RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 42, NUMBER 11 1 DECEMBER 1990

Multipole corrections to the angular distribution of photoelectrons at low energies

J. W. Cooper
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742
(Received 18 June 1990)

Higher multipole corrections to the dipole-approximation result for angular distributions of photoelectrons at low photon energies are discussed. The first-order corrections lead to a simplified formula for the angular distribution, which extends the dipole results for linearly, unpolarized, and partially polarized light. It is shown how atomic parameters can be obtained from experimental measurements, and relationships to previous work on photoelectron angular distributions are discussed briefly.

During the past two decades there has been considerable interest in the angular distribution of electrons produced by photoionization. Early theoretical and experimental work concentrated on the problem of obtaining individual subshell contributions to total cross sections via measured photoelectron cross sections[1,2] and investigations of this type have been extended to provide information on correlation effects by observing satellite lines[3] in photoelectron spectra which can only result from two-electron excitation processes. More recently, detailed studies of relativistic effects on angular distributions,[4] on the effects of angular momentum transport to core electrons during the photoionization process[5] and on the angular distributions of Auger electrons following photoionization[6] have been made.

While the above studies have increased our knowledge considerably of the photoionization process, with a few exceptions all of the theoretical calculations and interpretation of experimental results have been carried out within the framework of the dipole approximation. There are good reasons for this. First, at low incident energies for outer subshells with low binding energies deviations of calculated angular distributions, due to the neglect of higher multipoles, are expected to be of the order of a few percent which is of the same order as the accuracy of experimental angular distributions. Second, and perhaps more important, is the fact that within the dipole approximation the form of the angular distribution of electrons emitted in a photoionization process for systems which have no preferred orientation is completely general.[7] The formula

$$\frac{d\sigma}{d\Omega}=\frac{\sigma_t}{4\pi}[1+\beta P_2(\cos\theta)]\,, \tag{1}$$

where P_2 is a Legendre polynomial, θ is the angle between the polarization of incident photons and the direction of an observed electron, and σ_t the total cross section for a particular process, correctly describes the angular distribution of electrons regardless of whether they are produced in a single-electron process, via shakeoff processes or Auger processes following photoionization.

At higher energies, of course, the dipole approximation is no longer valid and detailed calculations for atoms of the angular distribution of photoelectrons from a particular subshell have been carried out within a one-electron relativistic central-field approximation.[8] The results of these calculations for unpolarized light are usually expressed in the form

$$\frac{d\sigma}{d\Omega}=\frac{\sigma_t}{4\pi}\sum_n B_n P_n(\cos\underline{\theta})\,, \tag{2}$$

where $\underline{\theta}$ is the angle between incident-photon and ejected-electron directions. In nonrelativistic dipole approximation, only $B_0=1$ and $B_2=-\beta/2$ are nonzero, so the form of the angular distribution is the same as Eq. (1) with β replaced by $-\beta/2$.

The one-electron relativistic central-field approximation can, of course, be used at lower energies, and it has been pointed out that deviations from the simple result of Eq. (1) occur at much lower energies than for total cross sections.[9] More recently[10] it has been shown that in a nonrelativistic central-field approximation, the angular distribution for K-subshell electrons can be approximated at low energies via an analytic formula which agrees well with the fully relativistic central-field calculations. While the formalism of the relativistic central-field approximation has been used to calculate angular distributions for polarized and unpolarized light,[8] numerical calculations for polarized light at low energies have only been performed recently.[11]

The above-mentioned work indicates that deviations from dipole approximation are important at low energies, and indicates that relativistic effects are relatively unimportant for K-shell angular distributions at low energies. Therefore, in order to sort out the important physical effects, it is desirable to consider only the leading terms in the dipole expansion in the nonrelativistic central-field approximation in order to see what new information can be obtained from experimentally observed deviations from Eq. (1). The procedure for doing this has been previously developed for molecular systems,[12] and the results presented here can be considered as a simplification of that work as well as an extension of the work of Ref. 10.

The angular distribution of photoelectrons for linearly polarized light is given in atomic units ($\alpha\sim\frac{1}{137}$) by the expression[13]

$$\frac{d\sigma(E,\theta,\phi)}{d\Omega}=\frac{4\pi^2\alpha}{\omega}|D_{if}|^2\,, \tag{3}$$

where E is the electron energy and ω the photon frequen-

cy and angles are relative to the direction of polarization. The nonrelativistic matrix element between initial and final states Ψ_i and Ψ_f is

$$D_{if}=\langle\Psi_{*i}|e^{i\mathbf{k}\cdot\mathbf{r}}p_z|\Psi_f\rangle\,, \tag{4}$$

where p_z is the momentum operator. Photon propagation and polarization are assumed to be in the x and z directions, respectively. Here it is assumed that the initial state represents a closed-shell atom and the final state an ion core plus a free electron. Thus a sum over substates of the core and spin states of the free electron is assumed. Core relaxation may be included if different orbitals are used in the initial state and ion-core wave functions.

Expanding the exponential term in Eq. (4), keeping only the first two terms and converting to the "length" form, the matrix element in Eq. (4) may be written as

$$D_{if}=\omega\langle z\rangle+\frac{i\omega^2\alpha}{2}\langle xz\rangle-\frac{\omega\alpha}{2}\langle L_y\rangle\,. \tag{5}$$

Here, $\langle z\rangle$ is the usual dipole matrix element, $\langle xz\rangle$ the matrix element for electric quadrupole transitions, $\langle L_y\rangle$ the matrix element for magnetic dipole transitions, and L_y the angular momentum operator in the y direction. In dipole approximation, of course, only the first term is retained and the angular distribution is given by Eq. (1). Using Eq. (5), to first order in $|\mathbf{k}|=\omega\alpha$ the differential cross section becomes

$$\frac{d\sigma}{d\Omega}=4\pi^2\alpha\omega\left[|\langle z\rangle|^2-\alpha\left(\frac{\omega}{2}(\mathrm{Im}\langle z\rangle^*\langle xz\rangle-\mathrm{Re}\langle z\rangle^*\langle L_y\rangle)\right)\right], \tag{6}$$

where Re and Im mean real and imaginary parts. Since only terms to first order in $\omega\alpha$ are included, Eq. (6) represents electric quadrupole and magnetic dipole corrections only in the long-wavelength limit.

The general form of the angular distribution for linearly polarized and unpolarized light retaining only the terms indicated above has been given previously.[12,14] For unpolarized light, Eq. (2) applies and only terms with B_1 and B_3 can occur in addition to the dipole B_2 term. For polarized light, the general form of the angular distribution will be

$$\frac{d\sigma}{d\Omega}=\frac{\sigma_t}{4\pi}\{1+\beta P_2(\cos\theta)+[(M+Q_1)P_1^1(\cos\theta)+Q_3P_3^1(\cos\theta)]\cos\phi\}\,, \tag{7}$$

where M, Q_1, and Q_3 will be coefficients arising from the magnetic dipole and electric quadrupole terms, respectively, and ϕ is the azimuthal angle with respect to the x axis. The coefficients Q_1, Q_3, and M are simply related to the coefficients B_n of Eq. (2):

$$Q_3=-2B_3/3;\quad B_1+B_3=M+Q_1-Q_3/2\,. \tag{8}$$

Using these relations Eq. (7) may be written in the form

$$\frac{d\sigma}{d\Omega}=\frac{\sigma_t}{4\pi}\{1+\beta P_2(\cos\theta)+[(B_1+B_3)\sin\theta-5B_3\sin\theta\cos^2\theta]\cos\phi\}\,. \tag{9}$$

The coefficients M, Q_1, and Q_3 may be evaluated in terms of final-state phase shifts and dipole and quadrupole matrix elements. In fact, this is the procedure used in calculations in the relativistic central-field approximation. A detailed report on the evaluation of these terms for atoms at low energies will appear in a forthcoming publication.[15] Here I summarize the two main results of this investigation.

First, note that the magnetic-dipole matrix element contains only the angular-momentum operator L_y. This means that in a one-electron unrelaxed core approximation there will be no magnetic dipole term contribution to the angular distribution owing to the orthogonality of initial- and final-state orbitals. However, the term will be present if core relaxation occurs.

Second, within the nonrelativistic one-electron approximation, regardless of whether or not there is core relaxation, the electric quadrupole terms are constrained to obey the relation $Q_1=Q_3/2$. This result comes from symmetry arguments similar to those used to obtain the dipole result, Eq. (1). If the outgoing electron direction is chosen as the axis of quantization, the outgoing electron may be represented by a wave function which is independent of the azimuthal quantum number m. In dipole approximation the average angular distribution can then be calculated in the form

$$\frac{d\sigma}{d\Omega}\propto A\sin^2\theta+B\cos^2\theta\,, \tag{10}$$

where A is the sum of the squared dipole matrix elements corresponding to $\Delta m=\pm1$ and B to a squared dipole matrix element representing $\Delta m=0$. A similar procedure can be used to calculate the average contribution of the dipole-electric quadrupole interference term $\sum_m\langle z\rangle_m^*\times\langle xz\rangle_m$. In this case, however, the $\langle z\rangle_m^*$ matrix element will change sign if the direction of propagation and quantization direction are changed, but $\langle xz\rangle_m$ will not. The end result is that only $\Delta m=0$ terms will contribute to the averaged dipole-electric quadrupole contribution, leading to the relation $Q_1=Q_3/2$, or $B_1=-B_3$. However, it must be noted that this result applies only for a one-electron model. It is not valid when angular momentum can be transferred to core electrons.

The above result has been derived previously for K-shell photoionization[10] and calculations indicate that $B_1\sim-B_3$ for all s subshells at low energies.[9,11] Within the nonrelativistic central-field approximation, this is true for all subshells.

Based on these results, it is suggested that Eq. (9) be parameterized as follows to compare with experimental data:

$$\frac{\sigma}{d\Omega}=\frac{\sigma_t}{4\pi}[1+\beta P_2(\cos\theta)+(\delta\sin\theta+\gamma\sin\theta\cos^2\theta)\cos\phi]\,, \tag{9'}$$

where $\delta=B_1+B_3$ and $\gamma=-5B_3$.

Within the nonrelativistic single-electron approximation, the parameter γ then represents the major correction term corresponding to dipole-electric quadrupole interference and δ, the magnetic-electric-dipole term, can only be present if core-relaxation occurs. The analogous expres-

sion for unpolarized light is

$$\frac{d\sigma}{d\Omega}=\frac{\sigma_t}{4\pi}[1-\beta/2P_2(\cos\underline{\theta})+(\gamma\sin^2\underline{\theta}/2+\delta)\cos\underline{\theta}]\,, \tag{11}$$

where $\underline{\theta}$ is, as in Eq. (1), the angle between incident-photon and ejected-electron directions.

For partially polarized light in dipole approximation, the angular distribution is expressed in terms of β, σ_t, and P,[16] where P is the polarization fraction. This result may be extended using Eq. (9'). The angular distribution in this case is

$$\frac{d\sigma}{d\Omega}=\frac{\sigma_t}{4\pi}(1+\beta/4+3/4P\beta\cos2\theta)\{\gamma[P\cos^2\theta-(P-1)/2(1-\sin^2\theta\cos^2\phi)]+\delta\}\sin\theta\cos\phi\,, \tag{12}$$

where now θ and ϕ are with respect to the principal axis of polarization.

Two things are to be noted in the above equations. First, if measurements are carried out perpendicular to the photon direction, i.e., in the plane of polarization, the interference terms vanish. This means that for partially polarized light, measurements made in the plane of polarization will yield values of σ_t and β correct to order α regardless of the degree of polarization. It should be noted that this will also be true if relativistic effects are included.[11] Conversely, information on the higher multipole corrections can only be obtained by measurements made not lying in the polarization plane. Second, the magnetic-dipole contribution δ is independent of the degree of polarization as has been noted previously.[14]

For s subshells, the relationships between atomic parameters and the parameters defined above is simple and serves to illustrate how information may be obtained from measured angular distributions. In a one-electron model, the s-subshell cross section is $\sigma_s=8\pi^2\omega/3|\langle r\rangle_p|^2$ is the s-p dipole matrix element and $\beta=2$. Assuming no core relaxation in this model, $\delta=0$ and γ may be written as

$$\gamma=3\omega\alpha\langle r^2\rangle_d/\langle r\rangle_p\cos(\delta_d-\delta_p)\,, \tag{13}$$

where $\langle r^2\rangle_d$ is the s-d quadrupole matrix element and δ_d and δ_p are d- and p-wave phase shifts. This result is identical to that of Ref. 10, which parameterizes corrections to dipole approximation via an energy-dependent parameter k which, in terms of the above parameters, is simply $\gamma/3$. It has been pointed out in Ref. 10 that k can be large for s subshells even in the near-threshold region. While this is true, Eq. (13) indicates that the correction term is proportional to photon energy. This means that large near-threshold deviations from the dipole result are expected only for deep inner subshells. Deviations might also be expected in regions where the ratio $\langle r^2\rangle_d/\langle r\rangle_p$ is large, but if this ratio is large due to $\langle r\rangle_p$ being small, the s subshell cross section will be small and deviations from the dipole result might be difficult to observe.

For an nl subshell in the one-electron approximation, the β parameter depends, as is well known, on the difference between $l+1$ and $l-1$ phase shifts and the dipole matrix elements $\langle r\rangle_{l+1}$ and $\langle r\rangle_{l-1}$.[17] In this approximation, an analogous expression can be derived for γ, which depends on the differences between the phase shifts for final states allowed by dipole selection rules $(l+1, l-1)$ and those allowed by quadrupole selection rules $(l-2, l, l+2)$ and the dipole and quadrupole matrix elements analogous to those in Eq. (13). The expression and its derivation will be given elsewhere.[15]

The only calculations that have been performed at low energies that include the effects of higher multipoles have employed a single-electron relativistic model.[9,11] These calculations indicate that relativistic effects are not important for s subshells ($B_2\sim2$, $B_1\sim-B_3$) except in regions close to threshold where the subshell cross section is extremely small. However, this does not appear to be true for p and d subshells. Moreover, these calculations do not include core-relaxation effects which will be important at energies near subshell thresholds. A comparison of experimental data on angular distributions with both relativistic and nonrelativistic calculations would be useful since it should be possible to obtain information on the relative importance of relativistic effects and core relaxation.

Finally, the above analysis serves to provide an indication of where deviations from the dipole approximation might be important. Note that the electric quadrupole interference term increases linearly with photon energy, whereas the only photon energy dependence of the magnetic-dipole interference term is contained in the dipole matrix elements. At low energies where only outer subshell photoionization is possible (<100 eV), both contributions are expected to be small compared to the dipole contribution. At higher energies (100 eV–10 keV), the effects of the added terms will produce observable effects on the angular distributions as has been predicted by detailed calculations,[9,11] and observed experimentally.[2,18] At energies above 10 keV, higher terms in the multipole expansion will become comparable to the interference terms, the above analysis does not apply, and angular distributions should be analyzed using Eq. (2) as has been done in the past.[9]

[1]J. W. Cooper and S. T. Manson, Phys. Rev. **177**, 157 (1969).
[2]M. O. Krause, Phys. Rev. **177**, 151 (1969).
[3]P. A. Heimann, C. M. Truesdale, H. G. Kerkhoff, D. W. Lindle, T. A. Ferrett, C. C. Bahr, W. D. Brewer, U. Becker, and D. A. Shirley, Phys. Rev. A **34**, 3782 (1986).
[4]W. Ong and S. T. Manson, Phys. Rev. A **19**, 88 (1978).
[5]D. Dill, A. F. Starace, and S. T. Manson, Phys. Rev. A **11**, 1596 (1975).
[6]S. H. Southworth, U. Becker, C. M. Truesdale, P. H. Kobrin, D. W. Lindle, S. Owaki, and D. A. Shirley, Phys. Rev. A **28**, 261 (1983).
[7]C. N. Yang, Phys. Rev. **74**, 764 (1948).

[8]R. H. Pratt, A. Ron, and H. K. Tseng, Rev. Mod. Phys. **45**, 273 (1973); R. H. Pratt, R. D. Levee, R. L. Paxton, and W. Aron, Phys. Rev. **134**, A898 (1964); R. D. Schmickley and R. H. Pratt, *ibid.* **164**, 104 (1967).

[9]H. K. Tseng, R. H. Pratt, S. Yu, and A. Ron, Phys. Rev. A **17**, 1061 (1978); M. S. Wang, Y. S. Kim, R. H. Pratt, and A. Ron, *ibid.* **25**, 857 (1982).

[10]A. Bechler and R. H. Pratt, Phys. Rev. A **39**, 1774 (1989).

[11]J. H. Scofield, Phys. Scr. (to be published); Phys. Rev. A **40**, 3054 (1989).

[12]J. C. Tully, R. S. Berry, and B. J. Dalton, Phys. Rev. **176**, 95 (1968).

[13]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-electron Systems* (Academic, New York, 1957), Sections 66, 69, and 72.

[14]M. Peskin, Adv. Chem. Phys. **18**, 1 (1970).

[15]J. W. Cooper (to be published.)

[16]J. A. R. Samson and A. F. Starace, J. Phys. B **8**, 1806 (1975).

[17]J. Cooper and R. N. Zare, J. Chem. Phys. **48**, 942 (1968).

[18]F. Wuilleumier and M. O. Krause, Phys. Rev. A **10**, 242 (1974).