Photoemission as a probe of coexisting and conflicting periodicities in low-dimensional solids

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Abstract. When two different periodic potentials are present at the same time in a solid, the electron wavefunctions must conform to the resulting overall periodicity. It is the case of the broken-symmetry phases which are often observed in low-dimensional systems. The rearrangement of the electronic states has some interesting and perhaps unexpected consequences on the momentum distribution of the spectral weight, which can be measured in an ARPES experiment.

Contents

1. Introduction 1
2. Results and discussion 2
3. Conclusions 8
Acknowledgments 8
References 8

1. Introduction

One of the most characteristic aspects of angle-resolved photoemission (ARPES) is its momentum selectivity, which allows the dispersion of the electronic states in a solid to be measured with considerable accuracy. Starting with pioneering work three decades ago, ARPES...
has probably contributed more than any other experimental tool to bring physical reality to the notion of electronic bands, and to fundamental concepts in solid state physics like crystal momentum, umklapp processes and Brillouin zone (BZ) [1]–[3]. Thanks to the high degree of sophistication reached by modern experiments, ARPES can now be exploited to test the properties of electrons in more complex situations, which challenge our understanding of band theory.

There is a fundamental ambiguity in the schemes introduced in textbooks to describe electronic bands [4]. All electronic states in a solid can be described using only wavevectors from within the first BZ, provided that bands are ‘folded back’ according to simple rules. The choice between the reduced and extended descriptions, or the redundant repeated zone scheme, is a matter of taste rather than a necessity. A real complication, however, arises when the symmetry of the crystalline lattice is changed (reduced), either in response to an external perturbation or as a consequence of a spontaneous symmetry breaking. Should the entire band structure be folded into the new first BZ? Are the reduced- and repeated-zone descriptions still equivalent? Or, more precisely, what is the physical meaning of the new-folded band structure? Equivalently, will an experiment like ARPES reflect the folded or the extended band structure?

These issues are not purely academic, because nature confronts us with solids which undergo, e.g. as a function of temperature, phase transitions which change the periodicity of the potential acting on the electrons. These instabilities can be found in ‘normal’ three-dimensional (3D) materials, but are especially frequent in lower dimensions, namely in 2D and, with special pathologies, in 1D systems [5]. Alternatively, in artificial ordered interfaces between two different materials, the relative periodicities of the substrate and overlayer can be tuned as a function of experimentally accessible parameters (temperature and coverage). Electronic states confined at the interface may find themselves in an ‘ambiguous’ situation due to the coexistence of two potentials with different and even conflicting translational periodicities. ARPES data help us to understand how electrons comply with these uncomfortable situations. They show that the relative strength of the potentials, rather than their simple geometrical relation, and the concept of spectral weight, as opposed to that of energy eigenvalues, are crucial factors. In this brief paper, we present recent ARPES data on selected low-dimensional systems, which illustrate various aspects of the problem of coexisting periodic potentials.

2. Results and discussion

The situation described in the introduction is sketched in figure 1, for the simple case of a half-filled tight-binding band in 1D. The dispersion $\varepsilon_0(k) = -2t \cos(ka)$ (red line in figure 1(a)) corresponds to a one-particle potential $V_0(x)$, with periodicity equal to ‘$a$’. The band is drawn within the first BZ, but it would be perfectly legitimate to represent it as a periodic function beyond the BZ boundaries at $\pm \pi/a$. This ambiguity is partially removed by ARPES and the simplest illustration of this point is from data on 1D compounds, e.g. in [6]–[8]. The ARPES spectra show the valence band—similar to the case of figure 1—in the first BZ, but also shadow bands in subsequent BZs. Their intensities, however, are generally small and most of the ARPES signal originates from the ‘main’ band. In this perspective, although the periodicity of the ARPES dispersion follows—as one expects—the repeated zone scheme, intensities are better described in an extended scheme, which does not explicitly reflect the translational periodicity.

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Figure 1. (a) Tight-binding bands (i) for a 1D potential $V_0(x)$ with periodicity $a$ (red line); and (ii) after adding a second potential $V_1(x)$ with periodicity $a_1 = 2a$ and amplitude $0.2t$ (black line). The same band is plotted in (b) with a line thickness proportional to the spectral weight $\rho(k, \omega)$.

Let us now suppose that a second periodic potential $V_1(x) = V_1 \cos(ka_1)$ is introduced into the system, so that the resulting total potential is $V(x) = V_0(x) + V_1(x)$. We will assume that the periodicity ‘$a_1$’ of $V_1(x)$ is commensurate with that of $V_0$: $a_1 = (n/m)a$ with $(n/m) > 1$. To be specific, we will consider $(n/m) = 2$ and $V_1 = 0.2t$. The periodicity of $V(x)$ is then $a_1 = 2a$, and the new first BZ is one half the original BZ. In the reduced zone scheme, the band is ‘folded back’ into the new BZ and a gap proportional to $V_1$ opens at the new zone boundaries $\pm \pi/2a$. Alternatively, in the repeated zone scheme, the band dispersion (black line in figure 1(a)) reflects the full periodicity of $V(x)$. In both representations, of course, states with the same energy which are connected by a reciprocal lattice vector $G' = \pi/a$ are indistinguishable. A rather different picture emerges if one considers not only the eigenvalues $\epsilon_i(k)$ ($i = 1, 2$) of the Schrödinger equation with potential $V(x)$, but also explicitly the corresponding eigenvectors $\psi_i(k)$. The spectral weight, which is proportional to the ARPES intensity for $\omega < 0$, can be written as $\rho_i(k, \omega) = u_i^2 \delta(\omega - \epsilon_i(k))$, in terms of the coherence factors $u_i^2 = |\langle \psi_i(k) | \psi_0(k) \rangle|^2 = [1 + (\epsilon_i(k)/\epsilon_0(k))] / 2$, where the $\psi_0(k)$ are the eigenvectors of $V_0$. Clearly $\rho(k, \omega)$ does not exhibit the new periodicity $\pi/a$ (figure 1(b)). The spectral weight is mainly distributed along the original band and the shadow band draws intensity from it only near the intersections at $\pm \pi/2a$. Although $\rho_1(k) + \rho_2(k) = 1$ for all values of $k$, independent of $V_1$, intensity is progressively transferred to the shadow band for increasing values of $V_1$. Therefore, ARPES spectra carry information on the relative strengths of the coexisting potentials. The situation sketched in figure 1 qualitatively describes the ARPES observations for the quasi-1D system (NbSe$_4$)$_3$I, where a periodic lattice distortion, possibly of electronic origin, doubles the natural lattice periodicity [9]. Even in the presence of the distortion, the overall band dispersion is determined by the ideal arrangement of the ions in the undistorted lattice.

A more complex situation is that of the blue bronze (BB) $K_0.3\text{MoO}_3$, another typical 1D material, which exhibits a low-temperature charge-density-wave (CDW) phase, with an associated periodic lattice distortion. The CDW in BB is well described by the Peierls ‘Fermi surface nesting’ mechanism [5]: nesting occurs between Fermi surface sheets which belong to two distinct bands, and the nesting vector tends to the commensurate value $Q_{\text{CDW}} = (3/2)\pi/b$ at low temperature [10]–[12]. The ARPES intensity map of figure 2(a) reveals a shallow...
Figure 2. (a) ARPES intensity map measured along the 1D direction of the CDW compound $K_{0.3}MoO_3$ (blue bronze), showing a shallow antibonding (AB) and a deeper bonding (B) band. (b) ARPES map measured in the perpendicular direction, for a $k_{\parallel}$ value corresponding to the red arrow in (a). (c) Expected dispersion (schematic). Solid lines, main B (red) and AB (blue) bands; long-dashed lines, $G$-umklapps; short dashed lines, $Q_{\text{CDW}}$ umklapps.

‘antibonding’ (AB) band within $\sim 0.4 \text{ eV}$ of the Fermi level and broader bonding (B) bands, extending beyond $1 \text{ eV}$ from $E_F$. Determining the Fermi level crossing for these metallic bands is not straightforward, because their intensities are strongly reduced as they approach $E_F$, but extrapolating the dispersion yields the Fermi wavevectors $k_{\text{B}} \sim (\pi/2b)$ and $k_{\text{AB}} \sim (\pi/b)$. Under the influence of the lattice and CDW potentials, the rather complicated band structure of figure 2(c) can be expected, with replicas of the main AB and B bands appearing displaced by multiples of the reciprocal vectors of the undistorted lattice ($G$) or of the CDW wavevector $Q_{\text{CDW}}$. Experimentally, strong shadow bands are observed for $|k| > (\pi/b)$ in the second BZ. They are dominated by the replica of the B band corresponding to a $G$-umklapp (long dash in figure 2(c)), i.e. by the effect of the (unperturbed) lattice potential. Weaker signatures of a shadow AB band, from a CDW-related umklapp (short dash) can also be identified [10]. That the scattering on the CDW potential is not negligible is evident from the analysis of the bands.
in the region $k_{FAB} < k < k_{FB}$. The ARPES intensity map of figure 2(b) represents the dispersion perpendicular to the 1D direction, measured for $k_{\|} \sim 0.6 (\pi/b)$, corresponding to the arrow in figure 2(a). It shows a cut through the B band at $\sim 0.8$ eV, but also a second feature at $\sim 0.3$ eV, symmetric around $k_{\perp} = 0$, which can only be attributed to a CDW-related shadow of the B band (short dash in figure 2(c)).

The electronic states respond to coexisting periodic potentials in CDW materials even when the two potentials are incommensurate, as in the 1D material (TaSe$_4$)$_2$I. In this case, the total potential $V(x)$ is strictly non-periodic: crystal momentum ceases to be a good quantum number, and one might expect Bloch theorem to break down. In other terms, it is not possible to fold back the electron bands into a suitable reduced BZ common to both potentials. Numerical solutions of a simple model clarify how the electrons can actually comply with these conflicting requirements [7]. They show that even if shadow bands uniformly fill the energy–momentum plane, the transferred weight rapidly decreases with the order of the umklapp processes involving combinations of the two reciprocal lattice vectors $G$ and $G_{CDW}$. As a result, only the lowest-order shadow bands, corresponding to the unperturbed lattice and to the CDW periodicities, can be observed. Similar considerations can be made for quasi-crystalline systems [13].

Examples of coexisting periodic potentials are not limited to one dimension. Selected layered materials and ordered interfaces, which can be considered as quasi-2D systems, also exhibit broken symmetry phases, with new emerging periodicities. A typical case is that of the 1T polytype of the layered chalcogenide TaS$_2$, whose electronic structure is dramatically affected below 180 K by a commensurate CDW [14,15]. In the CDW phase, the unit cell of the undistorted hexagonal lattice is replaced by a larger ($\sqrt{13} \times \sqrt{13}$) and rotated supercell. The ionic positions within the supercell are periodically modulated, with variations of the Ta–Ta distances as large as $\sim 8\%$ and the associated potential is strong enough to split the conduction band in separated subbands. Figure 3 shows the second derivative of the ARPES signal measured along the $\Gamma M$ direction. This representation, which enhances the weaker features, identifies very clearly a narrow band near $E_F$ and a second manifold centred around $-0.5$ eV, where at least two subbands oscillate and cross (e.g. in ‘A’) following the CDW superlattice periodicity. The as-measured map (not shown) shows that most of the ARPES intensity indeed remains confined along the original dispersion, schematically highlighted by the solid curve [17]. Once again, the spectral weight transferred to the CDW shadow bands is small, despite the considerable rearrangement of the ionic positions, which is confirmed by the observation of clear gaps between the subbands. The intensity of the shadow bands is rapidly suppressed by surface defects or contamination. On one hand, defects act as pinning centres which limit the coherence of the CDW phase, and therefore blur by a finite-size effect the superlattice potential. On the other hand, they scatter the quasi-particles, reducing the number of CDW supercells that can be coherently ‘visited’. The latter effect is of course also present in the undistorted phase, but it is more important in the CDW phase, due to the large size of the supercells.

The ARPES map of figure 3 reveals unexpected features. Two narrow subbands within the topmost band disperse with opposite phases near $\Gamma$, in contrast to band structure calculations which predicts only one band near $E_F$. The relative intensity of the two subbands is lost in the derivative plot, but from the unprocessed intensity map (not shown) it is clear that the higher subband, downward dispersing at $\Gamma$, is actually a shadow replica obtained by folding the second ‘main band’ at a new zone boundary ‘B’. A zone boundary at ‘B’ is incompatible with the CDW superlattice periodicity and would correspond to a larger supercell in real space. It is tempting to interpret it as the spectral signature of an underlying order parameter in the CDW phase. Strong
arguments suggest the localization of a Ta 5d electron at the centre of each CDW supercell [16], and there is a tendency for these electrons to order magnetically and form the Néel state predicted for spins on a triangular lattice. The ordered state has three ferromagnetic sublattices at 120° from each other, and a larger $(\sqrt{3} \times \sqrt{3})R30°$ unit cell with respect to the CDW supercell. This conjecture is supported by a calculation performed within the Hubbard model, which reproduces the observed dispersion [18]. The mean-field solution yields an ordered moment corresponding to $\sim 80\%$ of a fully localized spin, which should however be considered as an upper limit due to the neglect of fluctuations. There is no experimental evidence yet for an ordered magnetic state in TaS$_2$ from macroscopic probes. It is therefore likely that the ARPES shadow bands of figure 3 do not reflect long-range but rather fluctuating short-range magnetic order, a scenario previously proposed in the context of the high-$T_c$ cuprates [19].

The possibilities of studying coexisting periodicities in a bulk crystal are severely constrained by its crystalline and electronic structures. The constraints can be relaxed in epitaxial interfaces, where several ordered structures can be obtained depending on the chemical species, the temperature and coverage. The Moiré phases observed at various interfaces near monolayer coverage are especially intriguing [20]. The mismatch with the underlying substrate produces an incommensurate or nearly commensurate long-range modulation in the adlayer, which is graphically revealed by STM pictures. Electronic states confined at the interface will be affected by the conflicting potentials, but the signatures of the new periodicity may be more subtle than expected, as suggested by the following example.

Figure 4 shows a projection of the ordered structure of 1 ML of Pb on the Ag(1 1 1) surface, as determined by LEED. The in-plane Pb–Pb distance within the overlayer ($\sim 3.48 \text{ Å}$) is very close to the bulk Pb–Pb distance, but 20% larger than the ideal Ag–Ag distance at the Ag(1 1 1) surface, and the 2D hexagonal lattice of the overlayer is rotated by 4.7° with respect to the substrate. The figure suggests (near) commensurability with a large $(\sqrt{28} \times \sqrt{28})$ supercell, but the data are also consistent with a truly incommensurate superstructure. STM data reveal a Moiré
Figure 4. (a) Projected structure of the Pb/Ag(1 1 1) Moiré phase and (b) ARPES intensity map. The solid lines outline the dispersion of the broad p_z (green) and sharper p_{xy} (red) interface bands.

The most striking aspect of the data is the ‘fuzziness’ of the p_z band. Cuts through the band at either constant energy or constant wavevector (not shown) are unusually broad, and much broader than similar cuts through the p_{xy} band. It is tempting to relate such puzzling observation to the Moiré modulation. Ideally, the 2D band structure should be folded back into the surface BZ (SBZ) corresponding to the overall periodicity of the interface. Even assuming commensurability, the new SBZ is at least 28 times smaller than the Ag(1 1 1) SBZ, and folding requires umklapp processes with surface reciprocal lattice vectors \( G = mG_1 + nG_2 \) (\( G_1 \) and \( G_2 \) are unit vectors of the 2D reciprocal lattice), where \( m \) and \( n \) can be as large as 4. This would yield a dense web of superlattice bands in the energy-wavevector map of figure 4(b). For larger commensurate approximants, and eventually for a truly incommensurate structure, the SBZ would become progressively smaller, and higher and higher multiples of the \( G \)’s would be involved in the folding process. The previous discussion suggests that spectral weight will be transferred to the superlattice ‘shadow’ bands mainly in proximity of the crossings with the main bands, which will then be smeared. The ARPES data show that such smearing affects much more severely the p_z band. The striking contrast between the broad p_z and the sharp p_{xy} bands can be seen as a consequence of the polarization of the overlayer modulation. In the spirit of a tight-binding approach, transfer integral between atomic Pb p_z orbitals, and between the same orbitals and the Ag substrate, are certainly more drastically affected by an out-of-plane distortion than those involving in-plane p_{xy} orbitals. The effective potential acting on the latter is therefore considerably smaller, and the effects of the superlattice periodicity on the dispersion should be negligible, consistent with the experiment.
3. Conclusions

The selected examples discussed in this paper and a growing experimental set of data demonstrate that photoemission probes subtle aspects of the electronic response to periodic perturbations in a solid. The sensitivity of ARPES to the spectral weight, in contrast to the simple geometrical periodicity, is a valuable asset which can be used to highlight the fundamental importance of the strength of the perturbation. This distinction is quite relevant when electrons comply with the conflicting requirements of distinct periodic potentials. Further investigations of the explicit role of the electron wavefunctions and of the self-consistent coupling to the perturbation, beyond the simple model of an external potential considered here, could contribute to shed light on interesting and fundamental aspects of the electronic properties of broken-symmetry phases, overlayers and quasi-crystals.

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