Ab initio X^10^+ ground state potential curves of Pb….RG dimers (RG = He, Ne, Ar) including spin-orbit effects. Simulation of diffusion coefficients.

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The basis set extrapolation scheme was first tested on the homo-atomic RG….RG dimers (RG = He, Ne, Ar) where the use of basis sets up to dU5Z was affordable for He….He. The results indicate that for He….He, the use of dUDZ and dUTZ in the extrapolation formula (abbreviated as dU[DT]Z), Eq.(1) provides almost exactly the same results comparing to dU[TQ]Z and dU[Q5]Z extrapolations, see Figure S-1a. In Ne….Ne the extrapolation from dUDZ and dUTZ, i.e. the dU[DT]Z curve, is between the dUQZ and dU[TQ]Z curves, see Figure S-1b. In Ar….Ar, the dU[DT]Z extrapolated curve lies below dUQZ and even dU[TQ]Z curves, see Figure S-1c. The dU[DTQ]Z curves are shown in Figure S-1b,c for completeness. Evidently, in the case of He….He the extrapolation yields almost the same Complete Basis Set (CBS) potential depth irrespective of the consecutive cardinal numbers of the basis sets used in the extrapolation. In Ar….Ar such extrapolation leads to the improvement of the PES by more than one cardinal number with respect to the highest cardinal number basis set used in the extrapolation. This is in agreement with the findings of Feller et al. (D. Feller, K. A. Peterson, J. Grant Hill, *J. Chem. Phys.*, 2011, **135**, 044102), who claim that a two point extrapolation usually improves the values roughly by two cardinal numbers. Analogous trend, i.e. dU[DT]Z curve is below the dUQZ curve, can be seen in the Ne….Ne dimer. In this case, dU[DT]Z and dU[TQ]Z curves are close to each other. Nevertheless, it can be concluded that the dU[DT]Z extrapolation does not significantly exceed the dU[TQ]Z results, thus may be considered appropriate for further application.

$$E_N^{corr} = E_\infty^{corr} + \omega N^{-3} \qquad (1)$$

Extrapolation of the HF (Hartree Fock) energy provides no improvement to the PES. The dUTZ and dUQZ HF energies are already almost identical. Herein, the HF/dUQZ energies are used for the calculation of PES of the RG….RG dimers.
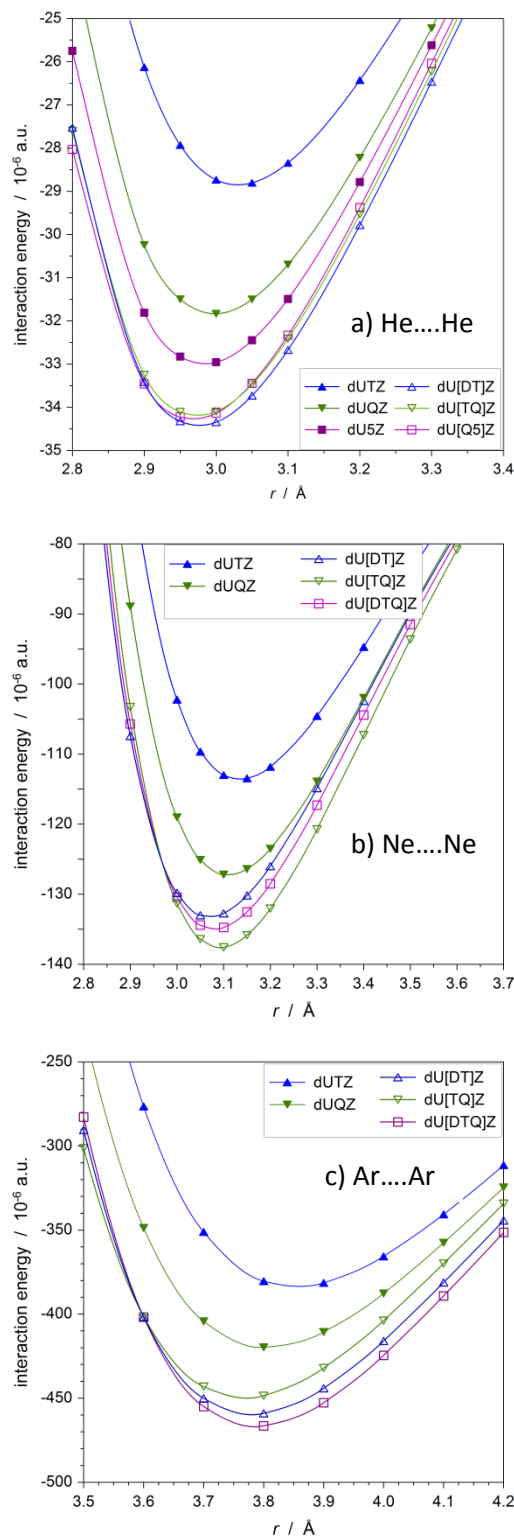

Figure S-1. Non relativistic CCSD(T) potential curves of a) He….He b) Ne….Ne c) Ar….Ar in dUXZ basis sets (X = D, T, Q, 5) and various extrapolation scenarios using equation (1). (The dUDZ curve is not shown in order to achieve better resolution of the remaining curves.)

In order to assess the effect of a larger active space on the CCSD(T) interaction energy, additional calculations of the Ar….Ar dimer were performed. The active space in the CCSD(T) calculations was extended to include also the $2s^2\ 2p^6$ electrons (in addition to the standard $3s^2\ 3p^6$) including all virtual orbitals. It has been found that such change did not bring any significant changes of the potential curve, e.g. the value of D_e in the dUQZ basis set changed from –416.540 to –419.759 μE_h. Analogously, D_e of the extrapolated dU[TQ]Z curve changed from –444.664 to –448.526 μE_h as a result of the extended active space. Thus, the difference is less than 0.8% in both cases.

The interaction energies of the Pb….He and Pb….Ar dimers were separated to the Hartree Fock (HF) and correlation contribution (corr). Figure S-2 displays this separation. It is clearly visible, that the BSSE corrected X2C HF curves do not correspond to a bound state (no minima on the curve) of the dimer and therefore the stabilization is exclusively due to the correlation energy. On the other hand, the BSSE corrected DKH2 potential curve does have a shallow minimum already at the HF level of calculation. These minima make up only 5% of the D_e for the DKH2/CCSD(T)/dUTZ curves. This may be considered to be in agreement with the analysis of the frontier orbitals and spin density as discussed in the paper. It has been argued, that the triplet state in the DKH2 calculation is stabilized by the sigma hole interaction.

Table S-1 displays the X2C HF energy differences of the open shell states with respect to the closed shell ground state HF energy. The energy differences were calculated for the lowest resolved HF states as well as for the lowest energy determinant in the CCSD(T) calculation.
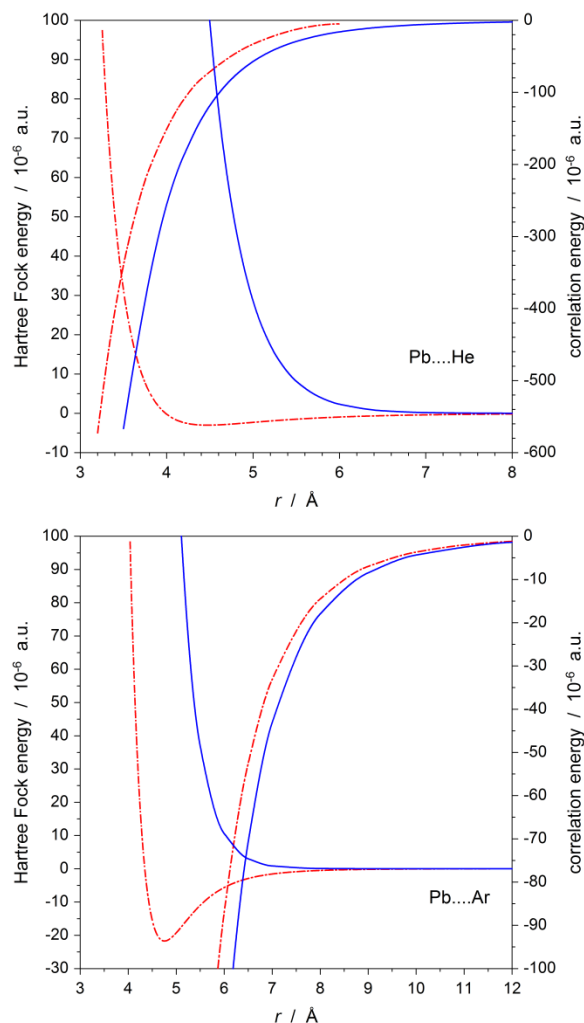

Figure S-2. The Hartree Fock and correlation energy contributions to the total interaction energy. Blue solid lines depict the X2C/dUTZ data and the dot-dashed red lines stand for the DKH2/dUTZ values.

Table S-1. Total energies of the closed shell ground state $E_0\ (6p_{1/2}^2)$ of Pb and the energy difference to the first excited state $(6p_{1/2}^1 6p_{3/2}^1)$.

	UDZ	UTZ	UQZ
$E_{(0)}$	-20904.9614	-20904.9780	-20904.9786
$E_{(1/2,1/2)} - E_{(0)}$ [a]	-0.02170	-0.02172	-0.02165
$E_{(1/2,1/4)} - E_{(0)}$ [a]	-0.02176	-0.02175	-0.02176
$E_{(2/6)} - E_{(0)}$ [a]	-0.02177	-0.02176	-0.02176
$E_{(1/2,1/2)} - E_{(0)}$ [b]	-0.02854	-0.02974	-0.02779
$E_{(1/2,1/4)} - E_{(0)}$ [b]	-	-	-
$E_{(2/6)} - E_{(0)}$ [b]	-0.02733	-0.02736	-0.02668

[a] The energy differences were calculated for the lowest resolved HF state (command .RESOLVE in the Dirac code).

[b] The energy differences were calculated for HF energies from the CCSD(T) calculation , i.e. the energetically most favoured determinat.