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An examination of exchange-correlation functionals in solid-state calculations

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[Introduction]

Density functional theory (DFT) raises the stakes in quantum chemistry in predicting and designing reactions and materials, because sophisticated exchange-correlation functionals have been developed for investigating large and complicated systems. However, conventional functionals represented by PBE have still been used in many solid state calculations, because these functionals tend to give even better band gaps for semi-conductors than those of sophisticated functionals with much less computational time. Kresse et al. actually suggested that LDA and GGA functionals slightly underestimate the band gaps of semi-conductors, while long-range corrected (LC) LDA functional significantly overestimate these band gaps.¹ However, note that LDA and GGA functionals always significantly underestimate the band gaps of insulators that are accurately reproduced by LC functionals. This appears to indicate that LC functionals lack something to give accurate band gap energies of semi-conductors and error cancellation causes the better band gaps for LDA and GGA functionals. In this study, we investigate the barrier gap energies of solids thoroughly by calculating them with various functionals, basis sets, and calculation models to make clear the reason for the band gap behaviors.

[Computational details]

The Kohn-Sham calculations of solid state properties are performed using DMol³ and the development version of Gaussian09 (G09), and Vienna Ab-initio Simulation Package (VASP) programs. DMol³ calculations are carried out using DNP (double numerical plus polarization) basis set with various types of functionals and 20×20×20 Monkhorst-Pack like *k*-point grids. To further extend this work to study the LC functionals, we also perform preliminary calculations using the development version of G09 program. Pure LDA and GGA calculations are performed using SVWN and SPW LDA, BOP, BLYP, BP, BP(VWN), PBE and PW91 GGA and semi-empirical HCTH exchange-correlation functionals. All the calculations on G09 program are performed using 6-31G and SDDALL basis sets. We also examine band calculations with plane wave basis set on the VASP program.

[Results and discussion]

Figure 1 displays the deviations of band gap energies calculated on DMol³ program from the experimentally-predicted values. As previously suggested, the figure shows that LDA and GGA functionals slightly underestimate band gap energies. However, we found that there are

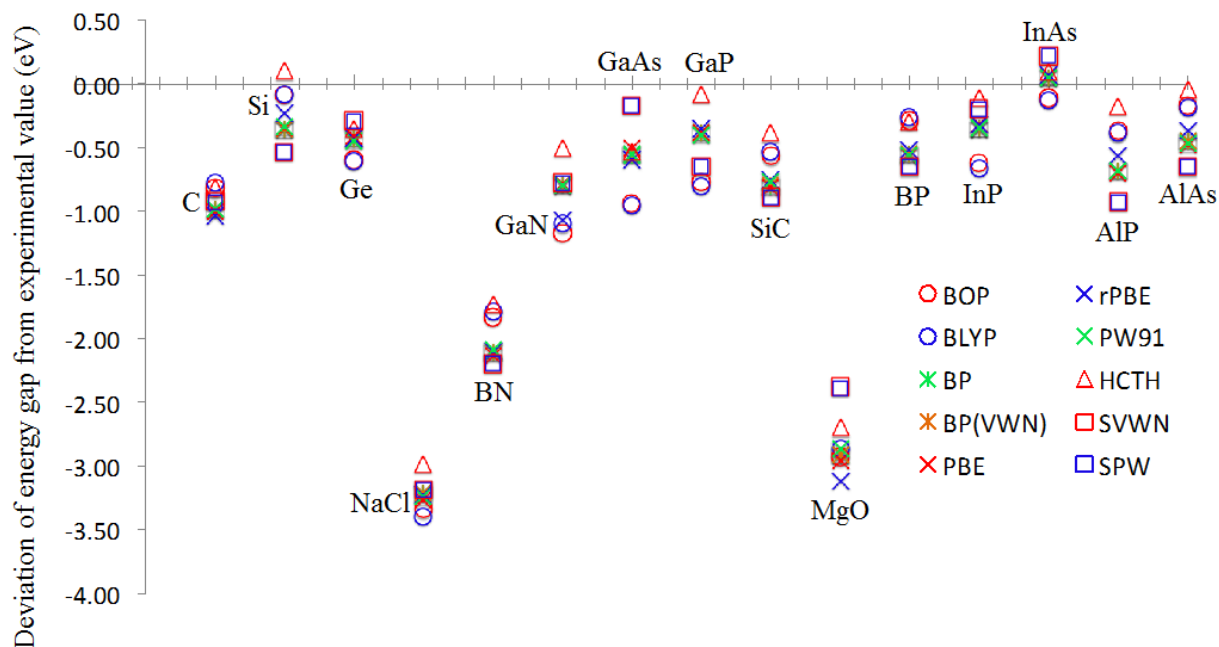


Fig. 1. The deviation of the band gap energies of various crystals calculated on Dmol³ in eV. systematic differences in the errors of the small band gaps for Ge and Sn crystals and Ga and In alloys: Functionals using PW91, PBE, and LDA correlation functionals provide better band gaps than others. The difference between them comes from exchange interactions, which are included as “parallel-spin correlation” in these correlation functionals.² That is, exchange interactions significantly affect band gap energies for near-degenerate bands. We therefore suppose that the near-degeneracy effects neglected in conventional functionals may be partly compensated by exchange interactions in LDA, PBE and PW91 correlation functionals, while these correlation functionals are usually used in band calculations. This result suggests the significance of near-degeneracy effects in solid state bands. We will further discuss the characteristics of band gap energies and other solid state properties in the presentation.

[References]

1. I. C. Gerber, J. G. Angyan, M. Marsman, and G. Kresse, J. Chem. Phys. 127, 054101, 2007.
2. 「密度汎関数法の基礎」常田貴夫著 (講談社) .