Picture-change-error-free Electric Field Gradients for Heavy Elements by the PCNQM-Method

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A point charge model for the nuclear quadrupole moment tensor (PCNQM) is presented in order to determine accurate electric field gradients (EFG) at the relativistic (Douglas-Kroll/Dirac-Fock) and correlated levels (CCSD(T)). This method helps to avoid the considerable picture change error resulting by the use of transformation schemes which are applied to reduce the Dirac equation to a two- or one-component form. Neglecting the field gradient operator transformation due to its complexity is the reason for the deviations especially at high nuclear charges. Therefore this alternative method was developed to count for relativistic and correlation effects avoiding the picture change error. It turned out that the variation of the point-charge Q is numerically stable and a suitable parameter for creating the PCNQM perturbation. An important aspect is that the correlation contribution to the resulting EFG at both the nonrelativistic and relativistic level of theory depends linearly on Q. This suggests that accurate EFG tensors can be obtained by performing only two correlated calculations for each atom and tensor component. The PCNQM model was successfully applied to one-electron systems and a whole range of diatomic molecules whose results are presented. The considered species were the fluorides of Cu, Cs and Ga and the coinage metal chlorides. For some of these nuclei a much more accurate value for the nuclear quadrupole moment could be given using the improved EFG values in combination with spectroscopical data. We obtained 220(10) mb for ^{63}Cu and -3.43(10) mb for ^{133}Cs and could considerably improve the values given in the literature bearing a large error bar.