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Supplementary material

Fully relativistic coupled cluster and DFT study of electric field gradients at Hg in ^{199}Hg compounds

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In order to obtain electron correlation corrections to the EFG at Hg, we used a finite difference method[1,2], in which one can either 1) differentiate the total energy, for example E_{CCSD-T}, with respect to the perturbation strength λ and obtain directly the total EFG value including the Hartree-Fock and electron correlation contribution to it or 2) differentiate the correlation energy E_{corr} with respect to the perturbation strength λ and then add this correction to the analytically obtained Hartree-Fock value. Consequently, using method 2) one can obtain the electron correlation correction to the EFGs using a two-point approximation

$$\left(\frac{\partial E_{corr}(\lambda)}{\partial \lambda}\right)\Big|_{\lambda=0} = \frac{E_{corr}(+\lambda) - E_{corr}(-\lambda)}{2\lambda} \tag{1}$$

and add it to the analytically obtained HF value. However, it was discussed by Pernpointner et al.[2], that a different behavior with respect to the applied perturbation strength, such as nonlinear dependence at larger λ values or almost perfect linear dependence, have been observed for the two methods. Method 1), or more precisely the Hartree-Fock contribution, either requires to use even smaller λ values in order to obtain linear dependence on the perturbation strength, which however, can lead to numerical inaccuracies, or to fit the curve to a n'th order polynomial

$$E(\lambda) = E(\lambda = 0) + c_1\lambda + c_2\lambda^2 + c_3\lambda^3 + ..., \tag{2}$$

where c_1 should then be in good agreement with the analytically obtained HF value. Therefore, Pernpointner et al.[2] concluded that it is more convenient to employ method 2).

Herein, we tested both methods (in combination with the dyall.cv3z/cc-pCVTZ basis set for Hg and Cl, respectively) in calculations of the electron correlation correction to the EFG at Hg in $HgCl_2$ and came to the same conclusions as Pernpointner et al.[2]. Method 2) required very small λ values ($\pm 1\times10^{-8}$ a.u., $\pm 5\times10^{-9}$ a.u., $\pm 1\times10^{-9}$ a.u.) to gain an almost linear dependence of the correlation energy on the values of λ as shown in Figure 1. We obtained thus an electron correlation correction to the EFG of 3.40 a.u. using Eq. 1 with any λ value in the range from $\pm 1\times10^{-8}$ a.u. to $\pm 1\times 10^{-9}$ a.u.. In order to get energy changes for Eq. 1 with such small λ values, tight gradient norm convergence criterium of 1×10^{-7} a.u. had to be applied. Alternatively, we calculated correlation energies also with larger λ values (between $\pm 1\times10^{-7}$ a.u. and $\pm 1\times10^{-8}$ a.u.), fitted them to a third order polynomial

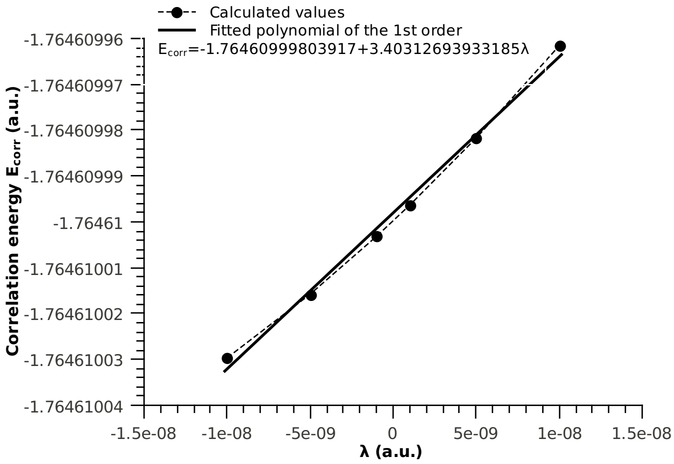

Figure 1: Electron correlation energies E_{corr} as a function of the perturbation strength λ in the range between $\pm1\times10^{-8}$ a.u. and $\pm1\times10^{-9}$ a.u..

(like in Eq.2), found the derivative of it for λ equal to 0 and in this way obtained c_1=3.40 a.u., which is the electron correlation correction to the EFG at Hg (see Figure 2).

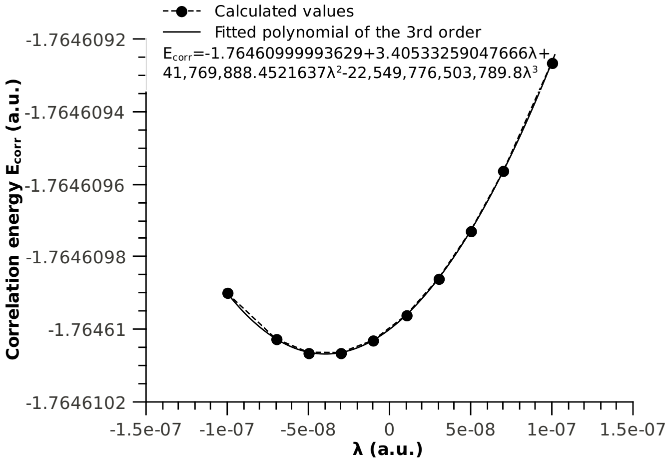

Figure 2: Electron correlation energies E_{corr} as a function of the perturbation strength λ in the range between $\pm\ 1\times10^{-7}$ a.u. and $\pm1\times10^{-8}$ a.u.

As pointed out by Pernpointner et al.[2], method 1) or, more precisely, the Hartree-Fock contribution, requires to include higher order terms compared to the electron correlation contribution. This was demonstrated by fitting the HF energies obtained at different λ values (between $\pm1\times10^{-7}$ a.u. and $\pm1\times10^{-8}$ a.u.) to a 5th order polynomial as shown in Figure 3, which gave a c_1, that is the Hartree-Fock contribution (electronic contribution) to the total EFG, of -13.83 a.u compared to the analytically obtained value of -13.79 a.u. For simplicity and accuracy reasons, in the rest of the study we obtain the electron correlation corrections using the two-point approximation (Eq. 1) with λ=1 $\times$ 10^{-8} a.u. and add this correction to the analytically obtained HF value.

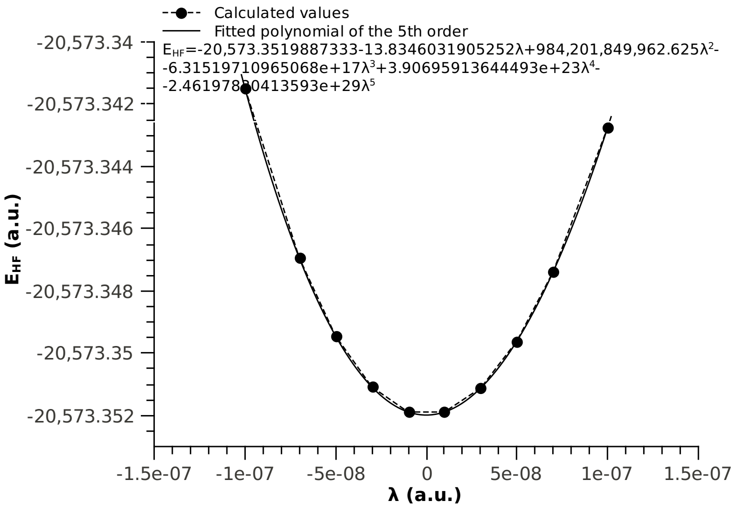

Figure 3: HF energies E_{HF} as a function of the perturbation strength λ in the range between $\pm 1\times10^{-7}$ a.u. and $\pm 1\times10^{-8}$ a.u.

References

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