JCTC Journal of Chemical Theory and Computation

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pubs.acs.org/JCTC

Strong Correlations in Density-Functional Theory: A Model of Spin-Charge and Spin−Orbital Separations

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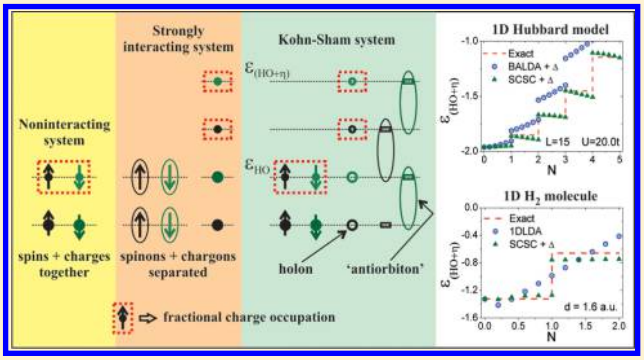
ABSTRACT: It is known that the separation of electrons into spinons and chargons, the spin-charge separation, plays a decisive role when describing one-dimensional (1D) strongly correlated systems [*Phys. Rev. B* **2012**, *86*, 075132]. In this paper, within the density-functional theory (DFT) formalism, we extend the investigation by considering a model for the third electron fractionalization: the separation into spinons, chargons and orbitons, the last associated with the electronic orbital degree of freedom. Specifically, we deal with two exact constraints of exchange-correlation (XC) density-functionals: (i) the constancy of the highest occupied (HO) Kohn−Sham (KS) eigenvalues upon fractional electron numbers and (ii) their discontinuities at integers. By means of 1D discrete Hubbard chains and 1D H_2 molecules in the continuum, we find that spin-charge separation yields almost constant HO KS eigenvalues, whereas the spin−orbital counterpart can be decisive when describing derivative discontinuities of XC potentials at strong correlations.



1. INTRODUCTION

Spin and charge are often treated as fundamental properties of ordinary electrons. However, when confined in one dimension, interacting electrons display the unusual property of separating their spin and charge into two independent quasiparticles: spinons and chargons.[1] Both behave just like ordinary electrons, but spinons have spin-1/2 and no electrical charge, whereas chargons are spinless charged electrons. Recently,[2,3] an additional fractionalization was shown to occur: the spin−orbital separation, for which spin and orbital degrees of freedom are decoupled to form the orbitons, particles with no spin and charge, carrying solely the orbital information. Both, the spin-charge and spin−orbital separations have recent evidence of experimental observation,[3,4] teaching us that ordinary electrons can be considered bounded states of spinons, chargons and orbitons.

The Kohn−Sham (KS) formalism of density-functional theory (DFT),[5,6] by construction, retains the spin, charge and orbital degrees of freedom together, once it considers an auxiliary system of noninteracting particles. In contrast, it has been shown that the separation into spinons and chargons is decisive when describing strongly correlated density distributions in one dimension.[7] W. Yang et al. have assumed strongly correlated systems as one of the modern challenges for DFT: "The challenge of strongly correlated systems is a very important frontier for DFT. To fully understand the importance of these systems, they must be looked at within the wider realm of electronic structure methods."[8] Here, we intend to give a contribution into this challenge; by means of one-dimensional (1D) discrete Hubbard chains and 1D H_2 molecules in the continuum, we extend the spin-charge investigation and propose a model for the spin−orbital separation in DFT. Specifically, we consider two exact constraints of exchange-correlation (XC) density-functionals: (i) the constancy of the highest occupied (HO) Kohn−Sham eigenvalues upon fractional electron numbers and (ii) their discontinuities at integers. These constraints are usually not satisfied even by modern approaches, and are the cause of dramatic errors when describing any generic situation involving transport of charges.[9−12]

In detail, we shall compare the performance of local-density functionals and their spin-charge separation corrections, including the spin−orbital fractionalization in both cases. We show that spin-charge separation yields almost constant HO KS eigenvalues, whereas the separation into orbitons can be decisive when dealing with derivative discontinuities of XC potentials at strong correlations.

2. THEORETICAL BACKGROUND

2.1. Fractional Electron Numbers. In a system with $M = N + w$ $(0 \le w \le 1)$ electrons, the total ground-state energy is given by[13]

$$E(N + w) = (1 - w)E(N) + wE(N + 1) \quad (1)$$

Assuming that only the HO KS orbital can be fractionally occupied, Janak[14] has proved that

$$\frac{\delta E}{\delta M} = \varepsilon_{\mathrm{HO}} = \text{constant} \quad (2)$$

Received: March 20, 2013
Published: June 11, 2014

 © 2014 American Chemical Society dx.doi.org/10.1021/ct400223d | *J. Chem. Theory Comput.* 2014, 10, 3641−3646

where ε_{HO} is the HO KS eigenvalue. By means of the Koopmans' theorem of DFT, it is known that the ionization potential (IP) is given by[15]

$$\mathrm{IP}(N) = E(N-1) - E(N) = -\varepsilon_{HO}(N) \tag{3}$$

that is, even though it is known that the KS eigenvectors and eigenvalues have, in general, no physical meaning, there is an exception: the negative of the HO KS eigenvalue is identical to the ionization potential of the interacting system.

The fundamental energy gap at each integer N is given by the difference between ionization potential and electronic affinity (EA):[15]

$$E_g(N) = \mathrm{IP}(N) - \mathrm{EA}(N) = \varepsilon_{HO}(N+1) - \varepsilon_{HO}(N) \tag{4}$$

because $\mathrm{EA}(N) = \mathrm{IP}(N+1)$.

The Kohn–Sham gap is defined as

$$E_{g,KS}(N) = \varepsilon_{HO+1}(N) - \varepsilon_{HO}(N) \tag{5}$$

where $\varepsilon_{HO+1}(N)$ is the lowest unoccupied state of the N-particle system.

Therefore, by means of eqs 4 and 5, one can write

$$E_g(N) = E_{g,KS}(N) + \delta_{xc} \tag{6}$$

where $\delta_{xc} = \varepsilon_{HO}(N+1) - \varepsilon_{HO+1}(N)$ is defined as the derivative discontinuity of the XC potential.[15] For open shell systems, $E_g(N) \equiv \delta_{xc}$, because $E_{g,KS}(N) = 0$ (in a spin-restricted KS calculation).

2.2. Spin-Charge Separation Correction. According to the Luttinger liquid conjecture, the total Hamiltonian of a 1D interacting system is believed to separate into two independent terms, of spin and charge, as schematically represented by[16−19]

$$\hat{H} = \hat{H}_\beta + \hat{H}_\rho = \hat{H}_0 + \hat{H}_I \tag{7}$$

where $\hat{H}_\beta$ and $\hat{H}_\rho$ stand for the spin and charge terms, respectively, with $\hat{H}_0$ indicating a noninteracting kinetic contribution and $\hat{H}_I$ including all interaction effects. The spin and charge components of eq 7 are related, respectively, to the spinon and chargon densities. Spinons and chargons are semions,[20,21] that is, particles which follow a fractional occupation statistics. At temperature $T = 0$, a generalization of Bose–Einstein and Fermi–Dirac statistics can be written as[20]

$$\begin{cases} 0 \le f_{i\sigma} \le 1/g, & \text{for } \varepsilon_{i\sigma} \le \varepsilon_{HO} \\ f_{i\sigma} = 0, & \text{for } \varepsilon_{i\sigma} > \varepsilon_{HO} \end{cases} \tag{8}$$

where $f_{i\sigma}$ indicates the average occupation of the $i\sigma$ orbital. Fermions are characterized by $g = 1$, whereas bosons by $g \to 0$. Semions are half way, with $g = 1/2$. This picture can be also associated with a phase change (given by $e^{i\theta}$) induced in the wave function upon exchange of two particles. Fermionic wave functions have $\theta = \pi$, whereas bosonic $\theta = 0$. Semions, half way, are described by $\theta = \pi/2$.[20] Considering spinons and chargons as independent entities, their occupied states should follow a semion distribution, where charge and spin are separated to form spin-1/2 spinons and spinless chargons. In Figure 1b, we display a strongly interacting semion distribution: spinons, with no charge, doubly occupy each state, whereas chargons, with the entire charges, are characterized by single occupations.[22]

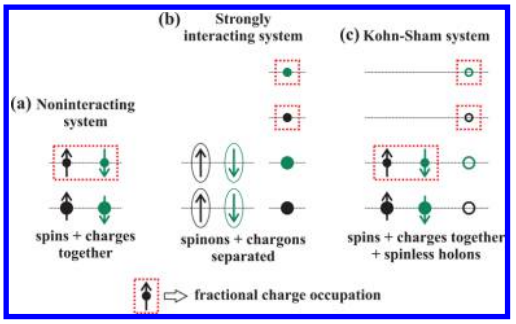


Figure 1. Schematic representation of occupied quantum states. (a) Noninteracting system, with spins and charges together. (b) Strongly interacting system, with spins and charges separated into spinons and chargons, respectively. (c) Noninteracting Kohn–Sham system: spins and charges together at expense of the presence of spinless holons (the chargons antiparticles). Fractional charge occupations are indicated by the dashed squares.

As shown in Figure 1c, it has been proposed[7] that the occupied states of a noninteracting KS system are built by retaining spin and charge together, at expense of the presence of holons (the chargon antiparticles), whose densities are given by $\rho^+(\mathbf{r})$. The KS potential is then proposed to be written as

$$v_{KS}[n](\mathbf{r}) = v_{ext}(\mathbf{r}) + \frac{\delta\langle H_I\rangle}{\delta n(\mathbf{r})} - \frac{\delta\langle H_I\rangle}{\delta \rho^+(\mathbf{r})} \tag{9}$$

where $n(\mathbf{r})$ is the ordinary total electronic density (of spins + charges together). In a nonmagnetic LDA formulation, for $N_{even} \le N \le (N_{even} + 2)$, we have that

$$n(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=0}^{N_{even}/2} |\psi_{i,\sigma}(\mathbf{r})|^2 + \sum_{\sigma=\uparrow,\downarrow} w|\psi_{(N_{even}+2)/2,\sigma}(\mathbf{r})|^2 \tag{10}$$

and

$$\rho^+(\mathbf{r}) = \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=0}^{N_{even}} |\psi_{i,\sigma}(\mathbf{r})|^2 + \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} w(|\psi_{N_{even}+1,\sigma}(\mathbf{r})|^2 + |\psi_{N_{even}+2,\sigma}(\mathbf{r})|^2) \tag{11}$$

with $0 \le w \le 1$, allowing fractional occupation. $N_{even} = 0, 2, 4, 6, \ldots$, and $\psi_{i,\sigma}(\mathbf{r})$ are the KS eigenvectors, with $\psi_{i=0,\sigma}(\mathbf{r}) = 0$. On the basis of eqs 9–11, the spin-charge separation correction (SCSC) is written as[7]

$$\begin{aligned} v_{KS}^{SCSC/approx}[n](\mathbf{r}) &= v_{ext}(\mathbf{r}) + v_H[n](\mathbf{r}) + v_{xc}^{approx}[n](\mathbf{r}) \\ &\quad - v_H[\rho^+](\mathbf{r}) - v_{xc}^{approx}[\rho^+](\mathbf{r}) \\ &\equiv v_{ext}(\mathbf{r}) + v_H[n](\mathbf{r}) + v_{xc}^{SCSC}[n](\mathbf{r}) \end{aligned} \tag{12}$$

where v_{ext}, v_H and v_{xc} label the external, Hartree and XC potentials, respectively. In other words, the SCSC approach can be described as follows: the KS system retains spins + charges together (once it is a noninteracting system, which includes interaction by means of a KS effective potential). Thus, in order to simulate the spin-charge separation, we compensate the absence of spinons and chargons by including an "external potential" to which spins + charges together are subjected: observe that the contributions due to holons in eqs 9 and 12

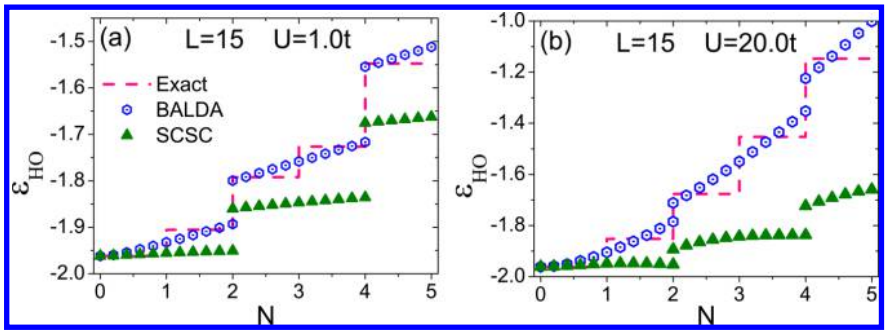


Figure 2. (Color online) Open Hubbard chains of $L = 15$ sites: HO KS eigenvalues (ε_{HO}) for $0 < N \leq 5$. The "exact" data come from total energies obtained by means of a Lanczos diagonalization of the Hubbard Hamiltonian of eq 13, that is, $\varepsilon_{HO}^{exact}(N) = E(N) - E(N-1)$, as follows from eq 3.

have the form of an external potential, which has then been intentionally incorporated to the $v_{xc}^{SCSC}[n](\mathbf{r})$ term. The negative signals are due to the positive holons charges. Note that the total electronic densities, $n(\mathbf{r})$, are calculated in the ordinary way, that is, by means of eq 10, without excitations or any further modification.

The XC SCSC potential of eq 12 is not a functional derivative of a known XC energy functional, that is, it is a direct correction to the KS potential. Even though model potentials may suffer from conceptual drawbacks when calculating the associated energy functionals, they are suggested to be a promising route to new developments in DFT.[23−25] For example, it is known that for KS potentials that are not functional derivatives, different paths of assigning energy functionals give different results,[26,27] evidencing an impossibility of unambiguously assigning energy values. On the other hand, although an ambiguous energy assignment represents a conceptual inconsistency, it is not necessarily meaningless, because the use of potentials as seeds can be also regarded as an interesting strategy for constructing new energy functionals.[26,27] In this sense, testing the SCSC model potential of eq 12 under different paths of assigning energies is certainly a topic of investigation, which, however, we judge to be out of the purposes of this paper.

3. RESULTS

3.1. One-Dimensional Hubbard Chains. In one dimension, and in second-quantized notation, the Hubbard model[28] (1DHM) is defined as

$$\hat{H} = -t \sum_{j,\sigma}^{L} (c_{j\sigma}^{\dagger} c_{j+1,\sigma} + \text{H.c.}) + U \sum_{j}^{L} c_{j\uparrow}^{\dagger} c_{j\uparrow} c_{j\downarrow}^{\dagger} c_{j\downarrow} \tag{13}$$

where L is the number of sites, t is the amplitude for hopping between neighboring sites and U is the local interaction acting on site j. Occupation of each site is limited to two particles, necessarily of opposite spin.[29] The 1DHM is a very instructive many-body laboratory, which enables us to investigate the effects of changing electronic correlation by just controlling the on-site electron−electron interaction U (which can be varied continuously). A different model, in the continuum and with long-ranged Coulomb interaction, will be considered in section 3.2.

With the density $n(\mathbf{r})$ replaced by the on-site occupation $n(j)$, the Hohenberg−Kohn and KS theorems of DFT also hold for the 1DHM.[30] In terms of this variable, local-(spin)-density approximations have been constructed,[31−34] including a recent extension to finite temperatures.[35] In this section, we chose the fully numerical Bethe Ansatz local-density approximation (BALDA-FN)[33] as the reference XC functional, considering only nonpolarized systems with $N_{\uparrow} = N_{\downarrow}$. There is no conceptual difference between the BALDA-FN functional and other L(S)DA approximations applied to three-dimensional (3D) systems. The only difference is that BALDA-FN is based on exact solutions of one-dimensional (1D) homogeneous Hubbard chains, and not on accurate solutions of 3D homogeneous systems. Throughout this section, we shall denote the SCSC/BALDA-FN approach simply as SCSC approximation.

Considering open Hubbard chains, in Figure 2a,b, we plot ε_{HO} versus fractional charge occupations for two values of U. The "exact" data, for all cases presented in this section, come from total energies obtained by means of a Lanczos diagonalization of the Hubbard Hamiltonian of eq 13, that is, $\varepsilon_{HO}^{exact}(N) = E(N) - E(N-1)$, as follows from eq 3. The DFT values of ε_{HO}, on the other hand, are the HO KS eigenvalues extracted from the KS equations, that is, we do not use DFT total energies. From Figure 2a,b, the BALDA yields a quasi-linear dependence for ε_{HO}. The slope of each straight line tends to increase as U is increased, with $E_g = 0$ at odd integers (open shells). Because we are dealing with 1D systems, the BALDA naturally yields $E_g \neq 0$ at even integers (closed shells), which, however, tend to be underestimated as U is increased. The SCSC performs much better, yielding almost constant values for ε_{HO}. The associated energy gaps, on the other hand, are also (i) equal to zero (open shells) or (ii) underestimated (closed shells), combined with severely incorrect ionization potentials (IP $= -\varepsilon_{HO}$).

3.1.1. Spin−Orbital Separation. The difficulty with energy gaps is intrinsic of most available density functionals. In this context, beyond spinons and chargons, we propose here a model for the third electron fractionalization: into orbitons. By definition, orbitons are excitations of the orbital degrees of freedom of electrons, which behave like spinless and uncharged particles. Consequently, when dealing with the noninteracting KS electrons of Figure 1c, we propose the KS eigenvalues should be increased by a constant Δ, which is equivalent to include the presence of an "antiorbiton", the extension of the SCSC idea of eq 12. Thus, we propose the XC potential to be given by

$$v_{xc}^{approx+\Delta}[n](j) = v_{xc}^{approx}[n](j) + \Delta \tag{14}$$

with

$$\Delta = \varepsilon_{(HO+\eta)} - \varepsilon_{HO}; \quad \eta = 0, 1, 2, \ldots \tag{15}$$

dx.doi.org/10.1021/ct400223d | J. Chem. Theory Comput. 2014, 10, 3641−3646

A schematic representation of this orbital separation model is shown in Figure 3, where, as conceptually thought, the parameter η is given by

$$\eta = \frac{N_{\text{even}}}{2} \tag{16}$$

for

$$N_{\text{even}} - 1 < N \leq N_{\text{even}} + 1 \tag{17}$$

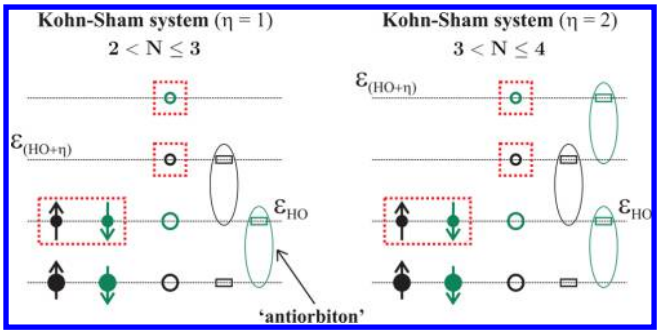


Figure 3. (Color online) Noninteracting Kohn–Sham systems: spins and charges together, at expense of the presence of spinless holons and the conjectured "antiorbitons". The antiorbitons are represented by excitations between orbital levels.

For example, in the strongly interacting limit, $\eta = 1$ for $1 < N \leq 3$ and $\eta = 2$ for $3 < N \leq 5$. Noninteracting systems (or systems with $0 < N \leq 1$) should have $\eta = 0$, indicating the absence of spin–orbital separation.

Let us define $\varepsilon_{\text{HO}}^{\Delta}$ as the HO KS eigenvalues yielded by the $v_{\text{xc}}^{\text{approx}+\Delta}$ potential. By means of eqs 14 and 15, $\varepsilon_{\text{HO}}^{\Delta}$ can be determined by means of the following KS equation:

$$\{\hat{t}_s + v_{\text{ext}}(j) + v_{\text{H}}[n](j) + v_{\text{xc}}^{\text{approx}}[n](j)\}\psi_{i\sigma}(j) = \varepsilon_{i\sigma}\psi_{i\sigma}(j) \tag{18}$$

with

$$\varepsilon_{\text{HO}}^{\Delta} = \varepsilon_{(\text{HO}+\eta)} \tag{19}$$

The orbital degrees of freedom we mention in this section do not come from a multiband Hubbard model. Instead, as shown in eqs 18 and 19, they come from the KS levels, as a solution of the KS equations under the Hubbard Hamiltonian of eq 13. Therefore, the idea represented by eqs 14–17 can be applied to other types of Hamiltonians, e.g., the one we shall consider in section 3.2.

In Figure 4a–d, we plot the results for the BALDA+Δ and SCSC+Δ. The inclusion of Δ yields $E_g \neq 0$ for open and closed shells. At strong correlations (when U is increased), the curves of SCSC+Δ fit in very good agreement with the exact data, including the constancy of ε_{HO}, the derivative discontinuities of the XC potentials and the ionization potentials. The BALDA +Δ also yields correct energy gaps, but combined with incorrect IPs and linear dependence of ε_{HO} between integers. Note that the good performance tends to deteriorate as U is reduced and N is increased. The reason is because the conjectures of eqs 9 and 14 have been specially conceived to deal with strong correlations, following the idea of the strongly interacting semion distribution, as displayed in Figure 1b. In this sense, the construction of XC potentials that can suitably link the weakly and strongly correlated regimes is certainly a topic of future investigation.

3.2. One-Dimensional H_2 Molecule in the Continuum.

In dissociation processes, to preserve neutrality of isolated atoms, it is known that the increment of nuclear separation uses are followed by an increment of correlation energy density.[8] To test the SCSC+Δ approach under this type of delimitation between weakly and strongly correlated systems, in this section, we consider the dissociation of a 1D H_2 molecule.

In contrast with the discrete Hubbard chains, a different way of describing interacting electrons in one dimension may take into account continuum space and long-ranged Coulomb interaction. This is a special case of interest, because chemistry, in general, is described by using both ingredients. The electronic Hamiltonian of a 1D H_2 molecule can be written as

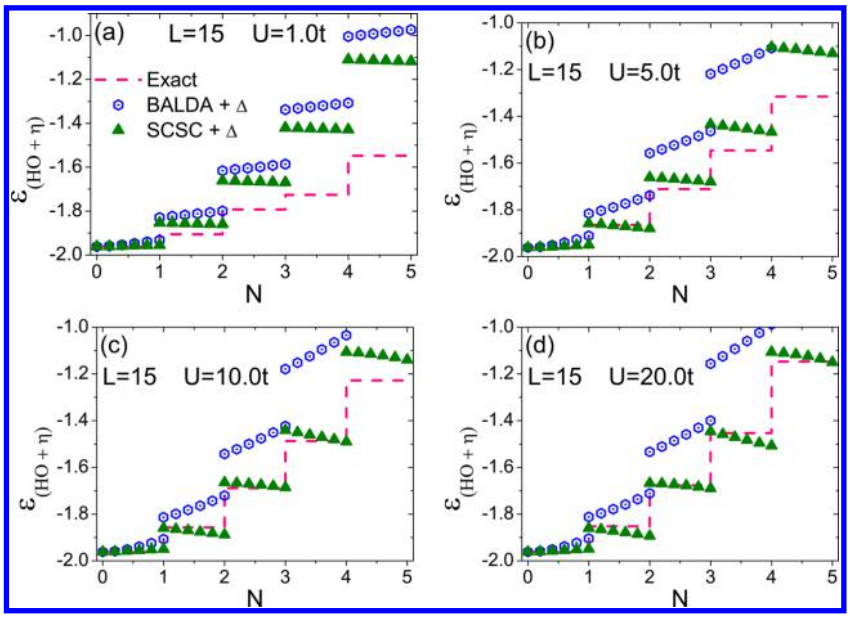


Figure 4. (Color online) Open Hubbard chains of $L = 15$ sites: HO KS eigenvalues (ε_{HO}) obtained by including the Δ factor of eqs 14 and 15, with η given by eqs 16 and 17.

dx.doi.org/10.1021/ct400223d | J. Chem. Theory Comput. 2014, 10, 3641–3646

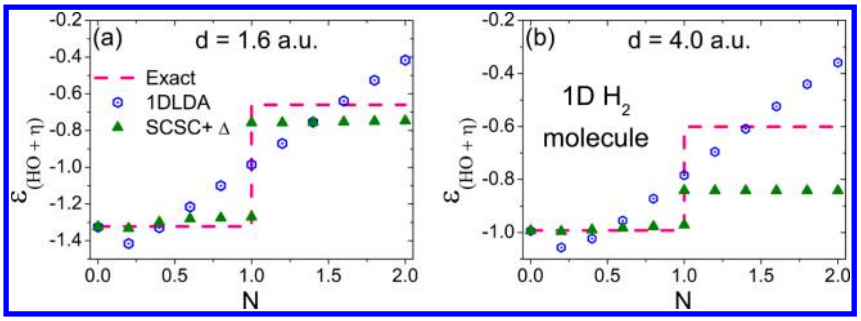


Figure 5. (Color online) One-dimensional H_2 molecule in the continuum. (a) HO KS eigenvalues (ε_{HO}) for $0 < N \leq 2$ and nuclear separation d = 1.6 au (b) the same as before, but for d = 4.0 au. Remember, for 1DLDA, $\eta = 0$ for $0 < N \leq 2$; in the case of SCSC+Δ, $\eta = 0$ for $0 < N \leq 1$ and $\eta = 1$ for $1 < N \leq 2$. The "exact" data come from total energies extracted from the literature,[38] with $\varepsilon_{HO}^{exact}(N) = E(N) - E(N-1)$, as follows from eq 3.

$$\hat{H} = \sum_{j=1}^{2}\left[-\frac{1}{2}\frac{d^2}{dx_j^2} + v_{ext}(x_j)\right] + \frac{1}{2}\sum_{\substack{j,k=1 \\ (j\neq k)}}^{2} v_{int}(x_j, x_k) \quad (20)$$

A common choice, which avoids singularities of the Coulomb interaction, is the soft-Coulomb potential:[36−39]

$$v_{int}(x_j, x_k) = \frac{q_j q_k}{\sqrt{b^2 + (x_j - x_k)^2}} \quad (21)$$

where q_j and q_k are the electron charges placed at positions x_j and x_k, respectively, and b is a softening parameter. The same idea holds for the electron−nucleus interactions:

$$v_{ext}(x_j) = \sum_{i=1}^{2} \frac{Z_i q_j}{\sqrt{b^2 + (x_j - X_i)^2}} \quad (22)$$

labeling the nuclear charge Z_i placed at position X_i. The repulsive nucleus−nucleus interaction (not shown) is also described by means of a soft-Coulomb potential (under the same parameter b). Specifically, for b = 1, a local-density approximation (1DLDA) has been used to describe 1D atoms and molecules within the DFT formalism.[37−39] Here we intend to use the 1DLDA and implement the corresponding SCSC+Δ correction to it. In this section, we shall denote the SCSC/1DLDA approach simply as SCSC approximation.

In Figure 5(a)−(b), considering $0 < N \leq 2$, we plot ε_{HO} for a 1D H_2 molecule with two nuclear separations: $d = X_2 - X_1$ = 1.6 au, which is the exact equilibrium distance,[38] and d = 4.0 au. In both cases, the 1DLDA yields a quasi-linear dependence for ε_{HO}, with no gap at N = 1. The SCSC+Δ, on the other hand, yields almost constant values for ε_{HO}, but with a reduced gap in comparison with the exact data. As the separation d is increased, the SCSC+Δ acts on leading E_g to zero, what can be seen as a delimitation between weakly and strongly correlated systems: in the limit of $d \to \infty$, the SCSC+Δ recovers the correct $E_g \to 0$ at N = 1 (as mentioned before, the conjectures of eqs 9 and 14 have been specially conceived to deal with strong correlations). These results are in accordance with the observation that correlation energy density is zero in isolated H atoms but substantial around each H atom in H_2 at long distances.[40,41]

In summary, we can conclude that (I) spin-charge separation, when included by means of the SCSC XC potential, yields almost constant highest occupied KS eigenvalues; (II) in the limits of strong correlations, the model we proposed here for the spin−orbital separation yields accurate energy gaps for both, open and closed shells (in association with correct derivative discontinuities of the XC potentials). Considering (I) and (II), we can argue that when dealing with strong correlations in one dimension, electrons should not be treated as unique particles. Instead, the separation into spinons, chargons and orbitons can be crucial. The way to include it in a noninteracting KS calculation, which by construction retains spin, charge and orbital degrees of freedom together, is a combination of (I) and (II).

4. CONCLUSIONS

Constancy of ε_{HO}. The BALDA-FN and 1DLDA yielded typical results attributed to delocalization errors of density functionals: Incorrect linear behavior of ε_{HO} upon fractional charge occupation. On the other hand, the SCSC/BALDA-FN and SCSC/1DLDA yielded almost constant values for ε_{HO}.

Derivative Discontinuity. By means of eq 14, we proposed the inclusion of the extra electron fractionalization, into orbitons, which yielded accurate energy gaps at strong correlations. We observed a delimitation between weak and strong correlations by simply changing the on-site interaction U in open Hubbard chains, or changing the nuclear separation in the dissociation of a 1D H_2 molecule. It has been recently pointed out that, beyond strong correlations, it is a basic challenge to understand whether the KS eigenvectors and eigenvalues have any further significance.[8] The spinon-chargon-orbiton separation can therefore be a step in this direction.

Energy Functionals. Testing the SCSC and SCSC+Δ potentials under different paths of assigning energy functionals[26,27] is a topic of future investigation. The resulting energy functionals may then be used in the derivation of even more accurate XC potentials, which, for example, could suitably link the weakly and strongly correlated regimes.

Extensions. Possible direct generalizations to higher dimensions, especially to three-dimensional (3D) systems, depend on a particular question: is electron fractionalization also possible in 3D? To our knowledge, this is still a topic of debate, and therefore deserves further investigation. Nevertheless, indirect generalizations are certainly possible, as the case of quasi-one-dimensional systems.

It should be noted that a successful alternative route to obtain accurate derivative discontinuities and constancy of ε_{HO}, the SCE approach, has been described in recent letters.[42,43] In this sense, understanding possible connections between using SCSC+Δ and other accurate approaches is also a topic of future investigation.

dx.doi.org/10.1021/ct400223d | J. Chem. Theory Comput. 2014, 10, 3641−3646

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Vivaldo L. Campo Jr. for his code of Lanczos exact diagonalization and for the original version of the BALDA-FN code.

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