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Photoelectron Spectroscopy and the Dipole Approximation

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Abstract. Over the past three decades, the dipole approximation has facilitated a basic understanding of the photoionization process in atoms and molecules. Advances in gas-phase photoemission experiments using synchrotron radiation have recently highlighted nondipole effects at relatively low photon energies while probing the limits of the dipole approximation. Breakdowns in this approximation are manifested primarily as deviations from dipolar angular distributions of photoelectrons. Detailed new results demonstrate nondipolar angular-distribution effects are easily observable in atomic gases at energies well below 1 keV, and, in molecules, a previously unexpected phenomenon greatly enhances the breakdown of the dipole approximation just above the core-level ionization threshold.

INTRODUCTION

Although breakdowns in the dipole approximation in the soft-X-ray photon energy range ($h\nu \leq 5$ keV) were first observed 30 years ago and have been studied theoretically for many years, their significance at low photon energies has remained generally unappreciated within the broader photoemission community. Ultraviolet (UV) and X-ray photoelectron spectroscopy (PES) is a common technique for studying matter of all kinds.

FIGURE 1. Geometry applicable to photoelectron angular-distribution measurements using polarized light. The polar angle θ is measured between the photon polarization vector $\mathbf{E}$ and the momentum vector $\mathbf{p}$ of the photoelectron. The azimuthal angle ϕ is defined by the photon propagation vector $\mathbf{k}$ and the projection of $\mathbf{p}$ into the x - z plane.

The power of PES stems from its ability to probe directly, via the measurement of electron kinetic energies, orbital and band structure in valence and core levels in a wide variety of samples: atoms, molecules, clusters, solids, surfaces and adsorbates.

The technique is even more powerful in an angle-resolved mode, where photoelectrons are distinguished not only by their kinetic energies but by their directions of emission as well. Probability of electron ejection as a function of angle is an excellent probe of quantum-mechanical channels available to a photoemission process because it is sensitive to phase differences among these channels. As a result, angle-resolved photoemission has been used successfully for many years to provide stringent tests of our understanding of basic physical processes underlying gas-phase and solid-state interactions with radiation, and also a tool to probe physical and chemical structure in solids and surfaces.

THE DIPOLE APPROXIMATION

One mainstay in the application of angle-resolved PES is the well-known dipole approximation (DA) for photon interactions, which leads to easily characterized and quantified behavior as a function of electron ejection angle. The electric-dipole ($E1$) approximation assumes the electromagnetic field of the photon beam, $\exp(i\mathbf{k}\cdot\mathbf{r})$, expressed as a Taylor-

series expansion, $1+i\mathbf{k}\mathbf{r}+\dots$, can be truncated to unity. In this simplification, all higher-order interactions, are neglected [1].

In the UV and far-UV photon-energy ranges, the DA for photoionization is grounded in solid physical reasoning based on two qualitative arguments: (1) photoelectron velocities following UV photoemission are extremely small compared to the speed of light, rendering relativistic effects unlikely, and (2) the wavelength of UV light (e.g., He I radiation) is much larger than the orbitals from which electrons are ejected, mitigating higher-order effects in the photon interaction. At the other extreme, in the hard-X-ray range ($h\nu \geq 5$ keV), the breakdown of the DA essentially becomes complete, requiring the use of the full Taylor-series expansion for the photon interaction. Somewhere between the UV and hard-X-ray ranges, it is clear effects due to interactions beyond the DA must eventually become important.

BEYOND THE DIPOLE APPROXIMATION – FIRST ORDER CORRECTIONS

The first hints of low-photon-energy deviations from the DA in angle-resolved photoemission were provided by Krause [2] and Wuilleumier and Krause [3] in measurements on rare gases using unpolarized Mg and Al $K\alpha$ X-rays. Recently, more extensive measurements, focusing on noble-gas core levels (Ar K and Kr L) and tunable photon energies between 2 keV and 5 keV, began to investigate nondipole effects in photoelectron angular distributions in more detail [4,5]. Probing the limits of the DA at lower energies ($0.15 \text{ keV} \leq h\nu \leq 1.2 \text{ keV}$), other experiments measured nondipolar angular distributions in Ne $2s$ and $2p$ valence photoionization [6-8]. Even at the lowest energy studied, nondipole effects are observable, bringing into question the usual assumption of the DA in soft-x-ray applications of PES. Finally, nondipole effects have been observed in molecules; in N1s photoemission from N_2 , deviations from dipolar angular distributions peak just 60 eV above threshold, due to an entirely new physical phenomenon [9]. At the peak, measured relative photoemission intensities as a function of angle vary by as much as 100% compared to DA expectations. At very high photon energies, where the DA is completely invalid, it is necessary to include the exact expression, $\exp(i\mathbf{k}\mathbf{r})$, for the electromagnetic field of the photon beam. For soft-x-ray photoionization, in contrast, the first-order correction to the DA is expected to be dominant [10,11]. The first step beyond the DA is to truncate the expansion of $\exp(i\mathbf{k}\mathbf{r})$ after the second term, $1+i\mathbf{k}\mathbf{r}$,

which amounts to including $E2$ and $M1$ interactions. These higher-order amplitudes contribute through cross terms with the $E1$ dipole amplitude (order k , or $O(k)$). They contribute only to odd multipoles, leaving σ and β unaffected, but leading to forward/backward asymmetries in the photoejection probability with respect to the photon propagation vector. In addition, $M1$ interactions vanish in a nonrelativistic treatment in which core relaxation is unimportant, and are generally considered to be much less significant than $E2$ interactions for soft-x-ray photoionization [10,11]. In the soft-x-ray range, cross terms yield the largest deviations from the DA. At a level of approximation in which nondipole effects are due only to first-order $E2$ - $E1$ (and the weaker $M1$ - $E1$) cross terms, two new nondipolar angular-distribution parameters, in addition to the dipole parameter β , are required. We adopt the parameterization used by Cooper [11] for the differential cross section in the first-order nondipole approximation,

$$\frac{d\sigma}{d\Omega} = \left(\frac{\sigma}{4\pi} \right) \left[1 + \frac{\beta}{2} (3 \cos^2 \theta - 1) + (\delta + \gamma \cos^2 \theta) \sin \theta \cos \phi \right] \quad (1)$$

which is valid for 100% linearly polarized light. The angles θ and ϕ are described in Fig. 1. As with σ and β , δ and γ depend on subshell and photon energy. Equation (1) makes it clear nondipolar angular-distribution patterns for photoelectrons exhibit forward/backward asymmetry, relative to the photon propagation direction ($\mathbf{k}$), due to the presence of $\cos(\phi)$ in the last term.

Enhanced probability in the forward direction corresponds to the classical notion of momentum transfer from the photon to the ionized electron. To illustrate graphically the extent to which nondipole effects can modify photoelectron angular distributions, Figure 2 shows δ and γ in the horizontal x - y plane,

FIGURE 2. Forward/backward asymmetries of the nondipolar angular-distribution patterns are shown for the γ and δ parameters. The shapes of the patterns stay the same for all values of γ and δ and there are in general no upper or lower limits unlike for β (-1 to 2).

containing the photon propagation ($\mathbf{k}$) and polarization ($\mathbf{E}$) vectors and in a side view (x - z plane) just containing the photon propagation vector. As under the DA, photoejection at the magic angle (θ_m) is independent of β , and also is independent of δ and γ in the dipole plane (see Fig. 2). Thus, one can refer to “magic directions,” for the combination of angles $\theta_m=54.74^\circ, 125.26^\circ, 234.74^\circ, 305.26^\circ$ and $\phi=90^\circ$; only in these (four) directions will the probability of photoejection depend solely on σ .

BEYOND THE DIPOLE APPROXIMATION – SECOND ORDER CORRECTIONS

The second step beyond the DA is to truncate the expansion of $\exp(i\mathbf{k}\mathbf{r})$ after the third term $1+i\mathbf{k}\mathbf{r}+0.5(i\mathbf{k}\mathbf{r})^2$, which amounts to including pure electric-quadrupole ($E2$) and magnetic-dipole ($M1$) interactions (order k^2 , or $O(k^2)$) and $E3$ and $M2$ cross terms. The even multipoles in the spherical-harmonic expansion, affect directly both σ and β . Four new parameters ($\Delta\beta, \eta, \xi, \mu$) have to be included in the differential cross section, which arise from interferences between $E1$ - $E3$, $E1$ - $M2$, $E2$ - $E2$, $E2$ - $M1$, $M1$ - $M1$ as well as from retardation corrections to $E1$ - $E1$. Three of the new parameters satisfy the constraint $\eta+\xi+\mu=0$ and their angular-distribution patterns are shown in Fig.3.

All parameters depend on subshell and photon energy and contribute intensities even to the above mentioned “magic directions”. The differential cross section including the second order corrections is given by Derevianko et al. [8] as,

$$\frac{d\sigma}{d\Omega} = \left(\frac{\sigma}{4\pi} \right) \left[\begin{aligned} &1 + (\beta + \Delta\beta) P_2(\cos \theta) \\ &+ (\delta + \gamma \cos^2 \theta) \sin \theta \cos \phi \\ &+ \eta P_2(\cos \theta) \cos 2\phi \\ &+ \xi (1 + \cos 2\phi) P_4(\cos \theta) \\ &+ \mu \cos 2\phi \end{aligned} \right] \quad (2)$$

with $P_2(\cos\theta) = 0.5(3\cos^2\theta-1)$ and $P_4(\cos\theta) = 1/8(35\cos^4\theta-30\cos^2\theta+3)$ and for 100% linear polarized light. The angles are the same as in Eq. (1).

The experiments were performed at the Advanced Light Source with four electron analyzers mounted in a chamber which can rotate about the photon beam [12]. At the nominal angular position of the apparatus, two analyzers are at θ_m and $\theta=0^\circ$ in the plane perpendicular to the photon beam ($\phi=90^\circ$), which we

FIGURE 3. The angular-distribution patterns correspond from left to right to the parameters η , ξ and μ . The photon propagation vector is in x -direction and the polarization vector is in y -direction. As for δ and γ the shapes of the patterns stay the same for all values of η , ξ and μ and there are in general no upper or lower limits.

refer to as the dipole plane because first-order corrections vanish, while two more analyzers are positioned on the forward 35.3° cone with respect to the photon beam. At the nominal position, these two “nondipole” analyzers are at $(\theta_m, \phi=0^\circ)$ and $(\theta=90^\circ, \phi=35.3^\circ)$. Photoemission intensities in the two magic-angle analyzers are independent of β and can differ only because of nondipole effects. While the magic angle is no longer strictly valid when second-order effects are included, calculations show they can be unimportant in certain geometries.

We present experimental results for Ne γ_{2s} and ζ_{2p} , assuming the validity of Eq. (1), for comparison with $O(k)$ and $O(k^2)$ calculations. The first data set is based on angle-resolved photoemission intensities from the two magic-angle analyzers. Figure 4 compiles old [6] and new values for γ_{2s} and ζ_{2p} (open squares) determined using this geometry. The solid curves represent $O(k)$ calculations [10,11,13], which agree well with the $2s$ results but disagree with the $2p$ results above 800 eV.

For the magic-angle geometry, Eq. (2) and calculated values for $\Delta\beta, \eta, \xi$, and μ [14] can be used to estimate $O(k^2)$ influences on the experimental determination of γ_{2s} and ζ_{2p} . Measured values of ζ_{2p} will be perturbed by second-order effects as follows:

$$\zeta(k^2) \approx \frac{\gamma + 3\delta + \sqrt{54}(\mu - 7\xi/18)}{1 - \mu} \quad (3)$$

Effective values for ζ_{2p} (and similarly γ_{2s}) have been determined, yielding the dotted curves in Fig. 4. We find excellent agreement for γ_{2s} and clearly improved agreement for ζ_{2p} . The second-order effects thus included account for much of the difference between first-order theory (solid curve) and experiment for ζ_{2p} .

To confirm this unexpected finding, new measurements in a different geometry were performed by rotating the apparatus to ten different angular

FIGURE 4. Experimental and theoretical values of γ_{2s} and ζ_{2p} for neon determined under different geometrical conditions: (1) open squares and dotted curves relate to the magic-angle geometry; (2) solid circles and curves relate to the nondipole-cone geometry. Both dotted and solid curves include effects up to $O(k^2)$. The solid curves also represent first-order theory, independent of geometry.

positions about the photon beam, yielding 20 angle-resolved intensities for Ne 2s and 2p photoemission at different angles θ and ϕ around the 35.3° nondipole cone. Here, influences of the $O(k^2)$ parameters are superimposed on intensity variations due to the dipole β and the $O(k)$ δ and γ parameters. But for both γ_{2s} and ζ_{2p} , our calculations predict effects due to η , μ , and ξ also mostly cancel in the nondipole-cone geometry, yielding the solid curves in Fig. 4. Furthermore, small residual effects around this cone are similar in sign and magnitude for 2s and 2p, which is relevant because 2s/2p intensity ratios are the raw input for data analysis. Assuming no influence of second-order effects in the nondipole cone, we modeled the measured ratios around this cone using Eq. (1) to derive values for γ_{2s} and ζ_{2p} . These results (solid circles in Fig. 4) agree extremely well with $O(k)$ calculations [10,11,13], confirming our prediction of near cancellation of $O(k^2)$ effects in this geometry.

In conclusion, the experimental study of breakdowns in the DA for soft-x-ray photoemission from gas-phase targets has experienced a resurgence in the past few years. Although DA breakdowns, and their effects on photoelectron angular distributions,

have been predicted for some time, their magnitude and potential significance have remained relatively unappreciated within this community.

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