Electronic density and other physical properties in solids by plane-wave auxiliary-field quantum Monte Carlo

Siyuan Chen[1], Mario Motta[3], Fengjie Ma[4], and Shiwei Zhang[2,1]

[1] *Department of Physics, College of William & Mary, Williamsburg, VA, USA*

[2] *Center for Computational Quantum Physics, Flatiron Institute, New York, NY, USA*

[3] *Division of Chemistry, California Institute of Technology, Pasadena, CA, USA*

[4] *Department of Physics, Beijing Normal University, Beijing, China*

We present accurate electronic densities in the ionic crystal NaCl and the covalent-bond semiconductor Si. These results are obtained using ab initio auxiliary-field quantum Monte Carlo (AFQMC) method[1] working in a plane-wave basis with norm-conserving pseudopotentials. AFQMC has been shown to be an excellent many-body total energy method. Computation of observables and correlation functions other than the ground-state energy requires back-propagation[2], which we have implemented in this work in the plane-wave basis AFQMC framework. This development allows us to compute correlation functions, electronic densities and atomic forces, and paves the way for geometry optimization in solids. We analyze the convergence of the electronic density towards the thermodynamic limit; finite supercell size effects are considerably more subtle in many-body framework than in independent-electron calculations. The densities from several typical density functionals are benchmarked against our (near-exact) results. The electronic densities we have obtained can also be used to help construct improved density functionals.

[1] S. Zhang and H. Krakauer, *Phys. Rev. Lett.* **90**, 136401 (2003); M. Suewattana, W. Purwanto, S. Zhang, H. Krakauer, and E. J. Walter, *Phys. Rev. B* **75**, 245123 (2007)

[2] S. Zhang, J. Carlson, and J. E. Gubernatis, *Phys. Rev. B* **55**, 7464 (1997); M. Motta and S. Zhang, *J. Chem. Theory Comput.* **13**, 5367 (2017)