Density functionals with spin-density accuracy for open shells: Supplementary material

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COMPARISON OF OEP SOLUTION FOR XC POTENTIAL WITH SIMPLE APPROXIMATIONS

As discussed in the main text, we compare the full OEP solution of Eq. 11 with the following simple approximations:

$$v_{xc}(\mathbf{r}) \approx v_{xc}^{\uparrow}(\mathbf{r})\,, \tag{S1}$$

$$v_{xc}(\mathbf{r}) \approx v_{xc}^{w}(\mathbf{r}) = \frac{\Delta^{\downarrow}v_{xc}^{\uparrow}(\mathbf{r}) + \Delta^{\uparrow}v_{xc}^{\downarrow}(\mathbf{r})}{\Delta^{\uparrow} + \Delta^{\downarrow}}\,,, \tag{S2}$$

where $\Delta^{\uparrow} = \epsilon_{N_e^{\uparrow}+1} - \epsilon_{N_e^{\uparrow}}$ is the HOMO-LUMO gap for the up-spin-channel, and $\Delta^{\downarrow} = \epsilon_{N_e^{\downarrow}+1} - \epsilon_{N_e^{\downarrow}}$ the HOMO-LUMO gap for the down-spin channel. We stress that the meaning of the "up"-spin-channel is just whichever contains more electrons, and vice-versa for the "down"-channel ($N_e^{\uparrow} > N_e^{\downarrow}$ for open shells). The first approximation therefore just uses the more 'dominant' spin-channel to define the whole potential, and the second is a weighted average of the two spin-dependent xc-potentials. The form of the weighted potential is motivated by the energy differences $\epsilon_i - \epsilon_a$ in the OEP equation.

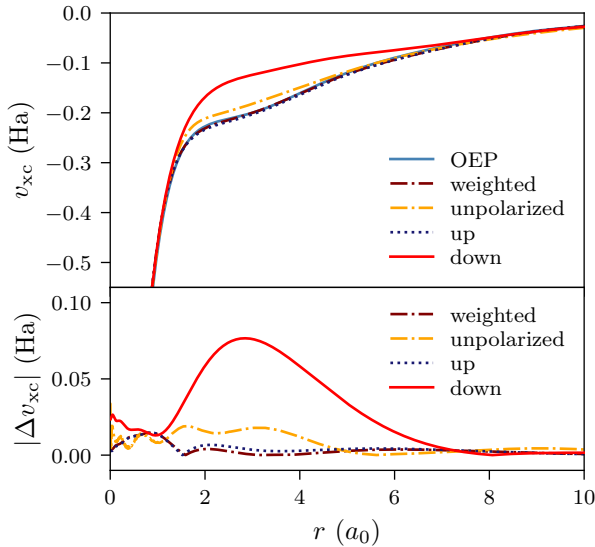In Fig. S1, we plot the spin-up and spin-down xc-potentials, alongside the full OEP and weighted (eq. S2)

FIG. S1: xc-potentials for Lithium (doublet). The lower panel shows the absolute difference $|\Delta v_{xc}|$ of the xc-potentials relative to the full OEP reference result.

	E_{tot} (Ha)	ΔE (mHa)
$E_{xc}[\rho^{\uparrow}, \rho^{\downarrow}]$, v_{xc}^{OEP}	-7.398144	0.011
$E_{xc}[\rho^{\uparrow}, \rho^{\downarrow}]$, v_{xc}^{w}	-7.398135	0.020
$E_{xc}[\rho^{\uparrow}, \rho^{\downarrow}]$, $v_{xc}^{\uparrow}$	-7.398136	0.019
$E_{xc}[\rho^{\uparrow}, \rho^{\downarrow}]$, $v_{xc}^{\downarrow}$	-7.396281	1.87
$E_{xc}[\rho]$, $v_{xc}[\rho]$	-7.388721	9.43

TABLE S1: Total energies for Lithium (doublet), obtained via different applications of the L(S)DA functional, and differences relative to the spin-DFT result. The final row uses the LDA functional of the total density (not spin-density), i.e. is contaminated by the ghost exchange error.

xc-potentials. We also plot the plain DFT potential $v_{xc}[\rho](\mathbf{r})$ (labelled 'unpolarized' in the figure) for comparison). From this figure, we see that both the weighted xc-potential and the up-only xc-potential are both in close agreement with the full OEP solution; the down-only and unpolarized potentials show much greater differences compared to the OEP solution. It might at first seem surprising that the up-only potential agrees so closely with the full OEP solution. However, because the up-spin-channel contains more electrons, it will have a smaller HOMO-LUMO energy difference ($\Delta^{\uparrow} < \Delta^{\downarrow}$); the weighting is therefore biased to the up-spin potential, explaining why this is such a good approximation.

In Table S1, we see that the the energies coming from the full OEP, weighted and up-only potentials are also similar, with any differences relative to the benchmark spin-DFT (LSDA) result being much lower (several orders of magnitude) than the result obtained using the plain LDA xc-functional of the total density (i.e. the ghost-exchange-contaminated result). In fact, we notice that even the result obtained using only the spin-down potential has a much smaller error than the the plain LDA result, even though the down-spin potential is differs much more from the full OEP potential than does the spin-unpolarized potential.

The accurate energetics using the up-only or weighted potentials holds for all the systems we have studied. For example, In Fig. S2 we show the energy dissociation curves for the OH radical (both doublet and quadruplet states where the energies have been obtained from the spin-up and full OEP potentials. From this figure, it is clear that there are only very minimal (in the order of a few mHa) differences between the approximate and full OEP solutions. The scheme we have presented above is
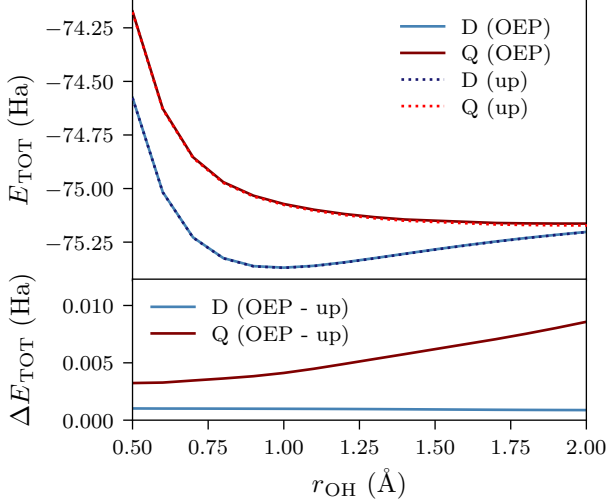
FIG. S2: Comparison of energies for the OH radical dissociation curve, where the KS equations have been solved with the full OEP xc-potential, and just the spin-up potential.

thus a practical way of performing ghost-exchange-free calculations at no extra cost or difficulty compared to a normal DFT calculation.

EMERGENCE OF UNRESTRICTED KS POTENTIAL FROM MINIMIZATION IN EQ. 18

The Euler-Lagrange equations which determine the minimising SDFT-KS system and the minimising spin-density in Eq. 18 of the main paper are ($\sigma = \uparrow, \downarrow$)

$$\frac{\partial T_s[\rho^\uparrow, \rho^\downarrow]}{\partial \rho^\sigma(\mathbf{r})}\bigg|_{\rho^\uparrow_\rho, \rho^\downarrow_\rho} + \frac{\partial E_{xc}[\rho^\uparrow, \rho^\downarrow]}{\partial \rho^\sigma(\mathbf{r})}\bigg|_{\rho^\uparrow_\rho, \rho^\downarrow_\rho} + v_{eff}[\rho](\mathbf{r}) = 0, \quad \text{(S3)}$$

where the local potential $v_{eff}[\rho](\mathbf{r})$ arises as a continuous set of Lagrange multipliers to satisfy the fixed total density constraint. It is convenient to write v_{eff} as the sum of the Hartree potential plus a remainder potential, $v_{eff}[\rho](\mathbf{r}) = v_H[\rho](\mathbf{r}) + v[\rho](\mathbf{r})$.

The functional derivative of the non-interacting kinetic energy at the spin-density $(\rho^\uparrow_\rho, \rho^\downarrow_\rho)$ is equal to minus the spin-dependent SDFT-KS potential for that spin-density

(within a spin-constant). Hence, the unrestricted KS potential with the correct spin-density is:

$$v_s^\sigma[\rho^\uparrow_\rho, \rho^\downarrow_\rho](\mathbf{r}) = v_{xc}^\sigma[\rho^\uparrow_\rho, \rho^\downarrow_\rho](\mathbf{r}) + v_H[\rho](\mathbf{r}) + v[\rho](\mathbf{r}) \quad \text{(S4)}$$

where all terms in (S4) are functionals of the total density ρ. By the HK theorem of SDFT (see Ref. 4) for non-interacting systems, the local potential $v[\rho](\mathbf{r})$ in (S4) is the external potential of the interacting system.

It is instructive to repeat the previous analysis for the DFT-KS system to establish how it differs from the DFT-GKS system. The minimising state of the non-interacting kinetic energy functional,

$$T_s[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} | \Psi \rangle, \quad \text{(S5)}$$

is the KS Slater determinant $\Phi[\rho]$. We separate again the minimisation in (S5) into two separate minimisations and obtain that DFT's non-interacting kinetic energy density functional can be obtained after an optimisation over spin-densities from SDFT's functional,

$$T_s[\rho] = \min_{(\rho^\uparrow, \rho^\downarrow) \to \rho} T_s[\rho^\uparrow, \rho^\downarrow]. \quad \text{(S6)}$$

However, the minimising spin-density, $(\rho^\uparrow[\rho], \rho^\downarrow[\rho])$, is the spin-density of $\Phi[\rho]$, which is different from the spin-density of the real interacting system Ψ_ρ. The Euler-Lagrange equations which determine the minimising spin-density and the minimising SDFT-KS system are ($\sigma = \uparrow, \downarrow$):

$$\frac{\partial T_s[\rho^\uparrow, \rho^\downarrow]}{\partial \rho^\sigma(\mathbf{r})}\bigg|_{\rho^\uparrow[\rho], \rho^\downarrow[\rho]} + u_{eff}[\rho](\mathbf{r}) = 0 \quad \text{(S7)}$$

where again the local potential $u_{eff}[\rho](\mathbf{r})$ arises as a continuous set of Lagrange multipliers to satisfy the fixed total density constraint. The functional derivative of the SDFT non-interacting kinetic energy is equal to minus the spin-dependent KS potential. However in this case, the functional derivative and the SDFT-KS potential lose their spin-dependence because $u_{eff}[\rho]$ is spin-independent:

$$v_s^\sigma[\rho^\uparrow[\rho], \rho^\downarrow[\rho]](\mathbf{r}) = u_{eff}[\rho](\mathbf{r}), \quad \sigma = \uparrow, \downarrow. \quad \text{(S8)}$$

By DFT's HK theorem, the DFT-KS potential is equal to $u_{eff}[\rho](\mathbf{r})$ in (S8), since there cannot be two local potentials with the same ground state density.