Accurate exact-exchange Kohn-Sham real space formalism

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Kohn-Sham density functional theory (KS-DFT) [1] is nowadays the most common and widely used computational method in physics, chemistry and materials science. There are many numerical packages employing the standard approximations to the DFT energy functionals available, based on the basis expansion of the Kohn-Sham (KS) wave functions like *VASP* [2] or *Quantum Espresso* [3]. An alternative way to determine K-S wave functions, is the solution of the Kohn-Sham equations on the real space grid. The advantage of the real space code over the other approaches (like VASP, QE codes) is much easier implementation on the computers of parallel architecture as well as the efficient treatment of the zero, one, and two-dimensional systems.

One of the aims of code development undertaken in our group is creation of the computational tool that could accurately describe carbon-based layered materials. This requires correct description of the van der Waals (vdW) interactions, which are not accounted for in the standard exchange-correlations functionals (such as LDA or GGA) of the KS-DFT implementations. The exact-exchange (EXX) KS-DFT with correlation energy calculated employing the random phase approximations (RPA) has proved to overcome many shortcomings of the standard KS-DFT approximations [4]. However, the EXX scheme is computationally demanding and requires large computational powers. Therefore, we have developed our own real space grid code implementing the EXX into KS real space method, in order to efficiently treat systems lacking periodicity in one, two or three dimensions, as well as accurately describe theirs properties.

In this communication, we present technical details of the implementation of a variational method of exact-exchange contribution [5] to the Kohn-Sham potential in a real-space version of the KS-DFT method with separable pseudo-potential. In order to check the efficiency (computational burden, CPU time) and the accuracy of our real space code with the other reciprocal space (i.e., plane-wave based) available codes (such as *VASP* or *QE)*, we examine the energetic properties and electronic structures of the representative systems exhibiting different periodicity, namely, 3D bulk systems - Si, Ge, and graphite; 2D systems - multi-layers of graphene, 1D systems – carbon nanotubes; and 0D systems - simple molecules C_2. Moreover, we calculate the energetic barriers of free standing single-, bi-, and multi-layer graphene in different stacking patterns and compare them with previously obtained results employing semiempirical vdW exchange correlations functionals [6]. In all of these cases we also examine the accuracy of the pseudopotential EXX scheme against the all-electron approach by performing calculations with the commercial all-electron code *FHI-aims* [7].

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