Determination of Complex Ionization Amplitudes by $(e,2e)$ Spectroscopy

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$(e,2e)$ spectroscopy has been used to investigate interference between resonant dipole and nonresonant monopole electron-impact ionization of Cd. A technique is described which allows the experimental determination of the relative magnitude and phase of the amplitudes for these processes. The method makes use of the rapid variation with energy of the continuum phase in the region of autoionizing resonances. The experimental relative dipole/monopole amplitude for momentum transfer 0.18 a.u. is found to be in substantial disagreement with a plane-wave Born approximation calculation.

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The electron-electron coincidence [or $(e,2e)$] technique provides detailed information on the electron-impact ionization process. $(e,2e)$ ejected-electron angular distributions show strong angular correlations between scattered and ejected electrons; the latter are preferentially ejected around the binary $(+\mathbf{K})$ and recoil $(-\mathbf{K})$ directions, where $\mathbf{K}$ is the momentum transferred in the collision [1].

A sensitive test of theory is the ability to obtain the correct binary-recoil intensity ratio, which is due to the angular behavior of complex interference cross terms in a partial wave expansion of the ejected-electron wave function. For s-shell ionization, there is a direct correspondence between this expansion and a multipole expansion of the scattering amplitude. Thus the calculation involves a coherent sum over complex amplitudes, rather than the incoherent sum in integrated scattering cross-section calculations.

It has long been known that the plane-wave Born approximation (PWBA) fails to predict the observed binary/recoil intensity ratio, even for fairly high incident electron energy and small momentum transfer [1]. A recent calculation by Botero and Macek [2] suggests that this failure of the PWBA is mainly due to incorrect *phase* predictions in the complex amplitudes. Using the Coulomb-Born approximation (CBA), good agreement was found between calculated and experimental $(e,2e)$ ejected-electron angular distributions for carbon inner-shell ionization, whereas an equivalent PWBA calculation was in very poor agreement. A term by term comparison of a multipole expansion (about $\mathbf{K}$) for the two calculations showed that the *magnitudes* of equivalent complex amplitudes were similar but the relative *phases* were very different.

The experimental determination of phase information of individual terms is clearly desirable. Traditional coplanar $(e,2e)$ experiments (incident, ejected, and scattered electrons in the same plane) are unable to yield complete information about the amplitudes of individual interference cross terms since angular distributions contain a sum over several such terms [3]. For the kinematic conditions investigated by Botero and Macek, where the multipole expansion may be truncated at $l=3$, there are six terms, each containing a magnitude *and* a phase. Even if only two cross terms are significant it is not possible to obtain unambiguous amplitudes; in previous work [4] involving autoionization we were forced to make a number of assumptions in the analysis of experimental data.

Recently, the first extensive *noncoplanar* $(e,2e)$ measurements in He have been carried out at low incident energy [5], resulting in angular distributions described by a set of fitted generalized parameters [6,7]. In principle, both magnitude and phase information may be extracted; the symmetric geometry and kinematic conditions used kept the number of parameters required to a large, but manageable, quantity. Angular distributions for the high-energy asymmetric case (where the two outgoing electrons have unequal energies) have also been analyzed using this parametrization [8]. Again, a fairly large number of fit parameters is required; the exact number to be included is fairly critical.

Here, we present the results of a novel coplanar asymmetric $(e,2e)$ experiment on atomic cadmium, which enables the extraction of both the magnitude and the phase of an individual cross term. The experiment is possible because we make use of the rapid change of phase with *energy* across autoionizing resonances.

Instead of measuring complete angular distributions for a fixed ejected-electron energy, as is done in more conventional experiments, we measure $(e,2e)$ energy spectra for two ejected-electron directions 180° apart. We make use of the experimental fact that the *dipole* allowed spectrum of Cd at low ejected electron energies is due only to autoionization, with no measurable contribution from direct ionization [9]. The principle of our experiment is outlined below, where, for the sake of clarity, it is assumed that there is a single autoionizing level.

We consider electron-impact ionization of an ns^2 atomic ground state resulting in an ns ionic state. We wish to model the $(e,2e)$ energy spectrum in the PWBA limit, as a function of ejected-electron direction and momentum transfer, for the special case where the dipole term is due only to autoionization and all other multipoles are due to direct ionization.

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The isolated autoionizing level has energy E_0, angular momentum $L=1$, and is excited by a dipole transition amplitude $A_1(K)=|A_1|e^{i\chi_1}$, followed by autoionization into the $nsEp$ continuum due to a discrete-continuum interaction V. With other multipole amplitudes $a_l(K)=|a_l|e^{i\chi_l}$ nonresonant, the $(e,2e)$ energy spectrum in the PWBA limit is of the form [10,11]

$$I(\theta,E,K)\sim\left|\frac{\sqrt{3}|A_1|}{\pi V}\sin\Delta e^{i(\delta_1+\Delta)}P_1(\cos\theta)-\sum_{l\neq 1}\sqrt{2l+1}|a_l|e^{i\delta_l}P_l(\cos\theta)\right|^2, \quad (1)$$

where θ is the ejected-electron direction with respect to the quantization axis $\mathbf{K}$, and the P_l are Legendre polynomials. The phases are

$$\delta_l=\chi_l-\tfrac{1}{2}l\pi+\sigma_l+\delta_l, \quad (2)$$

where σ_l is the hydrogenic Coulomb phase [12], and δ_l is the phase shift due to the unperturbed non-Coulombic ionic potential. Both these quantities are slowly varying functions of E. The rapidly varying extra phase due to autoionization is given by [13]

$$\cot\Delta=-\varepsilon=-\frac{E-E_0}{\Gamma/2}, \quad (3)$$

leading to a Lorentzian line shape $\sin^2\Delta$ with full width at half maximum $\Gamma=2\pi V^2$.

When $K\ll 1$, the PWBA magnitudes [4,14] are proportional to K^{l-2} for $l>0$, and are independent of K for $l=0$. It is therefore possible to find kinematic conditions where K is sufficiently small that the summation in Eq. (1) may be terminated at $l=2$. Furthermore, for experiments carried out at the "magic angles," $\theta=\theta_{\rm mag}$ and $\theta_{\rm mag}+180°$, the $l=2$ term vanishes since $P_2(\cos\theta)=0$. This leaves only one cross term in Eq. (1), between the monopole and dipole amplitudes. Defining $I^{\pm}$ as the spectra taken at these two angles, and $\delta_{l0}=\delta_l-\delta_0$, we then have the *sum* and *difference* spectra:

$$I^++I^-\sim 2\frac{|A_1|^2}{\pi^2V^2}\sin^2\Delta, \quad (4)$$

$$I^+-I^-\sim -4\frac{|A_1||a_0|}{\pi V}\sin\Delta\cos(\Delta+\delta_{10}), \quad (5)$$

where, in the summed spectrum, we have ignored the small contribution from the monopole cross section.

Figure 1 illustrates Eqs. (4) and (5) for $\pi V|a_0|/|A_1|=0.1$, and sample values $\delta_{10}=0,\pm\pi/4$. In Fig. 1(a) the peak of the Lorentzian has been normalized to unity, with the interference term in Fig. 1(b) plotted on the same relative scale. Note how the relative *magnitudes* of the excitation amplitudes determines the relative intensity in the two figures and the relative *phases* of the excitation amplitudes determine the shape of the interference term as a function of energy. Thus, because of the presence of autoionization, it is possible to obtain values of both quantities from experimental data.

An interesting relationship results by considering the ratio of the difference and sum intensities and expressing Δ in terms of the reduced energy ε. We then have

$$\frac{I^+-I^-}{I^++I^-}=2\pi V\frac{|a_0|}{|A_1|}\cos\delta_{10}[\varepsilon+\tan\delta_{10}], \quad (6)$$

which is a straight line whose intercept on the ε axis gives the relative phase and whose slope then gives the relative magnitude.

Equation (6) provides the most elegant analysis of experimental data involving a single level interacting with a single continuum. Cadmium, however, has a more complicated spectrum and modified forms of Eqs. (4) and (5) were used in the analysis of our data. Because of the magic angle condition, the new Eq. (4) still represents the dipole cross section. We have carried out extensive calculations, using pseudorelativistic Hartree-Fock (HFR) radial wave functions [14] and including configuration interaction (CI), in order to model the Cd sum and difference spectra. This requires the calculation of the dipole and monopole processes and their relative phase. Details of the calculations will be published elsewhere.

The Cd dipole-allowed autoionizing spectrum [15] at ejected-electron energies below 5 eV is dominated by the intermediate-coupling configuration $4d^95s^25p$, excited from the ground state $4d^{10}5s^2(^1S_0)$ by $4d\rightarrow 5p$. The most intense spectral line is $^1P_1$, with a near-Lorentzian profile of width 0.14 eV centered on 3.81 eV; less intense

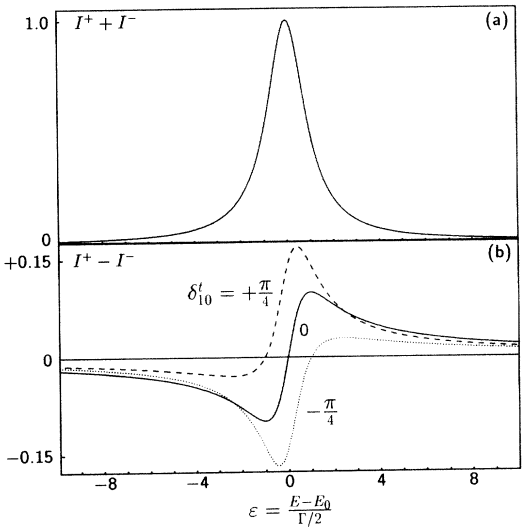

FIG. 1. Plots of Eqs. (4) and (5) for a representative monopole/dipole magnitude ratio and three different total relative phases δ_{l0}.

lines correspond to $^3P_1$ and $^3D_1$. Additional structure in the spectrum [15,16] is due to the doubly excited configurations $5pns$ ($n=6,7,8$) and $5p5d$. All the above levels couple to the $5sEp\ ^{1,3}P_1$ continua. The calculation of the dipole process, for the single configuration $4d^95s^25p$ and with empirical parameters used in a theory of overlapping resonances that couple to two continua [17], has been described in detail elsewhere [9]. For the present work a new, more detailed calculation has been carried out which includes *ab initio* CI HFR parameters for the doubly excited configurations. These levels are only weakly excited, via ground state correlation [18], and they mainly affect the shape of the spectrum but not its integrated intensity [16]; to a good approximation this latter quantity is determined by the $4d \rightarrow 5p$ transition amplitude.

The calculation of the monopole process included the even parity doubly excited $5pnp$ ($n=5,6,7$) $J=0$ autoionizing levels that autoionize into the $5sEs\ ^1S_0$ continuum [4]. However, since the (CI HFR) calculated level widths are more than an order of magnitude less than our experimental energy resolution and the levels are only weakly excited, they have little effect on the calculated difference spectrum. Thus the overall monopole process is mainly determined by the $5s \rightarrow Es$ direct ionization amplitude.

Calculations of the phase shifts δ_l were in excellent agreement with the extrapolated quantum defect behavior of $5snl$ Rydberg series [19,20], yielding a value $\delta_1 - \delta_0 = -(0.56 \pm 0.02)\pi$.

The free parameters in the calculation of the sum and difference spectra are the relative phase χ_{10}, and the (real) reduced matrix elements, $\langle Es||j_0(Kr)||5s\rangle$ and $\langle 5p||j_1(Kr)||4d\rangle$, where $j_l(Kr)$ is a spherical Bessel function [14]. For comparison with experimentally obtained values we calculated the PWBA reduced matrix elements; the relative phase is $\pi/2$ [21].

The coplanar $(e,2e)$ spectrometer used in the present experiments has been described in detail elsewhere [4]. A position sensitive detection system has recently been fitted to the ejected-electron channel resulting in both higher count rates and improved energy resolution.

The experiments were carried out with an electron-beam energy of 150 eV and a scattering angle of $+2°$, corresponding to a momentum transfer 0.18 a.u. in the spectral region of interest. $(e,2e)$ and noncoincident ejected-electron spectra were obtained for ejected-electron directions $\pm 90°$ with respect to the electron-beam axis, i.e., the magic angles away from the momentum transfer axis. Normalization (to better than 2%) and energy alignment (to within 2 meV) of the $(e,2e)$ spectra were achieved by using the axial symmetry of the noncoincident spectra.

The sum and difference $(e,2e)$ spectra are shown in Figs. 2(a) and 2(b). The experimental energy resolution is 0.04 eV full width at half maximum (FWHM). The solid line in Fig. 2(a) is the theoretical dipole cross section folded with a Gaussian of FWHM 0.04 eV and satisfactorily fitted to the experimental data to obtain the normalization constant (proportional to the dipole matrix element). The solid curve in Fig. 2(b) is the theoretical interference, folded with the experimental resolution and fitted to the data. The relative magnitude and phase from the fit are

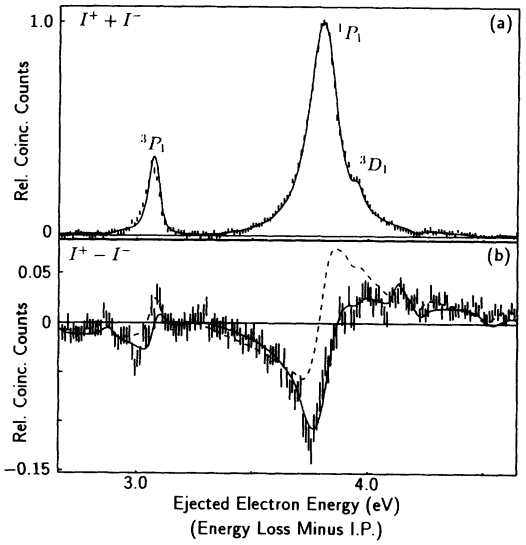

FIG. 2. (a) Experimental $(e,2e)$ sum spectrum for Cd. The vertical bars represent the statistical uncertainties. The solid line is the calculated dipole cross section fitted to the data. The three $4d^95s^25p$ autoionizing resonances are labeled. (b) Experimental $(e,2e)$ difference spectrum. The solid line is the calculated $J=0,1$ interference fitted to the experimental data. The dashed line is the same calculation but with the PWBA relative phase.

$$\frac{\langle Es||j_0(Kr)||5s\rangle}{\langle 5p||j_1(Kr)||4d\rangle} = 0.23 \pm 0.02\ \text{eV}^{-1/2}$$

and $\chi_{10}=(0.20\pm0.05)\pi$, for an ejected-electron energy $E \approx 4$ eV. Neither of these values is in agreement with our PWBA calculations. The fitted magnitude is 2.2 times the calculated value, and the fitted phase is 0.3π less than the PWBA relative phase $\pi/2$. The dashed curve in Fig. 2(b) corresponds to the fitted magnitude but with the PWBA phase; the difference is most marked in the region of the $^1P_1$ resonance.

Although the spectrum shown in Fig. 2(a) consists of a number of overlapping resonances, the $^1P_1$ resonance line shape is approximately Lorentzian, and it is possible to analyze the data in this restricted energy region in the manner suggested by Eq. (6). This is shown in Fig. 3 as a function of the reduced energy for $\Gamma(^1P_1)=0.14$ eV. The solid curve is the full theory, which includes all resonances, fitted to the data. The dotted line is the best straight line fit, which, using Eq. (6), corresponds to $\chi_{10}=0.17\pi$ and a relative magnitude within 10% of the above value. It is remarkable that the simple analysis is

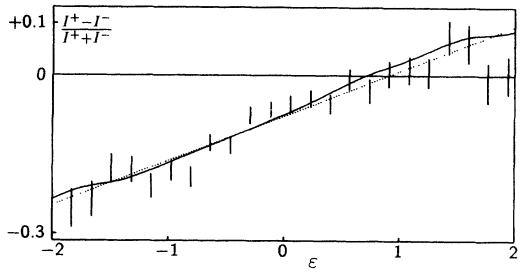

FIG. 3. The data of Fig. 2 presented as the ratio of the difference and sum spectra in the $^1P_1$ region. The solid line is a calculation including all autoionizing levels. The dotted line is a straight line fit in the spirit of Eq. (6).

applicable within the range $\varepsilon = \pm 2$, given the complexity of the dipole spectrum.

Although the system and kinematics investigated are very different from those in the CBA and PWBA calculations [2], some theoretical insight may be gained from a qualitative comparison. Whereas the experimental and PWBA *phase* discrepancy has both a similar size and sign to that found in the CBA and PWBA calculations, our experimental results do not show that a PWBA calculation should yield the correct dipole/monopole *magnitude* ratio.

In addition to the experiment described above, we have carried out experiments which yield the dipole/quadrupole ($J=1,2$) interference cross term. The analysis of these experiments is not as straightforward as the magic-angle experiment since it involves $J=0,1,2$ ionization with significant $J=2$ autoionization. The detailed results and analysis will be published elsewhere. Here, we note that a disagreement similar to that found above for the $J=1,0$ experimental and PWBA magnitudes also exists for $J=1,2$. The relative phase disagrees by a similar absolute value but with the opposite sign, which again agrees with the CBA and PWBA result.

Future experimental plans include repeating the measurements at larger scattering angles in order to find the K dependence of the amplitudes.

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