Electronic Supplimentary Information:

External Orthogonality in Subsystem Time-dependent Density Functional Theory

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1 EO Operator in MO Basis

In the following derivation, χ are atomic orbitals (AOs), ϕ are molecular orbitals (MOs), superscripts indicate the subsystem the particular matrix is describing (for only two subsystems, A or B), and subscripts indicate particular elements of the respective matrix. Roman subscripts i, j, ... indicate occupied MOs; a, b, ... indicate virtual MOs; p, q, ... indicate general MOs; and Greek subscripts α, β, ... describe AOs. Bold-face fonts (e.g. $\mathbf{A}$) indicate matrices in AO basis and blackboard-bold fonts (e.g. $\mathbb{A}$) indicate matrices in MO basis. The EO projection operator for subsystem A in the environment of B is[1]

$$\mathbf{V}^{\mathrm{EO,A(B)}} = \mathbf{S}^{\mathrm{A,B}}\mathbf{P}^{\mathrm{B}}\mathbf{S}^{\mathrm{B,A}} \tag{S1}$$

where $\mathbf{S}^{\mathrm{A,B}}$ is the AO overlap matrix between subsystems A and B ($\mathbf{S}^{\mathrm{A,B}}_{\alpha\beta} = \langle\chi^{\mathrm{A}}_{\alpha}|\chi^{\mathrm{B}}_{\beta}\rangle$), and $\mathbf{P}^{\mathrm{B}}$ is the density matrix of subsystem B, defined as

$$\mathbf{P}^{\mathrm{B}}_{\alpha\beta} = \mathbf{C}^{\mathrm{B}}\mathbf{n}^{\mathrm{B}}(\mathbf{n}^{\mathrm{B}})^{T}(\mathbf{C}^{\mathrm{B}})^{T} \tag{S2}$$

In this definition, $\mathbf{C}^{\mathrm{B}}$ is the MO coefficient matrix for all occupied and virtual orbitals of subsystem B and $\mathbf{n}^{\mathrm{B}}$ is a vector of the respective MO occupation numbers. We can therefore use this to write the MO density matrix as $\mathbb{P}^{\mathrm{B}} = \mathbf{n}^{\mathrm{B}}(\mathbf{n}^{\mathrm{B}})^{T}$. This allows us to write the EO operator in MO basis as

$$\begin{aligned}\mathbb{V}^{\mathrm{EO,A(B)}} &= (\mathbf{C}^{\mathrm{A}})^{T}\mathbf{S}^{\mathrm{A,B}}\mathbf{C}^{\mathrm{B}}\mathbb{P}^{\mathrm{B}}(\mathbf{C}^{\mathrm{B}})^{T}\mathbf{S}^{\mathrm{B,A}}\mathbf{C}^{\mathrm{A}} \\ &= \mathbb{S}^{\mathrm{A,B}}\mathbb{P}^{\mathrm{B}}\mathbb{S}^{\mathrm{B,A}}\end{aligned} \tag{S3}$$

where $\mathbb{S}^{\mathrm{A,B}}$ is the MO overlap matrix

$$\begin{aligned}\mathbb{S}^{\mathrm{A,B}}_{pq} &= \left[(\mathbf{C}^{\mathrm{A}})^{T}\mathbf{S}^{\mathrm{A,B}}\mathbf{C}^{\mathrm{B}}\right]_{pq} \\ &= \left(\sum_{\alpha}\langle\chi^{\mathrm{A}}_{\alpha}|\mathbf{C}^{\mathrm{A}}_{\alpha p}\right)\left(\sum_{\beta}\mathbf{C}^{\mathrm{B}}_{\beta q}|\chi^{\mathrm{B}}_{\beta}\rangle\right) \\ &= \langle\phi^{\mathrm{A}}_{p}|\phi^{\mathrm{B}}_{q}\rangle\end{aligned} \tag{S4}$$

2 Long-range correction to the NAKP

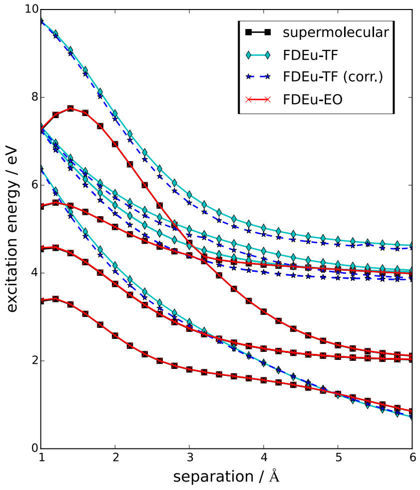

Fig. S1: Excitation energies of the five lowest transitions in the LiH system with respect to subsystem separation, showing the long-range correction to the NAKP (corr.).

3 Significance of the EO kernel

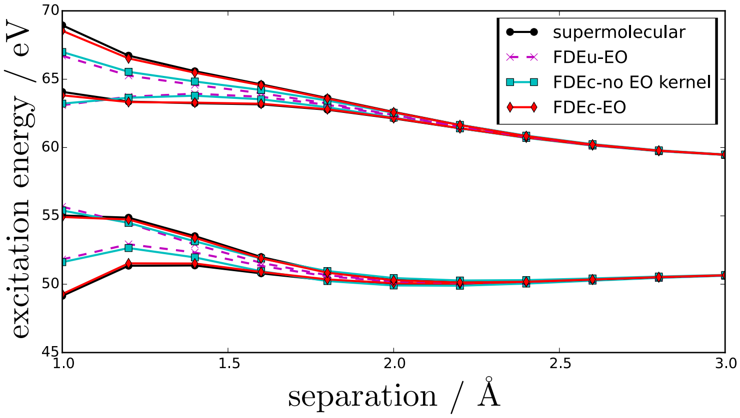

Fig. S2: Coupled excitation energies of the He-dimer showing the importance of the EO contribution to the coupled response kernel.

References

[1] D. V. Chulhai and L. Jensen, *J. Chem. Theor. Comput.*, 2015, **11**, 3080–3088.