11th International Workshop on Computational Electronics
TU Wien, 25-27 May 2006

Beyond the Local Density Approximation

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Ab initio density functional theory calculations have been widely successful in many fields, including bulk semiconductors, semiconductor-insulator interfaces, and semiconductor surfaces. For the modeling of semiconductor devices, the well known underestimation of band gaps, however, remains a yet unsolved problem; in some cases, the band structures are even qualitatively wrong. This makes prediction of effective masses, impurity levels or band alignments often unreliable or even impossible. The incorrect prediction of band gaps also possibly deteriorates the description of the energetics of defects.

Several remedies to this problem have been suggested over the last 10 years. Hybrid functionals, that include a fixed fraction of the exact non-local exchange operator, hold the promise to yield both, an improved description of the energetics of defects, as well an improved description of their energy levels. The drawback of this approach is that it is computationally more demanding than traditional semi-local density functionals, but with the rapid advances in computer performance, this has become less of an issue. The availability in widely used DFT codes, however, has been limited as well, with efficient implementations becoming available only very recently[1], [2].

Another approach, known even before the foundations of density functional theory were laid, is the GW method[3]. In this approach, the non-local exchange interaction is dynamically screened by the electrons, requiring the calculation of the frequency dependent non-local dielectric matrix $\epsilon(\mathbf{r}, \mathbf{r}', \Omega)$. The method is generally even more demanding than the aforementioned hybrid functionals, but should yield accurate band gaps and transport properties across all materials, including metals and wide gap insulators. Its application has yet been limited to very small systems, one major drawback being that easy to use implementations were not available in standard DFT packages.

In the present lecture, hybrid functionals and the GW method will be briefly introduced and discussed. Systematic studies for a large variety of systems are presented (see Fig. 1 and Fig. 2). We show that the GW approximation indeed improves significantly upon DFT, but the often applied approximation that the GW wavefunctions equal the DFT groundstate wavefunctions— the so called G_0W_0 approximation —can give unsatisfactory results. A novel hybrid scheme merging non-local exchange functionals with GW inspired screening is presented and discussed. It allows predictive band gap engineering, even in those cases, where the other two approaches fail.

Particular attention will be given to two case studies. The lead chalcogenides pose a critical test to any electronic structure method. Their band gaps are small and follow an usual trend with PbS $>$ PbSe $\approx$ PbTe. We show that, in this case, hybrid functionals as well as GW can recover the correct trend, if spin orbit coupling is properly included.

The second case study concentrates on ZnO, where the precise properties of native point defects are still a question of debate. We concentrate on native electron donors, such as oxygen vacancies, and address the question of their precise electronic structure by performing large scale density functional calculations with up to 700 atoms, and hybrid density functional studies for medium sized systems with more than 100 atoms.

References

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ISBN 3-901578-16-1

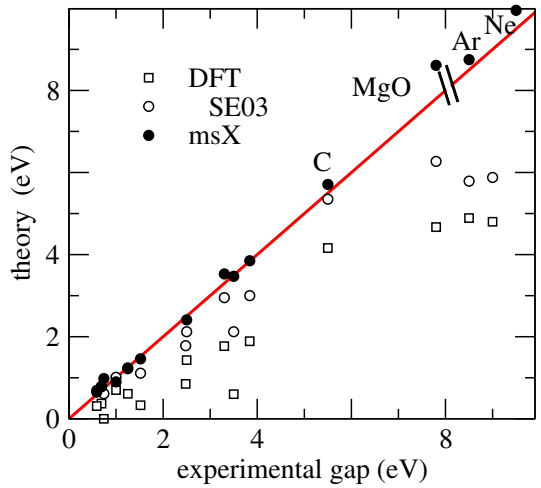

Fig. 1. Band gaps of 15 semiconductors and insulators using standard DFT, a hybrid functional with 25% non-local exchange (HSE03), and a G_0W_0 inspired model screened exchange (msX) approach

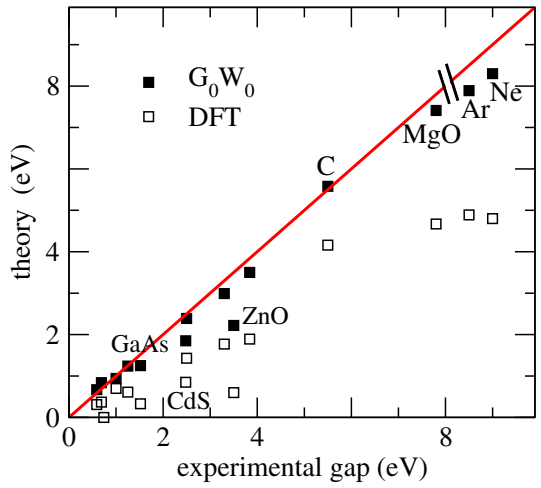

Fig. 2. Band gaps of 15 semiconductors and insulators using standard DFT and G_0W_0.