

3P090

Picture change effects and correction schemes in relativistic two-component methods

○Peng Daoling ^{1,2}, 平尾 公彦 ^{1,2}

¹ 理研, ²JST-CREST

Although full-relativistic four-component method provides benchmark results within chemical accuracy for molecular quantum chemistry calculation, especially, for the heavy elements containing systems. Its computational cost is heavy in contrast with normal non-relativistic calculation and, moreover, it suffers the existence of redundant negative energy solutions. While the two-component methods have removed the negative energy solutions. Furthermore, the computational cost was significantly reduced. The X2C version of relativistic two-component method can even provide same results as four-component level.

However, the two-component methods transform all physical operators, originally 4-component, to two-component picture via, typically, a unitary transformation. The transformed 2-component forms of electron operators are obviously different from its original version, and the differences were named picture change effects. The picture change effects of one-electron operators usually are fully considered in two-component approaches by means of applied the unitary transformation to one-electron 4-component operators and taken the positive diagonal 2-component part only. The two-electron interaction operator can be treated in the same way. But there is no computational advantages compare with the four-component method. Therefore, the bared (untransformed) Coulomb two-electron interaction operator is employed in the two-component calculation as the first step approximation. The effective term of picture change correction is added afterward. Since the picture correction term is small and can be approximated as sum of effective one-electron contributions. The picture change correction scheme of two-component method is a very efficient approach

without loss of accuracy.

The picture change effects in variant two-component methods, include X2C BSS and infinite order DKH, were studied. By analyzing the results of both atoms and molecules, several correction schemes were proposed. It is found that the picture change correction of two-electron interaction is very important for spin-orbit splitting. As the spin-orbit splitting of electron orbitals in close shell atoms is overestimated, especially for high angular momentum orbitals, and the spin-orbit splitting of molecular state in open-shell molecules is also overestimated.

Orbital	Bared	Corrected	Error		Orbital	Bared	Corrected	Error
2p	73.2303	71.5143	2.39%		3d	3.8670	3.3952	13.90%
3p	16.2484	15.8378	2.59%		4d	0.8215	0.7138	15.08%
4p	3.9422	3.8343	2.81%		5d	0.0793	0.0679	16.67%
5p	0.7002	0.6796	3.03%		4f	0.2332	0.1547	50.72%

Table: Spin-orbit splitting of electron orbitals (in a.u.) in Hg atom.

The bare approximation is very cheap, because the number of two-electron integrals is much less than the full Hamiltonian. Furthermore, the bare approximation is good for energies and electric properties of closed shell systems. However, picture change effect is important for spin-orbit splitting and properties of open shell molecules, bare approximation is bad in this case. Finally, the effective one-electron potential (matrix) correction schemes can reduce the picture change error.

References:

Wenjian Liu and Daoling Peng, *J. Chem. Phys.* 125, 044102 (2006)

Daoling Peng and Kimihiko Hirao, *J. Chem. Phys.* 130, 044102 (2009)