Supplementary Material for "Excitation energies along a range-separated adiabatic connection"

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The total energies $\mathcal{E}_k^\mu$ and excitation energies $\Delta\mathcal{E}_k^\mu = \mathcal{E}_k^\mu - \mathcal{E}_0^\mu$ of the partially interacting Hamiltonian given in Eq. (5) of the main article have been calculated with the `DALTON` program as a function of the range-separation parameter μ for the helium and beryllium atoms and for the dihydrogen molecule. The computational details can be found in Section IV. The total ground-state energies were then fitted to the following analytical expression which satisfies the form of the expansions at small μ and large μ given in Eqs. (27) and (39)

$$\mathcal{E}_0^\mu = E_0 + \frac{\mathcal{E}_0^{\rm KS} - E_0 + c_1\mu + c_2\mu^2 + c_3\mu^3}{1 + d_1\mu + d_2\mu^2 + d_3\mu^3 + d_4\mu^4 + d_5\mu^5},$$

where $c_1 = -N(N-1)/\sqrt{\pi} + (\mathcal{E}_0^{\rm KS} - E_0)d_1$ and $c_2 = -N(N-1)d_1/\sqrt{\pi} + (\mathcal{E}_0^{\rm KS} - E_0)d_2$ are fixed by the small-μ expansion, E_0 and $\mathcal{E}_0^{\rm KS}$ give the ground-state total energies of the physical system and of the Kohn-Sham (KS) system, and N is the number of electrons. The excitation energies were fitted to the expression

$$\Delta\mathcal{E}_k^\mu = \Delta E_k + \frac{\Delta\mathcal{E}_k^{\rm KS} - \Delta E_k + c_1\mu + c_2\mu^2 + c_3\mu^3}{1 + d_1\mu + d_2\mu^2 + d_3\mu^3 + d_4\mu^4 + d_5\mu^5},$$

where $c_1 = d_1(\Delta\mathcal{E}_k^{\rm KS} - \Delta E_k)$ and $c_2 = d_2(\Delta\mathcal{E}_k^{\rm KS} - \Delta E_k)$ to ensure the correct behavior at small μ, and ΔE_k and $\Delta\mathcal{E}_k^{\rm KS}$ give the excitation energies of the physical system and of the KS system.

The fits were performed on about 30 points for a range of μ going from 0 to 10 bohr^{-1}. The parameters of the fit can be found in Tables I, II, III and IV, and reproduce the calculated curves shown in the article with a maximum error of about 0.1 mhartree. All the energies are in hartree and μ is in bohr^{-1}.

Table I: Fitted parameters of the ground-state and excitation energies along the range-separated adiabatic connection for the helium atom using an uncontracted triple-augmented quintuple zeta basis set and a truncated singular-value decomposition cutoff of 10^{-7}.

Ground-state	$\mathcal{E}_0^{\rm KS}$	E_0	c_3	d_1	d_2	d_3	d_4	d_5
1^1S	-1.813977	-2.902589	0.2886122	-0.5256672	1.267965	0.7302989	1.729618	0.6215862
Transition	$\Delta\mathcal{E}_k^{\rm KS}$	ΔE_k	c_3	d_1	d_2	d_3	d_4	d_5
$1^1S \to 2^3S$	0.7476677	0.7281453	0.06186663	-1.148460	0.7875350	3.601280	-0.8453350	3.279870
$1^1S \to 2^1S$	0.7476670	0.7576321	-0.09598863	-1.799520	3.139774	9.153716	6.331953	8.164700
$1^1S \to 1^3P$	0.7787323	0.7701976	0.2572886	-4.517757	11.06152	37.53672	-27.73374	90.37671
$1^1S \to 1^1P$	0.7787322	0.7795772	0.05426567	11.97447	-47.11893	114.6076	-82.48554	51.72106

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Table II: Fitted parameters of the ground-state and excitation energies along the range-separated adiabatic connection for the beryllium atom using an uncontracted double-augmented double zeta basis set and a truncated singular-value decomposition cutoff of 10^{-6}.

Ground-state	$\mathcal{E}_0^{\mathrm{KS}}$	E_0	c_3	d_1	d_2	d_3	d_4	d_5
1^1S	-9.124165	-14.65438	46.83671	-0.2090221	-1.923411	3.658671	10.96260	5.215731
Transition	$\Delta\mathcal{E}_k^{\mathrm{KS}}$	ΔE_k	c_3	d_1	d_2	d_3	d_4	d_5
$1^1S \rightarrow 1^3P$	0.1336714	0.1009080	-0.02498641	2.675899	-1.103249	66.59735	-39.94845	24.42414
$1^1S \rightarrow 1^1P$	0.1336461	0.1974410	-0.3142418	2.670149	-5.243878	40.77140	-44.04497	36.69480

Table III: Fitted parameters of the excitation energies along the range-separated adiabatic connection for the dihydrogen molecule at the equilibrium distance using an uncontracted double-augmented triple zeta basis set and a truncated singular-value decomposition cutoff of 10^{-6}.

Transition	$\Delta\mathcal{E}_k^{\mathrm{KS}}$	ΔE_k	c_3	d_1	d_2	d_3	d_4	d_5
$1^1\Sigma_g^+ \rightarrow 1^3\Sigma_u^+$	0.4359619	0.3890173	0.2799389	1.767023	13.40149	19.23359	24.79910	19.29466
$1^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+$	0.4359571	0.4677408	-0.01241781	1.264479	-0.4431237	21.85013	-16.49858	12.33904
$1^1\Sigma_g^+ \rightarrow 2^3\Sigma_g^+$	0.4740336	0.4598110	0.2481387	0.9229492	-10.10530	21.52073	-16.87971	25.28795
$1^1\Sigma_g^+ \rightarrow 2^1\Sigma_g^+$	0.4740150	0.4814739	0.04156341	-5.018161	10.11410	-3.755105	-2.033443	8.145262
$1^1\Sigma_g^+ \rightarrow 1^3\Pi_u$	0.480003	0.4670848	0.1376852	30.80894	-13.52176	121.4909	-67.14926	32.50543
$1^1\Sigma_g^+ \rightarrow 1^1\Pi_u$	0.4799835	0.4852236	0.01995048	0.5766261	-5.036269	37.87564	-20.46073	10.75388

Table IV: Fitted parameters of the excitation energies along the range-separated adiabatic connection for the dihydrogen molecule at three times the equilibrium distance using an uncontracted double-augmented triple zeta basis set and a truncated singular-value decomposition cutoff of 10^{-6}.

Transition	$\Delta\mathcal{E}_k^{\mathrm{KS}}$	ΔE_k	c_3	d_1	d_2	d_3	d_4	d_5
$1^1\Sigma_g^+ \rightarrow 1^3\Sigma_u^+$	0.05176212	0.01700837	0.6515038	-1.415220	4.923966	118.7312	-176.1438	667.7109
$1^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+$	0.05174852	0.2813186	-9.042050	-9.080417	27.82670	57.35565	-188.3668	718.6815
$1^1\Sigma_g^+ \rightarrow 2^3\Sigma_g^+(\sigma_u^+)^2$	0.1034820	0.2988327	-8.364428	-6.876502	37.68192	51.86662	-151.0807	783.8883