

Relativistic 1s Core Orbital Shifts using Local Hybrid Functionals

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Relativistic effects play an important role in the accurate calculation of core properties, e.g. X-ray absorption spectra and core electron binding energies. Here, a common way to incorporate relativistic shifts of non-relativistic (NR) core-orbital energies is the a posteriori addition of atomic relativistic corrections, which, in many cases, are still determined using Hartree-Fock and a one-electron-relativistic Hamiltonian, i.e., two-electron relativistic effects and the dependence on the exchange-correlation (XC) functional, although being potentially significant, are fully neglected. In this work, the influence of the latter two factors on scalar-relativistic 1s core-orbital shifts has been investigated by employing the infinite-order two-component method^[1] together with local hybrid functionals,^[2,3] a recent class of hyper-generalized-gradient-approximation functionals, which, in contrast to most other XC functionals, is able to provide the correct high-density limit.

$$E_{xc}^{Lh} = E_x^{ex} + \sum_{\sigma} \int g_{\sigma}(\mathbf{r}) \cdot [e_{x,\sigma}^{ex}(\mathbf{r}) - e_{x,\sigma}^{sl}(\mathbf{r})] d\mathbf{r} + E_c^{sl} \quad (1)$$

First, we present the theoretical and technical details of our new scalar-relativistic implementation of local hybrid functionals in the RAQET program.^[4] This includes the introduction of a picture-change transformation of the density matrix for an efficient treatment of relativistic two-electron contributions, an improved new screening procedure for the semi-numerical evaluation of exact-exchange integrals, and the derivation of a gauge correction that restores the correct iso-orbital limit of the relativistic kinetic energy density (KED). The effectiveness of these three approaches is illustrated for several representative cases. Furthermore, we provide accurate two-electron-relativistic 1s core-orbital energy shifts using several local hybrid functionals. Respective two-electron relativistic contributions and deviations of different XC functionals, in particular those differing just in the definition of the KED (NR and relativistic, with and without gauge correction) and the choice of the local exchange functional (NR and relativistic), are found to be in the order of magnitude of errors of XC functionals specialized for the calculation of core excitations. The mentioned factors are thus essential for a technically accurate calculation of relativistic core-orbital shifts and a sound comparison of different XC functionals.

References

- [1] M. Barysz and A. J. Sadlej, *J. Chem. Phys.* **116**, 2696 (2002).
- [2] J. Jaramillo, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 1068 (2003).
- [3] T. M. Maier, A. V. Arbuznikov, and M. Kaupp, *WIREs Comput. Mol. Sci.* **9**, e1378 (2019).
- [4] M. Hayami, J. Seino, Y. Nakajima, M. Nakano, Y. Ikabata, T. Yoshikawa, T. Oyama, K. Hiraga, S. Hirata, and H. Nakai, *J. Comput. Chem.* **39**, 2333 (2019).