

Strong correlation and charge localisation in Kohn-Sham theories with fractional orbital occupations: the role of the potential

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Abstract

Strongly correlated electrons have been the subject of substantial theoretical interest for many years. Most work has focused on obtaining the energy in a low-cost fashion. Here, we show that even methods with good energies can yield significant “delocalization errors” that affect the orbitals and density, leading to large errors in predicting other important properties such as dipole moments. We illustrate this point by comparing existing state-of-art approaches with an accurate exchange correlation functional based on a generalised valence bond ansatz, in which *orbitals and fractional occupations* are treated as variational parameters via a common optimized effective potential (OEP). We show that the OEP exhibits step and peak features which, similar to the exact Kohn-Sham (KS) potential of DFT, are crucial to prevent charge delocalization. We

further show that the step is missing in common approximations within reduced density matrix functional theory resulting in delocalization errors comparable to those found in DFT approximations. Finally, we explain the delocalisation error as coming from an artificial mixing of the ground state with a charge-transfer excited state which is avoided if occupation numbers exhibit discontinuities.

Introduction

Electron delocalisation errors and related issues¹⁻⁴ have been the subject of intensive study in recent years, due to their importance to molecular modeling, particularly in charge transfer systems. These errors occur when an approximate quantum theory fails to correctly treat multi-reference physics (strong correlations), and, as a consequence, mis-predicts the electronic density. Delocalisation errors arise in most common *ab initio* approximations;⁵⁻⁷ within density functional theory (DFT) but also in more advanced many-body methods such as MP2, GW and beyond.⁸⁻¹¹ They are most prominent when breaking molecular bonds, and are responsible for the dramatic failures to correctly predict the charge distribution and energetics of heteronuclear dissociation into open-shell fragments,¹² exemplified by the LiH molecule.¹³

Much attention has been paid to overcoming static correlation and delocalization errors in density functional approaches.¹⁴⁻²³ An alternative pathway is to use reduced density matrix functional theory (RDMFT), by directly approximating the first- and second-order reduced density matrices.^{1,24,25} The resulting energy expression then becomes a simultaneous functional of (natural) orbital occupation factors, and a corresponding set of orthonormal (natural) orbitals. With an appropriate choice of RDMFT approximation, strong correlation effects can then be directly accommodated within a (natural) orbital framework.

It is also possible to accommodate orbitals within a DFT framework, by employing an optimized effective potential (OEP) approach^{26,27} together with an appropriate orbital functional. In so doing, one hopes that an appropriate choice of functional can lead to an

approach that intrinsically avoids delocalization errors. The best known OEP approach is the exact-exchange (EXX) approximation within DFT. In EXX, one looks for the Hartree-Fock-like energy of a system using orbital functions φ_i satisfying a common, local Hamiltonian $\hat{h}\varphi_i(\mathbf{r}) = [\hat{T} + V_{\text{KS}}(\mathbf{r})]\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r})$. EXX is known to reproduce many of the important features²⁸⁻³² of the true Kohn-Sham (KS) potential in molecular systems composed of closed-shell atoms.

However, unless the spin-symmetry is allowed to break,^{12,33} the EXX approximation does a poor job of predicting dissociation into open-shell atoms, where the outermost electrons are strongly correlated. The majority of the error comes from large delocalization errors caused by a failure to *localize* the outermost electrons on the different odd electron number atoms. Instead, the highest occupied molecular orbital (HOMO, H) is doubly occupied, with electrons shared across the two species. This allows “ghost interactions” to cause a static correlation error, with energy cost $1/2\langle\varphi_{\text{H}}^2|v|\varphi_{\text{H}}^2\rangle$ ⁹ between opposite-spin electrons that should be excluded by the multi-determinant nature of the groundstate. This issue also occurs at the Hartree-exchange level in the exact functional, but is remedied by the correct treatment of correlations, which are absent in EXX.

In this work we employ a multi-configurational approach that avoids ghost interactions and delocalisation errors via an optimized effective potential scheme. The energy is constructed from a wave function ansatz based on fractionally occupied KS orbitals, but integer occupation of a set of correlated orbitals defined as linear combinations of the KS orbitals. The KS orbitals are then optimized via a common local potential. This scheme differs from other OEP schemes utilising unoccupied orbitals^{9,34,35} in that the unoccupied orbitals are employed to remedy deficiencies of the reference system - similar to the local RDMFT approach³⁶ or other multi-configurational OEP methods.^{37,38}

We reveal the important role played by the effective potential in dealing with ghost interactions also in theories which depend explicitly on occupation numbers, and how a failure to correctly predict the potential (and thus orbitals) leads to delocalisation errors

even in methods that give, to leading order, correct correlation energies. This error manifests in measurable quantities, such as dipole moments.

Optimized effective potential

In this section we derive the OEP within theories that allow fractionally occupied KS orbitals. We employ a multiconfigurational approach similar to the ones proposed in Refs. 37,38 which we then, for two electrons, connect to the local RDMFT theory.³⁶

Wavefunction ansatz based on optimized Kohn-Sham orbitals

The use of doubly occupied KS orbitals in DFT is an, in principle, exact construction. But, it is a bad starting point for treating strongly correlated electrons which are spatially localised and thus more naturally treated by localized orbitals. Spin-DFT can sometimes achieve spatial localisation; at the expense of breaking the fundamental spin symmetries. A proper treatment of correlation is provided by multi-configurational wavefunction approaches, but with the drawback that several configurations may be needed to converge the energy (or density).

In the following will explore the possibility of optimising the orbitals via a KS system with a common local potential. Starting with a two electron system we construct a generalized-valance-bond-like ansatz of two Slater determinants built up from a set of nonorthogonal correlated orbitals that are allowed to localise via the HOMO and LUMO of the KS system

$$\psi_A(\mathbf{r}) = \cos \theta \varphi_H(\mathbf{r}) + \sin \theta \varphi_L(\mathbf{r}) \quad (1)$$

$$\psi_B(\mathbf{r}) = \cos \theta \varphi_H(\mathbf{r}) - \sin \theta \varphi_L(\mathbf{r}). \quad (2)$$

Unlike the KS orbitals, φ_H and φ_L , the correlated orbitals are not eigenstates of an effective Hamiltonian. Only at $\theta = 0$ do both ψ_A and ψ_B reduce to the KS HOMO orbital, and

we recover double occupancy. As θ is increased, more of the LUMO orbital is mixed in and eventually at $\theta = \pi/4$, ψ_A and ψ_B become orthogonal. The more the KS orbitals are delocalized, the more the correlated orbitals will be localized, and vice versa.

The two orbitals are then used to construct a singlet wavefunction

$$|\Psi\rangle = \frac{1}{\sqrt{N}}\{|A\uparrow B\downarrow\rangle + |B\uparrow A\downarrow\rangle\} \quad (3)$$

where $N = 4(\cos^4\theta + \sin^4\theta)$ is the normalization constant. We notice that when $\theta = 0$ this is just the Hartree-Fock (HF) wave function ansatz. We can also write (3) as

$$|\Psi\rangle = \frac{1}{\sqrt{N}}[\psi_A(\mathbf{r})\psi_B(\mathbf{r}') + \psi_B(\mathbf{r})\psi_A(\mathbf{r}')] |S\rangle \quad (4)$$

where $|S\rangle$ is the spin-singlet wavefunction.

Taking the expectation value of the full many-body Hamiltonian with respect to the wave function in Eq. (3) we find the density and kinetic energy to be

$$n^\theta(\mathbf{r}) = 2f_H|\varphi_H(\mathbf{r})|^2 + 2f_L|\varphi_L(\mathbf{r})|^2 \equiv \langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle \quad (5)$$

$$T_s^\theta = 2f_H\langle\varphi_H|\hat{T}|\varphi_H\rangle + 2f_L\langle\varphi_L|\hat{T}|\varphi_L\rangle \equiv \langle\Psi|\hat{T}|\Psi\rangle. \quad (6)$$

The occupation numbers $f_H = 4\cos^4\theta/N$ and $f_L = 4\sin^4\theta/N$ are related to the fourth power of the expansion coefficients of the correlated orbitals ψ_A and ψ_B and the factor of two comes from the spin-summation. The interaction energy term, which can be considered

as the sum of Hartree and exchange and correlation (Hxc) energies, is given by

$$\begin{aligned}
E_{\text{Hxc}}^\theta &= \frac{2}{N} \int d\mathbf{r}d\mathbf{r}' |\psi_A(\mathbf{r})|^2 v(\mathbf{r}, \mathbf{r}') |\psi_B(\mathbf{r}')|^2 \\
&\quad + \frac{2}{N} \int d\mathbf{r}d\mathbf{r}' \psi_A(\mathbf{r})\psi_B(\mathbf{r})v(\mathbf{r}, \mathbf{r}')\psi_A(\mathbf{r}')\psi_B(\mathbf{r}') \\
&= \int d\mathbf{r}d\mathbf{r}' n_{\text{HL}}^{1/2}(\mathbf{r}, \mathbf{r}')v(\mathbf{r}, \mathbf{r}')n_{\text{HL}}^{1/2}(\mathbf{r}', \mathbf{r})
\end{aligned} \tag{7}$$

where

$$n_{\text{HL}}^{1/2}(\mathbf{r}, \mathbf{r}') = \sqrt{f_{\text{H}}}\varphi_{\text{H}}(\mathbf{r})\varphi_{\text{H}}(\mathbf{r}') - \sqrt{f_{\text{L}}}\varphi_{\text{L}}(\mathbf{r})\varphi_{\text{L}}(\mathbf{r}'). \tag{8}$$

Finally, we use Eqs. (5)-(7) to generate the total energy

$$E = \min_{\theta} \left[T_s^\theta + \int d\mathbf{r} V_{\text{Ext}}(\mathbf{r})n^\theta(\mathbf{r}) + E_{\text{Hxc}}^\theta \right], \tag{9}$$

where the energy minimization over θ determines the amount of localization of $\psi_{A/B}$, via its optimizing value θ_0 . We henceforth implicitly define quantities using $\theta = \theta_0$ and drop the superscript θ , e.g. $n \equiv n^{\theta_0}$.

The ansatz described above is known to capture H_2 dissociation rather well if the correlated orbitals are expressed in a Gaussian basis and coefficients are optimized variationally. The crucial difference here is that the correlated orbitals are expressed in terms of the HOMO/LUMO KS orbitals that are optimised via a common local KS potential. This potential is obtained as the functional derivative of the energy with respect to the total potential V_s defined as

$$V_s(\mathbf{r}) = V_{\text{Ext}}(\mathbf{r}) + V_{\text{Hxc}}(\mathbf{r}). \tag{10}$$

It is straightforward to show that the Hxc potential can be determined by an OEP type

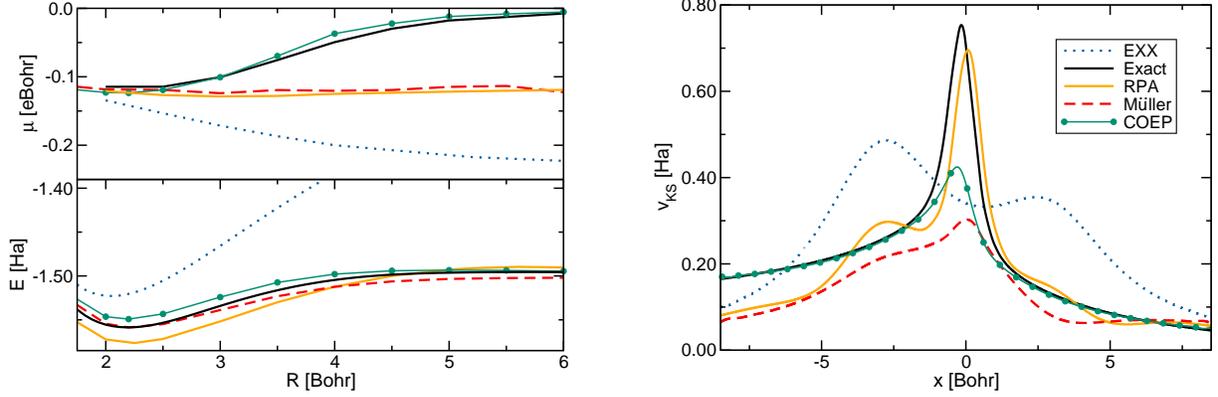


Figure 1: Left: The total energy E and dipole moment μ of the LiH molecule with EXX (blue dots), RPA (orange full), Müller (red dashed) and COEP (green filled circles) compared to exact results (black full). Right: The corresponding KS potentials at separation $R = 6$ Bohr.

of equation

$$\int d\mathbf{r}' \frac{\delta n(\mathbf{r}')}{\delta V_s(\mathbf{r})} V_{\text{Hxc}}(\mathbf{r}') = \frac{\delta E_{\text{Hxc}}}{\delta V_s(\mathbf{r})} \quad (11)$$

where the functional derivative is taken with respect to fixed occupations. The right hand side is easily evaluated using the functional chain rule $\frac{\delta}{\delta V_s} = \sum_i \int d\mathbf{r}' \frac{\delta \varphi_i}{\delta V_s} \frac{\delta}{\delta \varphi_i}$, and the functional derivative on the left hand side is just the linear density response function $\chi_0(\mathbf{r}, \mathbf{r}')$ obtained from the density in Eq. (5).

We note that the effective Hxc potential in Eq. (11) is different from the standard DFT Hxc potential with integer occupation numbers but serves a similar role. It is, in fact, equivalent to a potential generated through excited-state ensemble DFT^{39,40} and it thus inherits the usual good properties of KS potentials, such as uniqueness; and is fully amenable to the usual KS mechanics, such as division into kinetic, Hartree-exchange and correlation components.⁴¹

Although we restrict ourselves to two-electron systems the combination of a wavefunction ansatz with orbitals optimised via a KS potential is more general as demonstrated in Refs. 37,38. In this work our aim is to study the reliability and exact features of this local KS potential (from now on referred to as COEP [correlated orbital OEP]) in situations where

density errors can be significant.

Connection to reduced density matrix functional theory

The reduced density matrix of the many-electron wavefunction is defined as

$$n(\mathbf{x}, \mathbf{x}') = N \int d\mathbf{x}_{2-N} \Psi(\mathbf{x}, \mathbf{x}_2 \dots \mathbf{x}_N) \Psi^*(\mathbf{x}', \mathbf{x}_2 \dots \mathbf{x}_N) \quad (12)$$

where the variable \mathbf{x} carries both space and spin degrees of freedom. It is often written in terms of its spin eigenfunctions (natural orbitals) $\phi_i(\mathbf{x})$ and eigenvalues (occupation numbers) f_i

$$n(\mathbf{x}, \mathbf{x}') = \sum_i f_i \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}'). \quad (13)$$

It can be directly shown that the natural orbitals of the wavefunction in Eq. (4) are just the KS HOMO/LUMO orbitals, and the occupation numbers are given by the factors $f_{\text{H/L}}$ defined above. It is then easy to see that the derivations leading to the expression for the total energy Eqs. (6-7) are valid also for the exact wavefunction provided it is expressed in terms of its natural orbitals and occupation numbers.²⁴

The COEP approximation defined above can thus alternatively be derived from the exact RDMFT energy expression with the restriction of keeping only two natural orbitals further assumed to be generated by a common local potential. The use of a local potential in RDMFT is always approximate but recent studies suggest that it does not impose a severe restriction.³⁶

A standard approximation to the exchange correlation energy in RDMFT is the Müller (or BB⁴²) functional⁴³ obtained by taking the square root of the occupation numbers in the

Fock exchange term. It can thus be written as

$$E_{xc}^{\text{Müller}} = -\frac{1}{2} \int d\mathbf{x}d\mathbf{x}' n^{1/2}(\mathbf{x}, \mathbf{x}') v(\mathbf{r}, \mathbf{r}') n^{1/2}(\mathbf{x}', \mathbf{x}) \quad (14)$$

where $n^{1/2}(\mathbf{x}, \mathbf{x}') = \sum_i \sqrt{f_i} \phi_i(\mathbf{x}) \phi_i(\mathbf{x}')$. The corresponding local Müller potential at fixed occupations is determined by an OEP equation like Eq. (11) but with the xc part of the energy given by Eq. (14).

With some similarities to the nearly exact functional (Eq. (7)) the Müller functional captures static correlation rather well but tends to overestimate the correlation energy. In Ref. 44 it was shown that spurious magnetic instabilities occur in the Hubbard dimer and that an energy discontinuity is missing. Although simple improvements such as changing the square root of the occupation numbers to an optimised power improve energies⁴⁵ fundamental issues remain.⁴⁴

In the next section we will study how well the Müller functional performs in dissociating the heteronuclear LiH dimer. By restricting the functional to HOMO/LUMO we will show that despite energies of similar to quality to COEP defined above the delocalisation error is large and comparable to the LDA. We will further demonstrate that this error is related to a missing step of the local Müller potential captured by the more accurate local COEP potential.

Numerical analysis

In this section we present numerical results for the LiH dimer at dissociation. The molecule is modelled with soft-coulomb interactions in one dimension.⁴⁶ Thus, the electron-electron interaction is $v(x - x') = 1/\sqrt{1 + (x - x')^2}$ and the external potential is

$$V_{\text{Ext}} = \frac{Z_1}{\sqrt{1 + (x + R/2)^2}} + \frac{Z_2}{\sqrt{1 + (x - R/2)^2}}, \quad (15)$$

where $Z_1 = -1.2$ and $Z_2 = -1$. The core electrons on the Li atom are frozen and hence LiH is a two electron system for which we have a numerically exact solution to compare with. Calculations are done in a 1D spline basis-set previously proven suitable to solve OEP-type of problems.^{47,48} LDA and exact results are obtained with the OCTOPUS code.^{46,49}

All calculations are performed self-consistently. Energies are obtained from the relevant expressions. The potential for the COEP and Müller functionals are defined by applying Eq. (11) to Eq. (9) and Eq. (14), respectively. The RPA potential is found via the linearized Sham-Schlüter equation as described in previous works.^{47,50-52}

We will start by looking at the potential energy curve E and dipole moment μ and then analyse the ability of approximate functionals to deal with charge localisation, and relate this ability to energy derivative discontinuities and step features in the Hxc potential.

LiH dissociation

In a stretched symmetric or homonuclear system like H_2 the KS HOMO and LUMO are both delocalized by symmetry constraints. As a consequence, when $\theta = \pi/4$ the correlated orbitals are completely localized, and, due to the infinitesimal overlap between ψ_A and ψ_B , the interaction energy in Eq. (7) is close to zero. There is thus no static correlation error in COEP.

In the more challenging asymmetric or heteronuclear systems the KS orbitals may, or may not, be delocalized, depending crucially on the behavior of the KS potential. If the electrons were completely non-interacting the HOMO/LUMO would be localized on the atom with stronger/weaker nuclear potential. Hence, in the dissociation limit we would find both electrons on the atom with the largest ionization energy and zero on the other. In the LiH molecule the repulsive electron-electron interaction changes the charge distribution favouring one electron on each atom in the dissociation limit.

Standard KS DFT, which relies on a doubly occupied HOMO, solves this problem by aligning the effective HOMO of the two atoms via a step in the KS potential.^{13,53} In this

way the orbitals delocalize and the doubly occupied HOMO simulates localized electrons. However, all known approximate functionals in DFT fail to achieve the step when open shell atoms are dissociated and, consequently, fractionally charged atoms are found in the dissociation limit together with a diverging dipole moment: $|\mu(R)| \rightarrow \infty$ for $R \rightarrow \infty$.

How functionals that exploit fractionally occupied KS orbitals deal with the same situation is presently not well understood. From our accurate COEP approximation (Eq. (7)) we see that the KS orbitals *must* delocalize to ensure the interaction energy vanishes in the dissociation limit. Therefore, we expect a step feature similar to the one in DFT to develop in the KS potential of Eq. (11).

In Fig. 1 (left) we show the potential energy curves and dipole moment of the LiH molecule using the Müller, RPA, EXX and COEP functionals and compare them to the exact result. In Fig. 1 (right) we show the corresponding local Hxc potentials. As for H_2 , we see that both Müller and COEP are close to free from static correlation errors. Also state-of-the-art DFT-based perturbation theories, such as the RPA, perform well in the dissociation limit. All approximations (except EXX) perform similarly well in terms of total energies.

However, we see a drastically different behaviour for the dipole moment, which is an indirect measure of the charge distribution which has previously been used to assess the quality of densities from quantum chemical approximations.⁵⁴ While COEP gives very accurate results, both Müller and RPA fail. A diverging dipole moment implies that the molecule dissociates into fractionally charged atoms. This problem, previously discussed for RPA,^{9,11,55} has so far not been recognized for functionals in RDMFT.

The role of the potential

By looking at the corresponding KS potentials (Fig. 1, right) the origin of the density error becomes clear. The exact KS potential of DFT (black full line) exhibits a peak at around the bond midpoint, and a step that aligns the ionization potentials of the atoms. The peak has its origin in kinetic correlation and acts to separate the charges.^{56,57} This peak is present

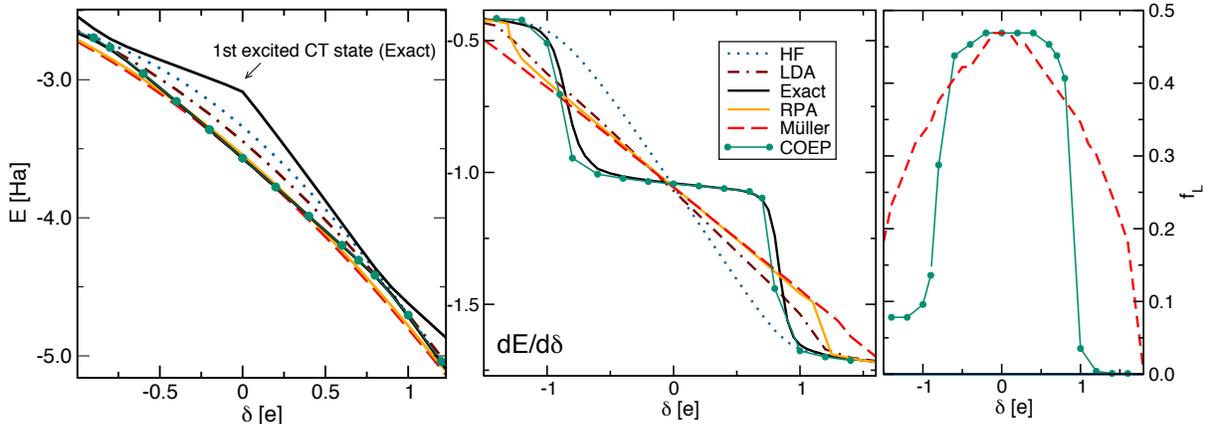


Figure 2: Left: Total energy as a function of the strength of the potential of atom 2 ($Z_2 = -2 - \delta$) with HF, LDA, RPA, Müller and COEP compared to exact result. Also the first excited singlet state is shown. Middle: Derivative of the ground state energy with respect to δ for the different approximations. Right: The corresponding occupation of the LUMO orbital within Müller and COEP.

also in the RPA but cannot alone prevent delocalisation.^{9,11} Due to the improved description of kinetic correlation in KS theories with fractional orbital occupations, like RDMFT, the peak is expected to be less relevant. This is, indeed, the case as demonstrated by the much smaller peak found in the nearly exact COEP.

We next turn our attention to the step. None of EXX, RPA or the Müller approach exhibit this feature. In contrast, COEP exhibits a step of exactly the same size as the exact KS potential of DFT. As noted above, this is not surprising as the size of the step must be equal to the difference in the ionization energy of the two atoms in order to accurately delocalize the KS orbital. The missing step in both Müller and RPA explains the error in their densities; and hence the divergent dipole moment.

From this simple demonstration we can conclude that the step is not only an essential feature of the DFT KS potential but also of the local potential used in local RDMFT theory or in wavefunction/ensemble theories that exploit optimized KS orbitals. We emphasise that the optimisation in LiH is crucial as the EXX orbitals are clearly unsuitable for either accurate energies or densities.

Delocalisation error and derivative discontinuity

We will now analyse in more detail the origin of the step in the KS potential. In DFT the step has been related to derivative discontinuities of the exact xc energy functional when studied as a function of particle number.^{13,58} To expose these discontinuities an extension of DFT functionals to ensembles composed of states with different particle numbers is required. Most approximate functionals have, however, been shown to miss the derivative discontinuity leading to an incorrect dissociation limit with atomic densities integrating to a fractional number of particles. The delocalisation error is therefore sometimes called fractional charge error.⁴

To continue our analysis, and uncover the properties of functionals involving fractionally occupied KS orbitals we will use an alternative approach, introduced in Ref. 59, which does not involve a direct treatment ensembles. Specifically, we study a stretched molecule at large separation and vary the nuclear charge on one of the atoms to transform the properties of the groundstate system. In our model system we set $R = 5$, set the charge on the first atom to $Z_1 = -2$ and, set the second to $Z_2 = -2 - \delta$ where δ is varied between -1.5 and 1.5. We then calculate the total ground state energy as a function δ .

In the exact calculation we have access to both ground and excited states. When $\delta < -0.9$ the exact ground state $|\Psi_0\rangle$ has two electrons on atom 2 and none on atom 1. The first *singlet* excited state $|\Psi_{1S}\rangle$ corresponds to a charge transfer state where one electron on atom 2 is transferred to atom 1 (see, e.g., Ref. 60). At around $\delta = -0.9$ $|\Psi_0\rangle$ and $|\Psi_{1S}\rangle$ become nearly degenerate (exactly so in the limit of infinite separation) and it is possible to form an arbitrary linear combination of them that has (almost) the same energy. These states are allowed to have fractional charges on the atoms even at infinite separation and hence the situation is similar to the one of studying one atom in an ensemble of states. As soon as $\delta > -0.9$ the excited state with one electron on each atom (i.e. the first excited charge-transfer state) becomes the ground state and vice versa.

In Fig. 2 we plot the energy and its derivative with respect to δ as functions of δ for

the exact case, COEP, Müller, EXX, LDA and RPA. In the energy plot we also include the energy of the first exact singlet excited state. The most notable feature is that, in the exact calculation, we see kinks or derivative discontinuities appearing at the "switching points" between the ground and the excited state. These discontinuities becomes sharper the further apart the atoms are.

Turning to the approximations, we see that EXX is clearly worst-performing compared to the exact calculation. Not only is its energy wrong, but fractional charges appear on the atoms as soon as δ crosses the point where the ground and excited state should become degenerate. This error is consistent with the large delocalisation errors found at dissociation of e.g. LiH (see Fig. 1), resulting from its poor treatment of strong static correlations. Based on these results we interpret the delocalisation (or fractional charge) error as an artificial mixing of the ground state with the first excited charge-transfer state beyond the point of degeneracy. A similar interpretation is often given to the fractional spin error but as an artificial mixing with the first *triplet* excited state (not shown in the figure as spin-symmetry is restricted here).

The RPA clearly performs better than EXX. Nonetheless, the derivative discontinuities are missed, leading to delocalisation errors of similar magnitude to LDA.¹¹ In view of the results in the previous section it is not surprising to see that the Müller functional fails as badly as RPA. Despite having an ostensibly good treatment of strong correlations, it lacks the ability to correctly treat charge localization.

Only the nearly exact COEP, which treats both the energy and potential in an appropriate fashion, is able to reproduce the correct behaviour with an energy discontinuity, or a step in the derivative. We note that restricting to a local potential does not impose any severe restriction even in this challenging situation. This can thus not be blamed for the failure of the Müller functional for example.

In the right panel of Fig. 2 we plot the occupation numbers in COEP and the Müller functional. While the occupation numbers of the Müller functional are smooth as a function

of δ , the occupation numbers of COEP exhibit discontinuities at the points where the energy has derivative discontinuities. Thus, just as in DFT, the problem of delocalization in RDMFT can be related to missing discontinuities in the energy functional. Fig. 2 (right) provides evidence that these discontinuities appear directly in the occupation numbers whenever charge localization is appropriately dealt with.

Conclusions

In this work we have: a) analyzed the optimized effective potential corresponding to multi-configurational DFT approaches and RDMFT in the challenging case of LiH dissociation; b) derived a nearly exact two-electron approximation based on a correlated orbital wavefunction ansatz and compared it against a selection of energy approximations from DFT, DFT-based perturbation theory, and RDMFT; c) introduced a stringent test of different functionals that highlights their strengths and weaknesses in dealing with charge localization.

We showed that approaches that give accurate energies such as the RPA and the Müller functional can still suffer from rather large delocalization errors, a surprising result that leads to errors in the dipole moment of molecules. Furthermore, by employing a multiplicative OEP, as in COEP, we showed that these errors can be avoided thanks to the appearance of step-like features in the effective potential. We thus recommend further attention be placed on the role played by potentials in theories that exploit fractional orbital occupation numbers such as RDMFT, wavefunction, and ensemble theories. Our work indicates that using optimized effective potentials might improve on existing techniques, and lead to improvements in the current state-of-art in electronic structure theory. Work along these lines is being pursued.

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Figure 3: For Table of Contents Only

A good potential tips the balance in favour of good energies, when modelling strong correlations

