In this paper, we use high-resolution ARPES of ZnO (0001) together with resonant photoemission as a test of theoretical treatments for ZnO. We show that GW calculations based on GGA, GGA+ U, and HSE wave functions exhibit similar too-high (overestimation) Zn d-

functional without further corrections due to quasiparticle energy shifts can be expected only if these shifts vanish for the respective functional.

III. RESULTS AND DISCUSSION

A comparison of theoretical and experimental band structure of ZnO is shown in Fig. 1. The arrows in Fig. 1(a) depict the sliced directions in the Γ-M-K plane where the measurements were taken, and the constant-energy contour plot in Fig. 1(b) exhibits hexagonal symmetry, reflecting the hexagonal Brillouin zone of wurtzite ZnO. The VBM is located at the binding energy $E_B = -3.45$ eV, and the Fermi level is approximately located near the bottom of conduction band due to our n-type Ga-doped ZnO. The valence bands observed in the Γ-K-M and Γ-M-Γ directions are highly dispersive, as can be seen in Figs. 1(c)–1(f). The ZnO valence band structure can be partitioned into three segments: (i) the O-p bands at -3.5 eV $< E_B < -7.5$ eV, (ii) the Zn-s/O-p band at -7.5 eV $< E_B < -9.5$ eV, which is formed due to hybridization between the empty s states of the Zn^{2+} cation and the occupied p states of the O^{2-} anion, and (iii) the Zn-d bands at -10 eV $< E_B < -12$ eV. The positions of O-p- and Zn-d bands are confirmed experimentally by resonant photoemission (see Supplemental Material, Fig. S1[41]) of O-p states.

Our results are in good agreement with previously reported work[8] for the O-p bands. However, here, we use an ultraviolet

FIG. 1. (Color online) k scans in hexagonal plane of the ZnO Brillouin zone and comparison between experimental and theoretical band structure. A photon energy of 135 eV is chosen to study the Γ-M-K basal plane. (a) The Γ-M-K plane and (b) its constant-energy contour plot of the photoemission intensity. The red lines denote Brillouin zone boundaries, and the dashed blue lines are connectors to the Γ points. The arrows indicate the sliced directions measured. (c) and (d) Comparison between experimental band structure (gray scale) and theoretical band structure within the GW(GGA) scheme. The origin of energy is chosen at the conduction band minimum. The red lines represent O-p bands, the green lines hybridized Zn-O-p bands, and the blue line Zn-d bands. It can be seen that the Zn-d band is too high, and there is overlap between Zn-O-p and Zn-d bands. (e) and (f) Comparison between experimental band structure (gray scale) and theoretical band structure within the GW$_d$(GGA + U) scheme. The Zn-d band is no longer too high, and the Zn-O-p and Zn-d bands do not overlap. The horizontal dashed line indicates VBM energy. All the experimental band structures (energy distribution curves) shown here are second derivatives.

TABLE I. Comparison of different computational schemes of DFT and GW for ZnO. The initial DFT wave functions are calculated using the GGA, GGA+ U, or HSE functionals. The GW + V_d with GGA + U input scheme is used as a reference [cf. Figs. 1(e) and 1(f)]. Here, E_{VBM} is the GW quasiparticle energy shift with respect to the single-particle energies of the respective initial DFT functional. The experimental band gap for ZnO is 3.44 eV[12] and d band position (Fig. 1) is Š 7.50 eV.

	E_g(DFT)	E_g(GW)	E_{VBM}	d band position from VBM
GW + V_d(GGA + U)	1.52	3.30	Š 0.99	Š 7.45
GW(GGA)	0.80	2.92	Š 1.42	Š 6.26
GW(GGA+ U)	1.52	2.94	Š 0.63	Š 6.33
GW(HSE)	3.46	3.22	+ 0.70	Š 6.21

shows the band structures for GGA, GGA+U, and HSE, and for each case the resulting GW(DFT) band structures. The GW + V_d(GGA + U) result is shown here only as a reference for the experimental band energies [Figs. 1(e) and 1(f)]. There are several important observations: (1) The band energies in GW are overestimated by a similar amount for all three initial Hamiltonians. Also, the trend of an underestimated GW band gap exists for all three DFT functionals, which can be interpreted as due to the d repulsion shifting the VBM upwards. (2) In the GGA calculation, the Zn-d bands are located at a very high energy and overlap with the Zn-s/O-p band causing a spurious rr 0 TD -0.0004 Tc (bands)Tj -22.2675 -1.15 TD -0.00s TD -081o4idiz0 TD 354.65 0.As22.26

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[41] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.86.235113 for Fig. S1. Resonant photoemission of O-p states at . The intensity modulation observed at $-3.5\ \text{eV} < E_B < -7\ \text{eV}$ (relative to conduction band minimum) confirmed the O-p character. In addition, the relatively high intensity as well as the lack of intensity modulation at $-10\ \text{eV} < E_B < -12\ \text{eV}$ imply Zn-d character.
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