4-COMPONENT RELATIVISTIC HAMILTONIAN WITH EFFECTIVE QED POTENTIALS FOR MOLECULAR CALCULATIONS

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Is the no-pair Dirac Hamiltonian sufficient to describe chemistry? A sophisticated electron-correlation calculation[1] improved the deviation from experiment[2] of the bond length for the CuCN and AgCN molecules, compared with a previous work[3]. In contrast, the Au-C bond length of the AuCN molecules in Ref.[1] was underestimated compared with that in Ref.[3]. Pyykko pointed out that this could be the effect of quantum electrodynamics (QED). The inclusion of the QED effects, in principle, means going beyond the no-pair approximation[4].

A well-balanced approach between accuracy and computational cost is effective QED (effQED) potentials. Some codes for atomic calculations with effective potentials are reported, but in the molecular case, previous study is limited to quasirelativistic calculations[5], where Pyykko and Zhao's model for vacuum polarization and self-energy were included.

In this work, we report the implementation of effQED potentials[6] in the DIRAC code[7]: the Uehling potential for vacuum polarization, Pyykko and Zhao's model, and Flambaum and Ginges's effective potential for self-energy effects. Recently Skripnikov also implemented effQED potentials in the DIRAC code[8]. From our application, the QED effect reduces the discrepancy of the corresponding substitution Au-C bond length r_s from 0.23 pm[1] to 0.04 pm[6] with respect to experiment[2]. To obtain r_s the ground-state rotational constant B_0 is calculated with vibration-rotation interaction constants α that are extracted from the potential energy surfaces of Ref.[1].

[1] J. Grant Hill, A. O. Mitrushchenkov, and K. A. Peterson, J. Chem. Phys. 138, 134314 (2013).
[2] T. Okabayashi, E. Y. Okabayashi, F. Koto, T. Ishida, and M. Tanimoto, J. Am. Chem. Soc. 131, 11712 (2009).
[3] P. Zaleski-Ejgierd, M. Patzschke, and P. Pyykko, J. Chem. Phys. 128, 1 (2008).
[4] T. Saue and L. Visscher, in Theoretical Chemistry and Physics of Heavy and Superheavy Elements, edited by S. Wilson and U. Kaldor (Kluwer, Dordrecht, 2003), pp. 211-267.
[5] B. C. Shepler, N. B. Balabanov, and K. A. Peterson, J. Chem. Phys. 127, 164304 (2007).
[6] A. Sunaga, M. Salman, and T. Saue, J. Chem. Phys. 157, 164101 (2022).
[7] http://www.diracprogram.org
[8] L. V. Skripnikov, J. Chem. Phys. 154, 201101 (2021).