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REGULAR ARTICLE

The localized Hartree–Fock method for a self-interaction free Kohn–Sham potential: applications to closed and open-shell molecules

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Abstract The localized Hartree–Fock and the open-shell LHF (OSLHF) approaches are reviewed and rederived under a unique formalism. Three different treatments of the OSLHF correction term are discussed and results for excitation energies are presented for small- and medium-size closed- and open-shell molecules.

Keywords Density-functional theory · Exact-exchange · Optimized effective potential · Open-shell molecules

1 Introduction

The main reason for the success of the density functional theory (DFT) [1,2] in the computation of the electronic properties of molecules is its high accuracy/computational cost ratio. Formally DFT scales as O(N^3), being N the number of basis functions, which is much lower than other common ab-initio approaches, such as Hartree–Fock (O(N^4)), MP2 (O(N^5)) or CCSD(T) (O(N^7)) [3]. The latter method is highly accurate but it cannot be applied to large organic molecules.

On the other hand the accuracy of DFT depends on the accuracy of the exchange-correlation (XC) functional, which is not yet know and it must be approximated. Conventional XC-functionals, i.e, the local-density approximation (LDA)[4–6] or the generalized gradient approximation (GGA)[7–9] are still widely used in solid-state physics, while for an accurate prediction of the electronic properties of organic molecules hybrid DFT methods [10,11], i.e., containing a fraction of the HF non-local exchange, are often required.

Several dozens of conventional/hybrid XC-functionals have been developed in the last decades to obtain an accurate description of the ground-state properties, such as bond-lengths and vibrational frequencies. However, with the advent of the time-dependent density functional theory (TD-DFT) [12–19] various short-comings of the XC-functional have been magnified[20]. While with conventional/hybrid XC-functionals accurate total energies can be obtained, the Kohn–Sham (KS) spectrum, which is the input quantity for TD-DFT, shows several problems. In particular, the conventional XC-functionals are not self-interaction-free and thus the XC-potential does not show the right, i.e., $-1/r$ asymptotic decay [21,22]. Thus, few bound-unoccupied orbitals are present in the KS spectrum and the energy of the highest occupied molecular orbital (HOMO) largely underestimates the ionization potential. In this case, hybrid functionals do not improve the quality of the KS spectrum as these methods are not pure-KS, i.e., in which KS orbitals are obtained from a multiplicative KS potential. The KS-gap, i.e., the difference between the energy of the lowest unoccupied molecular orbital (LUMO) and the HOMO, represents a zero-order approximation to the TD-DFT excitation energies [23–25] but is largely underestimated (overestimated) in conventional (hybrid) approaches.

To improve the KS spectra several asymptotically-corrected (AC) XC-functionals have been developed [26–36]. In these methods the KS potential is constructed in order to have the right $-1/r$ asymptotic decay. These methods strongly improve the KS spectra, but they are

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often not variational, i.e., the energy-functional is not know. In addition they do not solve fundamentally the self-interaction problem, because the $-1/r$ asymptotic decay is not a sufficient condition to be self-interaction free. Another approach to treat the self-interaction problem is to use self-interaction corrections [37], which lead to orbital-dependent potential and thus no longer within the framework of a pure KS formalism, or are not invariant with respect to unitary transformations of the orbitals [38–41].

The self-interaction problem can instead be solved if the exchange is treated exactly in the KS formalism. Various approach to treat Exact EXchange (EXX) in molecules have been presented in the last years [42–48]. However, numerical problems are always present for gaussian basis set[49,50]. For this reason the localized Hartree–Fock (LHF) approach have been developed [50].

2 Properties and applications of LHF method

The LHF was derived under the assumption that a local potential exists which generates the same determinant wavefunction of Hartree–Fock (HF), and numerical results showed that this assumption was almost valid [50]. The LHF approach is quite close to the one of Krieger et al. (KLI) [51], which was derived as an approximation to the EXX equation. However, the KLI method in not invariant under a rotation of occupied orbitals, a properties which is instead preserved in the LHF approach. Thus, it can be shown that KLI is an approximation of the LHF approach. The LHF approach is formally equivalent to the common-energy denominator approximation (CEDA)[52,53] which was also derived as an approximation of EXX equation.

The LHF potential is functional of orbitals and thus is *strong non-local functional of the density* . This property can be seen in Fig. 1 where we plot on a double log-scale the Slater–Dirac[4,5], the Becke[7] and the LHF exchange-potential for, e.g., the pyridine molecule.

The Slater–Dirac exchange potential is proportional to $\rho^{1/3}$, thus it is a straight line on Fig. 1. The non-locality can be seen on Fig. 1 when for a given density different values of the exchange potential are present. While the gradient-corrected Becke exchange potential contains a very small degree of non-locality, the LHF is strongly non-local. The non-locality increases far away from the system, i.e., when the density goes to very small values; the exchange-potential is also strongly non-local where the density is about 10^0–10^{-1} a.u., i.e., near atomic shells.

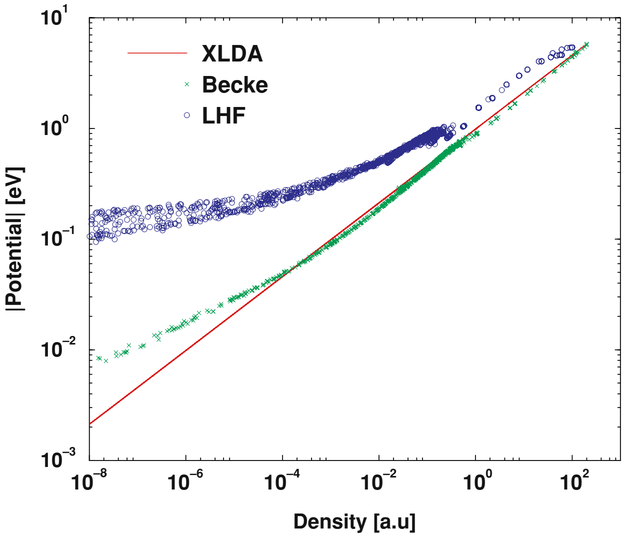

Fig. 1 Absolute value of the exchange potential as a function of the density for the pyridine molecule

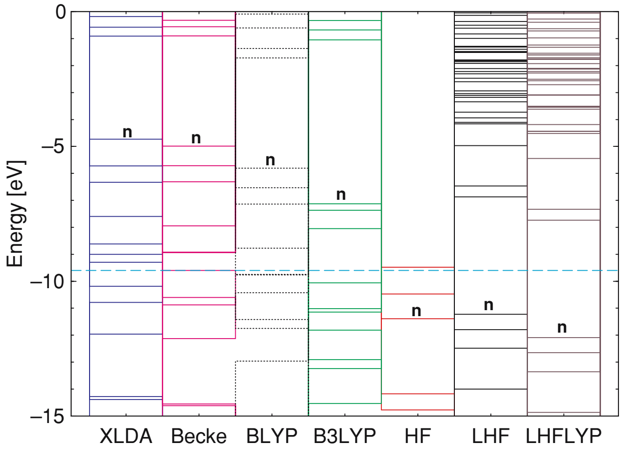

Fig. 2 KS orbital energies for the pyridine molecule using different methods. The experimental ionization potential is shown by a *dashed line*

The main advantage of the LHF approach is that it allows to obtain a *correct Kohn–Sham spectrum*. Often XC-functionals were approximated in order to obtain valid DFT total energy, while the KS orbitals were considered only auxiliary quantities. In Fig. 2 we report the Kohn–Sham energy levels for the pyridine molecules using different approaches. The *n* orbital is also indicated. The Slater–Dirac exchange potential (XLDA) leads to a Kohn–Sham spectrum with very few unbound virtual orbitals. In addition the energy of the HOMO is very far from the experimental ionization potential (IP) value of 9.60 eV [54] shown as a dashed line. The use of gradient correction (Becke) leads only to a shift-down of one tenth of an eV. The inclusion of correlation contribution (BLYP[7,8]) has instead larger effects and shifts down all orbitals by about 1 eV. Thus, the LYP correlation increases the number of bound virtual orbitals and decreases the HOMO energy. The use of hybrid functionals with a fraction of non-local HF exchange leads to a KS spectrum with a gap 2 eV larger than BLYP. Using B3LYP[10] the HOMO energy is 7.1 eV which is much closer to the experimental results than in XLDA, however fewer bound virtual orbitals than BLYP are present. In HF the HOMO energy is almost exactly the experimental IP, but it has the wrong character. The ionization potential has indeed a n-type character and thus it should be compared to the HF HOMO-3 energy, which is -11.4 eV. This means that for pyridine orbital-relaxation and correlation effect are as large as 1.8 eV, so in HF the energetical order of orbitals is not correct. In addition in HF no bound virtual orbitals are found, as the virtual orbitals are related to a system of $N + 1$ electron. The last but one column of Fig. 2 shows the orbital spectrum obtained with the LHF approach. Comparing to the previous methods three distinctive advantages are present: (1) a very large number of bound virtual orbital can be seen, due to the correct, i.e., $-1/r$ asymptotic decay of the exchange potential. (2) the HOMO has a n character as it should be; (3) the HOMO energy is 11.2 eV and it is closer to the experimental IP than all the previous approaches. Finally, we consider the LHF potential plus the LYP correlation. As in BLYP the LYP correlation shifts down all orbitals by about 1 eV. In this case the LYP correlation worsen the KS spectrum, as the HOMO is incorrectly shifted down.

The LHF potential showed surprising features in the asymptotic region [55,56]. The LHF exchange potential asymptotically approaches $-1/r$ only if the HOMO orbitals does not show nodal surfaces. Otherwise the asymptotic behavior is $C - 1/r$ where C is a constant. This constant can be several eV and it has been shown that it can affect the energies of Rydberg orbitals [55] meaning the all AC methods are not formally correct as they do not consider these constants. Note that these asymptotic properties will be retained also if the full exchange-correlation functional is employed[56,57]

In the last years, the LHF method have received a lot of attention. The reason of its success is not only the simple and elegant formalism, but its computational efficiency and the straightforward implementation is standard quantum-chemistry codes. Indeed a very simple approach to compute the Slater potential were proposed[50] which is based on the resolution of identity using orbital basis set, and thus without the use of new auxiliary-basis functions. Importantly, the computational cost of the LHF approach is equivalent to the one of hybrid methods. Recently, an auxiliary-basis approach for the computation of the Slater potential has been presented [58].

In the last years the LHF approach have been successfully used in different applications:
Della Sala and Görling [59] found that if LHF orbitals and eigenvalues are used in TD-DFT calculations accurate valence and Rydberg excitation energies can be obtained; Hupp et al. [60–62] found that LHF orbitals are well suited as single electron basis for multiple-reference configuration interaction calculations; Weimer et al. [63] found that the LHF potential for anion is attractive and thus it can bind anion species; different authors[64–66] investigated the NMR nuclear shielding constants: they found that thanks to the more accurate KS gap, the LHF potential leads to very good results. More recently it was found that LHF yields more accurate results than EXX, showing that approximations made in LHF probably lead to a correlation contribution[67]. In these NMR calculations localized hybrid functionals [64,66,68–70] were also considered. In these functionals the fraction of the non-local Hartree–Fock operator is substituted by the LHF potential, leading to a pure KS approach. However, such local hybrid functional has not the right asymptotic behavior; Arbuznikov and Kaupp [70–72] also considered the use of the LHF technique to construct *local* kinetic energy density dependent exchange-correlation potential; Teale and Tozer investigate the potential energy surfaces (PES) of molecules [73]. Only diatomic molecules were consider in order to extract optimized bond-lengths from the PES. We note in fact that the *LHF approach is not variational*, because the LHF energy functional is not know. The LHF energy functional is only approximately given by the Hartree–Fock exact exchange. This is not a practical limitation as the difference with respect HF are very small; Fabiano and Della Sala[74] studied the torsional potential of conjugate molecules, comparing different exchange functionals. It was found that using the LHF approach the resulting torsional barriers are lower than other exchange methods, and thus these can be improved by a correlation contribution. LHF has also been applied to molecular chains, such as polyenes/cumulenes [75] and oligothiophenes [76] in order to compared the KS energy gap with respect the chain-length and with respect other methods. It was found that for accurate TD-DFT excitation energies the improvement of the KS gap with respect conventional DFT approaches is not enough and better TD-DFT kernel are instead required; The CEDA (LHF) approach was applied to investigate the polarizabilities of hydrogen chains[52,53] showing that it is superior to the KLI approximations. The LHF method has been also applied to very large system[77,78] and it was found that LHF eigenvalues are well suited for the interpretation of scanning-tunneling microscopy images[78].

From a formal point of view various extensions of the LHF method have been considered.

In order to apply an effective exact exchange to open shell atoms and molecules the open-shell localized Hartree–Fock (OSLHF) method [79] have been developed. Open-shell systems in DFT are usually treated within an unrestricted formalism, which however has the problem of spin-contamination. While implementations of unrestricted or spin-dependent LHF [71,79,80] are also present in literature, the OSLHF is instead a restricted formalism based on the symmetrized Kohn–Sham theory [81–83] which allows the determination of the energetically lowest excited-state of a given symmetry. Within standard XC-functionals instead it is not possible to apply the KS formalism to states which are not ground states [84]. In fact symmetry dependent density-functionals and KS wave functions with well-defined symmetry labels referring to the full symmetry group of the molecule are required. If we consider, e.g., the lowest singlet and triplet excited state of a model closed-shell system where both states are characterized by a pure HOMO → LUMO transition, then it is clear that these states will show not differences using conventional XC-functional because the only variable entering these functionals is the electron density, which is identical in the two states. In an spin-polarized formalism it is possible to treat the triplet excited-state and the (ensemble) averaged singlet/triplet configuration. If the first state has energy E_t and the second one energy E_a then the energy of the singlet excited-state is $E_\mathrm{s} = 2E_\mathrm{a} - E_\mathrm{t}$[85]. These ΔSCF approaches [85–90] can also be generalized to configurations leading to more complicated multiplet structures. However, these approaches are only approximated because conventional XC-functionals, which are used for a description of individual states, are used to describe ensembles of states although such functionals are highly nonlinear. In addition these ΔSCF calculations are performed using conventional XC-functionals thus neglecting any state- and the symmetry-dependence[83]. The OSLHF potential instead depends directly on the symmetry of the state and thus can been used to computed many-particle states of atoms and molecules and thus this method should not be confused with the restricted-open Kohn–Sham (ROKS) formalism used in different context [88,91,92].

The OSLHF has been also generalized to compute excited state which are not the lowest of their symmetry [93]. This method is based on the generalized adiabatic connection (GAC) KS approach [82,83,94] which leads to a self-consistent KS treatment of individual excited state. Excitation energies can be computed as in ΔSCF, but the state- and the symmetry-dependence is included in the KS potential. In contrast to common time-dependent density-functional methods the GAC-OSLHF approach is capable of treating doubly or multiply excited states and it can be easily applied to molecules with an open-shell ground state. With the GAC-OSLHF approach it is possible to obtain an unique local multiplicative potential which acts on all orbitals. Such potential have been very recently used to compute excitation energies with a Quantum-Montecarlo approach [95]

Recently, Hesselman[96,97] extended the LHF approach by searching for a local potential which generated Brueckner orbitals instead of Hartree–Fock orbitals. In this way an effective exchange-correlation potential has been obtained. Results are comparable to ab-initio DFT approaches [98,99].

In this article, we will re-derive the LHF and the (GAC) OSLHF approach using an alternative formalism. The LHF and OSLHF were originally derived in different way considering the eigenvalues of a many-particles equation or using an approximation to the EXX equation. Here instead a more simple formalism is described which can be used to derive LHF and OSLHF. In this article we will also consider the effects of the different treatments of the off-diagonal elements in the OSLHF potential. We will present results on excitation energies for small- and medium-size closed- and open-shell system.

3 Method

In this section we derive the LHF and the OSLHF potential using a simple formalism.

We start from a generic *non-local* and *orbital dependent* operator $\hat{V}_i$ which satisfies

$$(\hat{H}_1 + \hat{V}_i)\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{1}$$

where $\hat{H}_1$ includes the one-electron operator and the coulomb potential. Then we consider a local KS exchange potential $v_x(\mathbf{r})$ which satisfies

$$(\hat{H}_1 + v_x(\mathbf{r}))\psi_i(\mathbf{r}) = \omega_i \psi_i(\mathbf{r}). \tag{2}$$

The KS orbitals ψ_i are not eigenfunctions of $\hat{H}_1 + \hat{V}_i$ but they are related by the following relation:

$$\begin{aligned}(\hat{H}_1 + \hat{V}_i)\psi_i(\mathbf{r}) &= (\hat{H}_1 + v_x(\mathbf{r}) - (v_x(\mathbf{r}) - \hat{V}_i))\psi_i(\mathbf{r}) \\ &= \omega_i \psi_i(\mathbf{r}) - (v_x(\mathbf{r}) - \hat{V}_i)\psi_i(\mathbf{r}).\end{aligned} \tag{3}$$

If we make the assumption that a local $v_x(\mathbf{r})$ potential exists that generates the *(partially) occupied* ψ_i orbitals which can be obtained as an unitary transformation of the *(partially) occupied* ϕ_i orbitals, i.e.,

$$\psi_i(\mathbf{r}) = \sum_j^{\text{occ.}} c_{ji}\phi_j(\mathbf{r}), \quad \forall\, i \in \text{occ.}$$

then we have

$$(\hat{H}_1 + \hat{V}_i)\psi_i(\mathbf{r}) = \sum_j^{\text{occ.}} c_{ji}\epsilon_j\phi_j(\mathbf{r}) = \sum_k^{\text{occ.}} d_{ki}\psi_k(\mathbf{r}) \tag{4}$$

with

$$d_{ki} = \sum_j^{occ.} c_{ji}\epsilon_j c_{jk}. \tag{5}$$

By equating the right-end side of Eq. (3) and (4), multiplying by $\psi_j(\mathbf{r})$ and integrating we obtain

$$\delta_{ij}\omega_i - \langle\psi_j|v_x(\mathbf{r}) - \hat{V}_i|\psi_i\rangle = d_{ji}. \tag{6}$$

Note that expression (6) is valid if ψ_j is a (partially) occupied orbital; if ψ_j is a virtual orbital we have

$$d_{ji} = \langle\psi_j|v_x(\mathbf{r}) - \hat{V}_i|\psi_i\rangle = 0. \tag{7}$$

Substituting Eq. (6) into (4) and equating to Eq. (3) we have

$$(v_x(\mathbf{r}) - \hat{V}_i)\psi_i(\mathbf{r}) = \sum_j^{\text{occ.}} \langle\psi_j|v_x(\mathbf{r}) - \hat{V}_i|\psi_i\rangle\psi_j(\mathbf{r}). \tag{8}$$

Considering that the total density is

$$\rho(\mathbf{r}) = n_\text{s}\sum_i^{\text{occ.}} f_i\psi_i(\mathbf{r}) \tag{9}$$

(where f_i is the occupation number and n_s the spin degeneration) we then multiply Eq. (8) by $f_i\psi_i(\mathbf{r})$ and sum over (partially) occupied orbitals:

$$\begin{aligned}\sum_i^{\text{occ.}} v_x(\mathbf{r})f_i\psi_i(\mathbf{r})\psi_i(\mathbf{r}) - f_i\psi_i(\mathbf{r})\hat{V}_i\psi_i(\mathbf{r}) \\ = \sum_{i,j}^{\text{occ.}} f_i\langle\psi_j|v_x(\mathbf{r}) - \hat{V}_i|\psi_i\rangle\psi_i(\mathbf{r})\psi_j(\mathbf{r}).\end{aligned} \tag{10}$$

Expression (10) can also be rewritten in a explicit form for $v_x(\mathbf{r})$:

$$v_x(\mathbf{r}) = v_x^{\text{Sla}}(\mathbf{r}) + v_x^{\text{corr}}(\mathbf{r}) \tag{11}$$

with

$$v_x^{\text{Sla}}(\mathbf{r}) = \frac{n_\text{s}}{\rho(\mathbf{r})}\sum_i^{\text{occ.}} f_i\psi_i(\mathbf{r})\hat{V}_i\psi_i(\mathbf{r}) \tag{12}$$

and

$$v_x^{\text{corr}}(\mathbf{r}) = \frac{n_\text{s}}{\rho(\mathbf{r})}\sum_{i,j}^{\text{occ.}} f_i\langle\psi_j|v_x(\mathbf{r}) - \hat{V}_i|\psi_i\rangle\psi_i(\mathbf{r})\psi_j(\mathbf{r}). \tag{13}$$

To obtain the LHF approximation for closed-shell systems[50] we set $n_\text{s} = 2, f_i = 1$, and $\hat{V}_i = \hat{v}_x^{\text{NL}}$, where the operator $\hat{v}_x^{\text{NL}}$ is the non-local exchange operator

$$\hat{v}_x^{\text{NL}}(\mathbf{r},\mathbf{r}') = -\sum_i^{\text{occ.}} f_i\,\frac{\psi_i(\mathbf{r})\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,. \tag{14}$$

In case of open-shell systems and/or orbital dependent operator the correction term so obtained is non-symmetric if i and j are interchanged. We can write the correction term as

$$v_x^{\text{corr}} = \frac{2}{\rho(\mathbf{r})}\sum_{j\le i}^{\text{occ.}} h_{ij}C_{ij}\psi_i(\mathbf{r})\psi_j(\mathbf{r}) \tag{15}$$

with $h_{ij} = 2$ if $j < i$ and $h_{ij} = 1$ if $j = i$. Simplest symmetrizations are

$$C_{ij} = \frac{f_i}{2}\langle\psi_j|v_x(\mathbf{r}) - \hat{V}_i|\psi_i\rangle + \frac{f_j}{2}\langle\psi_j|v_x(\mathbf{r}) - \hat{V}_j|\psi_i\rangle \tag{16}$$

or

$$C_{ij} = f_{\max(i,j)}\langle\psi_j|v_x(\mathbf{r}) - \hat{V}_{\max(i,j)}|\psi_i\rangle, \tag{17}$$

where $\max(i,j)$ indicates which orbital-index (or energy) is higher.

The OSLHF potential can be obtained in if we set $n_\text{s} = 2$ and

$$\hat{V}_i = \hat{v}_x^{\text{NL}} + \bar{u}_i(\mathbf{r}) + \hat{\bar{v}}_{x,i}^{\text{NL}}, \tag{18}$$

where

$$\bar{u}_i(\mathbf{r}) = \sum_j^{\text{occ.}} 2f_j(A_{ij}-1)\int \mathrm{d}\mathbf{r}'\,\frac{\psi_j(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,, \tag{19}$$

$$\hat{\bar{v}}_{x,i}^{\text{NL}}(\mathbf{r},\mathbf{r}') = \sum_j^{\text{occ.}} f_j(B_{ij}-1)\,\frac{\psi_j(\mathbf{r})\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{20}$$

(these operators are non-zero only for open-shell orbitals). The operators in Eq. (18) are the ones which appears in the restricted Hartree–Fock equations [100,101] and A_{ij}, B_{ij} are the Roothaan coefficients. We then obtain for the Slater potential

$$v_x^{\mathrm{Sla}}(\mathbf{r}) = \frac{n_{\mathrm{s}}}{\rho(\mathbf{r})}\sum_i^{\mathrm{occ.}} f_i\psi_i(\mathbf{r})\hat{v}_x^{\mathrm{NL}}\psi_i(\mathbf{r}) + \frac{n_{\mathrm{s}}}{\rho(\mathbf{r})}\sum_m^{\mathrm{open}} f_m\psi_i(\mathbf{r})\left[\bar{u}_m(\mathbf{r}) + \hat{\hat{v}}_{x,m}^{\mathrm{NL}}\right]\psi_i(\mathbf{r}) \quad (21)$$

and for the correction term

$$v_x^{corr}(\mathbf{r}) = \frac{n_s}{\rho(\mathbf{r})}\sum_{j\le i}^{occ.} h_{ji}f_i\langle\psi_j|v_x(\mathbf{r}) - \hat{v}_x^{\mathrm{NL}}|\psi_i\rangle\psi_i(\mathbf{r})\psi_j(\mathbf{r}) - \frac{n_s}{\rho(\mathbf{r})}\sum_m^{open}\sum_{j\le m}^{occ.} h_{mj}f_m \times\langle\psi_j|\bar{u}_m(\mathbf{r}) + \hat{\hat{v}}_{x,m}^{\mathrm{NL}}|\psi_m\rangle\psi_m(\mathbf{r})\psi_j(\mathbf{r}) \quad (22)$$

if the symmetrization of Eq. (17) is used. Equations (21) and (22) are identical to the one derived in the original OSLHF work [79].

If the symmetrization of Eq. (16) is used then the correction term is

$$\begin{aligned} v_x^{\mathrm{corr}}(\mathbf{r}) &= \frac{n_{\mathrm{s}}}{\rho(\mathbf{r})}\sum_{j\le i}^{\mathrm{occ.}} h_{ji}\frac{f_i+f_j}{2}\langle\psi_j|v_x(\mathbf{r}) - \hat{v}_x^{\mathrm{NL}}|\psi_i\rangle\psi_i(\mathbf{r})\psi_j(\mathbf{r}) \\ &- \frac{n_{\mathrm{s}}}{\rho(\mathbf{r})}\sum_m^{\mathrm{open}}\sum_j^{\mathrm{closed}} f_m\langle\psi_j|\bar{u}_m(\mathbf{r}) + \hat{\hat{v}}_{x,m}^{\mathrm{NL}}|\psi_m\rangle\psi_m(\mathbf{r})\psi_j(\mathbf{r}) \\ &- \frac{n_{\mathrm{s}}}{\rho(\mathbf{r})}\sum_m^{\mathrm{open}}\sum_{q\le m}^{\mathrm{open}} h_{mq}R_{mq}\psi_m(\mathbf{r})\psi_q(\mathbf{r}) \end{aligned} \quad (23)$$

with

$$R_{mq} = \frac{f_m}{2}\langle\psi_q|\bar{u}_m(\mathbf{r}) + \hat{\hat{v}}_{x,m}^{\mathrm{NL}}|\psi_m\rangle + \frac{f_q}{2}\langle\psi_q|\bar{u}_q(\mathbf{r}) + \hat{\hat{v}}_{x,q}^{\mathrm{NL}}|\psi_m\rangle \quad (24)$$

We shall call OSLHF-A this approach, i.e., with correction term coefficients of Eq. (23).

3.1 Diagonal approximation

A much simpler derivation can be obtained under the assumption that *HF and KS occupied orbitals coincides one by one*, i.e., without any rotation. The orbitals ψ are now eigenvectors of the non-local operator

$$(\hat{H}_1 + \hat{V}_i)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \quad (25)$$

and of the local KS Hamiltonian

$$(\hat{H}_1 + v_x(\mathbf{r}))\psi_i(\mathbf{r}) = \omega_i\psi_i(\mathbf{r}). \quad (26)$$

By subtracting these two equations we have

$$\begin{aligned} (v_x(\mathbf{r}) - \hat{V}_i)\psi_i(\mathbf{r}) &= (\omega_i - \epsilon_i)\psi_i(\mathbf{r}) \\ &= \langle\psi_i|v_x(\mathbf{r}) - \hat{V}_i|\psi_i\rangle\psi_i(\mathbf{r}). \end{aligned} \quad (27)$$

Multiplying by $f_i\psi_i(\mathbf{r})$ and summing over all (partially) occupied orbitals we have

$$v_x(\mathbf{r})\rho(\mathbf{r}) - \sum_i f_i\psi_i(\mathbf{r})\hat{V}_i\psi_i(\mathbf{r}) = \sum_i f_i\langle\psi_i|v_x(\mathbf{r}) - \hat{V}_i|\psi_i\rangle\psi_i(\mathbf{r})\psi_i(\mathbf{r}) \quad (28)$$

or

$$v_x(\mathbf{r}) = \frac{n_{\mathrm{s}}}{\rho(\mathbf{r})}\sum_i^{\mathrm{occ.}} f_i\psi_i(\mathbf{r})\hat{V}_i\psi_i(\mathbf{r}) + \frac{n_{\mathrm{s}}}{\rho(\mathbf{r})}\sum_i^{\mathrm{occ.}} f_i\langle\psi_i|v_x(\mathbf{r}) - \hat{V}_i|\psi_i\rangle\,|\psi_i(\mathbf{r})|^2\,. \quad (29)$$

If we set $n_{\mathrm{s}} = 2$, $f_i = 1$, and $\hat{V}_i = \hat{v}_x^{\mathrm{NL}}$ in Eq. (29) then we obtain the KLI[51] approximation to the exchange potential. Thus, the KLI approach can be derived under the assumption that KLI and HF orbitals are identical one-by-one. The KLI potential is identical to LHF if off-diagonals elements are neglected in the correction term. Casida et al. [102] considered the KLI approximation to the full exchange-correlation potential using the self-energy as the non-local operator. We here define the OSLHF-D approximation, i.e., using $n_{\mathrm{s}} = 2$ and

$$\hat{V}_i = \hat{v}_x^{\mathrm{NL}} + \bar{u}_i(\mathbf{r}) + \hat{\hat{v}}_{x,i}^{\mathrm{NL}} \quad (30)$$

in Eq. (29) which lead to a correction term given by

$$v_x^{\mathrm{corr}}(\mathbf{r}) = \frac{n_{\mathrm{s}}}{\rho(\mathbf{r})}\sum_i^{\mathrm{occ.}} f_i\langle\psi_i|v_x(\mathbf{r}) - \hat{v}_x^{\mathrm{NL}}|\psi_i\rangle\,|\psi_i(\mathbf{r})|^2 - \frac{n_{\mathrm{s}}}{\rho(\mathbf{r})}\sum_m^{\mathrm{open}} f_m\langle\psi_m|\bar{u}_m(\mathbf{r}) + \hat{\hat{v}}_{x,m}^{\mathrm{NL}}|\psi_m\rangle\,|\psi_m(\mathbf{r})|^2 \quad (31)$$

4 Computational Details

Calculations have been carried out a local version of the TURBOMOLE program package [103–107].

We either used experimental geometries (CO with bond distance of 1.128 Å, N_2 with bond distance of 1.098 Å, formaldehyde [108]) or geometries optimized with the B3LYP/TZVP [10,109] approach.

The (OS)LHF calculation have been performed using the XCU1T basis sets of Ref. [79] but for Benzyl, Pyridine and Naphthalene where a TZVP basis set was employed. For diatomic molecules an additional highly diffuse basis functions (geometric series with a half-width up to 20 a.u.) were placed in the center of mass of each molecule.

The quality of the grid was checked by calculating the norm of all virtual orbitals by numerical integration. The resulting norm in all cases lies within the range of 0.999–1.001.

For each open-shell (closed-shell) molecule and state we compare OSLHF(LHF), OSLHF-M(LHF), OSLHF-D(KLI) excitation energies and we calculated the corresponding excitation energies using the TD-UB3LYP(TD-B3YLP) approach.

5 Excitation energies on medium-size closed and open shell molecules

In Table 1 we report selected excitation energies of various closed- and open-shell systems using the three different OSLHF approaches and the standard TD-B3LYP approach. In the last column experimental results are reported. OSLHF excitation energies have been obtained by subtracting the (OS)LHF total energy in the ground-state from the OSLHF total energies in the excited states. Note that all the selected excitations are dominated by single electron transition. For all the systems the OSLHF values are higher than TD-B3LYP: this is due to the exact-exchange treatment and the neglect of the correlation. For CO, N_2 and BeF the OSLHF results are closer to the experimental results than TD-B3LYP, while for larger system TD-B3LYP is more accurate than OSLHF. However, the mean absolute error (MAE), reported in the bottom of Table 1 for all these selected systems/states is comparable. Concerning the three different OSLHF approaches we found than the OSLHF-A yields always excitation energies higher than OSLHF while OSLHF-D are in between

Table 1 Excitation energies in eV using the OSLHF, OSLHF-A and OSLHF-D approaches and comparison with TD-B3YLP and experimental results

System/State	OSLHF	OSLHF-A	OSLHF-D	TD-DFT	Exp.
CO					
$^1\Pi(5\sigma \rightarrow 3\pi^*)$	11.316	11.397	11.362	10.261	11.55[a]
$^3\Pi(5\sigma \rightarrow 3\pi^*)$	11.254	11.335	11.300	10.225	11.53[a]
$^1\Sigma(5\sigma \rightarrow 6\sigma)$	10.784	10.834	10.850	9.776	10.78[a]
$^3\Sigma(5\sigma \rightarrow 6\sigma)$	10.281	10.366	10.372	9.496	10.40[a]
$^1\Pi(5\sigma \rightarrow 2\pi^*)$	8.989	9.016	8.988	8.380	8.51[a]
$^3\Pi(5\sigma \rightarrow 2\pi^*)$	5.979	6.364	6.067	5.838	6.32[a]
N_2					
$^1\Sigma_g^+(3\sigma_g \rightarrow 4\sigma_g)$	12.962	12.998	12.982	11.207	12.20[a]
$^3\Sigma_g^+(3\sigma_g \rightarrow 4\sigma_g)$	12.616	12.633	12.611	10.960	12.00[a]
$^1\Pi_g(3\sigma_g \rightarrow 1\pi_g)$	10.216	10.260	10.223	9.260	9.31[a]
$^3\Pi_g(3\sigma_g \rightarrow 1\pi_g)$	8.247	8.260	8.236	7.572	8.04[a]
Formaldehyde					
$^3A_2(n \rightarrow \pi^*)$	3.400	3.553	3.527	3.159	3.50[b]
$^1A_2(n \rightarrow \pi^*)$	4.044	4.217	4.197	3.891	4.10[b]
$^3B_2(n \rightarrow 3s)$	6.979	7.131	7.079	6.326	7.09[b]
$^1B_2(n \rightarrow 3s)$	7.164	7.353	7.289	6.445	7.13[b]
Pyridine					
$^3A_1(\pi \rightarrow \pi^*)$	4.620	4.620	4.623	3.946	4.10[b]
$^3B_2(n \rightarrow \pi^*)$	5.267	5.530	5.433	4.052	4.10[b]
$^1B_2(n \rightarrow \pi^*)$	5.895	6.073	5.994	4.799	4.59[b]
$^3A_2(n \rightarrow \pi^*)$	6.476	6.686	6.610	4.939	5.40[b]
$^1A_2(n \rightarrow \pi^*)$	6.629	6.857	6.784	5.077	5.43[b]
BeF					
$2\Pi(5\sigma \rightarrow 2\pi)$	4.244	4.267	4.241	4.097	4.138[c]
$2\Sigma^+(5\sigma \rightarrow 6\sigma)$	6.260	6.262	6.261	5.566	6.158[c]
Benzyl					
$^2A_2(1a_2 \rightarrow 3b_2)$	4.046	4.042	4.025	3.17[c]	2.7[c]
$^2A_2(3b_2 \rightarrow 2a_2)$	4.219	4.217	4.209	3.84[c]	3.9[c]
Naphthalene$^+$					
$^2B_{1u}(\pi \rightarrow \pi^*)$	1.227	1.232	1.225	1.13[d]	0.73[d]
$^2B_{2g}(\pi \rightarrow \pi^*)$	2.742	2.742	2.744	2.15[d]	1.93[d]
MAE	0.508	0.535	0.521	0.507	

[a] See Ref. [110], [b] Ref. [108], [c] Ref. [111], [d] Ref. [112]

them. The difference between these approach are always very small: in fact several off-diagonal matrix elements vanished by symmetry. As an example, the OSLHF and OSLHF-A approaches yields exactly the same results for the $^2B_{2g}$ state of the Naphthalene cation because the only open shell orbital $1b_{2g}$ cannot mix with any other orbitals. The results presented here shows that the original OSLHF approach yields excitation energies slightly better than the OSLHF-D and OSLHF-K.

6 Conclusions

The LHF approach has received a lot of interest in the last 5 years as it is a very simple and very efficient approach to compute self-interaction free Kohn–Sham orbitals. The LHF orbitals have been used successfully for several applications. In this article all the LHF and OSLHF approaches and applications have been reviewed. The OSLHF method have been re-derived by localizing the non-local and orbital-dependent operators of the restricted Hartree–Fock method. As the correction term is non symmetric two different symmetrization techniques have been compared as well as the case in which only off-diagonal elements are not considered. Results selected for closed- and open-shell molecules show that the excitation energies computed with the OSLHF approaches has accuracy comparable to standard TD-DFT approaches.

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