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

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In a recent paper [Phys. Rev. Lett. 125, 043201 (2020)] (Ref. 1) Liao et al. propose a theory of the interferometric photoemission delay based on the concepts of the photoelectron phase and photoelectron effective mass. The present comment discusses the applicability and limitations of the proposed approach based on an ab initio analysis supported by vast literature. Two central assumptions of the paper are questioned, namely that the photoelectron can be characterized by a phase (have a well-defined phase velocity), and that it can always be ascribed an effective mass. Theories based on these assumptions are concluded to be inapplicable to real solids, which is illustrated by the example of the system addressed in Ref. 1. That the basic assumptions of the theory are never fulfilled in nature discredits the underlying idea of the “time-domain interferometric solid-state energy-momentum-dispersion imaging method” suggested in Ref. 1. Apart from providing a necessary caution to experimentalists, the present comment also gives an insight into the photoelectron wave function and points out problems and pitfalls inherent in modeling real crystals.

Critical notes on the use of the concepts of the effective mass and propagating phase in photoemission from solids

In Ref. [1], it is proposed to relate the interferometric photoemission delay to the photoelectron (PE) transport time, based on the PE phase $\xi$ and effective mass $m_{\text{eff}}$. Generally, the concept of effective mass is applicable neither to the PE transport in real solids nor to the PE interaction with light. While formally the effective mass tensor $m_{\text{eff}}$ can be defined for any bulk Bloch state, for the PE it is undefined in the following cases: (i) When the PE energy lies in a bulk gap, so the outgoing wave $\Psi_{\text{pe}}$ contains no propagating waves. (ii) When several propagating Bloch states contribute comparably to $\Psi_{\text{pe}}$. (iii) When the PE mean free path (MFP) is small enough so the weight of the evanescent waves (complex Bloch vector $k_\perp$) in the surface region relevant for photoemission is comparable to that of the propagating wave(s) (real $k_\parallel$). The ubiquity of the $k_\|\$-projected gaps and the multi-Bloch-wave character of $\Psi_{\text{pe}}$ is well documented for simple [3–6], noble and d-metals [7, 8], layered dichalcogenides [9, 10], etc. (see illustration in Fig. 1).

These fundamental and essential features are not allowed for in the basic Eq. (1) of Ref. [1], which depends on the ratio “between the effective energy-dependent PE masses” in the cases (i)–(iii) this equation becomes inapplicable because either $m_{\text{eff}}$ is undefined or PE is characterized by more than one $m_{\text{eff}}$. This is characteristic of all real solids, as illustrated for Mg in Fig. 1(a) by the complex band structure (CBS) [11] responsible for the PE transport. The role of each Bloch wave in photoemission is characterized by its contribution to the time-reversed LEED state $\Phi_{\text{LEED}}^*$ (low energy electron diffraction) [3]. We consider the same material (see Ref. 12 for a detailed study of photoemission from Mg up to photon energies of 320 eV) and parameters as in Ref. [1]: $\hbar\omega_{\text{ph}} = 1.6$ eV, $2q = 50$, and $2p$ initial states of $50$ eV binding energy. 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 at least three atomic layers ($15$ a.u.) the genuinely evanescent waves [13] generated by the surface [14] strongly contribute to $\Psi_{\text{pe}}$, as is evident from the density profile of $\Phi_{\text{LEED}}^*$ 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 optical transitions 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 $\delta \tau_{\text{as}}$ accumulated by PEs traveling over one lattice constant” inapplicable and Eqs. (7) and (8) of Ref. [1] meaningless.

Let us now imagine a situation when neither of the obstacles (i)–(iii) occurs, and the outgoing wave in the crystal is a single Bloch wave:

$$\Psi_{\text{pe}}(r) = \sum_{G_\|} \sum_g \psi_{G_\|g} \exp \left[i(k_\perp + g)z + iG_\|r\|\right]. \quad (1)$$

Here $g$ are surface-normal and $G_\|$ are surface-parallel reciprocal lattice vectors. The theory of Ref. [1] assumes that a propagation phase $\xi = k_\Delta z$ can be introduced for the PE wave [Eq. (2) of Ref. [1]]. This assumption is justified only if one of the plane waves $\{g, G_\|\}$ dominates the expansion (1). In reality, this is almost never the case,
FIG. 1. (a) Black lines: real band structure of Mg along ΓAΓ. Red: conducting CBS given by the dispersion Re \( k_\perp(E) \) of \( \Phi_{leed} \) constituents. Line thickness is proportional to the flux carried by the respective Bloch wave [9]. LEED is calculated for absorbing potential \( V_i = 0.2 \) eV [7]. Arrows show the \( 2q \pm 1 \) final states. (b), (c) Density profile \( \rho(z) \) of \( \Phi_{leed} \) (with \( V_i = 0 \)) for \( 2q + 1 \) (b) and \( 2q - 1 \) (c): full density (black) and single-plane-wave \( G_{\parallel} = 0 \) contribution (red). Gray area shows the contribution from the surface harmonics \( G_{\parallel} \neq 0 \).

see, e.g., the density profiles in Figs. 1(b) and 1(c): The weight of \( G_{\parallel} \neq 0 \) waves is of the same order as (and often larger than) the weight of the \( G_{\parallel} = 0 \) component. Thus, because each of the \( G_{\parallel} \) waves acquires its own phase \( \xi \), the propagation phase is ill-defined for a Bloch wave.

The conclusion of Ref. [1] that “interferometric spectroscopy addresses the material-dependent change of PE phase velocities inside the solids” contradicts the well-documented multi-plane-wave nature of the Bloch states, and the notion of effective mass conflicts both with the multi-Bloch-wave structure of the PE and with the surface sensitivity of photoemission. The concepts of PE phase and effective mass, which are plausible for one-dimensional models, turn out to be inapplicable to real solids, which makes the method to extract photoemission delays based on Eq. (1) of Ref. [1] unreliable.

Addendum: Critique of the Authors’ Response

A shorter version of this note has been published as a Comment [15]. For the benefit of the reader, we quote the main points of the Authors’ Response [16] to the Comment.

- Ref. 16: “... case (i) is irrelevant since the absence of “propagating waves” in direction normal to the surface prohibits electron emission.”

In fact, electron emission in the absence of propagating waves is not prohibited. This is known since early days of photoelectron spectroscopy [17] and is referred to as “band gap emission”. It is well-documented experimentally [18] and is discussed in classical textbooks [19, 20]: “it is a matter of common experience that EDCs in the UPS regime are also observed when the final state is in the gap.”—Hüfner 2003 [20], p. 383.

- Ref. 16: “With regard to case (ii), we point out that...
Electronic, not energetic, waves are specified by their momentum (vector), not energy. Should several propagating Bloch states with the same energy contribute, they must have different momenta, both inside and outside the solid, and thus do not contribute to the same outgoing wave. Such superpositions can be disentangled in time- and angle-resolved photoemission spectra.

This statement is incorrect. No experiment can distinguish between photoelectrons excited into different Bloch waves at the same energy and same momentum. This is especially obvious in the one-step theory of photoemission, in which the final state is represented by the time-reversed LEED state [3, 17, 21, 22], so the photoemission matrix element is a coherent sum of the contributions from different Bloch waves, see a typical example in Fig. 2 below. This gives rise to an interference between transitions to different Bloch waves, and the respective interference terms have been thoroughly studied in Ref. [9]. The presence of the interference terms makes it principally impossible to “disentangle” the individual contributions in angle-resolved photoemission spectra.

Apart from the general criticism above, we have to point out a serious error in the response by Liao et al.: They claim that different propagating Bloch states must have different momenta also outside the solid. Obviously, the wave that is defined both inside and outside the solid is not a Bloch wave, and the momentum outside the solid is uniquely determined by the kinetic energy and the emission direction.

- **Ref. 16:** “In case (iii), the damped amplitude of the evanescent wave does not directly influence the phase accumulation during propagation.”

This is not an answer to the case (iii) remark. Case (iii) is illustrated in Fig. 1(c), and it concerns the issue of effective mass rather than phase accumulation. Case (iii) is a generalization of case (ii), the difference being that in case (ii) there are several propagating waves, and in case (iii) there may be one propagating and many evanescent waves. For photoemission, propagating and evanescent waves are equally important, so there is no physical difference between the two cases. However, while case (ii) can be excluded at some energies, case (iii) should be taken into account at every energy, see the detailed discussions in Refs. [14, 23, 24].

- **Ref. 16:** “... photoelectron transport in the solid target while, to our knowledge, photoelectron transport times have not been clearly related to the directly observable phase (difference) information. Equation (1) in Ref. [1] provides this missing link based on the decisively different effect of photoelectron energy-momentum dispersion on the active electron’s phase and group velocity.”

It is exactly the validity of the concept of wave phase in application to photoelectron transport that we question in our Comment, in particular, the relevance of Eq. (1) in Ref. [1]. The authors made no attempt to respond to our criticism that the propagation phase is ill-defined for a Bloch wave.

- **Ref. 16:** “Clearly, the degree to which predictions from one-dimensional models and Eq. (1) in Ref. [1] are applicable to real (strong-field dressed three-dimensional solids) remains to be seen.”

It is not clear how the theory of Ref. [1] can make predictions for specific materials, but this is not our point. Whatever remains to be seen, ignoring the limitations of the model and using the concepts of effective mass and wave phase in cases when they are undefined are essential flaws of the theory.

- **Ref. 16:** “... one-dimensional numerical models have been applied with some success to model time-resolved photoemission from surfaces in the past”

One-dimensional models may be useful and instructive, but they cannot be used beyond their limitations.

- **Ref. 16:** “... we (i) disagree with the conclusion of Krasovskii and Kuzian (KK) that the concept of photoelectron phase and effective mass ... are inapplicable to
real solids and (ii) find the statement by KK that for the “cases (i)—(iii) Eq. (1) becomes inapplicable” overstated and inappropriate.”

It is important to reveal the limitations and delineate the applicability of the model. Here, we have questioned the main claim of Ref. [1], namely that “attosecond time-resolved interferometric spectroscopy addresses the material-dependent change of PE phase velocities inside the solids”, as well as the main message for experimentalists that the suggested method can be used “to extract accurately photoemission-time delays for imaging electronic dispersion in real solids”.

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