

AN ORBITAL DEPENDENT KOHN–SHAM POTENTIAL APPROACH TO THE SEMICONDUCTOR BAND GAP PROBLEM IMPLEMENTATION TO REAL SPACE PROJECTOR AUGMENTED WAVE CODE (GPAW)

M. KUISMA¹, J. OJANEN¹, J. ENKOVAARA² AND T. T. RANTALA¹

¹ Semiconductor Phys. Lab., Institute of Physics, Tampere University of Technology, P.O. Box 692 FIN-33101 Tampere, FINLAND

² CSC – Scientific Computing Ltd., P.O. Box 405, FI-02101, Espoo, FINLAND

INTRODUCTION

Conventional approximations for Kohn–Sham (KS) Density Functional Theory often yield good energetics. In the common approximative interpretation of KS-eigenvalues as quasiparticle energies, the KS-band gap E_g^{KS} remains generally too small.

The quasiparticle gap E_g^{QP} , relevant in comparison with experimental ionization energies (IP) and affinities, is obtained by adding the derivative discontinuity, that is

$$E_g^{QP} = E_g^{KS} + \Delta_{xc}, \quad (1)$$

where

$$\Delta_{xc} := \lim_{\alpha \rightarrow 0} \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \Big|_{\rho=\rho[N+\alpha](\mathbf{r})} - \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \Big|_{\rho=\rho[N](\mathbf{r})}. \quad (2)$$

OEP–EXX AND IT'S APPROXIMATIONS

The exchange potential can be obtained using the Optimized Effective Potential approach (OEP), or equivalently by indirect evaluation of the functional derivative $v_x = \frac{\delta E_x[\rho]}{\delta \rho(\mathbf{r})}$. In the KLI-approximation a model potential is used such that

$$v_x(\mathbf{r}) = v_{scr,x}(\mathbf{r}) + v_{resp,x}(\mathbf{r}) \quad (3)$$

$$\approx v_s(\mathbf{r}) + \sum_{i=1}^{N-1} w_i \frac{|\psi_i(\mathbf{r})|^2}{\rho(\mathbf{r})}, \quad (4)$$

where v_s is the Slater potential (called the screening part of exchange $v_{scr,x}$, the Coulomb potential due to the exchange hole) and the latter term is called the response part $v_{resp,x} \approx w_i \frac{|\psi_i|^2}{\rho}$. In the GLLB approach [1], v_s is approximated by GGA energy density by Becke, $v_{scr,x}(\mathbf{r}) \approx \frac{2c^{BSS}(\mathbf{r})}{\rho(\mathbf{r})}$ in order to increase effectiveness of computation. The response part is approximated by an eigenvalue dependent expression

$$v_{resp,x}(\mathbf{r}) \approx v_{resp,x}^{GLLB}(\mathbf{r}) := \sum_{i=1}^N K_G \sqrt{\epsilon_{ref} - \epsilon_i} \frac{|\psi_i(\mathbf{r})|^2}{\rho(\mathbf{r})}. \quad (5)$$

Due to the difference $\epsilon_{ref} - \epsilon_i$, where ϵ_{ref} is the HOMO-energy, the potential preserves the self interaction free $1/r$ asymptotic behaviour and potential gauge invariance. Due to $\sqrt{\cdot}$, it also fulfills the exchange only scaling relation. Finally, the coefficient K_G is derived to describe the homogenous electron gas limit correctly.

THE STEP IN POTENTIAL DUE TO THE DERIVATIVE DISCONTINUITY

The GLLB potential naturally includes a derivative discontinuity for non-metals, due to the change of HOMO reference on addition of an electron. The discontinuity has the form

$$\Delta_x^{GLLB}(\mathbf{r}) = \lim_{\alpha \rightarrow 0} v_x^{GLLB}(\mathbf{r}) \Big|_{\rho=\rho[N+\alpha]} - v_x^{GLLB}(\mathbf{r}) \Big|_{\rho=\rho[N]} \quad (6)$$

$$= \sum_{i=1}^N K_G (\sqrt{\epsilon_{N+1} - \epsilon_i} - \sqrt{\epsilon_N - \epsilon_i}) \frac{|\psi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \quad (7)$$

which, however, is not a constant function. To overcome this difficulty, we use first order perturbation theory to evaluate a step

$$\Delta_x^{GLLB} = \langle \psi_{N+1} | \Delta_x^{GLLB}(\mathbf{r}) | \psi_{N+1} \rangle. \quad (8)$$

Table 1: The HOMO eigenvalues of selected molecules (GPAW [2]).

| molecule | GLLB- v_s | GLLB-B88 | KLI* | -exp. IP |
|-------------------------------|-------------|----------|---------------|----------|
| H ₂ | -16.207 | -15.931 | -16.1805 (TM) | |
| LiH | - 8.842 | - 7.593 | - 8.19 | |
| CO | -12.117 | -12.242 | -14.85 | -14.01 |
| CH ₄ | -14.266 | -13.939 | -14.78 | -13.60 |
| C ₂ H ₄ | - 9.377 | - 9.206 | -10.28 | -10.68 |
| H ₂ O | -12.094 | -11.102 | -13.73 | |
| benzene | - 8.250 | - 8.280 | - 9.17 | |
| naphtalene | - 6.696 | - 6.854 | - 7.83 | |

* KLI values from JCP, 115, 5718

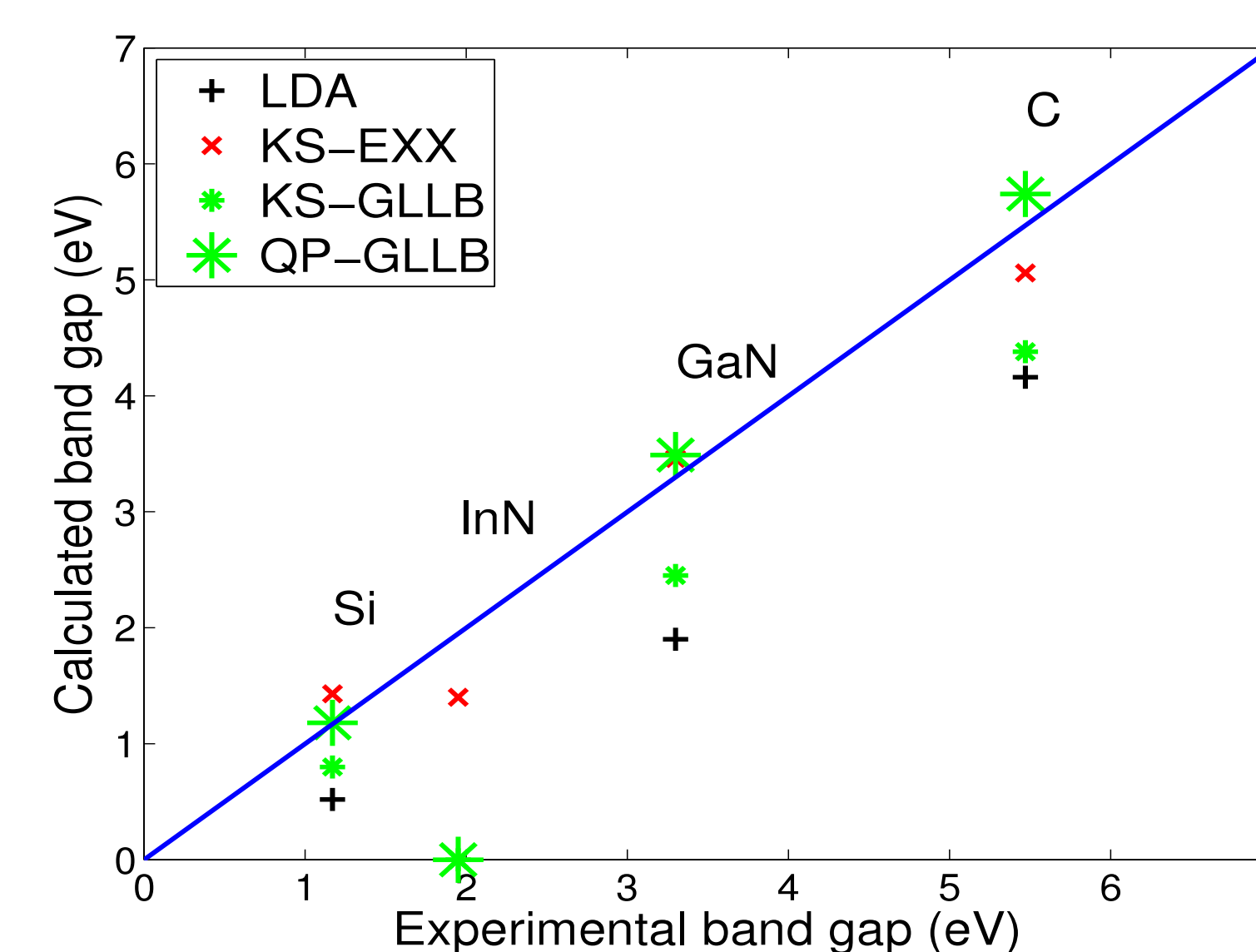


Figure 1: Calculated band gaps of selected semiconductors.

$\Delta_c?$
 $E_g^{GLLB+C}?$

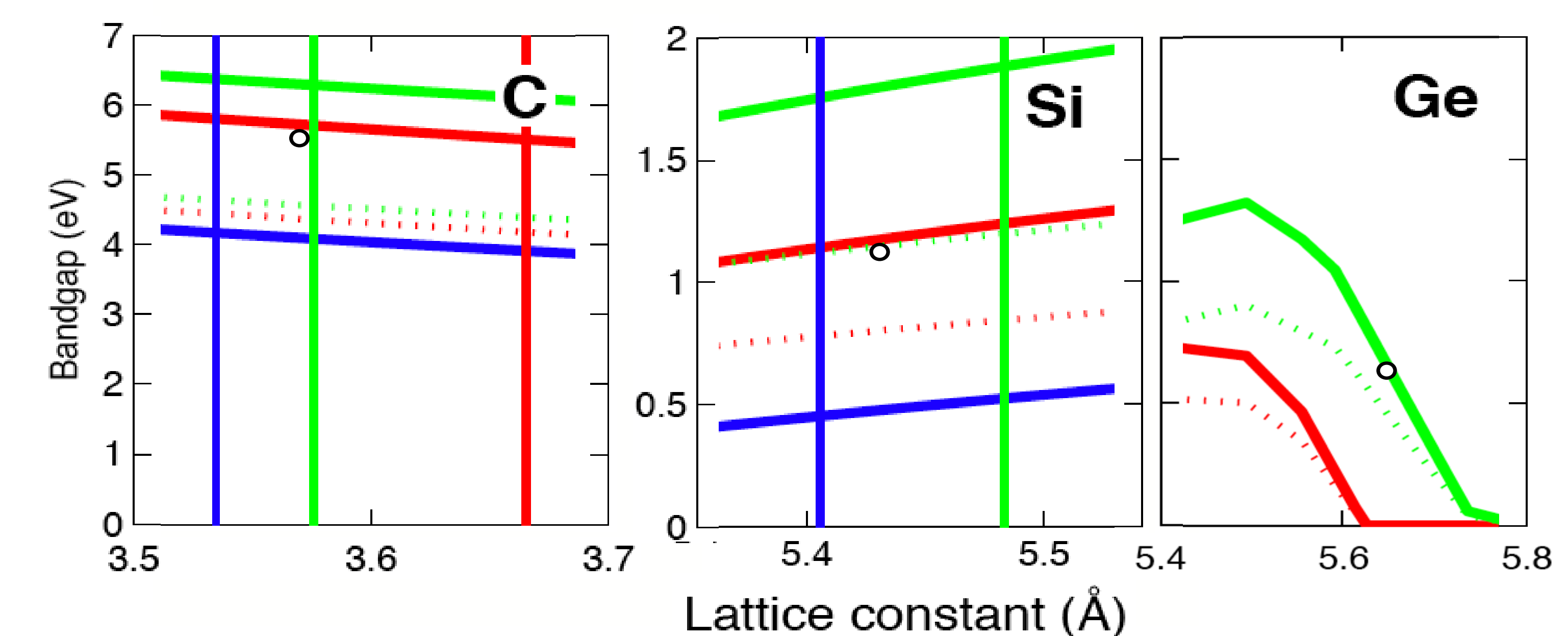


Figure 2: The lattice constant dependence of band gaps of elemental semiconductors. BLUE: LDA, RED: GLLB, GREEN: GLB, dashed: E_g^{KS} , solid: E_g^{QP} , vertical: energy minimum, black circle: exp.

CONCLUSION

In GLLB approximation, to be such a simple and computationally light method compared to $O(N^6)$ scaling GW approximation for example, E_g^{QP} is generally surprisingly close to the experimental results, although Germanium is still predicted to be a semimetal near the experimental lattice constant. This matching is also somewhat unexpected especially since GLLB is an X-only approximation.

Compared to correlated EXX + RPA – OEP scheme, GLLB potential seems to overestimate the KS-gap and underestimate the discontinuity. A compatible correlation should, therefore, correct this misbalance only.

REFERENCES

- [1] Gritsenko et al., Phys. Rev. A, 51, 1944 (1995).
- [2] Mortensen et al., Phys. Rev. B, 71, 035109 (2005).