Comment on "Distinction of Electron Dispersion in Time-Resolved Photoemission Spectroscopy"

In Ref. [1], it is proposed to relate the interferometric photoemission delay to the photoelectron (PE) transport time, based on the PE phase ξ and effective mass $m_{\rm eff}$. Generally, the concept of effective mass is applicable neither to the PE transport in crystals nor to the PE interaction with light. While formally $m_{\rm eff}$ can be defined for any bulk Bloch state [2], for the PE it is undefined when (i) the PE energy lies in a $\mathbf{k}_\parallel$-projected gap, so the outgoing wave $\Psi_{\rm PE}$ contains no propagating waves (real $k_\perp$); (ii) several propagating Bloch states contribute comparably to $\Psi_{\rm PE}$; (iii) the PE mean free path (MFP) is small enough so the weight of the evanescent waves (complex $k_\perp$) [3] in the surface region is comparable to that of the propagating wave(s). The ubiquity of the gaps and the multi-Bloch-wave character of $\Psi_{\rm PE}$ are well documented for a variety of materials [4–11].

These essential features are not allowed for in the basic Eq. (1) of Ref. [1], which depends on the ratio between energy-dependent $m_{\rm eff}$. In cases (i)–(iii) Eq. (1) becomes inapplicable because either $m_{\rm eff}$ is undefined or PE is characterized by more than one $m_{\rm eff}$. This is characteristic of all real solids, as illustrated for Mg in Fig. 1(a) by the complex band structure (CBS) [3] responsible for photoemission [4]: The role of each Bloch wave is characterized by its contribution to the time-reversed LEED state $\Phi^*_{\rm LEED}$ (low energy electron diffraction). We consider the setup of Ref. [1]: $\hbar\omega_{\rm IR} = 1.6$ eV, $2q = 50$, and $2p$ initial states at -50 eV. The $2q+1$ final state (31.6 eV) consists of two propagating waves, while the $2q-1$ state (28.4 eV) comprises only one. However, for 28.4 eV, down to a depth of 15 a.u. the evanescent waves [12] strongly contribute to $\Psi_{\rm PE}$, as is evident from the density profile of $\Phi^*_{\rm LEED}$ in Fig. 1(c). The depth of 15 a.u. is larger than the MFP, so the evanescent waves are important both in the PE transport and in forming the sidebands. Thus, even though there is only one real $k_\perp$, an effective mass cannot be ascribed to such wave. Furthermore, the strong admixture of the evanescent waves makes the notion of a *time delay per lattice constant* $\delta\tau_{a_s}$ inapplicable and Eqs. (7) and (8) meaningless.

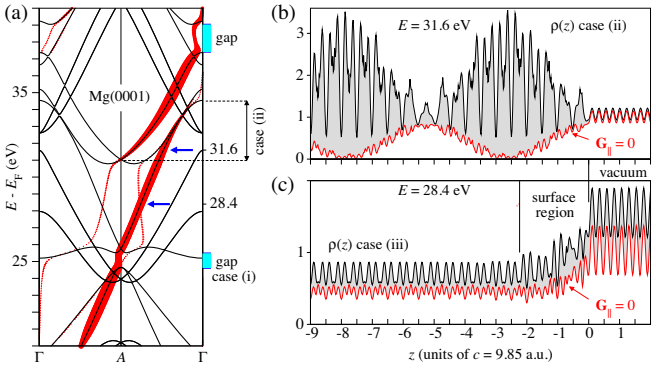

FIG. 1. (a) Band structure of Mg along $\Gamma A\Gamma$ (black lines) and conducting CBS (red): dispersion $\mathrm{Re}\,k_\perp(E)$ of $\Phi^*_{\rm LEED}$ constituents [8] for absorbing potential $V_{\rm i} = 0.2$ eV. Thickness shows flux carried by the Bloch wave [10]. Arrows show the $2q \pm 1$ energies. (b),(c) Density $\rho(z)$ of $\Phi^*_{\rm LEED}$ (with $V_{\rm i} = 0$) for $2q+1$ (b) and $2q-1$ (c): full density (black) and the $\mathbf{G}_\parallel = 0$ contribution (red). Gray area shows the $\mathbf{G}_\parallel \neq 0$ contribution.

Now consider the hypothetical case when $\Psi_{\rm PE}$ is a Bloch wave: $\Psi_{\rm PE} = \sum_{\mathbf{G}_\parallel} \psi^{k_\perp}_{\mathbf{G}_\parallel}(z)\exp(i\mathbf{G}_\parallel\mathbf{r}_\parallel)$, $\mathbf{G}_\parallel$ being surface reciprocal lattice vectors. Equation (2) of Ref. [1] assumes that a propagation phase $\xi = k\Delta z$ can be introduced for $\Psi_{\rm PE}(\mathbf{r})$. This is justified only if one $\mathbf{G}_\parallel$-harmonic dominates $\Psi_{\rm PE}(\mathbf{r})$. In reality, this is almost never the case, as illustrated in Figs. 1(b) and 1(c): The weight of $\mathbf{G}_\parallel \neq 0$ waves is comparable to (and often larger than) that of the $\mathbf{G}_\parallel = 0$ component. Because each $\mathbf{G}_\parallel$ wave acquires its own phase ξ the propagation phase is ill defined for a Bloch wave.

Thus, the conclusion that "interferometric spectroscopy addresses the material-dependent change of PE phase velocities" [1] contradicts the well-documented multi-plane-wave nature of Bloch states, and the notion of effective mass conflicts both with the multi-Bloch-wave structure of $\Psi_{\rm PE}$ and with the surface sensitivity of photoemission. The concepts of PE phase and effective mass are plausible for one-dimensional models but are inapplicable to real solids, which makes the method to extract photoemission delays based on Eq. (1) unreliable.

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