Projector Augmented Wave Formulation of Optimized Effective Potential Density Functional Theory – PAW-OEP[1]

Xiao Xu and N. A. W. Holzwarth

Department of Physics, Wake Forest University
Winston-Salem, NC, USA

The optimized effective potential (OEP) or exact exchange (EXX) formalism has recently received renewed attention as a method which can improve the accuracy of density functional theory with its ability to treat orbital-dependent functionals such as the Fock exchange and orbital-dependent correlation functionals.[2] Since the Projector Augmented Wave (PAW) formalism[3] enables an accurate treatment of the important multipole moments[4] as well as the core-valence contributions to the exchange interaction, it is a natural choice for implementing OEP within an efficient pseudopotential-like scheme. This poster presents a progress report on our PAW-OEP project. As a necessary first step, we have developed a frozen core approximation[5] to the all-electron OEP formalism, defining a valence optimized effective potential $V_x^{\rm vale}$. In assessing the accuracy for determining atomic excitation energies for elements across the periodic table, we find the frozen core errors to have a somewhat larger magnitude, and to depend differently on the atomic shell structure in comparison with density-dependent exchange-correlation functionals. The formalism for calculating $V_x^{\rm vale}$ can be directly adapted for use in the PAW method.

[1] Supported by NSF grant DMR-0705239.

[2] Stephan Kümmel and Leeor Kronik, *Rev. Mod. Phys.* **80**, 3 (2008).

[3] P. E. Blöchl, *Phys. Rev. B* **41**, 5414 (1990); A. R. Tackett and co-workers, *Comp. Phys. Comm.* **135**, 348 (2001).

[4] Joachim Paier and co-workers, *J. Chem. Phys.* **122**, 234102 (2005).

[5] U. von Barth and C. D. Gelatt, *Phys. Rev. B* **21**, 2222 (1980).