PHYSICAL REVIEW B **79**, 125109 (2009)

Using Kohn-Sham density functional theory to describe charged excitations in finite systems

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(Received 17 June 2008; revised manuscript received 3 December 2008; published 12 March 2009)

We use projector operators to correct the Kohn-Sham Hamiltonian of density functional theory (KS-DFT) so that, in finite systems, the resulting mean-field scheme yields virtual orbitals and energy gaps in better agreement with those predicted by quasiparticle theory. The proposed correction term is a scissorslike operator of the form $(\hat{I}-\hat{\rho})\delta\hat{H}(\hat{I}-\hat{\rho})$, where $\hat{I}$ is the identity operator, $\hat{\rho}$ is the N-particle KS-DFT density matrix, and $\delta\hat{H}$ is the difference between the $N+1$- and N-particle Kohn-Sham Hamiltonians. Such a term replaces the Kohn-Sham virtual orbitals of the N-particle system by the highest occupied molecular orbital and virtual orbitals of the system with $N+1$ particles in an attempt to mimic a true quasiparticle spectrum. The physical origin of the proposed correction is discussed and illustrated by considering a system of interacting electrons—the Moshinsky atom—where the gap can be computed exactly. A local-density approximation (LDA) is then used to evaluate $\delta\hat{H}$ in order to compute the gaps and orbitals of a variety of small molecules to find that the approximation improves the agreement with both experiment and computationally more demanding methods. The similarity between the corrected and Hartree-Fock virtual orbitals is illustrated and the extent to which the bare LDA virtual orbitals are improved is considered.

DOI: 10.1103/PhysRevB.79.125109 PACS number(s): 71.15.Mb, 71.15.Qe

I. INTRODUCTION

The accurate determination of charged excitation energies, such as electron affinities and the fundamental energy gaps, in many-electron systems by means of a computationally inexpensive mean-field method remains an open problem despite recent progress.[1–12]

The *interpretation* of the difference between the highest occupied and lowest unoccupied molecular-orbital (HOMO and LUMO) eigenvalues of Kohn-Sham density functional theory (KS-DFT) (Refs. 13 and 14) as the fundamental energy gap severely underestimates experimental values, both in finite and extended systems.[15–18] On the other hand, KS-DFT has been extremely successful in the computation of ground-state averages for which accurate density functionals are known, such as the total energy and magnetic moment.[19–21] This success is also due to the extremely good ratio between the accuracy and the computational demands of this method; KS-DFT not only yields accurate results for these quantities, but it is also very fast and simple to implement for most available exchange-correlation (XC) functionals.

KS-DFT is not designed to give addition and removal energies in a single calculation: the Kohn-Sham eigenvalues have no direct physical interpretation except for the ones associated with the highest occupied molecular orbital (HOMO) ;[22] Kohn-Sham orbitals are difficult to interpret physically; typically the Kohn-Sham virtual orbitals do not enter the self-consistent cycle and thus play a limited role in the theory.[23]

In this paper we consider a promising scheme proposed by Cehovin *et al.* in Ref. 10, where projector operators are used together with the KS-DFT Hamiltonians of the N- and $N+1$-particle systems to approximate the quasiparticle Hamiltonian and its orbital dependence thereby providing virtual orbitals that are able to describe charged excitations. In the remainder of the introduction we motivate the scheme by discussing the orbital dependence in different theoretical approaches and their ability to describe charged excitations.

In KS-DFT the ground-state N-particle electron density is obtained by the self-consistent solution of the Kohn-Sham equations, which are characterized by a noninteracting Hamiltonian of the form

$$H_N^{\mathrm{KS}} = -\frac{\nabla^2}{2} + v_s[n_N](\mathbf{r}), \tag{1}$$

where the effective Kohn-Sham potential, v_s, is a functional of the electron density of the N-particle system, n_N, and includes the external and Hartree potentials as well as the XC potential.

Note that v_s in Eq. (1) is the same for all of the Kohn-Sham orbitals, whether occupied or not. This fact is in clear contrast with the Hartree-Fock (HF) equations which in the basis of eigenstates of the HF Hamiltonian, ψ_i, can be written as

$$h_0(\mathbf{r})\psi_i(\mathbf{r}) + \sum_j^{\mathrm{occ}} V_{jj}\psi_i(\mathbf{r}) - \sum_j^{\mathrm{occ}} V_{ij}\psi_j(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \tag{2}$$

where $h_0(\mathbf{r})$ accounts for the kinetic energy and external potential, $V_{ii}(\mathbf{r}) = \int d^3\mathbf{r}' |\mathbf{r}-\mathbf{r}'|^{-1} |\psi_i(\mathbf{r}')|^2$ and $V_{ij}(\mathbf{r}) = \int d^3\mathbf{r}' \psi_j(\mathbf{r}') |\mathbf{r}-\mathbf{r}'|^{-1} \psi_i(\mathbf{r}')$. When ψ_i is occupied the electrostatic potentials that enter the HF equations are generated by $N-1$ particles because of the mutual cancellation between Hartree and exchange self-interaction terms. However, when ψ_i is unoccupied the electrostatic fields that enter the HF equations are generated by N particles since in this case $i \neq j$ in Eq. (2) and thus in the expression for V_{ij} the orbitals density $\psi_j(\mathbf{r}')\psi_i(\mathbf{r}')$ has zero net charge, i.e., $\langle\psi_i|\psi_j\rangle = 0$. In the HF approximation the potentials acting on occupied states are generated by $N-1$ particles while those acting on unoccupied states are generated by N particles and thus HF partially accounts for the effects of the added particle.[10,24–26] This type of *orbital dependence* is precisely what one would expect from simple electrostatic considerations of a charged particle added to or removed from a dielectric or metallic system. While the HF approximation has many drawbacks associated with the lack of correlation, this one physically appealing feature is totally absent in KS-DFT, yet it is intuitively necessary for the description of charged excitations: when an electron is added to a many-electron system one expects classical electrostatic effects to increase the fundamental energy gap with respect to its KS-DFT value. In simple terms: the eigenvalues of KS-DFT do not contain the effects of the added charge.

From the perspective of time-dependent density functional theory (TDDFT) (Ref. 27) it is possible to see why differences between the eigenvalues of static KS-DFT often provide a good zeroth-order approximation to neutral excitations: the first-order correction to the excitation energy depends on the sum of the Hartree and exchange-correlation kernels, which often have different signs, leading to partial cancellations and a small first-order correction at least in some systems. In contrast the HF approximation provides an approximation to charged excitations which is first order in the electron-electron interaction.

To summarize: the effective potential of KS-DFT makes no distinction between occupied and virtual orbitals and, as a result, the classical polarization of the N-electron system by the added electron is missing in KS-DFT.

The rest of this paper is organized as follows: in Sec. II we discuss the scheme proposed by Cehovin *et al.*,[10] which should correct the above-mentioned deficiency of KS-DFT; in Sec. III we present an illustration where we consider an exactly solvable model, the Moshinsky atom; in Sec. IV we present our numerical results for the HOMO-LUMO gaps and virtual orbitals of a few selected molecules. We end with the conclusions in Sec. V. Details of the calculations for the Moshinsky atom are included in the Appendix.

II. TWO KOHN-SHAM HAMILTONIANS TO APPROXIMATE THE QUASIPARTICLE HAMILTONIAN

The arguments put forward above show that to improve the description of charged excitations and thus the fundamental gap values, the N-particle Kohn-Sham Hamiltonian needs to be modified in order to include information about the singly-charged state with $N+1$ electrons. For all N, the vertical electron affinity (EA) of the N-particle system and the vertical ionization potential (IP) of the $N+1$-particle system satisfy[28]

$$\mathrm{EA}(N) = \mathrm{IP}(N+1). \tag{3}$$

Hence the fundamental gap can be obtained by means of two calculations of the Kohn-Sham HOMO energy, one for the N-particle system and another for the $N+1$-particle system[3,4,6–8,15–17] as

$$E_g = \mathrm{IP}(N) - \mathrm{EA}(N) = \mathrm{IP}(N) - \mathrm{IP}(N+1) = \epsilon_H^{N+1} - \epsilon_H^N, \tag{4}$$

where ϵ_H^N is the HOMO energy of the N-particle system. According to the ionization potential theorems of KS-DFT (Ref. 22) both ϵ_H^{N+1} and ϵ_H^N, and thus the gap, can be obtained exactly, provided that the exact XC potential is used to calculate these quantities. The difference between the exact and the Kohn-Sham gaps is thus given by

$$\Delta = E_g - E_g^{\mathrm{KS}} = (\epsilon_H^{N+1} - \epsilon_H^N) - (\epsilon_L^N - \epsilon_H^N) = \epsilon_H^{N+1} - \epsilon_L^N, \tag{5}$$

where ϵ_L^N is the N-electron KS LUMO energy. According to Refs. 7, 15, and 16 Δ directly gives the magnitude of the discontinuity of the exchange-correlation potential as the particle number is varied across an integer.

In order to provide a better description of charged excitations here we apply a variant of the method of *improved virtual orbitals*[24–26] and build an approximation to the quasiparticle Hamiltonian using the KS-DFT Hamiltonians of the $N+1$- and N-particle systems. Given the density matrix of the N-electron system, $\hat{\rho}_N$, we define a projector over the unoccupied states of the N-electron system, $\hat{I}-\hat{\rho}_N$ and a mean-field-like Hamiltonian,

$$\hat{H}_N \equiv \hat{H}_N^{\mathrm{KS}} + (\hat{I} - \hat{\rho}_N)\delta\hat{H}(\hat{I} - \hat{\rho}_N) \tag{6}$$

where $\delta\hat{H}$ is defined as

$$\delta\hat{H} = \hat{H}_{N+1}^{\mathrm{KS}} - \hat{H}_N^{\mathrm{KS}}. \tag{7}$$

Because of the action of $\hat{I}-\hat{\rho}_N$, δH acts only on the Kohn-Sham virtual orbitals of the N-particle system, leaving the ground-state properties invariant. The occupied orbitals of Eq. (6) are just the occupied Kohn-Sham orbitals. Equations (6) and (7) replace the virtual orbitals of the N-particle system by an approximation to the HOMO and virtual orbitals of the $N+1$ particle system, hence accounting for electrostatic and XC effects associated with the added particle. If the exact functional is used in H^{KS} then, according to Eq. (4), the exact gap would be obtained. In addition Eqs. (6) and (7) yield a set of altered virtual orbitals that include the effects of the added particle.

Note that in applications of the so-called *scissors operator* method,[29] $\delta\hat{H}=\epsilon\hat{I}$, where ϵ is typically a free parameter. This parameter can be defined as $\epsilon \equiv \epsilon_H^{N+1} - \epsilon_L^N$, and $\delta\hat{H}$ just shifts the virtual-orbital energies of the N-electron system so that Eqs. (3) and (4) are satisfied. Such an approach corrects the virtual orbital energies but leaves the virtual orbitals unchanged. In contrast to the scissors operator approach, Eqs. (6) and (7) do not only correct the gap but also alter the virtual orbitals: the virtual-orbital fields contain the effects of the added particle when these two equations are used.

In Secs. III and IV we provide an analytical illustration of the approach as well as an application to various small molecules.

III. ILLUSTRATION: THE MOSHINSKY ATOM

In a Moshinsky atom[30] electrons are confined in a harmonic potential $V_{\mathrm{ext}}(\mathbf{r}) = r^2/2$ and interact with each other via an attractive harmonic interaction $V_{e-e}(\mathbf{r},\mathbf{r}') = k(\mathbf{r}-\mathbf{r}')^2/2$, where k is the interaction strength parameter.[31] The model can be solved exactly for the two-electron ground state, and thus the exact gap can be obtained by evaluating the zero-, one- and two-particle ground-state total energies, the latter being available from Moshinsky's paper. In addition, Moshinsky provides the two-particle Hartree-Fock total energy from which the Hartree-Fock Δ-SCF gap is readily obtained. Here we derive the HF gap as given by Koopman's theorem. We obtain the exact-exchange potential for the two- and one-electron systems which are used to evaluate $\delta\hat{H}$ in Eq. (7) and thus obtain yet another approximation to the gap and the LUMO. These gaps are compared to each other and the relation between the LUMO obtained by means of Eqs. (6) and (7) and the HF LUMO is discussed. Finally we show how the electrostatics associated with the added particle lead—as argued in Sec. I—to a more confining potential, thus pushing the LUMO energy upward. In this section we present the results of our calculations for the model; details of the derivations can be found in the Appendix.

A. Exact gap and approximations

The exact gap of the Moshinsky atom can be obtained directly from Moshinsky's paper,[30] as $E_g = E(2) + E(0) - 2E(1)$ where $E(N)$ is the exact total energy of the N-electron atom. The exact fundamental energy gap is given by

$$E_g = \frac{3}{2}(1 + \sqrt{1+2k}) - 3. \quad \text{(EXACT)} \tag{8}$$

The HF ΔSCF gap can be similarly obtained by approximating $E(2) \approx E_{\text{HF}}(2)$, i.e., $E_g \approx E_g^{\text{HF}-\Delta\text{SCF}} = E_{\text{HF}}(2) + E(0) - 2E(1)$. The results is

$$E_g^{\text{HF}-\Delta\text{SCF}} = 3(\sqrt{1+k} - 1)\,. \quad (\text{HF} - \Delta\text{SCF}) \tag{9}$$

To calculate Koopman's theorem gap we solve the Hartree-Fock equations *for the one-electron system* and compute the difference between the one-electron HOMO and LUMO energies ($\epsilon_H^{\text{HF},1}$ and $\epsilon_L^{\text{HF},1}$), and hence an approximation to the gap given by their difference $E_g \approx E_g^K = \epsilon_L^{\text{HF},1} - \epsilon_H^{\text{HF},1}$. The details of the calculation are given in the Appendix and here we just write down Koopman's theorem gap

$$E_g^K = \frac{3}{2}\left(\frac{k-2}{2} + \sqrt{1+k}\right). \quad (\text{KOOPMAN'S}) \tag{10}$$

The exact-exchange (XX) KS-DFT gap is zero; in an open-shell system such as the one-electron Moshinsky atom the two noninteracting Kohn-Sham particles with opposite-spin occupy the lowest eigenstate of the isotropic harmonic oscillator. Therefore,

$$E_g^{\text{XX}} = 0. \quad \text{(XX-KS-DFT)} \tag{11}$$

Finally we calculate the gap and the orbitals as obtained from Eq. (6) and (7) where $\delta\hat{H} = \hat{H}^{2,\text{XX}} - \hat{H}^{1,\text{XX}}$, and $\hat{H}^{N,\text{XX}}$ is the XX KS-DFT Hamiltonian of the N electron system. In the Appendix we show that $\hat{H}^{2,\text{XX}}$ is given by

$$\hat{H}^{2,\text{XX}} = -\frac{\nabla^2}{2} + \frac{(1+k)r^2}{2} + \frac{3k}{4\sqrt{1+k}}. \tag{12}$$

The resulting HOMO-LUMO gap turns out to be given by

$$E_g^{\text{XXC}} = \frac{3}{2}\left(\sqrt{1+k}\,\frac{2+3k}{2+2k} - 1\right). \tag{13}$$

When applying Eqs. (6) and (7) we have not only corrected the gap but also altered the virtual orbitals. In particular we have replaced the XX-KS-DFT one-electron LUMO, $\psi_L^{1,\text{XX}}$, by the XX-KS-DFT two-electron HOMO, $\psi_H^{2,\text{XX}}$. These two orbitals can be compared with the HF one-electron LUMO, $\psi_L^{1,\text{HF}}$, by evaluating the overlaps

$$\langle \psi_L^{1,\text{HF}} | \psi_H^{2,\text{XX}} \rangle = 1\,, \tag{14}$$

$$\langle \psi_L^{1,\text{HF}} | \psi_L^{1,\text{XX}} \rangle = \sqrt{8}\,\frac{(1+k)^{3/8}}{(1+\sqrt{1+k})^{3/2}} \leq 1. \tag{15}$$

When replacing the N-particle KS-DFT Hamiltonian by means of the scheme proposed in Sec. II, i.e., using Eqs. (6) and (7), we expect to obtain virtual orbitals that are closer to the virtual orbitals of the N-particle HF Hamiltonian. The virtual orbitals of the HF Hamiltonian are obtained from potentials that partially account for the added particle and thus they should provide a good description of charged excitations, particularly when compared to the KS-DFT virtual orbitals.

B. Comparing the gaps

We have just seen that by considering Eqs. (6) and (7), the resulting LUMO resembles the HF LUMO. If our scheme replaced the KS-DFT LUMO energy by the HF LUMO energy perhaps nothing will be gained in terms of accuracy: HF typically overestimates the LUMO energy and thus the gap. However because some degree of electronic relaxation is included when adopting Eqs. (6) and (7), *the energy gaps are expected to be smaller than the HF gaps* obtained by means of Koopman's theorem.

This is confirmed by the results shown in Fig. 1 where the various gaps obtained in this section are compared to each other as a function of the interaction strength. The best approximation to the exact gap is provided by Eq. (13). By using two accurate functionals we have almost reproduced the exact gap.

It is worth pointing out that Koopman's theorem greatly improves over the XX-KS-DFT gap since the resulting gap has an approximate dependence on the interaction strength (exact in the small k limit), while the XX-KS-DFT gap is zero, independently of the interaction strength. Going back to what we stated in the introduction: the HF LUMO Hamiltonian partially accounts for the added particle.

C. Effective potentials

It is instructive to relate the inability of KS-DFT for the description of charged excitations to the asymptotics of the effective KS potential. In spherically symmetric systems the exact KS-DFT effective potential is self-interaction free and decays asymptotically into the vacuum as[9,32] $\propto -1/r$, where r is the radial distance, *both for unoccupied and occupied states*. According to Refs. 33 and 34 for unoccupied quasiparticle states, the effective quasiparticle potential should de-

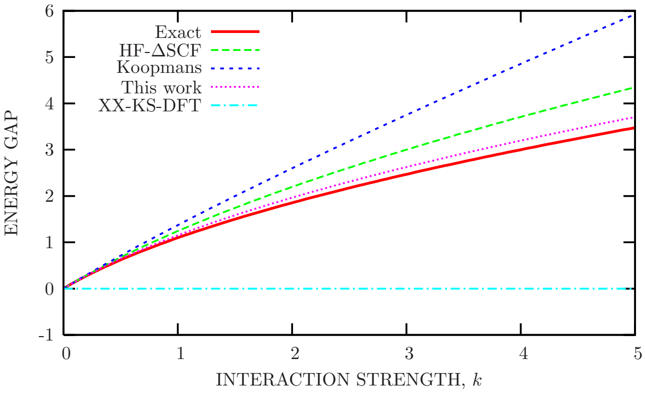

FIG. 1. (Color online) Various gaps as a function of the interaction strength, k. For the Moshinsky atom we show the exact gap [Eq. (8); solid], HF-ΔSCF gap [Eq. (9); long dashes], HF gap as obtained from Koopman's theorem [Eq. (10); short dashes] and the gap obtained by means of two exact-exchange Hamiltonians considered in this work [Eq. (13); dotted]. The dot-dashed line shows the exact-exchange KS-DFT result which predicts a zero gap for open-shell systems, independently of the interaction strength. Koopman's theorem gap is exact to first order in k. The best approximation to the exact gap is that given by Eq. (13).

cay asymptotically as $\propto -1/r^4$ because of classical polarization effects. Hence the quasiparticle and KS-DFT HOMO are both obtained from a potential with a $-1/r$ tail. The KS-DFT LUMO is also obtained from a potential with the $-1/r$ tail while the quasiparticle LUMO is obtained from a potential with a $-1/r^4$ tail. Since $-1/r$ is less confining than $-1/r^4$, the KS-DFT LUMO energy underestimates the experimental one,[35] contributing to the underestimation of the gap. These arguments are purely electrostatic in nature and similar to those leading to the correction proposed in Ref. 1 by Delerue *et al.* This correction explains the dependence of the fundamental energy gap on the system's size in silicon clusters[1] and molecular chains,[2] except for a constant which is taken to be the bulk value of the discontinuity[16,36,37] in the XC potential, v_{xc}.

Figure 2 shows that this trend is reproduced also in Moshinsky's model. The XX one-electron KS potential is given by $v^1_{\mathrm{XX}}=r^2/2$ and is shown in the left-panel of Fig. 2 together with its corresponding HOMO and HOMO energy. In contrast the XX two-particle potential, shown in the right panel of Fig. 2, is given by $v^2_{\mathrm{XX}}=(1+k)r^2/2+3k/(4\sqrt{1+k})$ and is thus more confining than v^1_{XX}. Both the extra confinement and the k-dependent shift observed in Fig. 2 originate from a (self-interaction-free) Hartree term and thus are a result of electrostatic interactions. These interactions push the LUMO level upward with respect to the one-electron XX-KS-DFT LUMO energy.

D. Summary

To summarize the results of this section: we have considered a simple model system where the gap can be computed exactly. Using the exact solution as a benchmark we have computed the gaps using various methods. Combined with the relevant exact-exchange potentials, Eqs. (6) and (7) give an excellent approximation to the exact gap, greatly improving over all the other approximations considered, particularly XX-KS-DFT. The LUMO resulting from Eqs. (6) and (7) is just the XX-KS-DFT HOMO of the two-electron system, which is shown to be identical to the HF LUMO. The gap correction arises solely from electrostatic terms.[38] These terms are responsible for a LUMO potential that is more confining than and shifted relative to the corresponding HOMO potential. In Sec. IV it is shown that some of the trends discussed in this section apply also to more "realistic" molecular models.

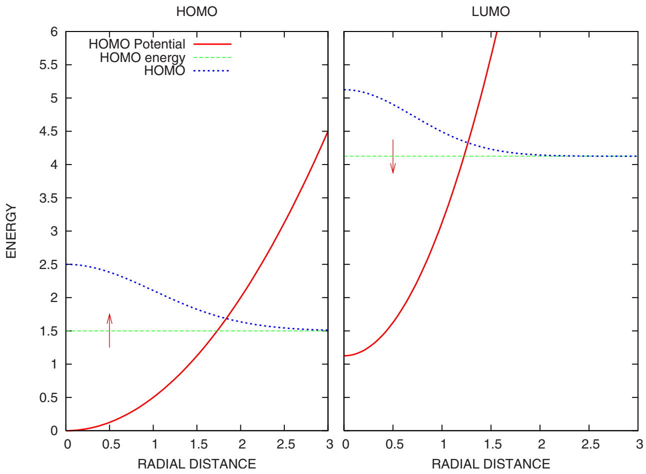

FIG. 2. (Color online) Left panel: effective XX-KS-DFT single-particle potential (see text) for the one-electron HOMO (solid), HOMO energy (dashed), and HOMO (dotted). Right panel: same as left but for the two-electron HOMO. The orbitals have been shifted upward for clarity. The relative spins of both states are also shown. The interaction strength was $k=3$.

IV. APPLICATION TO SMALL MOLECULES

In this section we evaluate the proposed correction for various small molecules, by means of the LDA KS potentials of the N- and $N+1$-electron systems. We find that the trends observed for the Moshinsky atom are reproduced.

The idea of computing gaps from two separate calculations of the KS-DFT HOMO energy goes back to the early eighties and the original "gap-problem" papers.[15–18] The earliest practical calculations that we are aware of were done by Capellini *et al.*[4] some ten years ago. This idea seems to have been recently rediscovered,[3,6–8] and in this paper we are showing how the associated KS-DFT Hamiltonians may be used to approximate the real part of the quasiparticle Hamiltonian.

A. Computational details

We calculate the HOMO-LUMO gap and LUMOs of several isolated molecules by means of Eqs. (6) and (7). In our calculations we approximate the XC potential by means of a spin-unpolarized LDA,[39] where the correlation part is given as in Ref. 40. We use either the self-consistent (SCF) LDA density matrix of the $N+1$ particle system or a non-self-

TABLE I. Calculated HOMO-LUMO gaps in electron-volts for several small molecules. Both the SCF and the NSCF approximations considered in this work yield gaps that are typically smaller than the HF gaps and larger than the KS-DFT gaps. The SCF gaps are smaller than the NSCF ones since the former includes electronic relaxation. The SCF and NSCF gaps are in fair agreement with experimental values reported in Ref. 45, except for the case of the water molecule. Those molecules without experimental gap (H_2, Li_2, CH_4) do not bind an extra electron in the gas phase.

Molecule	LDA	HF	SCF	NSCF	Expt.
H_2	12.2	22.5	20.6	21.2	
Li_2	1.4	5.2	4.9	5.2	
LiH	2.9	8.3	6.8	7.3	7.6
H_2O	7.3	19.1	14.8	15.6	11.4
CH_4	11.6	21.6	17.6	18.2	
Na_2	1.2	4.6	4.4	4.9	4.5
Na_4	0.4	3.7	3.4	3.9	3.4

consistent approximation (NSCF) to it, $\hat{\rho}_{N+1} \approx \hat{\rho}_N + |\psi_L^N\rangle\langle\psi_L^N|$, where ψ_L^N is the LUMO of the N-particle system. We use an open source quantum chemistry package[41] which we have tested by comparing the results of our calculations (HOMO energies and HOMO-LUMO gaps) with those reported in Ref. 42 as well as independent calculations using output from the GAMESS code.[43] From these experiences we estimate our numerical error bar in the orbital energies to be $\sim 1-2$ mHa for LDA-based calculations and typically less than 1 mHa for HF calculations.

We use the Gaussian basis set 6-31G** and perform our calculations at the generalized gradient approximation (GGA) geometries given in Ref. 42. The geometry of Na_4 was taken from Ref. 44. The choice of geometries is inconsistent with the LDA XC potentials used in our calculations, and is adopted to facilitate our analysis: we employ various methods to compute gaps which are then compared to each other; by using the same geometries for a given molecule we make sure that the external potential is the same for all the methods and thus that the differences in gap values arise solely from the treatment of electron-electron interactions.

B. Gaps

Calculated HOMO-LUMO gaps using different methods are presented in Table I, which clearly demonstrates that both the SCF and NSCF methods greatly improve the value of the gap, which is much closer to both the HF and experimental gaps relative to the bare LDA gaps, in line with previous calculations.[4,6–8] In most cases both the SCF and NSCF methods yield gaps that are somewhat smaller than the HF ones. In addition the SCF is shown to produce gaps that are smaller than those of the NSCF, since in the calculation of the NSCF gaps, no relaxation of the molecular orbitals is included. It is worth pointing out that the NSCF method is essentially as computationally expensive as the LDA, requiring only one additional iteration to build an approximation to $\hat{H}_{N+1}^{\mathrm{KS}}$ yet the gaps are improved. For some of these molecules we can compare with experiment:[45] in some cases (LiH, Na_2, and Na_4) using the LDA-based SCF and NSCF methods is sufficient to provide a good gap value, while for the case of H_2O this is clearly not the case and either a more accurate functional is needed or the geometrical relaxation of the water molecule upon addition of an extra electron needs to be accounted for.

In Fig. 3 we consider separately the Hartree, and LDA exchange and correlation contributions to the SCF gap correction for three of these molecules. The Hartree contribution is obtained from the difference between the Hartree potentials, v_h, of the $N+1$ and N particle system, by means of Eqs. (6) and (7) with $\delta\hat{H} = \hat{v}_h[\hat{\rho}_{N+1}] - \hat{v}_h[\hat{\rho}_N]$, and similarly for the exchange and correlation LDA potentials. For the systems considered the main effect is associated to the purely electrostatic correction which increases the LDA gap by a large amount ($\sim 7-8$ eV for the molecules shown), overestimating both the Hartree-Fock and experimental gaps. Both the exchange and the correlation contributions to the correction given by Eqs. (6) and (7) lower the value of the gap (by about 3–4 eV for the molecules shown) improve the agreement with the experiment and are consistent with a simple

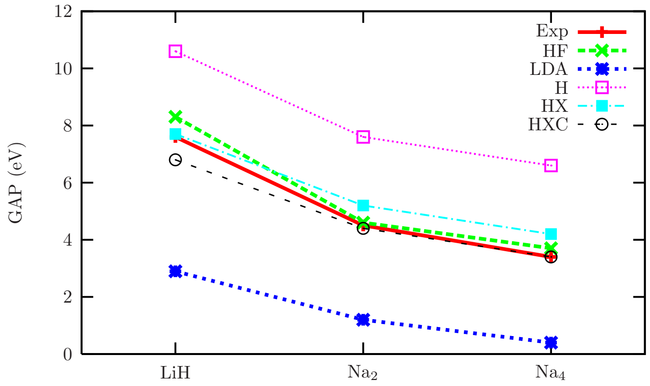

FIG. 3. (Color online) For the molecules shown, we compare the Hartree (h) Hartree-exchange (HX), contributions to the SCF gap correction (HXC) with the experimental (Expt.), HF, and LDA gaps (see text). All the lines are guides to the eyes. The Hartree-only correction overestimates the experimental gap. Adding both exchange and correlation to the correction lowers the gap value, bringing it closer to the HF and experimental values obtained from Ref. 45.

TABLE II. Second, third, and fourth columns: absolute values of the overlaps between the Hartree-Fock LUMO and the LUMOs obtained by means of the LDA, SCF, and NSCF. Fifth, sixth, and seventh columns: distance [as given by Eq. (16)] between the HF and LDA, SCF, and NSCF LUMO states, respectively.

	Overlap			Eq. (16)		
Molecule	LDA	SCF	NSCF	LDA	SCF	NSCF
H_2	0.998	1.000	1.000	0.050	0.003	0.012
Li_2	0.975	0.999	1.000	0.144	0.050	0.011
LiH	0.972	0.997	0.997	0.122	0.024	0.026
H_2O	0.994	0.999	1.000	0.057	0.019	0.007
CH_4	0.997	0.999	0.996	0.050	0.016	0.006
Na_2	0.955	0.996	0.999	0.174	0.056	0.021
Na_4	0.948	0.985	0.000	0.114	0.058	0.131

picture of screening of the classical Coulomb repulsion by exchange and correlation.

C. Virtual orbitals

An interesting question is whether the application of Eqs. (6) and (7) yields virtual orbitals in better agreement with quasiparticle orbitals. In Sec. III we have seen that the use of Eqs. (6) and (7) together with exact-exchange potentials leads to a LUMO which is identical to the HF LUMO, while obtaining much better gaps than those given by Koopman's theorem. To see whether this is also the case in our calculations we compute the quantum-mechanical overlap between the HF LUMO and the LDA, SCF, and NSCF LUMOs. In addition to this overlap we evaluate the following distance:

$$\sqrt{\sum_i (|c_{L,i}^{\mathrm{HF}}| - |c_{L,i}|)^2}, \tag{16}$$

where i labels a basis orbital, $c_{L,i}^{\mathrm{HF}}$ is the ith expansion coefficient of the HF LUMO, and $c_{L,i}$ is the corresponding coefficient of LDA, SCF, and NSCF LUMOs. Equation (16) gives another measure of the similarity between the HF LUMO and the LDA, SCF, and NSCF LUMO expansion coefficients. The results of this comparison are shown in Table II. We note that the excellent agreement between the HF and the bare LDA LUMOs is improved in the molecules shown, except for the NSCF calculation of the sodium tetramer, where the HF LUMO overlaps with the NSCF LUMO+1 instead of the LUMO.

The fact that the SCF/NSCF LUMO is in better agreement with the HF LUMO when compared to the KS-DFT LUMO is not surprising. When adopting Eqs. (6) and (7) we are replacing the KS-DFT N-particle virtual orbitals by the $N+1$-particle KS-DFT HOMO and virtual orbitals and thus effects associated with the added particle are being taken into account. As pointed out above the HF equations already account for some of these effects, while they are totally absent from any fixed-number KS-DFT Hamiltonian.

Due to the approximated nature of the calculations presented in this section we expect the agreement between the SCF/NSCF and HF LUMO to break down with system size: the XC functionals considered are continuous functionals of the density which are not self-interaction free. For the small molecules considered the electrostatic effect is large and its influence in the virtual orbitals seems to be captured by using the LDA in Eqs. (6) and (7). Self-interaction errors present in the functionals considered lead to HOMO and LUMO energies that are too high when compared with experiments. In finite systems, the LUMO energy could in principle be improved by considering functionals that are self-interaction free such as those of proposed in Refs. 46 and 47 or the exact-exchange functionals we consider in Sec. II.

However we believe that the gap values will be significantly better than those obtained by means of both HF and KS-DFT, even for pretty large molecules, since the effect we capture is essentially electrostatic in nature and decays slowly with system size, as noted by Delerue *et al.*[1]

V. CONCLUSIONS

In conclusion, we have used projector operators and two Kohn-Sham Hamiltonians to approximate the quasiparticle Hamiltonian. The resulting mean-field scheme approximates classical electrostatic and XC effects associated with the added particle. For the systems tested, the method systematically improves on the calculated fundamental gaps with respect to both KS-DFT and HF. The LUMO orbitals obtained from the correction have been shown to be similar to the HF LUMO. The non-self-consistent version of the proposed correction improves over the KS-DFT LDA without a significant increase in computational time and difficulty of implementation. The proposed mean-field scheme might be useful to improve the accuracy of KS-DFT-based calculations of the resistance of molecular junctions since these have proven to be highly sensitive both to the gap and the details of the mean-field orbitals.[10,48] Alternatively the proposed correction might be used to produce a better starting point for calculations of molecular systems based on many-body perturbation theory.

ACKNOWLEDGMENTS

We thank Aleksander Cehovin for many useful discussions and suggestions as well as numerical checks. We gratefully acknowledge useful discussions with the members of Rex Godby's group in York. We are thankful to Jan Jensen and Thomas Bondo for many useful discussions and suggestions. We acknowledge support from the Danish Research Agency, NABIIT project "Materials design using grid technology."

APPENDIX: EXACT AND APPROXIMATED ENERGY GAPS IN THE MOSHINSKY ATOM

1. Exact Gap

The exact total energies of the zero, one, and two-electron atoms can be easily obtained and thus the exact gap can be obtained as

$$E_g = E(2) + E(0) - 2E(1), \tag{A1}$$

where $E(N)$ is the exact total energy of the N-electron atom. Moshinsky[30] shows that, *for a spin singlet wave function*,

$$E(2) = \frac{3}{2}(1 + \sqrt{1+2k}), \tag{A2}$$

while from the textbook solution of the quantum isotropic harmonic oscillator we know $E(1)=3/2$, while $E(0)=0$. Hence the exact fundamental energy gap is just given by

$$E_g = \frac{3}{2}(1 + \sqrt{1+2k}) - 3. \tag{A3}$$

Note that we are dealing with an open-shell system and thus $\lim_{k\to\infty} E_g(k)=0$, i.e., in the absence of interaction two electrons with opposite spins occupy the same level. To first order in k we get

$$E_g = \frac{3k}{2} + o(k^2). \tag{A4}$$

2. Hartree-Fock Δ-SCF gap

Moshinsky also provides an analytical expression for $E(2)$ in the HF approximation,

$$E(2) \approx E_{\mathrm{HF}}(2) = 3\sqrt{1+k}, \tag{A5}$$

and since $E_{\mathrm{HF}}(1)=E(1)$ and $E_{\mathrm{HF}}(0)=E(0)=0$, the HF Δ-SCF gap is

$$E_g^{\mathrm{HF-}\Delta\mathrm{-SCF}} = E_{\mathrm{HF}}(2) - 2E(1) = 3(\sqrt{1+k} - 1). \tag{A6}$$

The approximation is exact to first order in k: $E_g^{\mathrm{HF-}\Delta\mathrm{-SCF}} = \frac{3k}{2} + o(k^2)$.

3. Koopman's theorem gap

Alternatively we can compute the gap by means of Koopman's theorem: we solve the Hartree-Fock equations *for the one-electron system* and compute the HOMO and LUMO energies, and hence an approximation to the gap given by

$$E_g \approx E_g^K = \epsilon_L^{\mathrm{HF},1} - \epsilon_H^{\mathrm{HF},1}, \tag{A7}$$

where $\epsilon_{H/L}^{\mathrm{HF},1}$ are the Hartree-Fock HOMO/LUMO energies as computed for a system with one electron. The HF equation for the HOMO is just the time-independent Schrödinger equation for the isotropic harmonic oscillator since the Hartree and exchange terms cancel each other; the HOMO is given by the lowest energy eigenstate and its energy is again $\epsilon_H^{\mathrm{HF},1}=E(1)=3/2$. Since $E(0)=0$, $\epsilon_H^{\mathrm{HF},1}$ gives the exact IP of the one-electron atom. Next, since the two-electron *exact* ground-state is known to be a singlet, we assume that HOMO and LUMO have opposite spins and that the exchange term in the one-electron HF equations vanishes. Then the HF Hamiltonian for the LUMO, $\hat{H}_L^{\mathrm{HF}}$,[49] is

$$\hat{H}_L^{\mathrm{HF}} = -\frac{\nabla^2}{2} + \frac{r^2}{2} + \frac{k}{2}\int d^3\mathbf{r}'|\psi_H^1(r)|^2(\mathbf{r}'-\mathbf{r})^2, \tag{A8}$$

where

$$\psi_H^1(r) = \frac{2^{3/2}}{(4\pi)^{3/4}}e^{-r^2/2} \tag{A9}$$

is the ground state of the isotropic quantum harmonic oscillator. Computing the Hartree term it can be shown that

$$\hat{H}_L^{\mathrm{HF}} = -\frac{\nabla^2}{2} + \frac{(1+k)r^2}{2} + \frac{3k}{4}, \tag{A10}$$

which can be trivially solved. The LUMO energy is just

$$\epsilon_L^{\mathrm{HF},1} = \frac{3k}{4} + \frac{3}{2}\sqrt{1+k}, \tag{A11}$$

and hence Koopman's theorem gap is just

$$E_g^K = \frac{3}{2}\left(\frac{k-2}{2} + \sqrt{1+k}\right). \tag{A12}$$

Again $\lim_{k\to\infty} E_g^K(k)=0$, and to first order in k we obtain $E_g^K=E_g+o(k^2)$. Thus for small k Koopman's theorem provides the exact gap.

4. Exact-exchange Kohn-Sham gap

In order for the exact one-electron density to be obtained, the XX potential needs to cancel the self-Hartree potential, and thus the XX Hamiltonian of the one-electron Moshinsky atom is just

$$\hat{H}^{1,\mathrm{XX}} = -\frac{\nabla^2}{2} + \frac{r^2}{2}, \tag{A13}$$

both for unoccupied and occupied states. Hence XX KS-DFT does not really give any gap that can be interpreted as the fundamental energy gap. It would be incorrect to think about the gap as being the difference between the lowest and second lowest eigenvalues of the above Hamiltonian since the resulting gap would be an *optical gap*, not the fundamental energy gap measured by adding and removing electrons (and not even that, because of the selection rules). Instead one should take the XX KS gap to be zero, representing a situation were two noninteracting Kohn-Sham particles with opposite-spin occupy the lowest eigenstate of the isotropic harmonic oscillator. N-particle KS-DFT does not give charging energies. As pointed out above exact KS-DFT does give a zeroth-order approximation to the excitations of the neutral system. Hence,

$$E_g^{\mathrm{XX}} = 0 \tag{A14}$$

5. Using exact-exchange potentials in Eqs. (6) and (7)

Here we calculate the gap and the orbitals that are obtained from the Hamiltonian

$$\hat{H} = \hat{H}^{1,\mathrm{XX}} + (1-\hat{\rho}^1)(\hat{H}^{2,\mathrm{XX}} - \hat{H}^{1,\mathrm{XX}})(1-\hat{\rho}^1) \tag{A15}$$

where $\hat{\rho}^1$ is the one-electron density matrix. Equation (A15) is just Eq. (6) with $\delta\hat{H}=\hat{H}^{2,\mathrm{XX}}-\hat{H}^{1,\mathrm{XX}}$ in Eq. (7). Clearly this scheme yields the same HOMO eigenpair as $\hat{H}^{1,\mathrm{XX}}$, but the LUMO eigenpair is the HOMO eigenpair of $\hat{H}^{2,\mathrm{XX}}$.

For the system under study the HOMO energy of the one-electron system is $\epsilon_H^1=3/2$. Next we calculate the XX-KS-DFT HOMO energy of the two-electron system. To do this we note that in two-electron systems the exact-exchange potential needs to cancel just half of the Hartree potential and hence

$$v_h(r) + v_x(r) = \frac{1}{2}\int d^3\mathbf{r}'\, V(\mathbf{r},\mathbf{r}')\, n_{\mathrm{HF}}^2(\mathbf{r}') \tag{A16}$$

where $n_{\mathrm{HF}}^2(\mathbf{r}')$ is the two-electron density obtained from the HF wave function, which we take from Moshinsky's paper. $v_h(r)+v_x(r)$ is thus a continuous functional of the two density, $n_{\mathrm{HF}}^2(\mathbf{r}')$. The resulting two-electron XX-KS-DFT Hamiltonian is

$$\hat{H}^{2,\mathrm{XX}} = -\frac{\nabla^2}{2} + \frac{r^2}{2} + v_h(\mathbf{r}) + v_x(\mathbf{r}), \tag{A17}$$

$$= -\frac{\nabla^2}{2} + \frac{(1+k)r^2}{2} + \frac{3k}{4\sqrt{1+k}}, \tag{A18}$$

$$= \hat{H}_L^{\mathrm{HF}} - \frac{3k}{4}\left(1 - \frac{1}{\sqrt{1+k}}\right). \tag{A19}$$

The last line has been added to show that the HF LUMO one-electron Hamiltonian differs from XX-KS-DFT two-electron Hamiltonian by a k-dependent constant. Note that for a two-electron system, the lowest eigenstate of the above equation, $\psi_H^{2,\mathrm{XX}}(r)$, can be obtained directly from the HF density, $n_{\mathrm{HF}}(\mathbf{r}')$, as

$$\psi_H^{2,\mathrm{XX}}(r) = \sqrt{n(\mathbf{r}')/2}, \tag{A20}$$

a result that can be confirmed by substitution. The resulting HOMO energy is

$$\epsilon_H^2 = \frac{3}{2}\sqrt{1+k}\left(\frac{2+3k}{2+2k}\right) \tag{A21}$$

which is equal to the HF HOMO energy of the two-electron system reported in Moshinsky's paper.[50] Hence we can compute the gap from Eq. (4),

$$E_g = \epsilon_H^2 - \epsilon_H^1 = \frac{3}{2}\left(\sqrt{1+k}\,\frac{2+3k}{2+2k} - 1\right) \tag{A22}$$

which again equals the exact gap to first order in k, and vanishes for $k=0$.

Next we discuss the HOMO and LUMO orbitals obtained from the Hamiltonian given by Eq. (A15). The one-electron XX-KS-DFT LUMO and HOMO have opposite spin but the same spatial part

$$\psi_H^{1,\mathrm{XX}}(r) = \frac{2^{3/2}}{(4\pi)^{3/4}} e^{-r^2/2} = \psi_L^{1,\mathrm{XX}}(r). \tag{A23}$$

The HOMO of the two-electron XX-KS-DFT system is given by

$$\psi_H^{2,\mathrm{XX}}(r) = \frac{2^{3/2}}{(4\pi)^{3/4}}(1+k)^{3/8} e^{-\sqrt{1+k}\,r^2/2}. \tag{A24}$$

Since the two-electron XX-KS-DFT and HF one-electron LUMO Hamiltonians differ by a constant the two-electron XX HOMO and the one-electron HF LUMO are identical,

$$\psi_L^{1,\mathrm{HF}}(r) = \psi_H^{2,\mathrm{XX}}(r). \tag{A25}$$

The overlaps given by Eqs. (14) and (15) are readily obtained from these orbitals.

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