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On the universality of the long-/short-range separation in multiconfigurational density-functional theory

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In many cases, the dynamic correlation can be calculated quite accurately and at a fairly low computational cost in Kohn-Sham density-functional theory (KS-DFT), using current standard approximate functionals. However, in general, KS-DFT does not treat static correlation effects (near degeneracy) adequately which, on the other hand, can be described in wave-function theory (WFT), for example, with a *multiconfigurational self-consistent field* (MCSCF) model. It is therefore of high interest to develop a hybrid model which combines the best of both WFT and DFT approaches. The merge of WFT and DFT can be achieved by splitting the two-electron interaction into long-range and short-range parts. The long-range part is then treated by WFT and the short-range part by DFT. In this work the authors consider the so-called "erf" long-range interaction $\mathrm{erf}(\mu r_{12})/r_{12}$, which is based on the standard error function, and where μ is a free parameter which controls the range of the long-/short-range decomposition. In order to formulate a general method, they propose a recipe for the definition of an optimal μ_{opt} parameter, which is independent of the approximate short-range functional and the approximate wave function, and they discuss its universality. Calculations on a test set consisting of He, Be, Ne, Mg, H_2, N_2, and H_2O yield $\mu_{\mathrm{opt}} \approx 0.4$ a.u.. A similar analysis on other types of test systems such as actinide compounds is currently in progress. Using the value of 0.4 a.u. for μ, encouraging results are obtained with the hybrid MCSCF-DFT method for the dissociation energies of H_2, N_2, and H_2O, with both short-range local-density approximation and PBE-type functionals. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2566459]

I. INTRODUCTION

Density-functional theory (DFT) is widely used nowadays in quantum chemistry, in particular, because it is computationally relatively cheap and thus can be used for large scale calculations. However, even if current standard approximate functionals in many cases provide a satisfactory description of the short-range dynamic correlation (Coulomb hole), the static correlation effects (degeneracy or near degeneracy) and the dispersion interaction effects are in general not treated adequately. On the other hand, the static correlation effects can be described in wave-function theory (WFT), for example, with a *multiconfigurational self-consistent field* (MCSCF) model,[1] but then an important part of the dynamic correlation has to be neglected. It can be recovered with perturbation-theory based methods, for example, CASPT2 (Ref. 2 and 3) or NEVPT2,[4] but their computational complexity prevents large scale calculations.

It is therefore of high interest to develop a hybrid WFT-DFT model which combines the best of both approaches. Different formulations have been proposed to merge WFT and DFT. One approach consists in calculating the dynamic correlation from the density of a MCSCF wave function (see, for example, Refs. 5 and 6). The correlation functional must then be adapted to the active space to avoid double counting of the dynamic correlation, which is technically not trivial. This complication can be overcome by splitting the two-electron interaction into long-range and short-range parts as proposed by Savin (see, for example, Ref. 7). In this approach the long-range interaction is treated within WFT and the short-range interaction treated within DFT. As we have to use approximate wave functions and approximate short-range functionals the following question arises: Can we define an optimal long-/short-range separation and is it universal?

The present work is an attempt to answer this question. It is organized as follows: in Sec. II we present the hybrid WFT-DFT model based on a long-/short-range decomposition of the two-electron interaction controlled by the parameter μ. The definition of an optimal μ parameter μ_{opt} is then investigated. In Sec. III A we show that system- and geometry-dependency problems occur when approximate short-range functionals and approximate wave functions are involved in this definition, preventing us to formulate a general method. A new definition, based on a clear and natural criterion for the assignment of the dynamic correlation to the short-range interaction and the static correlation (and dispersion interaction) effects to the long-range interaction, is then given in Sec. III B. After discussing the universality of this definition, we perform in Sec. III C a numerical investigation of μ_{opt} on a small selected set of atoms and molecules chosen to represent both systems without and with significant static correlation. Finally, the dissociation energies of H_2, N_2, and H_2O (fixed at the equilibrium angle) calculated at the hybrid MCSCF-DFT level are presented and compared to standard WFT and DFT results in Sec. IV.

II. THEORY

The hybrid WFT-DFT models discussed in the present paper are based on the separation of the regular two-electron Coulomb interaction W_{ee} into long- and short-range parts:[7]

$$W_{ee} = W_{ee}^{\text{lr},\mu} + W_{ee}^{\text{sr},\mu},$$
$$W_{ee}^{\text{lr},\mu} = \frac{1}{2}\sum_{i\neq j}\frac{\text{erf}(\mu r_{ij})}{r_{ij}}, \tag{1}$$

where erf is the standard error function and μ a free parameter in $[0,+\infty[$ which determines the long-/short-range separation. Thus the universal functional $F[n]$ introduced by Hohenberg and Kohn[8] can be decomposed into long-range and short-range contributions:

$$F[n] = F^{\text{lr},\mu}[n] + E_H^{\text{sr},\mu}[n] + E_{\text{xc}}^{\text{sr},\mu}[n],$$
$$F^{\text{lr},\mu}[n] = \min_{\Psi\to n}\{\langle\Psi|\hat{T} + \hat{W}_{ee}^{\text{lr},\mu}|\Psi\rangle\}, \tag{2}$$

where $E_H^{\text{sr},\mu}[n]$ and $E_{\text{xc}}^{\text{sr},\mu}[n]$ denote, respectively, the Hartree and the exchange and correlation energies related to the short-range interaction. In this approach the density is therefore obtained from a fictitious long-range interacting system whereas in Kohn-Sham DFT (Ref. 9) (KS-DFT) it is obtained from a fictitious noninteracting one. The KS-DFT is recovered in the $\mu=0$ limit, while the pure WFT is obtained in the $\mu=+\infty$ limit, as seen from Eqs. (1) and (2). The ground-state energy, which is obtained according to the variational principle[8] by

$$E_0 = \min_n\left\{F[n] + \int d\mathbf{r}\, v_{\text{ne}}(\mathbf{r})n(\mathbf{r})\right\}, \tag{3}$$

can then be expressed using Eq. (2) as

$$E_0 = \min_\Psi\left\{\langle\Psi|\hat{T} + \hat{W}_{ee}^{\text{lr},\mu}|\Psi\rangle + E_H^{\text{sr},\mu}[n_\Psi] + E_{\text{xc}}^{\text{sr},\mu}[n_\Psi] + \int d\mathbf{r}\, v_{\text{ne}}(\mathbf{r})n_\Psi(\mathbf{r})\right\}, \tag{4}$$

where n_Ψ is the electron density related to the wave function Ψ and $v_{\text{ne}}(\mathbf{r})$ the local nuclear attraction potential. The minimizing wave function $\Phi^{\text{lr},\mu}$ in Eq. (4) also fulfills the following self-consistent equation:

$$(\hat{T} + \hat{W}_{ee}^{\text{lr},\mu} + \hat{V}^{\text{sr},\mu})|\Phi^{\text{lr},\mu}\rangle = \mathcal{E}^\mu|\Phi^{\text{lr},\mu}\rangle, \tag{5}$$

where $\mathcal{E}^\mu$ is the Lagrange multiplier related to the normalization of $\Phi^{\text{lr},\mu}$ and $\hat{V}^{\text{sr},\mu}$ is the effective local potential operator defined as follows:

$$\hat{V}^{\text{sr},\mu} = \int d\mathbf{r}\, v^{\text{sr},\mu}(\mathbf{r})\hat{n}(\mathbf{r}),$$
$$v^{\text{sr},\mu}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + \frac{\delta E_H^{\text{sr},\mu}}{\delta n}(\mathbf{r}) + \frac{\delta E_{\text{xc}}^{\text{sr},\mu}}{\delta n}(\mathbf{r}), \tag{6}$$

with $\hat{n}(\mathbf{r})$ denoting the density operator. If $\mu=0$, the long-range interaction $W_{ee}^{\text{lr},\mu}$ vanishes so that the Kohn-Sham equation is recovered from Eq. (5). For $\mu\to+\infty$ the short-range interaction $W_{ee}^{\text{sr},\mu}$ vanishes and Eq. (5) reduces to the standard Schrödinger equation. For $0<\mu<+\infty$, the model is hybrid since long-range effects are treated in WFT and short-range effects are treated in DFT.

The theory is so far exact but, since the exact form of the short-range exchange and correlation functional $E_{\text{xc}}^{\text{sr},\mu}[n]$ is unknown, an approximate form must be used in practical calculations. Two approximations have been considered: the short-range local-density approximation[7,10] (SRLDA) and the short-range generalized gradient approximation (GGA) denoted PBEHSERI in the following, as an extension of the PBE functional.[11] In the latter case the short-range exchange PBE functional of the hybrid functional of Heyd *et al.*[12,13] is used. The short-range correlation functional is obtained by a rational interpolation between the standard PBE correlation functional at $\mu=0$ and the asymptotic expansion of the SRLDA correlation functional as $\mu\to+\infty$. The interpolation we use is the one of Eq. (29) in Ref. 14, except that the d_1 coefficient is multiplied by $\sqrt{2}$ according to Ref. 15.

Moreover, since $W_{ee}^{\text{lr},\mu}$ is a two-body operator, the exact wave function $\Phi^{\text{lr},\mu}$ is not anymore a single determinant [see Eq. (5)] as in KS-DFT. All standard approximations used in WFT (HF, MP2, CI, MCSCF, CC, NEVPT2, etc.) can therefore be adapted to the short-range DFT (SRDFT) approach. The following have been implemented recently: HF-SRDFT,[16,17] MP2-SRDFT,[16,18] CI-SRDFT,[17,19,20] MCSCF-SRDFT,[17] and CC-SRDFT.[18] In this work we focus on the MCSCF-SRDFT method. Combining the MCSCF and DFT models is envisaged to be an efficient way to treat simultaneously both static correlation (assigned to the long-range effects) and dynamic correlation (assigned to the short-range effects), compared to, e.g., CASPT2 and NEVPT2. A MCSCF-SRDFT combination is computationally interesting if the wave function has a rather short expansion. Our test calculations support our presumption that this is usually achieved if the μ parameter is not too large (see Sec. III C). However, in some systems like van der Waals complexes, the calculation of the dispersion energy requires large active spaces so that the long-range dispersion correlation can be described properly. The MP2-SRDFT (Refs. 16 and 18) or CC-SRDFT methods[18] are in this case obvious possibilities. But CC-SRDFT is still computationally expensive and unable to tackle cases with static correlation effects since it is a single-reference method. For such cases a multiconfigurational and size-consistent extension of the MP2-SRDFT approach, for example, a NEVPT2-SRDFT method [where Eq. (5) is solved in perturbation theory using a NEVPT2-type[4] zeroth order Hamiltonian], could be a good alternative. Work is currently in progress in this direction.

In this paper we use the HF-SRDFT and MCSCF-SRDFT methods, with both short-range LDA and PBEH-SERI spin-independent functionals mentioned previously, as implemented in a development version of the DALTON program package.[21] The computational implementation details are given in Ref. 17.

III. DEFINITION OF AN OPTIMAL μ PARAMETER

The μ parameter which defines the long-/short-range separation of the two-electron interaction can, in principle, be chosen arbitrarily. If the short-range exchange and correlation functionals as well as the wave function were exact, one would get the exact ground-state energy for any value of μ, but in practice the MCSCF-SRDFT energy depends on μ.[17] A criterion for choosing an optimal parameter μ_{opt} should therefore be defined for practical calculations. Different approaches can be adopted. A semiempirical one defines μ_{opt} as the minimum of the mean absolute error obtained on some properties. This type of calibration study has been performed on a large set of molecules for KS-DFT calculations where the long-/short-range separation was used for the exchange functional[22–26] and leads to a relatively narrow range of values ($0.33\ \text{a.u.} \leqslant \mu \leqslant 0.5\ \text{a.u.}$). Another approach consists in defining μ_{opt} from the minimum MCSCF-SRDFT energy,[17] but then system- and geometry-dependency problems occur, as shown in Sec. III A. In order to overcome such complications, we propose in Sec. III B a new definition of μ_{opt} that optimizes the assignment of the dynamic correlation to the short-range interaction and the static correlation to the long-range interaction, and discuss its universality. A numerical investigation of μ_{opt}, on a small set of atoms and molecules representing cases without and with significant static correlation, is finally presented in Sec. III C.

A. System-dependency problem

Considering the error of the KS-DFT functional at $\mu=0$ and the N-electron *ab initio* wave-function configuration error at $\mu=+\infty$, we could define the optimal parameter μ_{opt} as the minimum along the MCSCF-SRDFT energy curve, ensuring thus for a given molecule the optimal combination of a given approximate functional and approximate wave function. Pedersen and Jensen[17] and Pedersen[27] found that μ_{opt} is strongly system dependent if the SRLDA functional is used: the higher the core density of the system is, the larger μ_{opt} is. This can be interpreted as follows. On one hand, as $1/\mu$ is a measure of the r_{12} distance where the model changes from short-range to long-range interaction as illustrated in Fig. 1, for SRLDA (using the "erf" long-range interaction) to be a good approximation, $1/\mu$ should be smaller than the distance δ for which the density only varies slowly, and beyond this distance we need gradient corrections. Since this distance in a valence shell δ_{valence} is larger than its value in core shells δ_{core}, an optimal μ parameter common to both valence and core electrons must fulfill

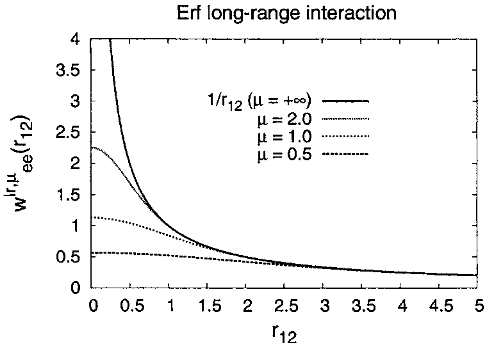

FIG. 1. The "erf" long-range interaction $w^{\text{lr},\mu}_{ee}(r_{12})=\text{erf}(\mu r_{12})/r_{12}$ plotted as a function of r_{12} for μ equal to 2.0, 1.0, and 0.5 a.u.

$$\mu \geqslant 1/\delta_{\text{core}} > 1/\delta_{\text{valence}}. \tag{7}$$

As a result, the higher the density in the core region is, the larger μ_{opt} is. On the other hand, the single configuration SRLDA approach is close to exact for the homogeneous electron gas if all effects of the two-electron interaction are treated with DFT, that is, if $1/\mu$ is larger than the Wigner-Seitz radius[20] $r_s=[3/(4\pi n)]^{1/3}$, where n denotes the density. A smaller $1/\mu$ value would put some part of the two-electron correlation into the long-range correlation, and thus a longer configuration expansion would be required for the wave function. For nonhomogeneous systems, a short configuration expansion of the wave function is highly desirable. Since the density is higher in the core shell than in the valence shell, the Wigner-Seitz radius for the core r_s^{core} is smaller than the one for the valence r_s^{valence}, and μ is thus optimal with respect to achieving a short configuration expansion of the wave function, for both core and valence electrons, if it fulfills

$$\mu \leqslant 1/r_s^{\text{valence}} < 1/r_s^{\text{core}}. \tag{8}$$

Since the core gives the highest contribution to the energy, the optimal μ_{opt} parameter fulfills $1/r_s^{\text{core}} \geqslant \mu_{\text{opt}} \geqslant 1/\delta_{\text{core}}$, which means that it is optimal for the core. However, $1/\delta_{\text{core}}$ is in general larger than $1/r_s^{\text{valence}}$, especially for many-shell atoms, and therefore μ_{opt} cannot also fulfill condition (8). Thus, it can only be optimal for the core, not for the valence, with respect to both the SRLDA functional and the configuration expansion of the wave function. Note that the long-/short-range separation for the valence thus becomes determined by the core, and as a consequence, a significant part of the valence dynamic correlation has to be treated by the MCSCF. In this respect this μ_{opt}, defined from the minimum MCSCF-SRDFT energy, does not optimize the combination of the MCSCF method and DFT.

Using effective core potentials is a possible alternative,[17,19] but then the model enables only the calculation of valence properties. On the other hand, μ_{opt} might be less system dependent if more accurate short-range functionals are used. Figures 2 and 3 show for both short-range LDA and PBEHSERI functionals the HF-SRDFT (uppermost curve) and MCSCF-SRDFT [lowest curve(s)] energies calcu-

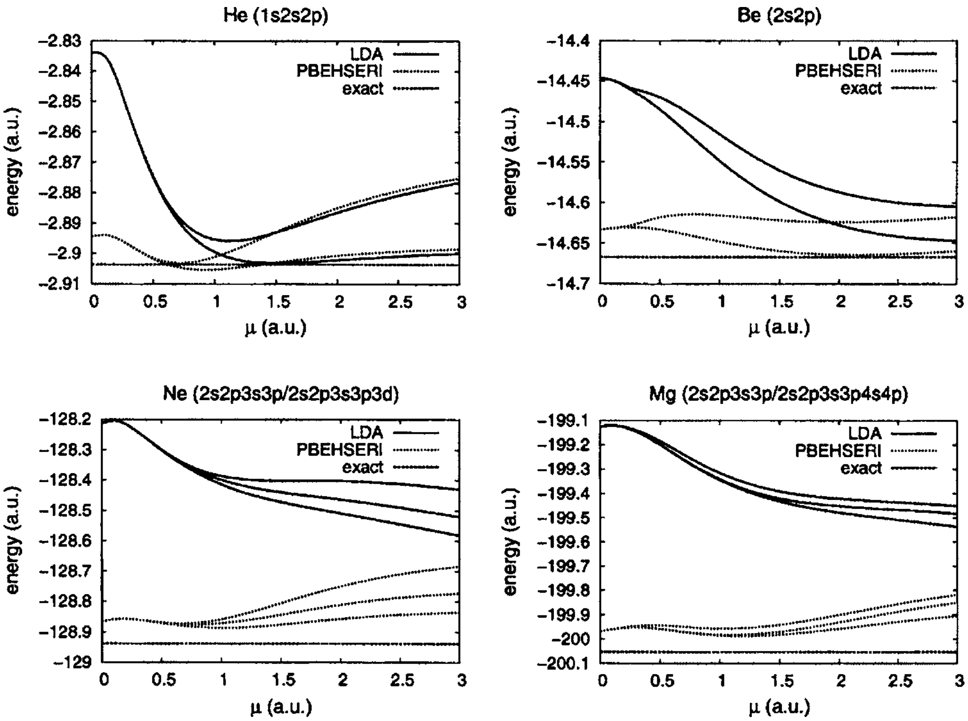

FIG. 2. Total ground-state energies of He, Be, Ne, and Mg calculated by the HF-SRDFT (uppermost curve) and MCSCF-SRDFT methods [lowest curve(s)] with respect to the μ parameter, with the short-range LDA and PBEHSERI functionals, and compared to the exact energy (Ref. 33). The MCSCF-SRDFT active spaces are given in parentheses. Basis sets are cc-pVTZ (Refs. 31 and 32) for He, Be, and Ne, and 6-311++G($3df$,$3pd$) (Ref. 37) for Mg.

lated with respect to μ on some selected atoms and molecules. When several MCSCF-SRDFT active spaces are used, the lowest curve corresponds, of course, to the largest one. As expected, the short-range GGA functional PBEHSERI does provide a more accurate treatment of the core correlation in comparison with LDA. Then μ_{opt} becomes smaller and less system dependent. As shown in Fig. 2, it is in the vicinity of 1 a.u. for He, Ne, and Mg. Nevertheless μ_{opt} is twice this value for Be. Moreover, such a minimum may not exist as observed for the stretched H_2 molecule, for example (see Fig. 3). In this case the pure MCSCF model at $\mu_{\text{opt}}=+\infty$ gives the lowest energy, which is exact in this special case. For N_2 at the experimental equilibrium geometry, the lowest energy is obtained with pure DFT ($\mu_{\text{opt}}=0$) when the short-range PBEHSERI functional is used. A similar result was already obtained by Savin and Flad[28] for the He series, performing CI-SRLDA calculations without the short-range exchange functional. Let us finally mention that μ_{opt} can also be geometry dependent. In H_2, for example, it is equal to 0.5 a.u. at the experimental equilibrium geometry and becomes $+\infty$ for the stretched geometry, when the short-range PBEHSERI functional is used (see Fig. 3).

In conclusion, these results show that it is currently impossible to define a universal optimal μ_{opt} parameter from the minimum MCSCF-SRDFT energy. They also show that the system dependency is strongly related to the approximate short-range functional used and thus can only be reduced by developing more complicated functionals, which is not trivial. Instead, we now propose to address the possibility of defining a universal long-range/short-range separation from a new angle of view. The initial motivation for merging WFT and DFT was the lack of significant improvements in the derivation of approximate KS functionals able to tackle long-range effects such as static correlation and dispersion interaction effects. Thus, we would like to formulate a hybrid WFT-DFT method that is able to treat in DFT the dynamic correlation, which can be described fairly accurately by current standard-type functionals (LDA, GGA, or hybrid), and able to treat in WFT the remaining (long-range) correlation effects. A μ parameter which leads to a maximal separation of the long-range and dynamic correlations would be optimal in this respect.

B. Definition of a universal μ_{opt} parameter

The analysis of Sec. III A shows that defining μ_{opt} from the minimum MCSCF-SRDFT energy involves the approximate short-range functional (SRLDA, SRPBEHSERI, etc.) as well as the approximate wave function (MCSCF), which leads to system- and geometry-dependency problems. We advocate here that, instead of optimizing the combination of the two approximations (short-range functionals and wave function), the criterion for the long-range/short-range separation should be chosen such that the static correlation (and dispersion interaction) effects are assigned to the long-range interaction and the dynamic correlation effects to the short-range interaction to the maximum possible extent. According to Eq. (5), this means that the chosen long-/short-range separation should ensure that the wave function is multiconfigurational only in systems where static correlation (or dispersion interaction) effects are significant. With such a separation, the dynamic correlation could be calculated with short-range extensions of the current standard KS-DFT functionals and the static correlation within the MCSCF method, which is expected to be optimal with respect to the computational effort as well as the feasibility of deriving adequate functionals. Note that in the case of significant dispersion interaction effects, the MP2-, CC-, or NEVPT2-SRDFT methods are more appropriate than the MCSCF-SRDFT (see Sec. II). In the particular case of a long-/short-range separa-

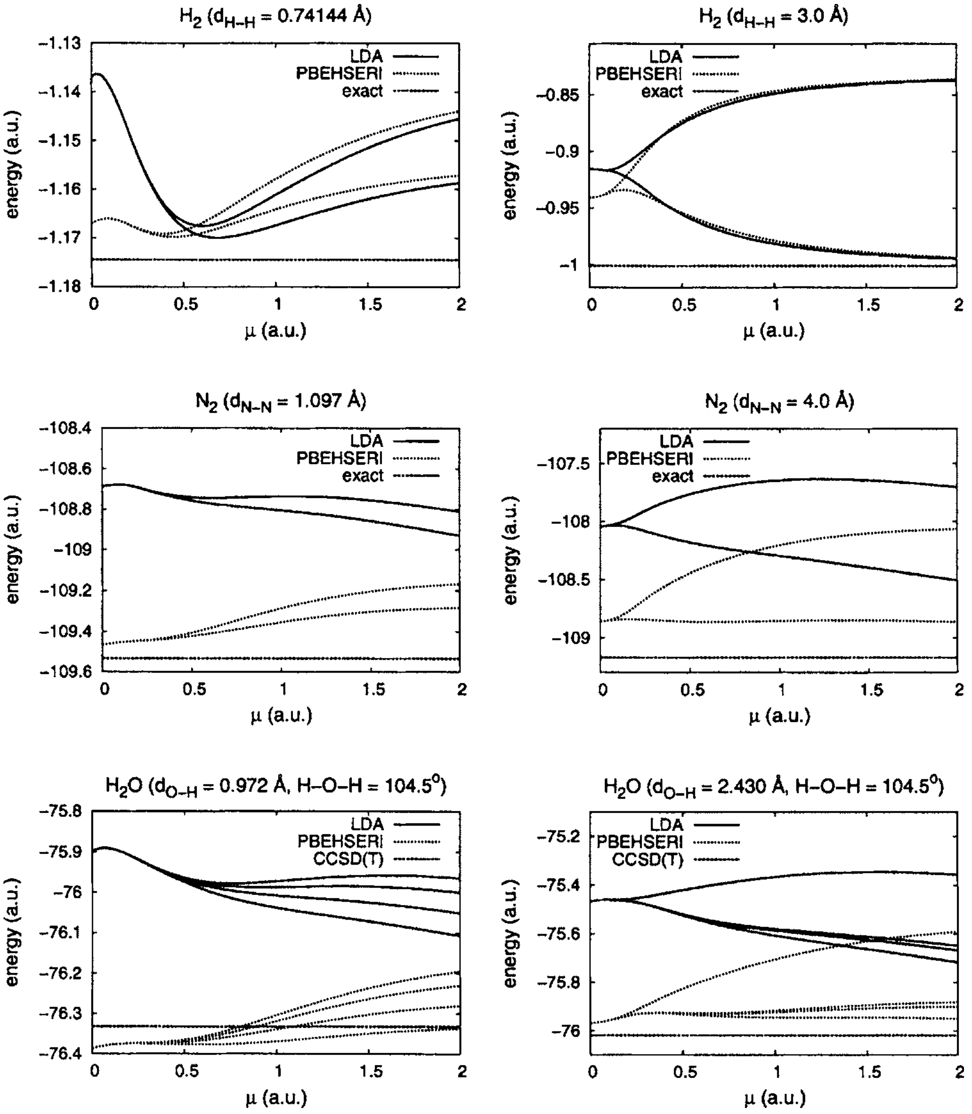

FIG. 3. Total ground-state energies of H_2, N_2, and H_2O calculated at both equilibrium (left side) and stretched (right side) geometries by the HF-SRDFT (uppermost curve) and MCSCF-SRDFT methods [lowest curve(s)] with respect to the μ parameter, with the short-range LDA and PBEHSERI functionals, and compared to the CCSD(T) for H_2O or exact energy (Ref. 34) for H_2 and N_2. The MCSCF-SRDFT active spaces are for H_2 $1\sigma_g 1\sigma_u$, for N_2 $2\sigma_g 2\sigma_u 1\pi_u 3\sigma_g 1\pi_g 3\sigma_u$, and for H_2O, given as number of orbitals of $(a_1.b_1.b_2.a_2)$ symmetry: 3.1.2.0, 4.2.2.0, and 6.3.3.1. Basis sets are cc-pVTZ (Refs. 31 and 32).

tion based on the erf long-range interaction of Eq. (1), the optimal μ_{opt} parameter should ensure, according to this new definition, that the wave function is a single determinant in static correlation- and dispersion interaction-free systems. For sufficiently small μ, so that $\mu r_{12} \ll 1$, where r_{12} denotes the average correlation distance between two electrons, the long-range interaction $\text{erf}(\mu r_{12})/r_{12}$ equals approximately $2\mu/\sqrt{\pi}$, which is constant. There are thus, in this case, no correlation effects related to the long-range interaction. As a result, we can find a range of suitable nonzero μ_{opt} values. On the other hand, μ_{opt} should be chosen as large as possible in order to ensure that, when it is used on systems with significant static correlation or dispersion interaction effects, those are fully treated in WFT. Therefore the optimal μ_{opt} parameter can be defined as the largest μ value for which the wave function is a single determinant in systems with no significant static correlation and dispersion interaction effects. Note that this definition is, in principle, independent of the approximate short-range functional and the approximate wave function used, since, as shown in Eq. (5), the multiconfigurational character of the wave function is only determined by the long-range interaction. It means that further improvements on the functionals should not change the value of μ_{opt}. Moreover, μ_{opt} can be interpreted as the inverse of the average dynamic correlation distance, r_{12}^{valence}, between the valence electrons. Thus, the universality of the optimal μ_{opt} parameter depends only on the interval of the r_{12}^{valence} distances obtained in all the systems with no significant static correlation and dispersion interaction effects. If this interval is not loo large, an averaged μ_{opt} value might be a good compromise for assigning most of the static correlation to the long-range interaction. In addition, if we consider, for example, rare-gas dimers,[18] the averaged distance $1/\mu_{\text{opt}}$ is expected to be smaller than half of the interatomic distance, which means this μ_{opt} should also assign the dispersion interaction effects to the long-range interaction. A numerical investigation of μ_{opt} on some selected test systems containing light elements (He and Ne, as well as H_2, N_2, and H_2O at equilibrium) is presented in Sec. III C. Note that, in our approach, r_{12}^{valence} is a measure of the distance where the correlation changes from dynamic to long range (static correlation or dispersion interaction effects). So far, the definition of μ_{opt} ensures that the wave function is well approximated by a single determinant in systems with only dynamic correlation. In order to ensure a maximal separation of the dynamic and long-range correlations, it should also allow the wave function to be multiconfigurational in systems with significant long-range correlations. Numerical tests on such systems containing light elements (Be and Mg, as well as the stretched H_2, N_2, and H_2O molecules) are presented in Sec. III C. A similar analysis on actinide compounds is currently in progress.

C. Numerical investigation of μ_{opt}

In order to get a first estimate of the optimal μ_{opt} parameter defined in Sec. III B, we consider a set of five closed-shell systems with no significant static correlation and dispersion interaction effects: two atoms (He and Ne) and three molecules at the experimental equilibrium geometry (H_2, N_2, and H_2O). To investigate the multiconfigurational character of the wave function with respect to μ we first compare the HF-SRDFT and MCSCF-SRDFT energies. If the short-range LDA functional is used, the HF-SRDFT and MCSCF-SRDFT energy curves split (within an accuracy of 10^{-3} a.u.) in the vicinity of 0.5 a.u. for the five systems, as shown in Figs. 2 and 3. As expected, a similar result is indeed obtained using the more accurate short-range PBEHSERI functional. On the other hand, the occupation numbers of the natural active orbitals in the MCSCF-SRDFT calculation indicate that the wave function is a single determinant for $\mu \leqslant 0.4$ a.u. within an accuracy of 10^{-4} for He, Ne, H_2, and H_2O and 10^{-3} for N_2 (see Fig. 4). So far we can conclude that μ_{opt} should be in the vicinity of 0.4 a.u. Note that this value is in agreement with previous calibration studies, based on KS-DFT calculations using the long-/short-range separation for the exchange term only, which also have been taken as reference for the choice of μ in SRDFT calculations such as MP2-SRDFT (Refs. 16 and 29) or CC-SRDFT.[30] Iikura *et al.*[22] have, for example, shown that the mean absolute error on the 4*s*-3*d* interconfigurational energies of the first-row transition metals is minimal for $\mu=0.4$ a.u. The recent calibration studies of Vydrov *et al.*[23] and Vydrov and Scuseria[24] also show that $\mu=0.4$ a.u. works well for enthalpies of formation, barrier heights, and ionization potentials. Gerber and Ángyán[25] have reported a slightly larger optimal value (0.5 a.u.) based on the calculation of enthalpies of formation for a set of 56 molecules, and Tawada *et al.*[26] found a slightly smaller value (0.33 a.u.) minimizing the mean absolute deviation of the calculated equilibrium distances for the dimers of the first- to third-row atoms (except rare-gas dimers).

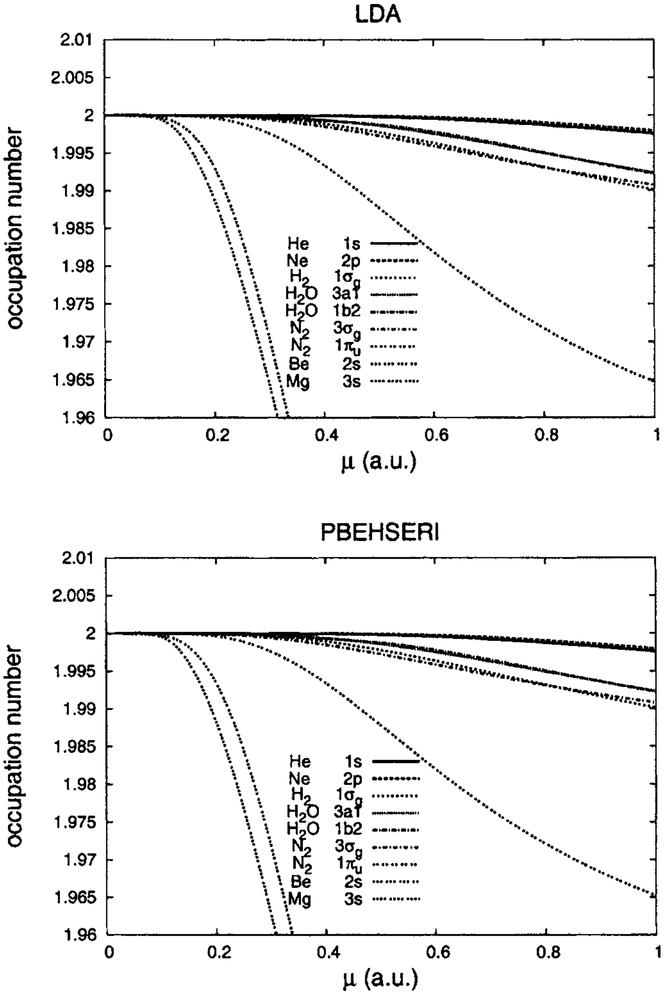

FIG. 4. Occupation numbers of MCSCF-SRDFT natural orbitals of He, Be, Ne, Mg as well as H_2, N_2, and H_2O at the equilibrium geometry, calculated with respect to the μ parameter with the short-range LDA and PBEHSERI functionals. The active spaces are given in Figs. 2 and 3. For Ne, Mg, and H_2O the smallest ones have been used. Basis sets are 6-311++G(3*df*,3*pd*) (Ref. 37) for Mg and cc-pVTZ (Refs. 31 and 32) for the other atoms.

We now consider a set of five systems where static correlation effects are significant: two atoms (Be and Mg) and three stretched molecules (H_2, N_2, and H_2O). In all cases, the HF-SRDFT and MCSCF-SRDFT energies are different for $\mu=0.4$ a.u. (see Figs. 2 and 3). It means that the wave function is multiconfigurational, as confirmed by the occupation numbers of the natural active orbitals of Be and Mg in the MCSCF-SRDFT (see Fig. 4). It is an indication that a significant part of the static correlation is assigned to the long-range interaction. But we still have to check that, in those systems, most of the dynamic correlation is assigned to the short-range interaction. We thus investigate the configuration expansion of the wave function. Figure 2 shows that the MCSCF-SRDFT energies obtained for Mg with two different active spaces (2*s*2*p*3*s*3*p* and 2*s*2*p*3*s*3*p*4*s*4*p*) are identical for $\mu=0.4$ a.u. but still differ from the HF-SRDFT energy. The same was observed for the symmetrically stretched water molecule using three different active spaces (see Fig. 3). If we now compare with static correlation-free systems such as Ne or H_2O at the experimental equilibrium geometry, both HF-SRDFT energy curve and all the MCSCF-SRDFT energy curves (obtained with the different active spaces) split from $\mu=0.4$ a.u. This clearly shows that for $\mu=0.4$ a.u. the static correlation is treated within the MCSCF model and the dynamic correlation with DFT. In this respect, choosing the optimal μ_{opt} parameter to be 0.4 a.u. ensures a maximal separation of the dynamic and static correlations for all the systems considered in this work. In order to discuss the universality of the 0.4 a.u. value, it is also of high interest to investigate molecules with heavier elements. Work is currently in progress in this direction on actinide compounds.

TABLE I. Equilibrium bond distances R_e (Å) and dissociation energies D_e (eV) for the ground states of H_2 and N_2 calculated by MCSCF, RKS-DFT, HF-SRDFT, and MCSCF-SRDFT (with the short-range LDA and PBEHSERI functionals and μ=0.4 a.u.) methods. The MCSCF and MCSCF-SRDFT active spaces are $1\sigma_g 1\sigma_u$ for H_2 and $2\sigma_g 2\sigma_u 1\pi_u 3\sigma_g 1\pi_g 3\sigma_u$ for N_2. Basis sets are cc-pVTZ (Refs. 31 and 32).

	H_2		N_2	
Method	R_e (Å)	D_e (eV)	R_e (Å)	D_e (eV)
MCSCF	0.755	4.13	1.106	9.18
RKS-LDA	0.766	6.72	1.096	17.69
RKS-PBE	0.751	6.79	1.103	16.85
RKS-B3LYP	0.743	7.75	1.092	20.44
HF-SRLDA	0.755	10.70	1.082	30.84
MCSCF-SRLDA	0.757	6.05	1.088	16.17
HF-SRPBEHSERI	0.742	10.85	1.086	30.41
MCSCF-SRPBEHSERI	0.744	6.17	1.092	15.73
Expt.[a]	0.741	4.75	1.097	9.91

[a] Reference 35.

IV. RESULTS AND DISCUSSIONS

In this section the dissociation energies of H_2 and N_2, as well as the symmetric dissociation energy of H_2O at the experimental equilibrium angle H–O–H=104.5°, are calculated within the MCSCF-SRDFT method using cc-pVTZ basis sets.[31,32] Both short-range LDA and PBEHSERI spin-independent functionals are tested and the μ parameter is set to 0.4 a.u. according to the analysis of Sec. III C. The results obtained for the diatomic molecules are presented in Table I. We note that the equilibrium bond distances obtained at the MCSCF-SRDFT are in very good agreement with experiment, in particular, when the PBEHSERI functional is used. They are also very similar to the HF-SRDFT ones, which was expected since, at the equilibrium geometry, there is very little static correlation (see Sec. III C). Secondly, the large difference between the HF-SRDFT and MCSCF-SRDFT dissociation energies is a sign of the ability of the MCSCF-SRDFT to tackle the static correlation at dissociation, i.e., to dissociate correctly. The occupation numbers of the active natural orbitals indicate that, for both H_2 and N_2 at dissociation, the proper multiconfigurational wave function is obtained (see Fig. 5). The MCSCF-SRDFT dissociation energies are closer to experiment than all the restricted KS-DFT values but they are still too high. The approximate short-range functionals used are responsible for this overestimation. Let us consider the case of H_2, for example. At dissociation the wave function becomes $|\Phi^{\mathrm{lr},\mu}\rangle = 1/\sqrt{2}(|\sigma_g\overline{\sigma_g}\rangle - |\sigma_u\overline{\sigma_u}\rangle)$ according to Fig. 5, which means that H_2 is dissociated into two neutral hydrogen atoms within the MCSCF-SRDFT approach. The two electrons, both localized on one hydrogen, have therefore no long-range interaction at dissociation. Moreover, the short-range energy should be, in principle, equal to zero unless the electron is self-interacting. With the LDA functional, for example, the short-range Hartree term equals 0.2306 a.u. and is not compensated by the short-range exchange and correlation contribution (−0.1784 a.u.). Their sum (0.0522 a.u.) corresponds essentially to the difference between the MCSCF-SRLDA energy and the exact energy (see Fig. 6). For a single hydrogen atom, the short-range Hartree term, obtained at the HF-SRLDA level, equals 0.1154 a.u. and is not compensated by the short-range exchange and correlation contribution (−0.0892 a.u.). Their sum multiplied by 2 (0.0523 a.u.) is almost identical to the energy error obtained for H_2 at dissociation. The same conclusion can be drawn for the short-range PBEHSERI functional. In this respect our energy error at dissociation is a self-interaction error. On the other hand, although the MCSCF method, using the $\sigma_g\sigma_u$ active space, describes the dissociation properly, a significant

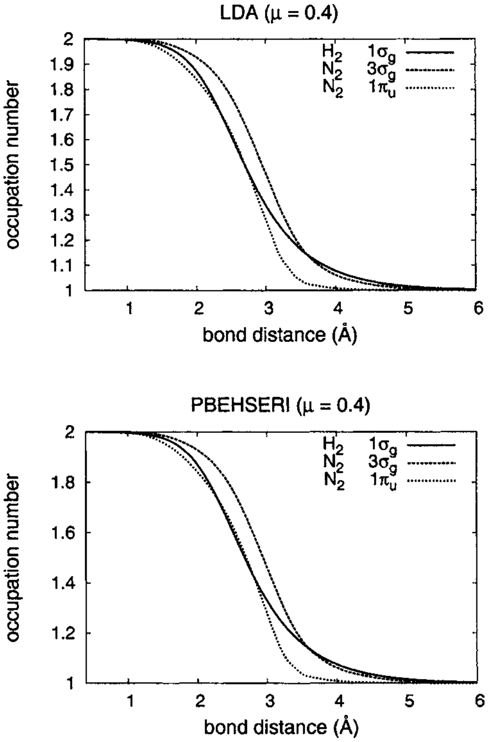

FIG. 5. Occupation numbers of MCSCF-SRDFT natural orbitals of H_2 and N_2 calculated with respect to the bond distance using the short-range LDA and PBEHSERI functionals and μ=0.4 a.u.. The active space is $1\sigma_g 1\sigma_u$ for H_2 and $2\sigma_g 2\sigma_u 1\pi_u 3\sigma_g 1\pi_g 3\sigma_u$ for N_2. Basis sets are cc-pVTZ (Refs. 31 and 32).

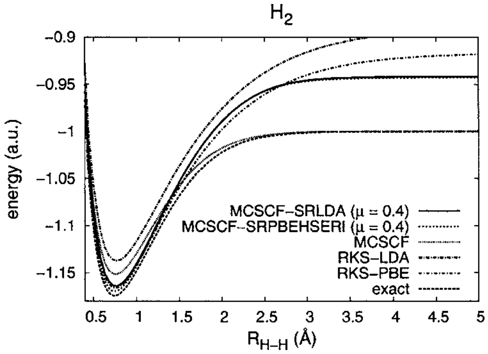

FIG. 6. Potential energy surfaces of H_2 calculated by the RKS-DFT (with both LDA and PBE functionals), MCSCF, and MCSCF-SRDFT methods (with both short-range LDA and PBEHSERI functionals and μ=0.4 a.u.) using the active space $1\sigma_g 1\sigma_u$, and compared to the exact surface (Ref. 34). Basis set is cc-pVTZ (Refs. 31 and 32).

TABLE II. Equilibrium O–H bond distance R_e (Å) and symmetric dissociation energy D_e (eV) for the ground state of H_2O (with a fixed H–O–H angle of 104.5°) calculated by MCSCF, RKS-DFT (with the LDA and PBE functionals), HF-SRDFT, and MCSCF-SRDFT (with the short-range LDA and PBEHSERI functionals and $\mu=0.4$ a.u.) methods. The active space 3.1.2.0, given as number of orbitals of $(a_1.b_1.b_2.a_2)$ symmetry has been used for both MCSCF and MCSCF-SRDFT calculations. Basis sets are cc-pVTZ (Refs. 31 and 32).

Method	R_e (Å)	D_e (eV)
MCSCF	0.963	8.31
RKS-LDA	0.970	16.06
RKS-PBE	0.969	15.14
HF-SRLDA	0.961	19.30
MCSCF-SRLDA	0.962	13.32
HF-SRPBEHSERI	0.958	18.82
MCSCF-SRPBEHSERI	0.959	13.05
Expt.	0.957[a]	10.06[b]

[a] Reference 36.
[b] Reference 11.

part of the dynamic correlation at the equilibrium is not included, and therefore the dissociation energy is underestimated, as shown in Table I. It is clear from Fig. 6 that the MCSCF-SRDFT method recovers much more dynamic correlation than the MCSCF.

The results obtained for the water molecule are given in Table II. As already observed for the diatomic molecules, the HF-SRDFT and MCSCF-SRDFT equilibrium bond distances are almost identical and in very good agreement with experiment. As expected both HF-SRDFT methods overestimate the symmetric dissociation energy significantly, because of the wrong dissociation limit for a single determinant $[O(^1S)+H_2(\sigma_g^2)]$, whereas the MCSCF-SRDFT results (13.32 and 13.05 eV) are much closer to the experimental value (10.06 eV), but still not satisfactory. Two problems can be identified: (1) the self-interaction error at dissociation also needs to be corrected in this case and (2) the dissociation limit for the oxygen atom is the ^1S state instead of the ^3P state. Again, the MCSCF model dissociates correctly but neglects a bigger fraction of the dynamic correlation at the equilibrium distance than at dissociation and therefore underestimates the dissociation energy.

V. CONCLUSIONS

In order to formulate a general hybrid MCSCF-SRDFT method, we have investigated the possibility of defining an optimal and universal long-/short-range separation of the two-electron interaction, characterized by the μ parameter in Eq. (1). We advocate that this parameter should be chosen so that the static correlation (and dispersion interaction) effects are assigned to the long-range interaction and the dynamic correlation effects to the short-range interaction. We thus propose to define the optimal μ_{opt} parameter as the largest μ value for which the wave function is a single determinant in systems with no significant static correlation and dispersion interaction effects. Such a definition is general because it involves neither the approximate short-range functional (SRLDA, SRPBEHSERI, etc.) nor the approximate wave function (HF, MCSCF, CI, CC, etc.). It is only determined by the form of the short-/long-range separation, for example, the erfgau separation[14] would lead to another optimal μ value. We have shown that its universality depends only on the interval of the average dynamic correlation distances between the valence electrons obtained in all the systems with no significant static correlation and dispersion interaction effects. If it is not loo large, an averaged μ_{opt} value might be a good compromise. Calculations on He and Ne, as well as H_2, N_2, and H_2O at their experimental equilibrium geometries, all yield $\mu_{\text{opt}} \approx 0.4$ a.u. Moreover, investigating Be and Mg, as well as the stretched H_2, N_2, and H_2O molecules, we observed that such a value leads to a maximal separation of the static and dynamic correlations. In order to discuss the universality of the 0.4 a.u. value, a similar analysis on actinide compounds is currently in progress.

Using the MCSCF-SRDFT method with $\mu=0.4$ a.u. gives very encouraging results for the dissociation energies of H_2 and N_2 as well as for the symmetric dissociation energy of the water molecule. Improvements on the short-range functionals are nevertheless necessary, in particular, to correct the self-interaction of the unpaired electrons at dissociation. Note that such improvements should not, in principle, modify the optimal μ_{opt} parameter since its definition does not involve the approximate short-range functionals. It is also clear that enhancements are needed for handling of open-shell systems, which cannot be completely handled with the proposed spin-dependent short-range functionals,[30] cf. the wrong state obtained for the oxygen atom when investigating the symmetric dissociation of water.

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