Strain effects and band parameters in MgO, ZnO and CdO

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Supplementary Material

Convergence of G_0W_0 quasiparticle calculations. In 2010, Shih *et al.* claimed [1] that G_0W_0 calculations based on the local-density approximation (LDA) would give a bandgap of 3.4 eV for wurtzite ZnO and that all previous reports of a significantly lower bandgap around 2.4 eV [2–4] had been due to an underconvergence with respect to the number of unoccupied states included in the calculation of the G_0W_0 polarizability and the self-energy. Although it was later shown that the particular plasmon pole model of Shih *et al.*'s work was responsible for the larger bandgap [5], it remains true that the convergence with respect to the number of unoccupied states is much slower in ZnO [5, 6] than in, e.g., silicon [7].

Figure 1 shows the convergence of the G_0W_0@OEPx(cLDA) bandgap in wurtzite ZnO. The band convergence is indeed slow and the bandgap only converges when approximately as many unoccupied states are included as can be resolved with a plane wave cutoff of 35 Ha. We checked that increasing the plane-wave cutoff further does not change the final value, i.e. the bandgap is converged with respect to the plane-wave cutoff. The final G_0W_0@OEPx(cLDA) gap amounts to 3.26 eV and is noticeably larger and therefore closer to experiment than the G_0W_0@LDA gap of $\sim$2.4 eV [2–4]. The same convergence criteria were applied to the calculations for CdO and MgO.

Sensitivity to HSE parameters. Since the bandgaps calculated from HSE06 with default parameters for ZnO and MgO are somewhat different from those obtained with G_0W_0 and from experiment, we checked the sensitivity of the band parameters and deformation potentials to modifying the parameters in HSE06. We calculated the band parameters and deformation potentials with HSE06 using a modified mixing parameter α=0.36, which produces a bandgap of 3.41 eV at theoretical equilibrium lattice parameters. Band parameters of ZnO obtained with different mixing parameters are shown in Table I. The optimization of the mixing parameter for ZnO only slightly affects these parameters and the changes in band parameters are relatively small. Interestingly, HSE06 calculations with default mixing parameter (as reported in the paper) provide a better agreement with G_0W_0 results.

Table II shows the deformation potentials obtained by HSE06 with different mixing parameters. Although the mixing parameter α strongly changes the bandgap, it only slightly affects the deformation potentials for ZnO. The absolute changes in deformation potentials are within 0.3 eV, while the relative changes are within 10%.

Comparison of effective mass calculations. Overall, the effective masses obtained from our

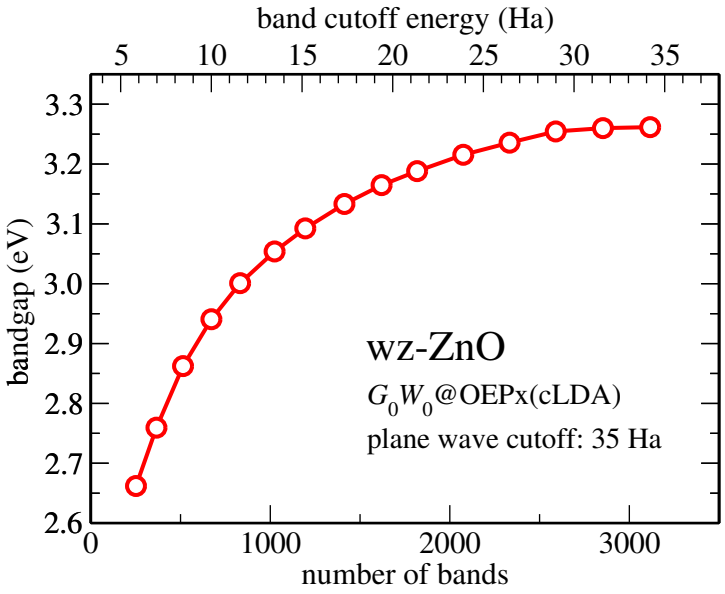

FIG. 1: Dependence of the G_0W_0@OEPx(cLDA) bandgap of wurtzite ZnO at the experimental lattice parameters on the number of unoccupied bands included in the calculation. The corresponding energy cutoff is given on the upper axis.

TABLE I: Luttinger parameters (A_7 is in eV Å, all others are dimensionless), transition matrix elements E_P (in eV), and effective masses of wurtzite ZnO at experimental lattice constants obtained with HSE06 approach with different mixing parameter α. Band parameters obtained by the G_0W_0@OEPx(cLDA) approach are also listed in the table.

param.	ZnO		
method	HSE06 (α=0.25)	HSE06 (α=0.36)	G_0W_0
A_1	−2.747	−2.633	−2.743
A_2	−0.386	−0.402	−0.393
A_3	2.386	2.255	2.377
A_4	−2.089	−1.829	−2.069
A_5	−2.059	−1.797	−2.051
A_6	−2.103	−1.863	−2.099
A_7	0.028	0.011	0.001
$E_P^{\parallel}$	12.443	12.834	13.042
$E_P^{\perp}$	9.658	9.906	9.604
$m_e^{\parallel}$	0.239	0.259	0.246
$m_e^{\perp}$	0.244	0.267	0.250
$m_{\Gamma 9}^{\parallel}$	2.769	2.641	2.732
$m_{\Gamma 9}^{\perp}$	0.404	0.448	0.406
$m_{\Gamma 7+v}^{\parallel}$	2.563	2.456	2.567
$m_{\Gamma 7+v}^{\perp}$	0.408	0.453	0.410
$m_{\Gamma 7-v}^{\parallel}$	0.368	0.384	0.368
$m_{\Gamma 7-v}^{\perp}$	2.434	2.351	2.417

TABLE II: Deformation potentials (in eV) of wurtzite ZnO obtained by HSE06 calculations with different mixing parameters.

Method	$a_{cz}-D_1$	$a_{ct}-D_2$	D_3	D_4	D_5	D_6
HSE06 (α=0.25)	-3.06	-2.46	0.47	-0.84	-1.21	-1.77
HSE06 (α=0.36)	-3.38	-2.67	0.54	-0.92	-1.22	-

G_0W_0@OEPx(cLDA) quasiparticle calculations are in good agreement with previous G_0W_0@HSE calculations by Schleife *et al.* [8] However, one noticeable difference exists. From our calculations, the effective masses for the conduction band of all three oxides are almost isotropic, while the effective masses in Ref. 8 exhibit distinct anisotropies (being larger along directions perpendicular to *c*-axis). We suggest that the difference is due to our use of a more sophisticated fitting scheme to obtain the effective masses from G_0W_0 band structures. First of all, we employ a higher density of data points along the relevant lines through the Brillouin zone (BZ). Second, we are fitting a $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian to the quasiparticle band structure along several lines through the BZ simultaneously, whereas in Ref. 8 the fitting (to second- or third-order polynomials) is performed along individual high symmetry lines near the Γ point.

We note that our calculations show that the band parameters and effective masses obtained by HSE06 and G_0W_0@OEPx(cLDA) agree very well with each other, providing further evidence that HSE06 is an accurate band structure method.

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