Relativistic density functional theory with the finite-light-speed correction for Coulomb interaction[†]

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The periodic table of elements is determined by the electronic configuration and represents the periodicity of fundamental atomic properties. However, the positions of super-heavy elements (SHEs) in the periodic table are tentative because their chemical properties have not been established. Owing to the short half-lives of SHEs, experimental measurements of their chemical properties are difficult. Thus, first-principles numerical simulations are complementary tools to such experimental measurements.

The first-principles calculation for SHEs requires proper treatment of the relativistic effect. The relativistic effect can modify the Coulomb interaction between the charged particles, which is significant in SHEs. The non-relativistic form is of the order $O(Z\alpha)$, whereas the second dominant contribution is of the order $O\left((Z\alpha)^2\right)$, which is called the Breit correction.[1] Here, $\alpha \simeq 1/137$ is the fine-structure constant. The Breit correction is usually called the relativistic effect or finite-light-speed effect. The lowest order of relativistic effects incorporated using the Dirac equation is also $O\left((Z\alpha)^2\right) \sim O\left(1/c^2\right)$. Once the relativistic effects incorporated by the Dirac equation are considered, the Breit correction between two electrons should also be considered to keep consistency. Hereafter, we refer to both the Breit correction and effects incorporated using the Dirac equation as "relativistic effect" for simplicity.

So far, the electronic structure calculation with the relativistic effects in $O\left(1/c^2\right)$ has been performed based on wave-function theory. In contrast, density functional theory (DFT)[2,3] with the consistent inclusion of the relativistic effects up to the order $O\left(1/c^2\right)$ is unprecedented. Although the accuracy of DFT is lower than that of wave-function theory, DFT with the relativistic effects is highly desired, because DFT is applicable to larger systems such as molecules and coordination complex ions, the experimental syntheses of which are ongoing, and even solids.

In this paper, we formulate the Hartree-exchange-correlation functional for electron systems with the correction of $O\left(1/c^2\right)$. As a benchmark calculation, the all-electron calculation of atoms is performed.

We calculated the energy of the lawrencium atom with two electronic configurations, where one valence electron occupies the $6d$ orbital ([Rn] $5f^{14}\,6d^1\,7s^2$) or $7p$ orbital ([Rn] $5f^{14}\,7s^2\,7p^1$). For comparison, that of

Table 1. Total energies for lutetium and lawrencium atoms. All values are in the Hartree atomic unit.

	Outermost	Non-rel	SRel-CB
Lu	$5d^1$	**−13848.19912**	**−14527.46807**
	$6p^1$	−13848.12376	−14527.42700
Lr	$6d^1$	**−33551.48205**	Unbound
	$7p^1$	−33551.38274	**−37331.31054**

the lutetium atom is also calculated, where one valence electron occupies the $5d$ orbital ([Xe] $4f^{14}\,5d^1\,6s^2$) or $6p$ orbital ([Xe] $4f^{14}\,6s^2\,6p^1$). The energies calculated with these configurations in the non-relativistic (Non-rel) and the newly-developed relativistic (SRel-CB) schemes are listed in Table 1. The smaller values for the respective approximations in each atom are written in bold. In the lutetium atom, the outermost valence electron prefers to occupy the d orbital rather than the p orbital with all schemes. In contrast, in the lawrencium atom, the electron prefers to occupy the p orbital rather than the d orbital with the SRel-CB scheme, whereas it still prefers the d orbital in the Non-rel scheme, as in the lutetium case. The occupation of the p orbital could be the origin of the anomalous behavior of lawrencium.[4] This result is consistent with previous calculations using wave-function theory.[5,6] Note that we obtained the consistent results with far less computational cost than those previous calculations. It should also be noted that the p-block elements are defined as those in which the outer-most electrons occupy the p orbitals.[7] Lawrencium, thus, belongs to the p block, rather than d according to the definition. It seems, however, more appropriate to regard that the concept of "block" is ambiguous for the heavy and super-heavy elements, because the electronic configuration of lawrencium is almost the same as that of lutetium, and the only difference is in the outermost electron. Therefore, reconsideration of the classification appropriate for SHEs is mandatory.

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