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Hoefener, S.; Visscher, L.

published in

Journal of Chemical Physics
2012

DOI (link to publisher)

[10.1063/1.4767981](https://doi.org/10.1063/1.4767981)

document version

Publisher's PDF, also known as Version of record

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citation for published version (APA)

Hoefener, S., & Visscher, L. (2012). Calculation of electronic excitations using wave-function in wave-function frozen-density embedding. *Journal of Chemical Physics*, 137(20), [204120]. <https://doi.org/10.1063/1.4767981>

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Citation: *J. Chem. Phys.* **137**, 204120 (2012); doi: 10.1063/1.4767981

View online: <http://dx.doi.org/10.1063/1.4767981>

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Calculation of electronic excitations using wave-function in wave-function frozen-density embedding

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(Received 21 August 2012; accepted 2 November 2012; published online 29 November 2012)

Recently, a general framework suitable for general frozen-density embedding (FDE) methods was published [S. Höfener, A. S. P. Gomes, and L. Visscher, *J. Chem. Phys.* **136**, 044104 (2012)]. In the present article, we report the fragmentation of a supermolecule while treating all subsystems with coupled-cluster theory and the interaction of the subsystems with density-functional theory. This variant is denoted wave-function theory in wave-function theory FDE, or coupled-cluster theory in coupled-cluster theory FDE. Main target of this approach is not the embedding of a single molecule in large solvation shells, but rather the possibility to divide a complex system consisting of several molecules when all subsystems are to be treated with, e.g., coupled-cluster methods to provide a balanced and unbiased description. We present numerical results for hydrogen-bonded complexes which exhibit rather strong interactions. Cases with weakly interacting subsystems are expected to exhibit even higher accuracy. This facilitates the study of properties of larger complexes such as DNA base pairs with coupled-cluster methods. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4767981>]

I. INTRODUCTION

Properties of molecules can be strongly influenced by their surroundings, leading to significant changes in their responses to external electric and magnetic fields. While properties such as molecular polarizabilities, local excitation energies, and molecular vibrations are conceptually well defined, it is difficult to define computational models to provide unambiguous values for such local properties. A simple example is the water... ammonia complex¹ in which orbitals are delocalized over the whole complex and even individual molecular charges are not well defined in a super molecular approach.

Subsystem methods therefore make an *a priori* subdivision of a complex system into smaller subunits, allowing for a convenient definition of subsystem properties. This also makes it easier to introduce approximations in selected subsystems and improve the computational feasibility of the calculations. Many quantum-mechanics/molecular-mechanics (QM/MM) as well as QM/QM methods have been developed and applied in virtually all areas of chemistry. In cases in which the electronic structure of only a relatively small number of atoms needs to be considered explicitly, such as for molecules in solution or an active site in a protein, QM/MM methods are typically chosen because they offer the possibility to include ten thousands of atoms, albeit with most atoms treated using molecular mechanics. In such a case, there is a trade-off between the accuracy in terms of the size of the QM region and the accuracy in terms of the level of theory applied in the QM region that can be addressed by applying multilevel partitioning, e.g., using the flexible ONIOM scheme^{2–4} (ONIOM is short-hand for “our own n-layered integrated molecular orbital and molecular mechanics”).

The situation is different when the system consists of similar molecules that are all equally important for the pro-

cess under investigation. Examples are light-harvesting complexes in natural systems, in which one would like to study all individual chromophores using the same level of theory. Such problems call for homogeneous partitionings in which subsystems are defined, but in which each system is treated with the same method. This is possible with local coupled cluster (CC) schemes, e.g., as developed by Schütz and Werner,^{5,6} in which non-orthogonal unoccupied projected atomic orbitals are used and only “local” coupled-cluster amplitudes are determined. In the present work, we report a new alternative, namely, wave-function theory in wave-function theory (WFT-in-WFT) frozen-density embedding (FDE), which can be derived from density-functional theory in density-functional theory (DFT-in-DFT), developed by Wesolowski and Warshel,⁷ but in essence already contained in earlier works by Senatore and Subbaswamy⁸ and later Cortona.⁹ WFT-in-WFT FDE offers the possibility to choose any WFT method well suited for the system and property of interest, which is of importance when Kohn-Sham approaches are unsuitable or have too limited accuracy. Comparing to WFT-in-DFT FDE, the computational cost of the new approach is even slightly decreased, because only one iterative scheme has to be carried out instead of two WFT-in-DFT FDE schemes with interchanged roles of WFT and DFT treatment, provided that WFT results are required for all subsystems.

This approach’s formalism is included in earlier work¹⁰ and is thus closely related to FDE work in the literature. For instance, for the time-dependent generalization¹¹ of DFT-in-DFT, Neugebauer and co-workers^{12–18} have shown how to formulate the exact treatment in case of time-dependent properties such as excitation energies to account for polarization effects due to the environment response and how to introduce systematically approximations to obtain an efficient and fast treatment. It does, however, exhibit significant

differences to other subsystem methods. The present approach is distinct from the density-matrix embedding theory by Chan and Knizia,¹⁹ in which, starting from the supermolecule, subunits are reproduced exactly allowing for cutting chemical bonds, or the exact embedding recently reported by Manby,²⁰ in avoiding all explicit supermolecular treatments. The goal is to obtain a scheme that enables the calculation of chemical subunits in complex systems that are too large to be accessible otherwise. The key feature is to describe the interaction between the subsystems by a purely DFT-based ansatz. This enables a general combination of arbitrary WFT methods without possibly complicated projection operators and overlaps.

The article is organized as follows. In Sec. II, the theory is outlined, followed by the computational details in Sec. III. In Sec. IV, results for three different examples are presented and discussed.

II. METHOD

The fundamental CC orbital-unrelaxed Lagrangian $\mathcal{H}$ is obtained from the energy expression and the amplitude equations Ω_{μ_i}

$$\mathcal{H} = \langle \text{HF} | \exp(-T) H \exp(T) | \text{HF} \rangle + \sum_{\mu_i} \tilde{t}_{\mu_i} \Omega_{\mu_i}, \quad (1)$$

$$\Omega_{\mu_i} = \langle \mu_i | \exp(-T) H \exp(T) | \text{HF} \rangle, \quad (2)$$

T denotes the (truncated) cluster operator. In FDE, the supermolecule Lagrange functional $\mathcal{L}$ consists of the subsystem I ($\mathcal{H}_I$), subsystem II ($\mathcal{H}_{II}$), and the interaction contribution (Q_{int})

$$\mathcal{L} = \mathcal{H}_I + Q_{\text{int}} + \mathcal{H}_{II}. \quad (3)$$

For details the reader is referred to Ref. 10. In our previous work, a DFT energy expression was always used for subsystem II. In the current work when investigating CC-in-CC, a coupled-cluster Lagrange functional is used for both subsystems. However, the interaction contribution remains to be expressed in terms of DFT using only the densities of the two subsystems (ρ_I and ρ_{II})

$$\begin{aligned} Q_{\text{int}} = & \int \rho_I(\mathbf{r}) v_{\text{nuc}}^{\text{II}}(\mathbf{r}) d\mathbf{r} + \int \rho_{II}(\mathbf{r}) v_{\text{nuc}}^{\text{I}}(\mathbf{r}) d\mathbf{r} \\ & + E_{\text{nuc}}^{\text{I,II}} + \iint \frac{\rho_I(\mathbf{r}) \rho_{II}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ & + Q_{\text{xc}}^{\text{nadd}}[\rho_I, \rho_{II}] + Q_T^{\text{nadd}}[\rho_I, \rho_{II}]. \end{aligned} \quad (4)$$

When employing coupled cluster for the subsystems, the coupled-cluster densities are used in this expression.

The embedding contributions to the coupled-cluster amplitudes are obtained from the constraint that the quasienergy Lagrangian has to be stationary with respect to the Lagrangian multipliers. One thus obtains for either subsystem¹⁰

$$0 = \frac{\partial \mathcal{L}}{\partial \tilde{t}_{\mu_i}} = \Omega_{\mu_i} + \sum_{pq} \langle p | v_{\text{int}} | q \rangle \langle \mu_i | e^{-T} E_{pq} | \text{CC} \rangle. \quad (5)$$

This equation connects the DFT contribution with the coupled-cluster treatment since a potential as used in DFT is

contracted with a coupled-cluster density. Similarly, contributions are derived for the Lagrangian multipliers. New terms, qualitatively analogous to kernel contributions in DFT, are included in the coupled-cluster Jacobian when time-dependent properties are to be calculated.^{10,21} The uncoupled procedure yields, e.g., two Jacobians, and the spectrum of the whole system is obtained as the superposition of both subsystem spectra. The size extensivity of the subsystem approach is an important advantage; even when the subsystems are treated with non-size extensive methods like configuration interaction, the method provides the correct limit for non-interacting subsystems.

As discussed in Ref. 21 for WFT-in-DFT FDE, at all levels the coupled-cluster density is to be used whenever terms originating from the interaction contribution are calculated. The WFT density is therefore not decomposed into uncorrelated and correlated parts, and the embedding potential (if used) in the Hartree-Fock step and (always used) in the coupled-cluster step are taken to be the same.

Each subsystem is converged according to schemes as proposed for WFT-in-DFT FDE,^{10,21} followed by an update of the other subsystem according to the same criteria. This is commonly denoted freeze-thaw iterations in FDE methods: first, a calculation for an isolated fragment is carried out, followed by the computation of the second subsystem in the presence of the potential (represented on a numerical grid) due to the first subsystem. After intra-molecular relaxation, the density is stored and the first subsystem is relaxed. These intra- and inter-molecular relaxation cycles are carried out until the requested convergence is reached.

While the repeated computation of Hartree-Fock orbitals and the coupled-cluster density may seem computationally rather expensive, relative to treatment of a single subsystem, the scheme is rather cheap compared with supermolecule coupled-cluster calculations in which orbitals and amplitudes are determined for the full system. The approach may also easily be made more computationally efficient by combining micro- and macro-iterations, i.e., restarting the micro-iterations needed for the coupled-cluster density with the amplitudes determined in the previous macro-cycle.

III. COMPUTATIONAL DETAILS

We have implemented the scheme in a local version of the DALTON2011 release.²² The full model including couplings of the subsystems is the aim of future work. Here, results obtained from the uncoupled model are presented, so that strong couplings between excitations between the separated subsystems cannot be described. All calculations have been carried out using the full supermolecule grid as generated by the Dirac code²³ with default parameters. Local density approximation (“LDA”) refers to an embedding potential created with Slater exchange and Thomas-Fermi kinetic energy, whereas generalized gradient approximation (GGA) refers to an embedding potential created with the PBE²⁴ functional in combination with the PW91 kinetic²⁵ energy functional. Whereas in DFT-in-DFT embedding differences between the explicit density functional and the Kohn-Sham kinetic energy representation is the only source of discrepancy between supermolecule

and embedding calculations, for WFT-in-WFT FDE also differences between the explicit exchange-correlation density functional and the WFT way of representing exchange and correlation may play a role. Because the kinetic energy contribution to the interaction energy and embedding potential is usually much larger than the exchange-correlation contribution, we expect that these additional errors are relatively small. In the following, we will therefore not attempt to disentangle these two sources of errors but rather discuss the influence of the functionals using two different functional sets in which the kinetic and the exchange-correlation energy belong to the same class of functionals.

If not indicated otherwise, Dunning's correlation consistent double zeta basis (cc-pVDZ)²⁶ was used and the frozen-core approximation was applied. Coupled-cluster methods used were coupled-cluster singles (CCS), singles and doubles (CCSD), as well as coupled-cluster singles and doubles with a perturbational treatment of the doubles (CC2).²⁷ Clearly, these excitation energies obtained are not converged with respect to the basis set or the truncation level of the cluster operator but the accuracy should be sufficient for the comparison of supermolecule and embedding calculations, for which we only need to focus on differences in the treatment of the intermolecular interaction.

All WFT-in-WFT FDE procedures include both micro- and macro-iterations, where the latter ones are denoted "freeze-thaw" iterations in FDE theory. In each macro-iteration, two micro-iterations were carried out to relax the active fragment with respect to the frozen density of the inactive fragment. The number of macro-iterations was limited in most cases to one relaxation cycle, which turned out to be sufficient for excitation energies within the presented accuracy. Although we observed that the densities and energies were converged after about 5 iterations, the small density changes after the first iteration had no impact on the excitation energies. All results were obtained with perturbed Hartree-Fock orbitals ("p") in the presence of the embedding potential, which is reflected in the acronym {p,r,-}, where "r" denotes relaxed embedding potentials and "-" the absence of kernel contributions. If kernel contributions are included, the abbreviation {p,r,ALDA} is used, denoting the use of the adiabatic local density approximation.

We have also carried out a WFT-in-DFT approach as proposed earlier by Gomes *et al.*,²⁸ in which DFT-in-DFT freeze-thaw iterations are carried out using the ADF program,²⁹ followed by a coupled-cluster calculation using DALTON. Since this approach uses a static ("s") embedding potential in the final coupled-cluster treatment, this method is abbreviated with {p,s,-}, although the potential was relaxed during freeze-thaw iterations. We have chosen to carry out this procedure rather than a "true" WFT-in-DFT treatment, i.e., employing the coupled-cluster density to polarize the environment, because the subsystems should be treated at the same level of theory to avoid an unbalanced description. It should be noted that a comparison of a supermolecule coupled-cluster calculation to such an approach is rather ambiguous. If, for instance, the coupled-cluster density and the DFT density differ due to some failures of either method for a given molecule, the comparison will reveal different shifts for the right rea-

son and similar shifts would indeed indicate errors. Thus, the main conclusion of such a comparison is that if the densities are expected to be of similar accuracy and the observed shifts are also akin, the results can be considered reliable. In particular, this holds for the frozen-core approximation used in the coupled-cluster treatment, in which the "frozen" electrons are not neglected but treated at Hartree-Fock level of theory within the coupled-cluster density.

IV. RESULTS

A. Water . . . ammonia complex

In the first example, a water . . . ammonia complex is investigated with CC-in-CC. The geometries were taken from Ref. 1; the basis set used was aug-cc-pVDZ^{26,30} and the frozen-core approximation was applied. In Table I, results of supermolecule calculations are listed, showing that in this example the influence due to the geometry change is small and amounts to at most 0.06 eV. Embedding results are collected in Table II. The biggest difference stems from the choice of the coupled-cluster model, and the 0.1–0.3 eV embedding error for the lowest excitation is in case of CCS significantly below the CCS method error of 1–2 eV. In case of CC2, the error of the method decreases to a few tenths of an eV and both errors have approximately the same order of magnitude which is also comparable to basis set truncation effects for the aug-cc-pVDZ basis in this example.¹ To evaluate the influence of basis set truncation errors on the environment shifts, we carried out calculations with larger basis sets and found in the case of CCSD (employing "GGA embedding" without kernel) that the shifts become +0.65 eV and -0.29 eV, respectively. Since these values exhibit differences less than 0.01 eV to the ones obtained with the aug-cc-pVDZ basis, it indicates that the basis-set effect on the shift is negligible in this case.

The old protocol yields, e.g., CC2 {p,s,-} excitation energies of 7.04 eV and 6.70 eV for NH₃ and H₂O, respectively. It can be seen that the differences to the CC-in-CC treatment amount to about 0.06 eV and no clear trend is observed: whereas for ammonia the absolute error is decreased with the new method, it is increased slightly for the water molecule.

TABLE I. Vertical excitation energies and corresponding shifts of the water . . . ammonia complex for the lowest two excitations in eV. In these calculations, the aug-cc-pVDZ basis and the frozen-core approximation was used. "Monomer" refers to relaxed monomer structures.

Method	Source	Monomer	Isol. ^a	Geom. ^b	Superm.	Env. ^c	Total ^d
CCS	NH ₃	7.44	7.50	+0.06	8.05	+0.55	+0.61
	H ₂ O	8.67	8.63	-0.04	8.59	-0.04	-0.08
CC2	NH ₃	6.25	6.31	+0.06	6.79	+0.48	+0.54
	H ₂ O	7.09	7.05	-0.04	6.84	-0.21	-0.25
CCSD	NH ₃	6.46	6.51	+0.05	7.00	+0.49	+0.54
	H ₂ O	7.45	7.41	-0.04	7.26	-0.15	-0.19

^aIsolated molecules at the dimer geometry.

^bGeometric shift relative to monomer geometry.

^cEnvironment shift relative to isolated molecules at dimer geometry.

^dTotal shift relative to monomer geometry.

TABLE II. Vertical excitation energies and corresponding shifts of the water...ammonia complex calculated with embedding for the lowest two excitations in eV. In these calculations, the aug-cc-pVDZ basis and the frozen-core approximation was used.

Method		Source	{p,s,-}	Env. ^a	Error ^b	{p,r,-}	Env. ^a	Error ^b	{p,r,ALDA}	Env. ^a	Error ^b
CCS	LDA	NH ₃				8.16 ^c	+0.66	+0.11	8.17 ^c	+0.67	+0.12
		H ₂ O				8.48 ^c	-0.15	-0.11	8.49 ^c	-0.14	-0.10
	GGA	NH ₃				8.15 ^c	+0.65	+0.10	8.18 ^d	+0.68	+0.13
		H ₂ O				8.39 ^c	-0.24	-0.20	8.40 ^d	-0.23	-0.19
CC2	LDA	NH ₃				6.97 ^c	+0.66	+0.18	7.00 ^d	+0.69	+0.21
		H ₂ O				6.79 ^c	-0.26	-0.05	6.80 ^d	-0.25	-0.04
	GGA	NH ₃	7.04	+0.73	+0.25	6.97 ^c	+0.66	+0.18	7.01 ^d	+0.70	+0.22
		H ₂ O	6.70	-0.35	-0.14	6.66 ^c	-0.39	-0.18	6.67 ^d	-0.38	-0.17
CCSD	LDA	NH ₃				7.16 ^c	+0.65	+0.16	7.19 ^d	+0.69	+0.20
		H ₂ O				7.22 ^c	-0.19	-0.04	7.22 ^d	-0.19	-0.04
	GGA	NH ₃	7.23	+0.72	+0.23	7.18 ^d	+0.67	+0.18	7.19 ^d	+0.69	+0.20
		H ₂ O	7.14	-0.27	-0.12	7.11 ^d	-0.30	-0.15	7.12 ^d	-0.29	-0.14

^aEnvironment shift relative to isolated molecules at dimer geometry, see Table I.^bError relative to supermolecule treatment.^cOne macro-relaxation cycle was used.^dTwo macro-relaxation cycles were used.

The lowest excitation in the complex corresponds to the excitation of the nitrogen lone pair,¹ and the second lowest excitation corresponds to an excitation of the oxygen lone pair, so that in general the perturbation of the lowest excitation is more pronounced: In Ref. 1, the most accurate shifts were calculated (using CCSD with d-aug-cc-pVQZ³¹) to be +0.47 eV and -0.17 eV for the lowest and the second lowest excitation, respectively.¹ In the present work, the environment shifts are overestimated, which can lead to a wrong order of the excited states due to the small energy differences between the excited states. As our tests indicated that we can rule out basis set errors, this error should originate from deficiencies in the density functionals used to describe the intermolecular exchange correlation and kinetic energy contributions and the neglect of couplings between the intramolecular excitations.

B. Uracil in 6 water molecules

As a second example, excitation energies of the micro-solvated uracil molecule in presence of 6 water molecules are presented, of which the geometry was taken from Ref. 32. In this case, the lowest excitation occurs from the oxygen lone pair denoted n_O to the lowest unoccupied molecular orbital (LUMO), denoted π_L^* . Table III reveals that both the in-

fluence due to the geometry change and the intermolecular electronic interactions introduce significant modifications for the lowest excitation energies. Because of the different sign, these shifts partially cancel each other, so that the final solvatochromic shift is comparatively small. A quite good description of the $n_O \rightarrow \pi_L^*$ excitation energy is observed, with errors compared to the supermolecule calculation of less than 0.05 eV. Concerning the $\pi \rightarrow \pi_L^*$ excitation energy, larger errors of slightly less than 0.1 eV occur.

We have also carried out a WFT-in-DFT approach as introduced for the first example. This yields, e.g., CC2 {p,s,-} excitation energies of 5.43 eV and 5.48 eV for the $n_O \rightarrow \pi_L^*$ and $\pi \rightarrow \pi_L^*$ excitation, respectively. For this example, the new method is able to decrease the errors below 0.1 eV.

C. Guanine...cytosine (GC) base pair

The third and last examples are concerned with the Watson-Crick GC base pair, which is naturally divided in the two subsystems guanine and cytosine. The dimer geometries were taken from Refs. 33 and 34. The monomer structures were optimized at Hartree-Fock level of theory using the 6-31++G** basis³⁵⁻³⁷ to ensure the same level of theory as for the dimers. Differences arising from coordinates obtained at

TABLE III. Lowest two vertical excitation energies of uracil in eV, calculated with CC2. n_O is the lone pair of the oxygen orbital, and π_L denotes the lowest unoccupied molecular orbital (LUMO). Excitation energies for the relaxed monomer structures are 5.05 eV and 5.69 eV for the excitations $n_O \rightarrow \pi_L^*$ and $\pi \rightarrow \pi_L^*$, respectively.

	Isol. ^a	Geom. ^b	Superm.	Env. ^c	Total ^d	LDA			GGA			Env. ^c	Error ^e
						{p,r,-}	Env. ^c	Error ^e	{p,s,-}	Env. ^c	Error ^e		
$n_O \rightarrow \pi_L^*$	4.66	-0.39	5.31	+0.65	+0.26	5.34	+0.68	+0.03	5.43	+0.77	+0.12	5.36	+0.70
$\pi \rightarrow \pi_L^*$	5.48	-0.21	5.36	-0.12	-0.33	5.45	-0.03	+0.09	5.48	-0.00	+0.12	5.45	-0.03

^aIsolated molecules at the dimer geometry.^bGeometric shift relative to molecules at monomer geometry.^cEnvironment shift relative to isolated molecules at dimer geometry.^dTotal shift relative to molecules at monomer geometry.^eError relative to supermolecule treatment.

TABLE IV. Results for DNA base pair guanine...cytosine (GC) in eV. "Monomer" refers to relaxed monomer structures. All embedding calculations were carried out with the GGA functional set.

Method	Source	Monomer	Isol. ^a	Geom. ^b	Superm.	Env. ^c	{p,s,-}	Env. ^c	Error ^d	{p,r,-}	Env. ^c	Error ^d
CC2	G $\pi \rightarrow \pi^*$	5.57	5.47	-0.10	5.42	-0.05	5.48	+0.01	+0.06	5.49	+0.02	+0.07
	C $\pi \rightarrow \pi^*$	5.15	4.98	-0.17	5.25	+0.27	5.27	+0.29	+0.02	5.22	+0.24	-0.03
CCSD	G $\pi \rightarrow \pi^*$	5.65	5.56	-0.09	$\times^e$		5.58	+0.02		5.58	+0.02	
	C $\pi \rightarrow \pi^*$	5.30	5.17	-0.13	$\times^e$		5.44	+0.27		5.40	+0.23	

^aIsolated molecules at the dimer geometry.^bGeometric shift relative to monomer geometry.^cEnvironment shift relative to isolated molecules at dimer geometry.^dError relative to supermolecule treatment.^eNot calculated.

a better level of theory³⁸ are unimportant for the current purpose.

Using the embedding procedure at the CC2 level of theory, shifts of -0.08 eV and +0.07 eV are found for guanine and cytosine, respectively, see Table IV. For guanine the lowest excitation shifts by -0.10 eV due to the structure change, and for cytosine the same effects leads to a shift of -0.17 eV. The interaction of the electronic structures of the two molecules leads then to an additional shift of +0.05 eV for guanine, and +0.27 eV for cytosine. This is partially captured by the embedding approach. For cytosine, the embedding yields a shift of +0.24 eV, which deviates only by 0.03 eV from the supermolecule calculation. In case of guanine, the shift has the wrong sign, but the error of 0.07 eV is distinctly below, e.g., the influence of the coupled-cluster ansatz. The larger error occurs due to the character of the excitation, because it contains some charge-transfer (CT) character which cannot be described with the FDE approach. However, when comparing the shift with respect to the relaxed monomer geometries, this error is overshadowed by the larger geometry shift, resulting in acceptable solvatochromic shifts.

We also present CCSD embedding results, which give similar shifts compared to those obtained with CC2. Due to the fragmentation, it is computationally affordable, in particular for the DNA base pairs, to increase the basis and/or the level of theory, which would lead to very expensive calculations in the supermolecule approach. In addition, it will be possible to include environment effects via explicit solvation to provide a better description of experimentally obtained spectra.

Applying the WFT-in-DFT {p,s,-} scheme, e.g., CC2 excitation energies of 5.48 eV and 5.27 eV are obtained for guanine and cytosine, respectively. An analogous treatment at CCSD level of theory yields excitation energies of 5.58 eV and 5.44 eV, respectively. The differences of the two schemes amount to about 0.01 eV for guanine and are thus negligible in the context of other error sources. For cytosine, the differences are 0.04 eV, which is slightly larger but still very small. Since for these examples neither coupled-cluster nor DFT is expected to exhibit severe failures, it can be concluded that both approaches yield similar densities and thus similar environment shifts for the right reason. We therefore consider the CC-in-CC FDE approach a valuable tool due to its symmetry for all subsystems, allowing for a straight-forward extension

to more accurate treatments such as the formulation of coupled excitations.

V. CONCLUSIONS AND OUTLOOK

In the present work, excitation energies are obtained from dividing a molecular arrangement into fragments with all subsystems calculated with coupled-cluster methods and the interaction treated with DFT, denoted WFT-in-WFT frozen-density embedding. The theory of this approach is described in detail in Refs. 10 and 21. The sample calculations presented show that the main contribution to the solvatochromic shift is accounted for using uncoupled WFT-in-WFT embedding, leading to an efficient treatment especially for larger systems. The observed differences of up to 0.2 eV in comparison to supermolecule calculations can be traced back to the interaction between the subsystems which is replaced by a DFT description with approximate kinetic as well as exchange-correlation energy functionals. In order to study these discrepancies, it is of interest to also study this approach with optimized effective potentials to avoid the error originating from the approximate kinetic energy functional. This is not yet possible within the computational setup used, but needs to be addressed in future work. However, differences of this size are smaller than errors, e.g., due to the truncation of the coupled-cluster excitation operator in these examples. It is understood that the current procedure is not applicable when highly accurate results are required. This is not only due to the density functionals used to calculate the interaction, but it is also inherent to the FDE ansatz which is not able to describe, e.g., inter-fragment CT excitations.

The current implementation does not allow to treat strongly coupled excitations. Future work will be also concerned with the coupling of the subsystems, which corresponds to the calculation of off-diagonal matrix elements as outlined in Ref. 10, or Ref. 15 for DFT-in-DFT. The importance of this can be illustrated in the example of two identical subsystems: in such a case, the uncoupled approach yields numerically identical lowest excitation energies for both subsystems, but the interaction will result in symmetry breaking and a splitting. In this situation, when two similar subsystems are to be treated with WFT methods and the inclusion of the coupling becomes mandatory, combinations of, e.g., two separate WFT-in-DFT calculations is not possible in a consistent fashion.

The reported CC-in-CC approach is only one example of WFT-in-WFT embedding and represents a first step towards more generalized setups which can consist of embedding, e.g., a relativistic calculation in a one-component treatment. In WFT-in-WFT FDE, approximations are being made that lead to a reduced numerical accuracy compared to the supermolecule case, but we believe that the FDE approach offers the possibility to study cases which are not accessible otherwise, such as using relativistic methods with (saturated) solvation shells.

ACKNOWLEDGMENTS

S.H. has been supported by the European Commission under a Marie-Curie Intra-European Fellowship (Contract No. PIEF-GA-2010-274224). L.V. has been supported by a VICI grant by the Netherlands Organisation for Scientific Research (NWO).

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