Direct Observations of Relativistic Effects in Single-Electron Momentum Distributions in Xenon Outer Shells

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The $5p_{3/2}$ and $5p_{1/2}$ one-electron momentum probability distributions in xenon, measured by means of the noncoplanar symmetric $(e, 2e)$ reaction, show clear and direct manifestations of relativistic effects. The momentum densities and branching ratios cannot be described by nonrelativistic wave functions, but they are in very good agreement with those given by Dirac-Fock wave functions.

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The measurement of electron momentum distributions has become a powerful tool for investigating the detailed electronic structure of atoms and molecules.[1-3] The noncoplanar symmetric $(e, 2e)$ reaction (or electron coincidence spectroscopy) has been shown[2,3] to be particularly valuable in measuring electron momentum distributions, as well as electron correlation effects and the influence of chemical bonding on momentum distributions. The cross section for this reaction at high enough electron energies is essentially directly proportional to the square of the momentum-space overlap between the initial target state and final ion state. If the target atom or molecule can be well described by the Hartree-Fock (HF) approximation, the momentum-space overlap reduces to the square of the momentum-space wave function of the characteristic orbital from which the particle is ejected, multipled by a constant of proportionality. This constant of proportionality is the pole strength (or spectroscopic factor) for the transition, and describes the probability that the ion state contains the configuration consisting of a hole in the characteristic orbital coupled to the ground state of the target. For pole strengths close to unity the transition can be well described in single-particle terms.

Recently the reaction has been used to measure the electron momentum distribution in atomic hydrogen,[4] and in helium the ground-state transition has been shown to be accurately described by the Hartree-Fock wave function.[3,5] The $(e, 2e)$ transitions to higher excited states in He^+ are, however, extremely sensitive to electron correlations in the helium ground-state wave function,[3] and in a recent experiment[5] the $(e, 2e)$ measurements to the $n = 2$ ion states were able to discriminate between several accurate correlated helium wave functions, two of the wave functions obtaining 98% of the correlation energy.

Accurate single-particle momentum-distribution measurements have been confined to low- and medium-Z atoms (and molecules), and for the dominant single-particle transitions the measured momentum distributions are found to be in good agreement with those given by the nonrelativistic Hartree-Fock wave functions for the characteristic orbital.

In the case of heavy elements relativistic effects may become important in the one-electron momentum distributions. Electrons with the same n and l quantum numbers but with different values of total angular momentum j need not necessarily have the same radial momentum distributions, as they would in nonrelativistic approximations. While attention has been focused on the deviations between HF and relativistic bound-state wave functions,[6] most of it has concerned the single-particle energies and to a lesser extent the position-space radial distributions of the orbitals. For instance, in the observation of spin-orbit branching ratios in photoelectron spectroscopy, relativistic effects are found to play an important role, but they are often obscured by other effects such as the "kinetic-energy" effect.[7,8] A direct test of relativistic structure theories can, however, be obtained by measuring the electron momentum probability distributions for a high-Z atom, since the probability distribution is the observable most closely related to the electronic wave function. We have therefore carried out accurate momentum-profile measurements for the valence $5p_{3/2}$ and $5p_{1/2}$ orbitals of xenon using the noncoplanar symmetric $(e, 2e)$ reaction. The measurements are the first to show the direct effects of relativity in one-electron probability distributions. The $5p$ outer valence orbital of xenon provides a suitable case for comparing one-electron momentum densities with those given by structure theories. Firstly xenon with $Z = 54$ should begin to show the influence of relativistic effects in its ground-state wave function. Secondly, since the pole strength for the $5p$ hole state is essentially unity,[9-11] final- and initial-state configuration-interaction effects will have only a minimal influence on the results. Such effects will of course have no influence on the branching ratios in the nonrelativistic limit.

The measurements were carried out with a recently modified coincidence spectrometer which has been fully described elsewhere.[5] The modified spectrometer employed two position-sensitive microchannel plate electron detectors which were aligned with the energy-dispersing direction of the two hemispherical analyzers. The mode of data acquisition has also been described in Ref. 5. The sum of the outgoing electron energies was chosen to be 1200 eV, the incident electron energy being 1200 eV plus the electron binding energy. The separation energy spectrum for the $5p_{3/2,1/2}$ doublet was recorded as a function of the out-of-plane azimuthal angle, which is directly related to the momentum of the struck electron.[2]

The energy resolution of 1.6 eV was not sufficient to resolve the $5p_{3/2}$ and $5p_{1/2}$ doublet clearly. Therefore a deconvolution procedure was employed. First a careful measurement was made of the helium $(e,2e)$ ground-state separation-energy spectrum in order to accurately establish the experimental resolution function. This line spectrum was fitted with three Gaussians; the fixed widths and relative heights of these Gaussians were then used to fit the two xenon $5p$ lines, the only variable being the relative intensity of the two lines in the doublet.

The resulting $(e,2e)$ momentum profiles are shown in Fig. 1, where the $(e,2e)$ cross sections for the doublet have been divided by the multiplicity $(2j+1)$ for each level. The observed momentum distributions are clearly different for the two j values. The $j=\frac{3}{2}$ momentum distribution is significantly greater than the $j=\frac{1}{2}$ momentum distribution at low values of electron momentum, but at high values of momentum (>0.9 a.u.) the $j=\frac{1}{2}$ momentum distribution is greater than the $j=\frac{3}{2}$ one. This is clearly in violation of any nonrelativistic structure theory, which would predict the two distributions to be equal.

A relativistic HF, otherwise called a Dirac-Fock (DF),[12] calculation has been carried out for the ground state of xenon. The resulting squares of the DF momentum-space wave functions for the $5p_{3/2}$ and $5p_{1/2}$ orbitals in xenon are shown by the solid

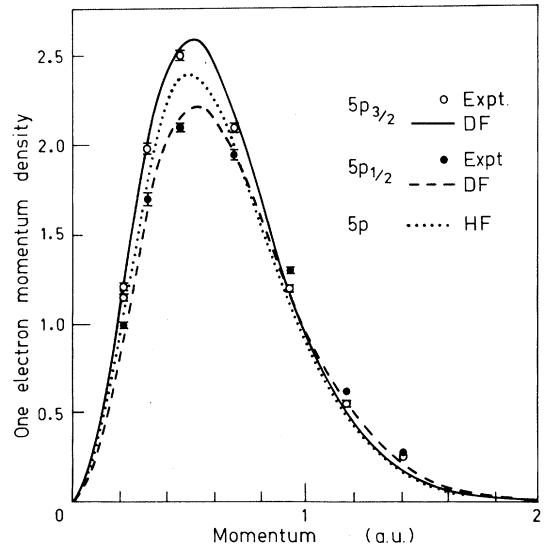

FIG. 1. The one-electron momentum probability distributions for the $5p_{3/2,1/2}$ orbitals in xenon compared with DF (solid line and dashed line) and HF (dotted line) wave functions.

and dashed curves in Fig. 1. Since the measured $(e,2e)$ momentum profiles are not absolute, the total $5p$ cross section at the out-of-plane azimuthal angle ϕ of 6°, corresponding to a momentum p of 0.46 a.u., was normalized to the total summed $5p$ DF probability distribution. The figure shows that the DF one-electron momentum probability distributions are in very good agreement with the measurements, showing clearly that the DF wave functions are realistic.

Also shown in Fig. 1 by the dotted curve is the HF one-electron momentum probability distribution (again normalized to the summed $5p$ data at $\phi = 6°$). Clearly the nonrelativistic wave function is quite inadequate, giving the same shape and magnitude for both momentum distributions.

Nonrelativistic structure theories predict that the ratio of $5p_{3/2}$:$5p_{1/2}$ cross sections should be independent of the momentum of the struck electron and be given simply by the relative statistical weights, namely 2:1. The observed branching ratio is plotted in Fig. 2 as a function of the momentum. It deviates significantly from the value of 2, being greater than 2 at momenta below approximately 0.9 a.u., and smaller than 2 at higher momenta. Also shown in the figure is the branching ratio given by the DF wave functions. It is in very good agreement with the data over the measured range of momenta.

Because of numerical problems, the DF momen-

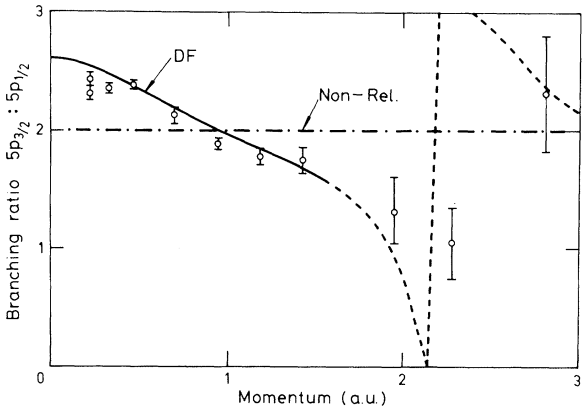

FIG. 2. The 1200-eV noncoplanar symmetric $(e, 2e)$ branching ratios plotted as a function of the momentum.

tum distributions may be inaccurate above 1.5 a.u., and so the DF branching ratios in this momentum region have been indicated by a dashed curve. The sharp minimum and maximum at about 2.2 a.u. are due to the fact that the first nodes in the two DF momentum-space wave functions occur at slightly different values of momentum. Unfortunately zeros in the wave functions also correspond to zeros in the $(e, 2e)$ cross section in the plane-wave impulse approximation, making the measurement of these effects extremely difficult. In addition, distortion effects in the continuum electron waves become important at high momentum and in regions where the plane-wave approximation gives zero or small cross sections.[2,5] Therefore comparison between experiment and the present calculation must be treated with caution above about 2 a.u.

While the theoretical results discussed above were obtained with a single-configuration DF wave function, more extensive calculations were also carried out within a relativistic configuration-interaction framework. The DF program was used to define a set of virtual single-particle spinors, which were used to form configuration-interaction basis sets for the initial target and final ion states, each composed of about 1000 Slater determinants. Below 1.5 a.u., deviations from the DF results shown in Fig. 1 were negligible, while the branching ratios were indistinguishable from the DF results shown in Fig. 2.

We conclude that relativistic effects are important even in the outer valence shell of a medium-Z element such as xenon, and that shape differences between the $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ momentum distributions, which are not predicted by the nonrelativistic structure models, are indeed directly observable. Further, Dirac-Fock wave functions give good agreement with the observed electron momentum distributions and cross-section branching ratios.

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