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Diverse manifestations of barriers to atomic electrons*

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Attention is called to phenomena that should serve as sensitive indicators of the field acting upon slow electrons as they traverse the edge of atoms.

Certain resonances observed in photoabsorption spectra of inner-shell electrons have been attributed to the presence of potential barriers at the edge of an atom or molecule, which hinder the escape of the ejected electron. The barrier may, but need not, originate simply from the centrifugal potential experienced by electrons with high orbital momenta ($l \geq 2$). These phenomena have been discussed repeatedly[1-5] but additional comments may be warranted by the recent observation of related effects in different settings, namely, in bremsstrahlung emission[6] and in photoabsorption by valence electrons.[7] The comments aim at drawing the attention of a wider public, because a reasonably detailed mapping and understanding of the situation may require a variety of experimental and theoretical approaches.

We shall first state the comments and then illustrate them by outlining the recent evidence. Since the newer phenomena have been observed in barium and lanthanum atoms ($Z = 56, 57$) and are attributed to the effect of the centrifugal field on f electrons, we deal explicitly with this particular but important case. In these examples the barrier peaks at the edge of the atom, i.e., at a radius of the order of 1 Å from the nucleus where the nuclear attraction and the centrifugal repulsion balance out. The potential decreases outwards from the peak owing to the declining strength of centrifugal repulsion and inward owing to the increasing strength of nuclear attraction.

(a) Because of the near cancellation of two strong fields, the location and the height of the barrier peak depend critically on the screening of the nuclear attraction by the other electrons, as well as on the presence of any external field. (The centrifugal field is, of course, known exactly but the screening depends on such poorly predictable details as exchange and correlations.) Furthermore, the effect of a barrier upon an electron changes critically when the phase of the radial wave function attains a multiple of π in the classically forbidden region near the peak.

(b) Major changes of the attractive field may result from the presence of inner shell vacancies, especially from their exchange interaction with the electron of interest.[2] Thus, e.g., a photoelectron being ejected from the $4d$ shell of La into an f orbit experiences attraction by the $4d$ vacancy while a $4f$ electron of the same atom does not; the barrier height is accordingly different in the two cases.

(c) The physico-chemical environment of the atom may also exert a critical influence, through crystal fields and especially by inducing variations of covalent bonding which shift the mean position of valence electrons and thereby the barrier radius.

(d) Accordingly, observations of resonances due to the barrier should serve as critical indicators of the environment of each atom. By contrast, theory is today in a poor position to predict the position of each resonance with any accuracy.

One of the recent investigations deals with the emission of x rays near the tip of the bremsstrahlung spectrum, i.e., with photon energies close to the energy of the incident electron. This process must occur in the interior of an atom where the field has sufficient strength to absorb the incident momentum. The electron remains even more strongly influenced by the atomic field after having spent nearly its full energy in the radiation process; hence it combines with the target atom into an (unstable or metastable) complex. The probability of radiating photons of specific energy is thus proportional to the *local* density of states of this complex in the interior of the atom. (This circumstance can distort the spectrum near the tip, frustrating attempts to utilize precise observations of its Duane-Hunt limit as a measurement of e/h.[8]) In particular, the local density of states may be enhanced resonantly by any obstacle to the decay of the complex by escape of the radiating electron. Indeed Liefeld *et al.*[6] bombarding a La target with monoenergetic electrons of 500–1000 eV, have observed a narrow peak rising above the ray spectrum at 5.5 eV below its tip (Fig. 1). They attribute the peak to capture of the radiating electron into an empty discrete $4f$ orbital in the interior of the atom, but a similar effect might also have been produced by a shape resonance in the continuum slightly above the peak of the barrier. (Atoms of La vapor do possess an inner $4f$

orbital at a level higher than the ground state but the same need not hold for the negative e + La complex.) A $4f$ level lies presumably below the barrier peak; accordingly the interpretation of the resonance bears on the height of this peak. Very recent calculations[9] aimed at accounting for the tip bremsstrahlung peak have shown the result to depend critically on whether the atom is regarded as isolated, in vapor phase.

Additional peaks were observed when the incident electron energy traverses the thresholds for excitation of the M_4 and M_5 characteristic x rays, near 850 eV. Their pattern arises from the superposition of the characteristic lines and of the bremsstrahlung tip and varies as a function of energy. In this range the incident energy may be utilized either to radiate a photon, leaving one residual slow electron, or to excite an M shell electron, yielding *two* slow electrons. Liefeld *et al.* suggest plausibly that both of these slow electrons are trapped into $4f$ levels. Yet a dependable interpretation should rest on broader inputs of evidence which remain to be developed. For example, one might investigate whether and how these x-ray spectra depend on the degree of oxidation of the target material. Thus, e.g., a qualitative difference has been observed in the photoabsorption spectra of di- and trivalent Yb at the $4d$ threshold.[10]

The second, and quite recent, type of evidence emerges from observations by Roig and Tondello[7] of the ultraviolet absorption spectrum of Ba$^+$ in a shock tube. Specifically, the wavelengths and the relative intensities of the $5d \to nf$ transitions were measured for n ranging from 4 to 13. The nf level positions showed a striking rise of their quantum defects, from small values to nearly unity, which follows the familiar behavior of a resonant phase shift (Fig. 2). The oscillator strength dependence on n seemed initially complicated but it also revealed a clear resonance behavior when reduced by Lin[11] to the form of a spectral density, $df/dE = f_n\,(dE/dn)^{-1}$. Note, however, in Fig. 2 that the two familiar indices of resonance position, namely, the peak of the oscillator strength density and the point of steepest rise of the quantum defect, do not coincide on the energy scale. Actually, these indices are related but need not quite coincide. The effects displayed in Fig. 2 imply a rapid shift of the radial wave functions of f electrons toward smaller values of the radial coordinate. Such a shift might occur at an energy lower than the barrier peak, for which the depth and width of the potential well inside the barrier are just sufficient to accommodate a half-wavelength, that is, when the phase of the wave function reaches π near the barrier peak. In this event the resonance effect would appear very sharply and at the same energy in both plots of Fig. 2. These plots indicate instead a more gradual evolution of the nf wave functions with increasing energy, such as would occur at energies near or above the peak of the barrier.

In conclusion the evidence and the discussion presented in this paper indicate that effective potential barriers to the radial motion of low-energy electrons manifest themselves in various and rather unexpected ways. These manifestations may serve as sensitive indicators of the state of an atom or molecule, but accurate characterization

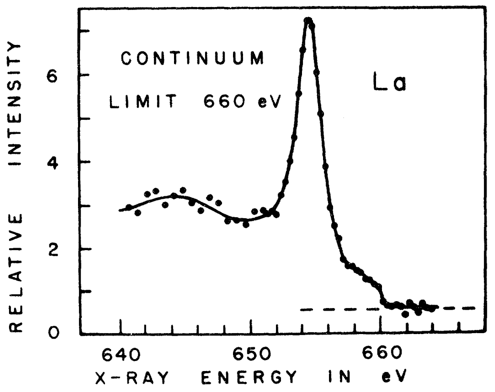

FIG. 1. Continuous x-ray spectrum emitted by 660-eV electrons incident on lanthanum (Ref. 6).

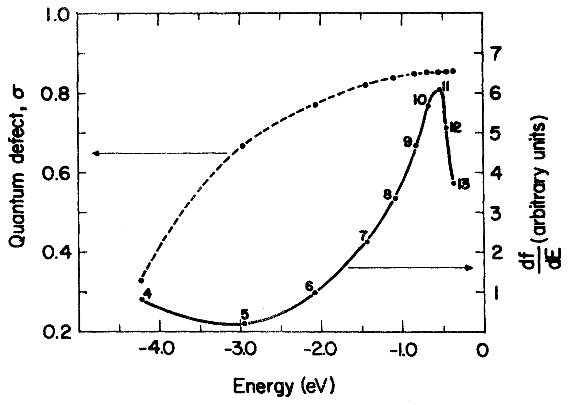

FIG. 2. Quantum defects of nf levels of Ba$^+$ ions and spectral density df/dE of $5d \to f$ transitions. (The occurrence of a minimum of df/dE near $n = 5$ is unexplained.) Courtesy C. D. Lin, Harvard University Observatory; data from Ref. 7.

of the barriers may require new, imaginative approaches, experimental and/or theoretical. The escape of an electron is a particularly sensitive probe when it leaves behind a neutral atom.

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