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Some future perspectives in soft- and hard- X-ray photoemission☆

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ABSTRACT

We discuss several recent developments in photoemission, with comments on their perspectives for the future. These include an adequate allowance for differential cross section effects in core- and valence-angular distributions, as well as more accurate one-step modeling of angle-resolved photoemission (ARPES); the use of higher photon energies from the soft- to hard- X-ray regime to permit probing bulk electronic structure and buried layers and interfaces; extending ARPES into the soft- and hard- X-ray regimes; tailoring the X-ray wave field through X-ray optical effects including standing waves, total reflection, and tuning through resonances; using standing-wave excitation to provide much enhanced depth sensitivity in studying solid/gas and solid/liquid interfaces; and applying photoelectron holography to time-resolved studies of molecular reactions and dissociation. Specific application examples include a magnetic semiconductor, multilayer structures of complex metal oxides, a thin water solution on a metal oxide surface, and a halo-substituted benzene molecule.

1. Introduction

We will in this article discuss a few recent developments in soft- and hard- X-ray photoemission that relate to the overall topic of this issue: structure determination and wave-function analysis, with special emphasis on the future perspectives that these suggest. Structure determination will be considered both from the point of view of using (SW) standing-wave excitation, together with other X-ray optical effects and total reflection, in studies of multilayer solid samples, but also at the atomic level from the point of view of photoelectron diffraction (PD) and holography (PH), including potential time-resolved studies with free-electron lasers. Wave-function analysis will be discussed in the context of angle-resolved photoemission (ARPES) using higher-energy soft and hard X-ray excitation so as to probe more deeply into materials.

We begin by introducing some of the basic parameters of the photoemission process related to these developments, and then consider more specific topics and applications. We will also point in several places in this article to discussions by other authors in this issue, so as to be complementary, but not repetitive, to them. For example, Gray [1] has written an excellent article on standing-wave effects whose contents we will not repeat here, but try to complement in a couple of case studies. The experimental results presented here have been obtained at several different synchrotron radiation facilities, as indicated specifically for each case below.

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2. Some basic parameters and phenomena

2.1. Differential photoelectric cross sections for atomic orbitals in arbitrary experimental geometries

Photoelectron spectrometers, both dispersive and time-of-flight, are rapidly being developed that can simultaneously measure intensities over an increasingly broader two-dimensional angle range, as e.g. those discussed by Matsuda [2] and Matsushita [3] in this issue. One can thus ask a very basic question in studying both core- and valence- electron emission as to the precise form of the differential photoelectric cross sections involved, and how they will vary over the detection range of the spectrometer. Such variations can influence both PD and ARPES, for example. With polarized radiation for excitation, it is well known that the cross section is strongly affected by the experimental geometry, but there is no readily accessible source of differential cross sections for individual atomic orbitals such as e.g. the t_{2g} set d_{xy}, d_{yz}, and d_{zx} and the e_g set $d_{x^2-y^2}$ and d_{z^2}. A program has thus been written in our group [4] that will be made available to the community at large and which permits calculating the differential photoelectric cross sections for core and valence atomic orbitals for arbitrary experimental geometries and light polarizations. This makes use of analytical formulas developed by our group some time ago [5], to which are added a database of photoelectric cross sections and continuum-wave phase shifts. These should be generally useful to many groups in trying to estimate the relative contributions of different orbitals to in particular valence-band spectra, whether density-of-states like or momentum-resolved as in ARPES. In ARPES one certainly has additional selection rules on wave vector **k** and matrix elements that depend on the orbital makeup of a given band that are critical for describing the full dispersion curves, and these can only be assessed by more accurate photoemission calculations, for example, with the surface explicity included in a time-reversed low energy electron diffraction or so-called "one-step" picture [6]. However, atomic cross sections can nonetheless provide insight as to what bands should be strong in which directions.

As an illustrative example of these atomic orbital differential cross sections, in Fig. 1, we show some first results from this program, actually calculated for two closely-related experimental geometries we have used for soft X-ray ARPES at both the Advanced Light Source (ALS) and the Swiss Light Source (SLS). In Fig. 1(a), the experimental geometry we have used is shown, and in Fig. 1(b) the cross sections of the various d orbitals at the ca. 833 eV excitation energy used in experimental results that will be discussed in subsequent figures, for both s- and p-polarizations. Gray [1] has also considered data obtained at this photon energy. The red highlights indicate orbitals that would be directly seen strongly (solid line) or weakly (dashed line) in the precise emission direction shown in 1(a), and an "x" indicates orbitals that are not expected to be seen at all. But the fact that a given two-dimensional spectrometer might see well beyond this direction can also be judged from the forms of these profiles. The complex form of these cross section profiles makes it clear that the planning of many future experiment with variable polarization and a spectrometer accepting a wide angle range will much benefit from having these simple atomic references, and that not considering these effects could lead to erroneous interpretations. We illustrate such effects in experimental standing-wave ARPES (SWARPES) results below.

2.2. Inelastic mean free paths

In work in both solid samples looking into vacuum, or studies with a significantly high background pressure in the multi-Torr range, in what has been termed ambient-pressure X-ray photoemission (APXPS, APPS) [7,8], the inelastic mean free path (IMFP)

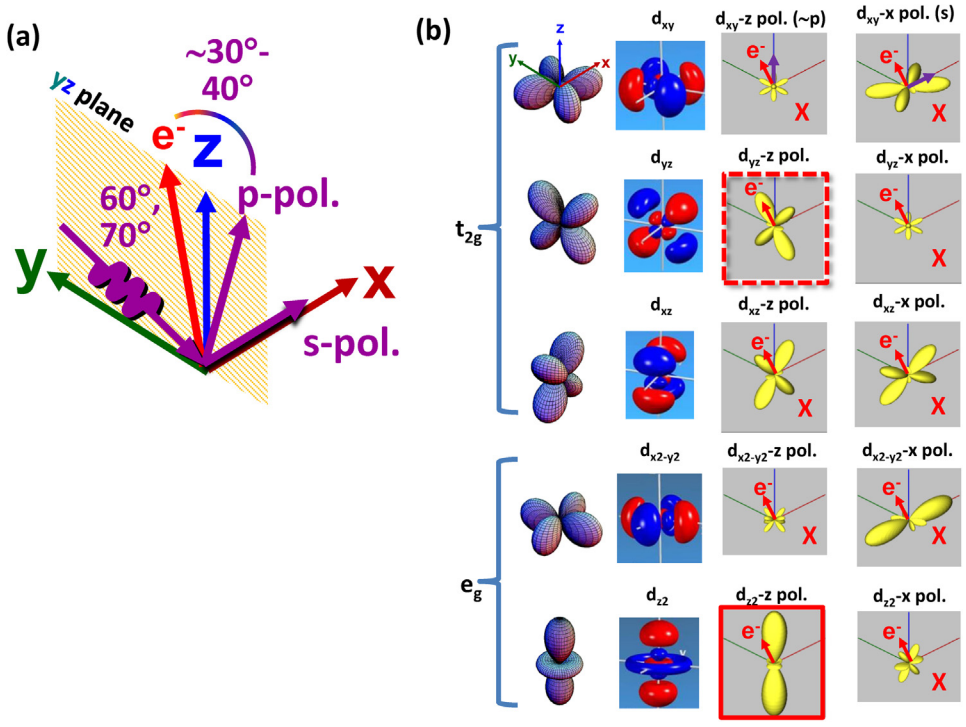

Fig. 1. Theoretical differential photoelectric cross sections for Mn 3d atomic orbitals at a photon energy of 833 eV just below the La M_5 absorption resonance. (a) The experimental geometry used in our group's soft X-ray standing-wave and ARPES measurements at the ALS and the SLS. (b) The 3d orbitals of Mn, in both angular and spatial form (plotted through contours of equal probability density), together with their three-dimensional differential cross sections in both s and p polarization, as defined in (a). Cross-section contours are all plotted on the same absolute scale: that is, the distance from the origin to the contour surface is proportional to the absolute cross section. The orbitals marked with X are not expected to contribute in, and those outlined in red/dashed red should be strongly/less strongly seen [From ref. 4].