

# Strain influence on valence-band ordering and excitons in ZnO: An *ab initio* study

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Modern parameter-free methods to treat single- and two-particle electronic excitations are applied to compute the band structure and the lowest optical transitions of wurtzite ZnO under biaxial strain. The calculations are based on density functional theory with a spatially nonlocal exchange and correlation functional and include spin-orbit interaction. Quasiparticle shifts and excitonic effects are computed. In addition to the band parameters, also their dependence on biaxial strain and the ordering of the *A*, *B*, and *C* excitons are investigated. While the crystal-field splitting is very sensitive to strain, the spin-orbit splittings and the exciton binding energies remain unaffected.

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For more than 40 years the ordering of the crystal-field (CF) and spin-orbit coupling (SOC) split levels of the *p*-type states  $\Gamma_{9v}$ ,  $\Gamma_{7+v}$ , and  $\Gamma_{7-v}$  at the valence-band maximum in wurtzite ZnO has been subject of controversy (see Ref. 1 and references therein). Moreover, the corresponding optical transitions into the *s*-like  $\Gamma_{7c}$  conduction-band minimum are influenced by strong electron-hole interaction (see, e.g., Ref. 2). In recent years the situation became more confusing due to the fabrication of high-quality ZnO films on various substrates (see, e.g., Refs. 3 and 4) which show different energetic orderings of the  $A(\Gamma_{9v} \rightarrow \Gamma_{7c})$ ,  $B(\Gamma_{7+v} \rightarrow \Gamma_{7c})$ , and  $C(\Gamma_{7-v} \rightarrow \Gamma_{7c})$  excitons (we use this nomenclature also for large tensile biaxial strain). Contradictory spectroscopic fingerprints indicate positive or negative CF splittings as well as varying signs of the SOC.<sup>1,2</sup>

In principle, modern electronic-structure theory including quasiparticle (QP) effects<sup>5</sup> and electron-hole interaction<sup>6</sup> should be able to predict the relative energetic ordering of the optical transitions and the absolute transition energies.<sup>1,7</sup> One difficulty that arises for ZnO is the treatment of the shallow semicore Zn 3*d* electrons, whose binding energies are underestimated in all local and quasiloc approaches to density functional theory (DFT). Accordingly, due to the overestimated *pd* repulsion, the DFT gap underestimation is more pronounced.<sup>8</sup> The inclusion of spin-orbit interaction is also a challenge. In this letter, we compute the band structure and exciton parameters for biaxially strained ZnO in wurtzite structure without taking experimental parameters into account.

First, the structural calculations for the ground state are carried out within DFT as implemented in the VASP package<sup>9</sup> applying the generalized gradient approximation (GGA) for the exchange and correlation (XC) functional. The computational parameters are the same as described in Ref. 8. The shallow Zn 3*d* electrons are treated as valence electrons. To account for biaxial strain, we fix the lattice constant *a* at several values, whereas the lattice constant *c* and the internal cell parameter *u* are allowed to relax. The biaxial strain is then defined as  $\epsilon_b = \epsilon_{xx} = \epsilon_{yy} = (a - a_0)/a_0$  with  $a_0 = 3.283 \text{ \AA}$  as the theoretical lattice constant for the unstrained case. The

resulting strain in the *c*-axis direction is given by  $\epsilon_{zz} = -R^b \epsilon_b$  with  $R^b = 2C_{13}/C_{33}$ .<sup>10</sup> The elastic stiffness constants  $C_{13} = 94 \text{ GPa}$  and  $C_{33} = 202 \text{ GPa}$  are close to the experimental values  $C_{13} = 104.6 \text{ GPa}$  and  $C_{33} = 210.6 \text{ GPa}$ .<sup>11</sup> We compute a value of  $R^b = 0.929$  for the biaxial strain coefficient of ZnO. The biaxial stress is given by  $\sigma_b = \sigma_{xx} = \sigma_{yy} = Y \epsilon_b$  with the biaxial modulus  $Y = C_{11} + C_{12} - 2C_{13}^2/C_{33}$ . From the computed value  $C_{11} + C_{12} = 303 \text{ GPa}$ , we derive  $Y = 216 \text{ GPa}$ .

The electronic structure is calculated using a very recent implementation<sup>12</sup> of Hedin's GW approximation.<sup>5</sup> Starting from eigenvalues and eigenfunctions of the ground state DFT-GGA calculation and adding QP corrections computed in first-order perturbation theory is the standard approach, but it fails for ZnO (Refs. 13 and 14) because the perturbational treatment is not justified for this system. For that reason we apply the spatially nonlocal HSE03 XC functional,<sup>15</sup> whose eigenvalues are much closer to the QP ones than the DFT-GGA values, as an alternative starting point. We use a mesh of  $8 \times 8 \times 6$  Monkhorst-Pack (MP) *k*-points to sample the Brillouin zone (BZ), resulting in QP energies converged up to 10–20 meV. For the three states  $\Gamma_{1c}$ ,  $\Gamma_{5v}$ , and  $\Gamma_{1v}$  without SOC, the QP energies versus biaxial strain  $\epsilon_b$  are plotted in Fig. 1. The strain and stress coefficients in Table I are derived from the calculated strain dependences. For all energies and splittings  $X(\epsilon_b)$  we present the quantities  $X_0 = X(0)$ , their biaxial deformation potentials  $A = \partial X(\epsilon_b)/\partial \epsilon_b|_{\epsilon_b=0}$ , and the stress coefficients  $A' = A/Y$ .

Using the combination of HSE03 and GW (Ref. 14) yields a value for the strain-free fundamental gap of  $E_g^{\text{HSE03+GW}} = 3.21 \text{ eV}$  which is close to the experimental result of 3.4 eV.<sup>3</sup> The computed QP energies in Fig. 1 show an almost vanishing influence of strain on the energy difference  $\epsilon(\Gamma_{1c}) - \epsilon(\Gamma_{5v})$ . Accordingly, only a very small negative biaxial deformation potential of about  $-0.37 \text{ eV}$  is derived. This value is influenced by the nonlinear strain variation of the  $\Gamma_{1c}$  level (cf. Fig. 1). The situation is different for the CF splitting  $\Delta_1 = \epsilon(\Gamma_{5v}) - \epsilon(\Gamma_{1v})$ . It exhibits an almost linear decrease with the biaxial strain  $\epsilon_b$  with a positive value for vanishing strain. The absolute value of the CF splitting depends on the details of the calculation, namely, the treatment of XC. The crossing of  $\Gamma_{1v}$  and  $\Gamma_{5v}$  levels for small tensile strains is a consequence of the negative value of their relative

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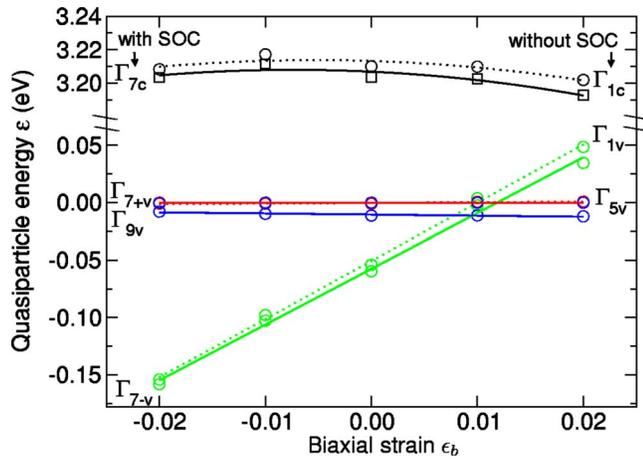


FIG. 1. (Color online) QP bands in the HSE03+GW approach at the  $\Gamma$  point without (dotted lines) and with (solid lines) spin-orbit interaction vs biaxial strain. The  $\Gamma_{5v}$  level (without SOC) and the  $\Gamma_{7+v}$  (with SOC) are taken as energy zero.

QP shift. For negative and zero strains, the situation is similar to that in GaN, whereas for positive strains, the CF splitting becomes negative as in AlN,<sup>10</sup> i.e., the levels  $\Gamma_{1v}$  and  $\Gamma_{5v}$  are exchanged. The strain-free CF splitting  $\Delta_1=54$  meV is slightly larger than those of experimental [30.5,<sup>2</sup> 38.3,<sup>16</sup> 39.4 meV (Ref. 17)] or other calculated [38 meV (Ref. 17)] values. The relatively large stress coefficient of  $-2.35$  meV/kbar of  $\Delta_1$  approaches the experimental value of  $-1.93$  meV/kbar.<sup>2</sup> For  $\varepsilon(\Gamma_{1c})-\varepsilon(\Gamma_{5v})$ , the strain/stress coefficients are smaller compared to the deformation potentials/pressure coefficients measured for hydrostatic pressure.<sup>17</sup>

Assuming only a small modification of the SOC due to the QP effects, we calculate these non-scalar relativistic effects on the DFT level. Apart from the change of the level denotation in the double-group representation, the most important effect of the SOC is the splitting of the degenerate  $\Gamma_{5v}$  state into  $\Gamma_{9v}$  and  $\Gamma_{7+v}$  levels. A symmetry analysis indicates that the uppermost state possesses  $\Gamma_{7+v}$  symmetry resulting in a level ordering  $\Gamma_{7+v}/\Gamma_{9v}/\Gamma_{7-v}$ , at least for not too large tensile biaxial strains (see Fig. 1). This picture seems to be in agreement with very early but also recent spectroscopic studies (see Refs. 1, 7, and 18) but is in contradiction to other recent experiments.<sup>2,4</sup> In contrast to the  $\Delta_1$ -dominated

TABLE I. Gap (in eV), energy splittings of valence bands, and exciton binding energies (in meV) at the equilibrium coordinates  $X_0$  as well as their linear biaxial strain  $A$  (in eV) and stress  $A'$  (in meV/kbar) coefficients.

Quantity	$X_0$	$A$	$A'$
$E_g = \varepsilon(\Gamma_{1c}) - \varepsilon(\Gamma_{5v})$	3.21	-0.37	-0.17
$\Delta_1 = \varepsilon(\Gamma_{5v}) - \varepsilon(\Gamma_{1v})$	54.0	-5.08	-2.35
$\varepsilon(\Gamma_{9v}) - \varepsilon(\Gamma_{7+v})$	-11.3	-0.07	-0.03
$\varepsilon(\Gamma_{9v}) - \varepsilon(\Gamma_{7-v})$	48.3	-5.09	-2.36
$\Delta_2$	-5.7	-0.04	-0.02
	(-5.2)	(-0.05)	(-0.02)
$\Delta_3$	$\approx 0.0$	$\approx 0.0$	$\approx 0.0$
	(-5.2)	(-0.05)	(-0.02)
$E_B(A)$	59.3	-0.44	-0.20
$E_B(B)$	60.1	-0.36	-0.17
$E_B(C)$	63.4	-0.61	-0.28

$\varepsilon(\Gamma_{9v}) - \varepsilon(\Gamma_{7-v})$  splitting, the SOC-induced splitting of the levels  $\varepsilon(\Gamma_{7+v}) - \varepsilon(\Gamma_{9v})$  in Fig. 1 and Table I as well as its biaxial strain or stress dependence remain relatively small. The sign of the splitting indicates a negative SOC constant.

From  $\mathbf{k} \cdot \mathbf{p}$  theory,<sup>19</sup> one finds for the energy differences of valence levels in a wurtzite crystal

$$\varepsilon(\Gamma_{9v}) - \varepsilon(\Gamma_{7+v}) = \frac{1}{2} [(\Delta_1 + 3\Delta_2) \mp \sqrt{(\Delta_1 - \Delta_2)^2 + 8\Delta_3^2}] \quad (1)$$

with the two spin-orbit splitting parameters  $\Delta_2$  and  $\Delta_3$ . The values for  $\Delta_1$  from the calculation without SOC are almost in agreement with the average distance  $\frac{1}{2}[\varepsilon(\Gamma_{7+v}) + \varepsilon(\Gamma_{9v})] - \varepsilon(\Gamma_{7-v})$  between the valence levels. The use of this relation for  $\Delta_1$  is equivalent to vanishing SOC matrix elements between the  $p_z$  state and the states perpendicular to the  $c$  axis,  $\Delta_3 \equiv 0$ . This results in a small spin-orbit interaction  $\Delta_2 = -5.7$  meV for  $\varepsilon_b = 0$  and a weak strain/stress variation (cf. Table I). We compare this approach with the quasicubic approximation, i.e.,  $\Delta_2 = \Delta_3$ . The resulting values are quite similar and are given in brackets in Table I. The predicted small splitting of  $\Delta_2$  is in rough agreement with a value computed with a local XC potential.<sup>1</sup> As a consequence of the inverted valence-band ordering the sign of  $\Delta_2$  differs from that in Ref. 2, while we find almost agreement with other measured values of  $\Delta_2 = -2.1$  meV ( $\Delta_3 = -9.1$  meV) (Ref. 16) and  $\Delta_2 = \Delta_3 = -3.5$  meV.<sup>17</sup> The linear strain and stress coefficients of  $\Delta_2$  match the experimental values measured for hydrostatic pressure in Ref. 17 concerning the order of magnitude but disagree with the values given in Ref. 2.

In the last step, we calculate optical transitions including the screened electron-hole attraction and unscreened electron-hole exchange interaction to account for excitonic and local-field effects.<sup>6,7</sup> To this end the eigenvalue problem of the electron-hole pair Hamiltonian is solved.<sup>20</sup> The main difficulty to obtain converged results for the lowest exciton states belonging to the band edges shown in Fig. 1 is the  $\mathbf{k}$ -point convergence. By using an inhomogeneous  $\mathbf{k}$ -point mesh, we improve the convergence without increasing the size of the electron-hole pair Hamiltonian. As the strongest contributions to the bound excitons are expected from the inner region of the BZ around  $\Gamma$ , this region is sampled with a higher density corresponding to 31 000  $\mathbf{k}$ -points in the full BZ. The computation of the wave functions and eigenvalues of the HSE03 problem at the resulting 3064  $\mathbf{k}$ -points is impossible for computer-time reasons. Therefore, we use the GGA+ $U$  method with  $U=6.5$  eV to generate eigenvalues and eigenfunctions<sup>7</sup> and obtain a band structure which is within several 10 meV similar to the HSE03+GW band structure regarding  $d$ -band positions and valence-band ordering. The static electronic dielectric constants  $\varepsilon_\infty$  in random-phase approximation which enter the expression for the electron-hole attraction are strain dependent. Neglecting the very small polarization anisotropy, we find a linear increase from  $\varepsilon_\infty = 4.29$  ( $\varepsilon_b = -0.02$ ) to  $\varepsilon_\infty = 4.49$  ( $\varepsilon_b = 0.02$ ). Spin-orbit shifts are obtained as differences of GGA+ $U$  eigenvalues from two calculations with and without SOC and incorporated into the QP shifts to take the correct valence-band structure into account within perturbation theory.

The optical transitions between the bands in Fig. 1 lead to excitons with symmetries according to  $\Gamma_7 \times \Gamma_9 \rightarrow \Gamma_5 + \Gamma_6$  and  $\Gamma_7 \times \Gamma_7 \rightarrow \Gamma_5 + \Gamma_1 + \Gamma_2$ . We focus our attention on the

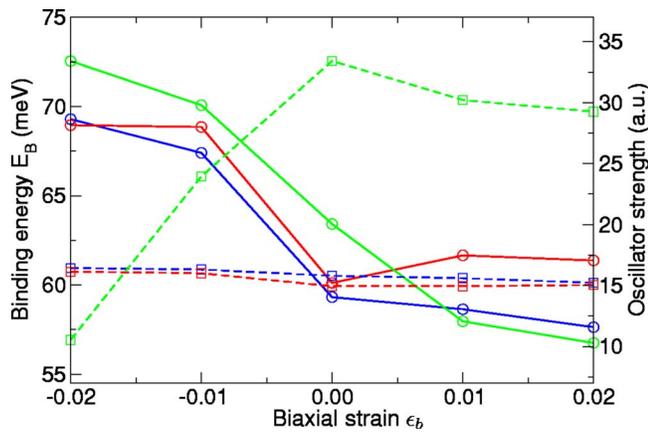


FIG. 2. (Color online) Binding energies (solid lines, circles) and oscillator strengths (dashed lines, squares) vs biaxial strain of A (blue), B (red), and C (green) excitons.

dipole-allowed  $\Gamma_5$  and  $\Gamma_1$  excitons. The  $\Gamma_5$  exciton mainly derived from  $\Gamma_{9v} \rightarrow \Gamma_{7c}$  ( $\Gamma_{7+} \rightarrow \Gamma_{7c}$ ) transitions is called A(B) exciton. It is allowed for light polarized perpendicular to the  $c$  axis. The  $\Gamma_1$  or C exciton is mainly derived from  $\Gamma_{7-v} \rightarrow \Gamma_{7c}$  transitions and is allowed for light polarization parallel to the  $c$  axis. We measure the exciton binding energies  $E_B(A)$ ,  $E_B(B)$ , and  $E_B(C)$  with respect to the corresponding noninteracting electron-hole pair energy and not with respect to the fundamental gap.

The computed exciton binding energies in Fig. 2 and Table I are in excellent agreement with the experimental values of about 60 meV.<sup>3,4</sup> The binding energies for the A, B, and C excitons are rather similar. Figure 2 also shows a clear strain dependence for the binding energies and oscillator strengths. In general, one observes a trend for decreasing binding energies from compressive to tensile strains. The linear strain and stress coefficients are very small and negative for the A, B, and C excitons. The strongest strain-induced variation of the oscillator strengths is the increase with positive strain which we observe for the C exciton. The strengths of the A and B excitons remain uninfluenced by strain. For vanishing and compressive strain, we predict a clear energetic ordering B, A, and C but with energetically close B and A excitons. The energy distance between A and B remains almost uninfluenced. However, for tensile strain the C

exciton may have the smallest pair excitation energy. This is a consequence of the change of the valence-band ordering from  $\Gamma_7-\Gamma_9-\Gamma_7$  ( $\Gamma_5-\Gamma_1$  without SOC) to  $\Gamma_7-\Gamma_7-\Gamma_9$  ( $\Gamma_1-\Gamma_5$  without SOC) with increasing strain. Our findings may give an explanation of the contradictory experimental findings.<sup>1-4</sup> The actual band ordering may be governed by the residual (biaxial) strain in the studied sample.

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