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

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(Dated: July 3, 2014)

I. FIT FORM AND PARAMETERS

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}.

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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	$\mathcal{E}_0^{\mathrm{KS}}$	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	$\Delta\mathcal{E}_k^{\mathrm{KS}}$	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

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
$1^1S \to 1^3P$	0.1336714	0.1009080	-0.02498641	2.675899	-1.103249	66.59735	-39.94845	24.42414
$1^1S \to 1^1P$	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
$1^1\Sigma_g^+ \to 1^3\Sigma_u^+$	0.4359619	0.3890173	0.2799389	1.767023	13.40149	19.23359	24.79910	19.29466
$1^1\Sigma_g^+ \to 1^1\Sigma_u^+$	0.4359571	0.4677408	-0.01241781	1.264479	-0.4431237	21.85013	-16.49858	12.33904
$1^1\Sigma_g^+ \to 2^3\Sigma_g^+$	0.4740336	0.4598110	0.2481387	0.9229492	-10.10530	21.52073	-16.87971	25.28795
$1^1\Sigma_g^+ \to 2^1\Sigma_g^+$	0.4740150	0.4814739	0.04156341	-5.018161	10.11410	-3.755105	-2.033443	8.145262
$1^1\Sigma_g^+ \to 1^3\Pi_u$	0.480003	0.4670848	0.1376852	30.80894	-13.52176	121.4909	-67.14926	32.50543
$1^1\Sigma_g^+ \to 1^1\Pi_u$	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
$1^1\Sigma_g^+ \to 1^3\Sigma_u^+$	0.05176212	0.01700837	0.6515038	-1.415220	4.923966	118.7312	-176.1438	667.7109
$1^1\Sigma_g^+ \to 1^1\Sigma_u^+$	0.05174852	0.2813186	-9.042050	-9.080417	27.82670	57.35565	-188.3668	718.6815
$1^1\Sigma_g^+ \to 2^3\Sigma_g^+(\sigma_u^+)^2$	0.1034820	0.2988327	-8.364428	-6.876502	37.68192	51.86662	-151.0807	783.8883

II. BASIS SET CONVERGENCE

The short-range potential changes regime at about $r \simeq 1/\mu$. If the basis set is not large enough, this region of the potential is not well described. The higher in energy, the more affected the excited states are, which might result in a bump as observed in the the singlet $1^1\mathrm{S} \to 1^1\mathrm{P}$ excitation energy of the helium atom . The evolution of this excitation energy is shown in Figure 1 as a function of μ, for different

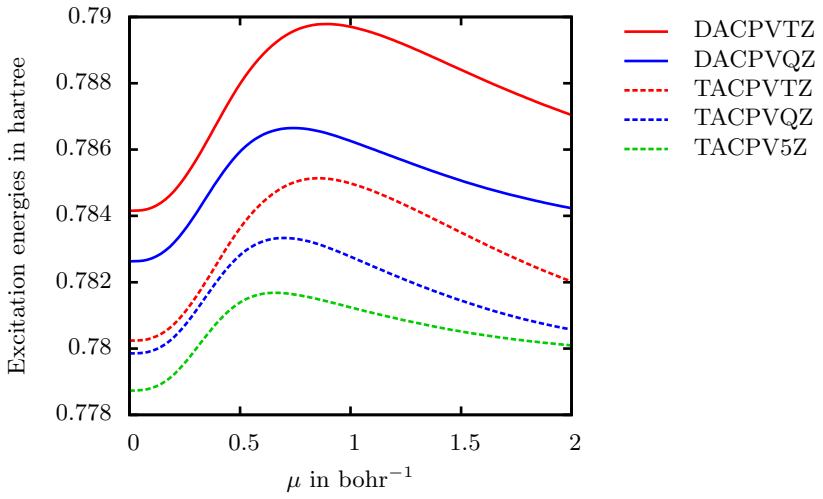

Figure 1: Singlet $1^1\mathrm{S} \rightarrow 1^1\mathrm{P}$ excitation energy $\Delta\mathcal{E}_k^\mu = \mathcal{E}_k^\mu - \mathcal{E}_0^\mu$ (in hartree) of the He atom as a function of μ (in bohr^{-1}) for different basis sets.

basis sets, going from a triple to a quintuple zeta, and with double or triple augmentation. As the size of the basis set increases, and especially, its diffuse nature, the amplitude of the bump and the position of its maximum decreases. Similar observations were obtained for singlet $1^1\mathrm{S} \rightarrow 2^1\mathrm{S}$ excitation energy but as the $2^1\mathrm{S}$ is lower in energy, smaller basis set were soon sufficient to recover what we believe to be the correct behavior. In this case, as the excited state is more diffuse, larger basis set are required, and memory issues prevented us to increase the basis set further more.