

Fully numerical calculations on atoms and diatomic molecules

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Although fully numerical electronic structure calculations on atoms and diatomic molecules have a long history [1], running such calculations has traditionally required extensive effort and the available programs have been restricted to e.g. only restricted open-shell configurations, a low-order numerical approach (e.g. only cubic basis functions), and to few density functionals. I have recently developed a new program called HELFEM [2] that solves these issues. HELFEM employs a basis set composed of numerical shape functions for the radial part and spherical harmonics for the angular part, both in the case of atoms [3] and diatomic molecules [4], and yields fully variational energies. The approach used in HELFEM affords stable and fast convergence to the self-consistent field solution thanks to modern convergence accelerators, as well as to the basis set limit thanks to its support for high-order polynomial basis functions (15 by default) [3]. The fully numerical approach in HELFEM allows reproduction of accurate reference values for various systems or functionals of interest. In addition to strong electric fields [3,4], atoms and diatomic molecules can also be calculated in extremely strong magnetic fields [6], found e.g. in the atmospheres of white dwarfs and magnetars, which change not only the ground state geometry of a molecule, but also have significant effects on its ground spin state. At present, HELFEM supports non-relativistic calculations on atoms [3] as well as diatomic molecules [4] at the Hartree–Fock or density functional level of theory. Hundreds of local density approximation (LDA), generalized gradient approximation (GGA) and meta-GGA functionals are supported via an interface to LIBXC [5], also including global hybrid functionals such as B3LYP and TPSSh. Fully spin restricted, spin-restricted open-shell or unrestricted orbitals can be employed in calculations, which may be run using full molecular symmetry, partial symmetry, or no symmetry. The program is fully self-initializing, and can be started from e.g. the core guess or the superposition of atomic potentials (SAP) [7]; the program can also calculate the radial potentials needed for SAP.

References

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