All-electron relativistic four-component Dirac–Kohn–Sham theory for solids using Gaussian-type functions

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First-principle predictions of electronic structure and properties of solid-state materials containing heavy elements pose numerous challenges to computational methods, as the variational treatment of relativistic effects is in many cases required and multiple wavefunction components coupled by the spin–orbit interaction increase the complexity of the formalism and the computational cost. Here, we present a four-component Dirac–Kohn–Sham theory for obtaining relativistic band structures of spin–orbit-coupled solids. The method was recently developed in our group [1,2], and uses restricted kinetically balanced Gaussian-type orbitals (GTOs) to compactly express all operators in real space. The atom-centered nature of GTOs allows for explicit handling of one-, two-, and three-dimensional periodic systems while avoiding the need to introduce vacuum layers. We provide a detailed description of how key components of such a method are altered in the four-component regime, and show the necessary steps that need to be overcome when employing GTOs on periodic systems. Finally, we demonstrate the validity of the method on 3-dimensional silver halide (AgX) crystals with strong scalar-relativistic effects, and 2-dimensional honeycomb structures (silicene and germanene) exhibiting the quantum spin Hall effect due to a strong spin–orbit coupling.

References

[1] Marius Kadek, Michal Repisky, and Kenneth Ruud, *Phys. Rev. B* **99**, 205103 (2019).

[2] http://www.respectprogram.org