug-ET-pVQZ and when going from QZ4P to ET-QZ3P-3DIFFUSE/aug-QZ4P results in a large increase in the induced dipole moments. For the basis sets which do already include diffuse functions, the difference in the induced dipole moments when going from

TABLE III. Induced dipole moments (in debye) of $\text{CO}_2 \cdots X$ complexes calculated from supermolecule KS-DFT calculations with the PW91 functional using different basis sets. For comparison, the experimental values and the results of the previous MP2 and CCSD(T) calculations are also given.

		He	Ne	Ar	Kr	Xe	Hg
KS-DFT	ET-pVQZ	0.0123	0.0228	0.0611	0.0890		
	aug-ET-pVQZ	0.0132	0.0229	0.0743	0.0995		
	QZ4P	0.0102	0.0211	0.0712	0.0916	0.1132	0.1385
	ET-QZ3P-3DIFFUSE ^a	0.0134	0.0253	0.0736	0.0943	0.1194	0.1464
MP2 ^b		0.0160	0.0274	0.0714	0.0877	0.0976	
CCSD(T) ^c		0.0158	0.0267				
Experiment ^d			0.0244	0.0679	0.0829	0.1029	0.1070

^aBasis set aug-QZ4P was used for Xe and Hg.^bReference 32.^cReference 32.^dReferences 26 and 27.

TABLE IV. Dipole moments μ (in debye) of $X \cdots \text{CO}_2$ complexes and static dipole polarizabilities α (in a.u.) of X calculated from supermolecular KS-DFT calculations using both PW91 and SAOP. In all calculations, the largest basis set available (aug-QZ4P for Xe and Hg and ET-QZ3P-3DIFFUSE for all other elements) have been used. For comparison, the experimental values and the results of the previous MP2 and CCSD(T) calculations are also given.

		He	Ne	Ar	Kr	Xe	Hg
Dipole moment μ	KS-DFT (PW91)	0.0134	0.0253	0.0736	0.0943	0.1194	0.1494
	KS-DFT (SAOP)	0.0190	0.0286	0.0831	0.1112	0.1375	0.1651
	MP2 ^a	0.0160	0.0274	0.0714	0.0877	0.0976	
	CCSD(T) ^b	0.0158	0.0267				
	Experiment ^c		0.0244	0.0679	0.0829	0.1029	0.1070
Polarizability α	KS-DFT (PW91)	1.59	3.13	12.10	18.09	29.11	35.14
	KS-DFT (SAOP)	1.42	2.57	11.56	17.30	28.28	30.02
	Experiment ^d	1.38	2.67	11.07	16.77	27.29	33.91

^aReference 32.

^bReference 32.

^cReferences 26 and 27.

^dReferences 53 and 54.

the aug-ET-pVQZ basis set to the largest basis set used (ET-QZ3P-3DIFFUSE) is significantly smaller. The negligibly small BSSE correction gives another indication that the results obtained with the largest basis set are close to the basis set limit. All calculations presented in the following section use these large basis sets, e.g., ET-QZ3P-3DIFFUSE for the elements up to Kr and aug-QZ4P for Xe and Hg.

Comparing the results of the PW91 calculations to the experimental values, one notices that, except for $\text{CO}_2 \cdots \text{He}$, the induced dipole moments are overestimated in all cases. For $\text{CO}_2 \cdots \text{He}$, where no experimental value is available, the calculated dipole moment is slightly below the CCSD(T) calculation by Maroulis and Haskopoulos.

In the previous section, it was pointed out that to be able to describe the induced dipole moments correctly, it is important to describe the polarizability of the attached atom accurately. GGA potentials like PW91 are known to overestimate polarizabilities³⁸ because they do not give the correct asymptotic behavior of the KS potential.⁵⁶ Therefore, we also use the SAOP potential, which does have the correct asymptotic behavior and which is known to perform well in the calculation of polarizabilities.³⁸ In Table IV, the calculated induced dipole moments and static dipole polarizabilities calculated using PW91 and SAOP are given together with the experimental values.

We notice that PW91 overestimates indeed the polarizabilities of the rare gases and mercury while the SAOP potential gives polarizabilities which are in good agreement with the experiment. Even though SAOP gives better polarizabilities, for the induced dipole moments the agreement with experiment calculated is much worse than for PW91. These surprising findings are explained by looking at quadrupole moments of CO_2 calculated with KS-DFT using PW91 and SAOP, which are given in Table V. While the quadrupole moment calculated using PW91 is in good agreement with the experimental value, the SAOP potential overestimates the CO_2 quadrupole moment by 15%.

Summarizing the results of the supermolecular KS-DFT calculations, we can conclude that both PW91 and SAOP fail to reproduce the induced dipole moments of the investigated

$\text{CO}_2 \cdots X$ complexes, but for quite different reasons. PW91 overestimates the dipole polarizability of the rare gases, a consequence of the wrong asymptotic behavior of GGA potentials. On the other hand SAOP does describe the polarizabilities of the rare gases correctly, due to its correct asymptotic behavior, but it gives a poor description of the quadrupole moment of CO_2 .

C. KSCED embedding calculations

To assess the performance of the orbital-free KSCED embedding scheme we compared the induced dipole moments calculated using this scheme to the results of the supermolecular KS-DFT calculations presented in the previous section. This comparison was done for the two approximations to the exchange-correlation potential considered in the previous section: PW91 and SAOP.

We applied the KSCED scheme in freeze-and-thaw iterations as described above. In all the calculations done here the dipole moment was converged to an accuracy of 0.0001 D after only two or three freeze-and-thaw iterations. The dipole moments calculated for the two subsystems were added to yield the total induced dipole moment.

Following the formalism presented in the Introduction, applying the KSCED scheme in freeze-and-thaw iterations should result in the same electron density and thus the same total dipole moment as the supermolecular KS-DFT calculation. However, there are some approximations involved, which can lead to differences between the KSCED results and the results of supermolecular KS-DFT calculations.

TABLE V. Quadrupole moment Q_{xx} (in atomic units) of CO_2 calculated using KS-DFT with the ET-QZ3P-3DIFFUSE basis set.

	Q_{xx}
PW91	1.55
SAOP	1.85
Experiment ^a	1.595

^aReference 55.

TABLE VI. Induced dipole moments (in debye) in $\text{CO}_2 \cdots X$ complexes calculated using the KSCED embedding scheme with different approximations for the exchange-correlation potential (KSCED/PW91, KSCED/SAOP, and KSCED/combi; see text for details). In all calculations, the largest basis set available (aug-QZ4P for Xe and Hg and ET-QZ3P-3DIFFUSE for all other elements) have been used. For comparison, the results of the corresponding supermolecule KS-DFT calculations are also given, as well as the experimental values and the results of the previous MP2 and CCSD(T) calculations.

		He	Ne	Ar	Kr	Xe	Hg
KSCED/PW91	KSCED(<i>m</i>)	0.0136	0.0261	0.0747	0.0949	0.1136	0.1529
	KSCED(<i>s</i>)	0.0121	0.0258	0.0761	0.1028	0.1231	0.1771
PW91	KS-DFT	0.0134	0.0253	0.0736	0.0943	0.1194	0.1464
KSCED/SAOP	KSCED(<i>m</i>)	0.0128	0.0225	0.0775	0.0999	0.1204	0.1467
	KSCED(<i>s</i>)	0.0116	0.0220	0.0780	0.1042	0.1273	0.1606
SAOP	KS-DFT	0.0190	0.0286	0.0831	0.1112	0.1375	0.1651
KSCED/combi	KSCED(<i>m</i>)	0.0103	0.0200	0.0668	0.0859	0.1017	0.1249
MP2 ^a		0.0160	0.0274	0.0714	0.0877	0.0976	
CCSD(T) ^b		0.0158	0.0267				
Experiment ^c			0.0244	0.0679	0.0829	0.1029	0.1070

^aReference 32.

^bReference 32.

^cReferences 26 and 27.

First, in all KSCED calculation, the approximated non-additive kinetic-energy functional is not exact and its functional derivative, which is used in the construction of the embedding potential, is not exact either. Second, in calculations using orbital-dependent approximations to the exchange-correlation potential like SAOP, one furthermore encounters the complication that the supermolecular exchange-correlation potential is constructed in terms of a set of supermolecular orbitals. This potential cannot be reconstructed in a KSCED calculation since only the subsystem orbitals are available. This makes it necessary to choose a non-orbital-dependent form for the nonadditive exchange-correlation contribution [Eq. (9)], introducing an additional inconsistency relative to the supermolecular calculation. This is not the case with a GGA potential like PW91, because then the same approximation can be used for the exchange-correlation potential in the subsystems and for the nonadditive exchange-correlation contribution to the embedding potential. Therefore, the treatment of the exchange-correlation potential in KS-DFT and KSCED calculations is consistent.

With regard to possible basis set errors, there are two possibilities for the choice of the basis functions which are used to expand the densities of the two subsystems.¹³ The most obvious choice is to use only basis functions that are centered on the atoms in the considered subsystem to expand the corresponding density. This choice is in line with the “divide-and-conquer” strategy mentioned earlier since the size of the KS-Fock matrix is reduced in the separate calculations of $\rho_I(\mathbf{r})$ and $\rho_{II}(\mathbf{r})$. Calculations using this monomolecular basis set expansion will be labeled KSCED(*m*) following the convention of Ref. 13. However, this choice of the basis functions introduces an additional source of differences to the supermolecular calculation. In the expansion of the total electron density the products of basis functions centered at atoms in different subsystems are neglected. Further-

more, since the total number of electrons in both subsystems is fixed, a charge transfer between the two subsystems is not possible.

These problems are both removed in the KSCED(*s*) scheme which uses the full supermolecular basis set to expand the density of both subsystems. In this scheme, the advantage of the computational efficiency is lost. However, it is interesting from a theoretical point of view because the only sources of differences between KSCED(*s*) and supermolecular KS-DFT calculations are the approximation to the nonadditive kinetic-energy functional which is used when constructing the embedding potential and, in SAOP calculations, the approximations in the nonadditive exchange-correlation component of the embedding potential. It was, however, noticed in earlier works^{13,33} that in the KSCED(*s*) scheme the results are more sensitive to the problems in the kinetic-energy potential because the electron density is more flexible. Furthermore it should be noted that the differences between the KSCED(*s*) and KSCED(*m*) schemes should become smaller for larger basis sets as they approach the basis set limit.⁴

In Table VI, the induced dipole moments calculated with the KSCED scheme using different approximations to the exchange-correlation potential are presented and compared to the results of the corresponding supermolecule KS-DFT calculations and to the experimental dipole moments.

In the KSCED/PW91 calculations the induced dipole moments calculated using the KSCED(*m*) scheme are in excellent agreement with the results of the corresponding supermolecular KS-DFT calculations. For all considered complexes these differences are below 5%. Opposite to what would be expected, the agreement with the supermolecular KS-DFT calculations is worse for KSCED(*s*). For the Ar, Kr, Xe, and Hg complexes, the dipole moment calculated within the KSCED(*s*) scheme overestimates the dipole moments by up to 20%, with the differences becoming larger when mov-

ing to the heavier attached atoms. While for the Ne complex the KSCED(*s*) result is in good agreement with both the KSCED(*m*) and the supermolecular KS-DFT result, for the He complex the KSCED(*s*) dipole moment underestimates the supermolecular result by 10%.

The increase in the dipole moment which is observed for the complexes with the heavier attached atoms when going from KSCED(*m*) to KSCED(*s*) corresponds to electron density of the rare-gas or mercury atom being moved in the direction of the CO₂ molecule, and the decrease for the CO₂···He complex corresponds to electron density of the CO₂ molecule which is moved in the direction of the He atom. We think that these artificial differences between KSCED(*m*) and KSCED(*s*) are mainly caused by problems of the embedding potential in the region close to the nuclei of the frozen subsystem. Near these nuclei the embedding potential has to compensate the large attractive Coulomb potential of the nuclear charge. The observed differences indicate that this is not achieved completely. In the calculation of a rare-gas or mercury atom next to a frozen CO₂ fragment there is a small amount of electron density that is pulled to the C and O nuclei, leading to an artificial increase of the dipole moment. This effect shows up the most for the fragment which is more polarizable, e.g., the rare gas or mercury in the complexes with the heavier attached atoms. In the CO₂···He complex the effect is the other way around. In the calculation of the He fragment, a small amount of the more polarizable CO₂ electron density is attracted by the He nucleus. This kind of charge transfer can only occur if the basis set used is flexible enough near these nuclei in the frozen fragment, which is only the case in the KSCED(*s*) scheme. In the KSCED(*m*) calculations, the basis functions centered on the nuclei of the frozen subsystem are not available so that the amount of spurious charge transfer is smaller or not existent. It is important to note that the dipole moment, which is investigated here, is very sensitive to this kind of charge transfer so that small problems in the embedding potential have already a significant effect.

For the KSCED(*m*)/SAOP calculations, the agreement with the corresponding supermolecular KS-DFT calculations is not as good as in the KSCED/PW91 calculations. This is not surprising because of the contribution of the nonadditive exchange-correlation potential to the KSCED embedding potential an additional inconsistency is introduced. For the Ar, Kr, Xe, and Hg complexes the differences are rather small (below 13%), but for the He and Ne complexes the differences are larger (up to 32% for He). A reason for this behavior can be found in the way the SAOP potential is constructed. SAOP uses a statistical averaging over orbital potentials, in which the difference between the orbital energy and the orbital energy of the highest occupied molecular orbital (HOMO) is used to interpolate between two functional forms of the exchange-correlation potential: one that is optimal for the core region and one that is optimal for the valence region. For the He and Ne complexes, the highest occupied rare-gas orbitals, which are most important for the induced dipole moments, are more than 5 eV lower in energy than the HOMO and give rise to a “core” contribution to the exchange-correlation potential. In the KSCED embedding

calculations, the two subsystems are calculated separately, however, so that the rare-gas HOMO is then considered a valence orbital with corresponding contribution to the exchange-correlation potential. In the Kr, Xe, and Hg complexes, the rare-gas HOMO is also the HOMO in the supermolecular calculation, while for the Ar complex it is only about 1 eV below the HOMO of the supermolecule, so that these differences between the supermolecular KS-DFT calculation and the KSCED embedding calculation are then much smaller.

Comparing the KSCED(*s*)/SAOP calculations to the KSCED(*m*)/SAOP ones shows the same differences that were observed with KSCED/PW91. Even with the large basis sets used here, the KSCED(*s*) results differ significantly from the KSCED(*m*) results. As with KSCED/PW91, for the Kr, Xe, and Hg complexes, the dipole moments calculated using KSCED(*s*) are larger than the KSCED(*m*) values, with the difference increasing when going to the heavier elements. For the Ne and Ar complexes, the differences between KSCED(*m*) and KSCED(*s*) are not significant, while for the He complex the KSCED(*s*) dipole moment is smaller than the KSCED(*m*) one. These differences can be explained in the same way as it was done above for the KSCED/PW91 results. The fact that the KSCED(*s*) results are actually closer to the supermolecular KS-DFT results than the KSCED(*m*) results seems only to be a fortunate error cancellation between the nonadditive exchange-correlation and kinetic-energy contributions to the embedding potential.

D. Embedding with a combination of different exchange-correlation approximations

The supermolecular KS-DFT calculations in Sec. III B showed that both GGA potentials like PW91 as well as the asymptotically correct SAOP potential are not able to reproduce the experimental dipole moments of the investigated CO₂···X complexes correctly, because none of them is able to accurately describe the quadrupole moment of CO₂ and the polarizability of the attached atom at the same time.

One advantage of the KSCED embedding scheme presented here is that it allows one to use different approximations for the exchange-correlation potential in the two subsystems in a straightforward way. Therefore, we performed KSCED calculations (KSCED/combi) using PW91 to approximate the exchange-correlation potential in the KS potential of the CO₂ fragment (because it reproduces the quadrupole moment of CO₂ correctly) and SAOP in the KS potential of the rare-gas or mercury fragment (because it is able to describe the polarizability of the attached atom correctly). We would like to note that the use of this combination of different approximations is not just an arbitrary choice but one that is based on both physical knowledge about the systems under investigation (see the simple electrostatic interaction model presented in Sec. III A) and on the knowledge about the ability of different approximations to describe the polarizabilities and molecular multipole moments correctly.

In the previous section, we have demonstrated that the KSCED scheme works well for the considered complexes

both with PW91 and with SAOP. Therefore, we are confident that the embedding scheme will also work when these different approximations are combined by using them for the two subsystems. We can expect that the errors introduced by the use of the embedding scheme will be similar to the errors observed in the previous section. To get around the problems with the nonadditive kinetic-energy potential which were found in the previous section, we only applied the KSCED(m) scheme here, that is less affected by these problems.

The results of these calculations are shown in Table VI. For the Ar, Kr, Xe, and Hg complexes the embedding calculations using a combination of different approximations significantly improve the results of the simple electrostatic interaction model of Sec. III A, while giving dipole moments of comparable quality for the He and Ne complexes.

The results obtained in the KSCED/combi calculations are, for the Ar, Kr, and Xe complexes, in perfect agreement with the experimental values, with the differences being smaller than 5%. For $\text{CO}_2 \cdots \text{Ne}$, the experimental dipole moment is underestimated by about 20% and an underestimation is also observed for $\text{CO}_2 \cdots \text{He}$, where we have to compare to CCSD(T) calculations because no experimental value is available. For $\text{CO}_2 \cdots \text{Hg}$, the experimental value is overestimated by about 20%. These differences are of about the same size as the differences between the KSCED(m)/SAOP calculations and the corresponding supermolecular KS-DFT calculations in the previous section, so that these differences can be mainly attributed to the approximation which has to be made in the nonadditive exchange-correlation potential and the nonadditive kinetic-energy functional.

IV. CONCLUSIONS

In this study, we have for the first time applied the KSCED embedding scheme to the calculation of induced dipole moments in van der Waals complexes. We have shown that the embedding calculations are able to reproduce the results of the supermolecular KS-DFT calculations, if only basis functions centered on atoms of the nonfrozen subsystem are included [KSCED(m)]. The agreement is much better with a GGA potential like PW91 than for the calculations using the orbital-dependent SAOP potential, which can be explained by the additional approximations in the exchange-correlation part of the embedding potential that have to be made in this case.

Including the basis functions of the frozen subsystem in the embedding calculations [KSCED(s)] lead to a spurious charge transfer. We attribute this to the approximation used for the nonadditive kinetic-energy part of the embedding potential. These problems are most important if there are larger differences between the nuclear charges in the two subsystems, like in the $\text{CO}_2 \cdots X$ complexes where X is a heavier rare-gas or a mercury atom.

For the van der Waals complexes investigated here, it is possible to circumvent these problems by using the KSCED(m) scheme that does not probe the embedding potential in the region around the nuclei of the frozen subsystem as much as the KSCED(s) scheme does. However,

this will not be possible in systems with a stronger interaction or where a charge transfer between the subsystems occurs indeed, because for these systems the inclusion of the additional basis functions in the KSCED(s) is very important. Therefore, it will be interesting for future work to analyze these problems in more detail and to develop more advanced approximations to the nonadditive kinetic-energy functional.

Furthermore, we have demonstrated that the KSCED embedding scheme is a useful tool for combining different approximated exchange-correlation potentials by applying different approximations in the different subsystems. In this study, we have made use of this feature for the calculation of induced dipole moments, where both the GGA potential PW91 and the asymptotically correct SAOP potential fail to give a correct overall description. The KSCED embedding scheme made it possible to use in both subsystems an approximation to the exchange-correlation potential that is able to describe those properties of the fragments correctly that are important for the induced dipole moment of the complex: the polarizability for the rare-gas or mercury atom and the quadrupole moment for the CO_2 molecule. This strategy makes it possible to get induced dipole moments for the $\text{CO}_2 \cdots X$ van der Waals complexes that are in good agreement with the experiment, whereas KS-DFT calculations fail to achieve this. We mention here that a similar scheme was recently, mainly for reasons of computational efficiency, also used in studies on solvatochromism.^{7,8} While the SAOP potential was used to get accurate excitation energies for the solute, the local-density approximation (LDA) was used to describe the solvent molecules.

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