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Perturbed-Stationary-State Theory of Atomic Inner-Shell Ionization by Heavy Charged Particles*

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Cross sections for inner-shell ionization by slow heavy charged particles, if compared to predictions given in the plane-wave Born approximation, are reduced strongly by the Coulomb deflection of the particle in the field of the target nucleus, and by the increase in binding energy of the target electrons induced by the presence of the particle. We use the framework of the perturbed-stationary-state approximation to incorporate these effects *ab initio* into the theory of inner-shell ionization and derive the binding effect given by Brandt, Laubert, and Sellin. Our result formally unifies the Coulomb deflection of the particle trajectory with the perturbation of the atomic states in their effect on the ionization cross section and suggests systematic ways for further improvements.

I. INTRODUCTION

When an energetic charged point particle passes through matter it may eject inner-shell electrons of the target atom into excited or ionized states by direct Coulomb encounters. The resulting vacancies may be detected by observing characteristic x-radiation or Auger-electron spectra. Theoretical ionization cross sections for production of these vacancies have been studied in the plane-wave Born approximation (PWBA), usually employing hydrogenic wave functions for the atomic system,[1-3] and in a classical binary-encounter approximation.[4]

Consider the regime where the incident velocity v_1 of the particle is so low that $(v_1/Z_2^* v_0) \ll 1$, where Z_2^* is the effective atomic number of the target for the shell in question and $v_0 = e^2/\hbar$. In this regime two substantial v_1-dependent effects appear which are not included in these approximations: (i) Coulomb deflection of the particle by the target nucleus, and (ii) increased binding of the target electrons owing to the presence of the slowly moving particle. The theory of the first of these effects has been studied thoroughly by Bang and Hansteen,[5] who obtain cross sections in a semiclassical approximation in the sense that they incorporate the hyperbolic trajectory of the (heavy) particle in the Coulomb field of the bare target nucleus.

Brandt, Laubert, and Sellin,[6] hereafter referred to as BLS, discovered that the binding effect may give rise to K-shell ionization cross sections considerably smaller than those calculated from these theories. They arrive at a successful description of their experimental results by employing the deflection-corrected PWBA formula for the cross section, but, in addition, they replace the binding energy of the K electron for the isolated atom as it occurs in this formula by an augmented energy which allows for the binding effect of the finite positive charge of the particle. The incremental binding energy is evaluated by bound-state perturbation theory at a given impact parameter and averaged over impact parameters according to the excitation probability, before integrating the cross section over all final electron states. This approach was reviewed recently[2] and has been studied

further.[3]

The BLS approach is based on reasonable physical arguments. This paper intends to derive the binding effect *ab initio* in the framework of the perturbed-stationary-state (PSS) theory. We find that at low speeds of impact, where the PSS theory is most accurate, the BLS procedure gives the correct theoretical description of the cross sections. Possible improvements are discussed.

II. THEORY

The incident particle of charge $Z_1 e$, moves on a prescribed trajectory with radius vector $\vec{R}(t)$ measured from the nucleus of the target atom at time t (Fig. 1.) The Hamiltonian of the N-electron atomic system is taken to be $H_a(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ in the absence of the charged particle, where $\vec{r}_j$ is the position vector of the jth electron relative to the nucleus. The effect of the charged particle is given by the additive energy operator

$$V(t)=\sum_{j=1}^{N} \frac{-Z_1 e^2}{|\vec{r}_j-\vec{R}(t)|} ,$$

which appears in the time-dependent Schrödinger equation as $[H_a+V(t)]\Psi = i\hbar\partial\Psi/\partial t$. Following standard developments of PSS theory,[7,8] we expand Ψ in terms of time-dependent adiabatic wave functions;

$$\Psi_i=\sum_{m=0}^{\infty} a_m(t)u_m(\vec{R}(t))\exp\left(\frac{-i}{\hbar}\int_{-\infty}^{t} W_m(\vec{R}(t'))\,dt'\right), \tag{1}$$

where the subscript i denotes the initial condition $a_m(-\infty)=\delta_{mi}$. Here,

$$[H_a+V(t)]u_m(\vec{R}(t))=W_m(\vec{R}(t))u_m(\vec{R}(t))$$

is understood to generate the set of wave functions $u_n(\vec{R}(t))$ corresponding to the nth excited or ionized configuration of the N-electron system at fixed separation $\vec{R}(t)$ between the target nucleus and the charged particle. The interaction causing transitions between adiabatic states is taken to be weak enough that only the first term in a perturbation expansion is important. This should be a good expansion for slow collisions since in the small-velocity limit, the state Ψ_i is purely adiabatic and no transitions occur. Expanding the excited-state amplitudes in a standard way, one finds

$$a_n(\infty)=-e^{-i\phi}\int_{-\infty}^{\infty} dt\,[W_{in}(t)]^{-1}\left(\frac{\partial V(t)}{\partial t}\right)_{ni} \times\exp\left(\frac{-i}{\hbar}\int_0^t W_{in}(t')\,dt'\right), \tag{2}$$

where $a_n(\infty)$ is the probability amplitude that the nth state is occupied after the collision is over. Here $W_{in}(t)\equiv W_i(\vec{R}(t))-W_n(\vec{R}(t))$, and

$$\left(\frac{\partial V(t)}{\partial t}\right)_{ni}=\int d^3r_1\int d^3r_2\cdots\int d^3r_N \times u_n^*(\vec{R}(t))\left(\frac{\partial V(t)}{\partial t}\right)u_i(\vec{R}(t)) . \tag{3}$$

The phase $\phi=(1/\hbar)\int_{-\infty}^{0} W_{in}(t')\,dt'$ in Eq. (2) is a constant for a given collision and will be neglected hereafter since it disappears when computing $|a_n|^2$ for the final result. Equation (2) incorporates the identity

$$\int d^3r_1\int d^3r_2\cdots\int d^3r_N\, u_n^*(\vec{R}(t))\left(\frac{\partial u_i(\vec{R}(t))}{\partial t}\right) =\left(\frac{\partial V(t)}{\partial t}\right)_{ni}\Big/ W_{in}(t) .$$

This is easily shown to hold for the many-electron system by following the proof of the corresponding result for a one-electron system given by Mott.[7] Using the Bethe integral for the Coulomb potential, the matrix element may be written as

$$\left(\frac{\partial V(t)}{\partial t}\right)_{ni}=\frac{-iZ_1e^2}{2\pi^2}\int\frac{d^3p}{p^2}\left(\vec{p}\cdot\frac{\partial\vec{R}(t)}{\partial t}\right)e^{i\vec{p}\cdot\vec{R}(t)} \times\left(\sum_{j=1}^{N} e^{-i\vec{p}\cdot\vec{r}_j}\right)_{ni} . \tag{4}$$

Figure 1 shows a set of Cartesian coordinates

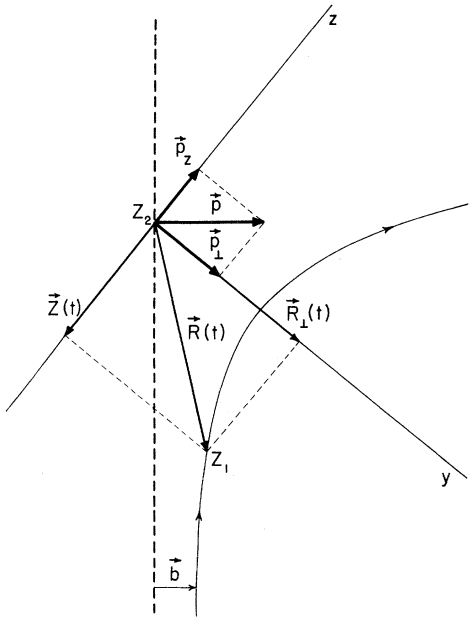

FIG. 1. This figure displays the coordinate system, with origin at the target nucleus, used to describe the collision problem in the y-z plane. The trajectory of the particle is marked by the curved line. In the special case of a straight-line trajectory the dotted line coincides with the z axis. Then, $\vec{R}_\perp(t)=\vec{b}$ and $\vec{Z}(t)=v_1t\hat{z}$, where $\hat{z}$ is the unit vector for the z axis.

(y, z) centered at the nucleus. The y axis is chosen to pass through the point of closest approach, and the z axis is taken parallel with the velocity vector of the charged particle when the latter is at that point. The vector $\vec{p}$ which appears in Eq. (4) may be resolved into the components $\vec{p}_\perp$, perpendicular to the z axis, and the component p_z along the z axis. $\vec{R}(t)$ is resolved similarly into components $\vec{R}_\perp(t)$ and $Z(t)$. In these terms

$$a_n(\infty) = (iZ_1e^2/2\pi^2)\int d^2p_\perp \int_{-\infty}^{\infty} dZ \times \int_{-\infty}^{\infty} dp_z\, e^{i[\vec{p}_\perp\cdot\vec{R}_\perp(Z)+(p_z-\Omega(Z))Z]} G_{\vec{p}_\perp,p_z}(\vec{R}_\perp(Z), Z) , \tag{5}$$

where it is assumed that orders of integration may be changed. Here

$$G_{\vec{p}_\perp,p_z}(\vec{R}_\perp(Z), Z) \equiv \frac{\vec{p}_\perp\cdot d\vec{R}_\perp(Z)/dZ + p_z}{W_{in}(\vec{R}_\perp(Z), Z)(p_\perp^2+p_z^2)} \times \left(\sum_{j=1}^{N} e^{-i\vec{p}\cdot\vec{r}_j}\right)_{ni} \tag{6}$$

and

$$\Omega(Z) \equiv \frac{1}{\hbar Z}\int_0^Z W_{in}(\vec{R}_\perp(Z'), Z')\frac{dt'}{dZ'}\,dZ' , \tag{7}$$

where $Z(t=0)=0$ and $W_{in}(\vec{R}_\perp(Z), Z)\equiv W_{in}(t)$. $\vec{R}(t)$ is replaced by $(\vec{R}_\perp(Z), Z)$ everywhere. These equations are obtained through a change of integration variable from t to Z. Introducing the wave number variable $P\equiv p_z-\Omega(Z)$, Eq. (5) becomes

$$a_n(\infty) = \frac{iZ_1e^2}{2\pi^2}\int d^2p_\perp\int_{-\infty}^{\infty} dZ\int_{-\infty}^{\infty} dP\, e^{iPZ}F_{\vec{p}_\perp}(P, Z), \tag{8}$$

where

$$F_{\vec{p}_\perp}(P, Z) \equiv F = e^{i\vec{p}_\perp\cdot\vec{R}_\perp(Z)}G_{\vec{p}_\perp,p_z}(\vec{R}_\perp(Z), Z) . \tag{9}$$

A Maclaurin's series expansion in powers of P,

$$F = \sum_{s=0}^{\infty}\frac{1}{s!}P^s\frac{d^sF}{dP^s} ,$$

permits integration of Eq. (8) over P in formal terms. A series in successively higher derivatives of $\delta(Z)$ results. Integration by parts yields

$$a_n(\infty) = \frac{iZ_1e^2}{\pi}\int d^2p_\perp\sum_{s=0}^{\infty}\frac{i^s}{s!}\frac{d^{2s}}{dZ^s dP^s}F_{\vec{p}_\perp}(0,0) \equiv \sum_{s=0}^{\infty} a_n^{(s)} , \tag{10}$$

where it is assumed that F and all of its derivatives vanish as $|Z|\to\infty$. The cross section for a transition from state i to state n is given by $\sigma_{ni} = 2\pi\int_0^\infty b\,db\,|a_n(\infty)|^2$.

The expansion displayed in Eq. (10) consists of derivatives of F with respect to (i) the z component of the particle trajectory, Z, evaluated at the point of closest approach, $\vec{R}_\perp(0)$, $Z=0$, and (ii) the z component of the wave number, p_z, evaluated at $W_{in}(\vec{R}_\perp(0), 0)/\hbar v_1(0) \equiv q_0(0)$, where $v_1(Z)\equiv dZ/dt$ is the z component of the particle velocity for a given value of Z; $\hbar q_0(0)$ is just the minimum momentum transfer necessary in the process of imparting energy $W_{in}(\vec{R}_\perp(0), 0)$ to the atom and $v_1(0) = [b/R_\perp(0)]v_1$, from the conservation of angular momentum for impact parameter b.

The convergence of the series, Eq. (10), depends essentially upon the near constancy of F as a function of the orbit parameter Z evaluated at the point of closest approach. If $W_{in}(\vec{R}_\perp(Z), Z)$ and the matrix element $\rho_{ni}\equiv(\sum_{j=1}^{N} e^{-i\vec{p}\cdot\vec{r}_j})_{ni}$ appearing in Eq. (6) both vary slowly enough as a function of Z, the first term in the series should give an excellent approximation to the entire sum. We demonstrate in Sec. III that for reasonable approximations to F this is true. It is expected to hold also for the exact form of F.

III. DISCUSSION

Consider first the approximation to Eq. (10) obtained by neglecting all except the $s=0$ term in the series. It follows readily, then, that the cross section for the $i\to f$ transition can be written in the form

$$\sigma_{fi}^{(0)} \equiv 2\pi\int_0^\infty b\,db\,|a_f^{(0)}(\infty)|^2 = \frac{4\pi Z_1^2e^4}{\hbar^2}\int_0^\infty\frac{b\,db}{v_1^2(0)}|M_b|^2 = \frac{4\pi Z_1^2e^4}{\hbar^2v_1^2}\int_0^\infty R_1^2(0)\frac{db}{b}|M_b|^2 , \tag{11}$$

where

$$M_b = \int d^3r_1\int d^3r_2\cdots\int d^3r_N\, u_f^*(\vec{R}_\perp(0), 0) \times\sum_{j=1}^{N} e^{-iq_0(0)z_j}K_0(q_0(0)|\vec{r}_{\perp j}-\vec{R}_\perp(0)|)u_i(\vec{R}_\perp(0), 0) \tag{12}$$

and $K_\nu(x)$ is the modified Bessel function of the second kind. In the case of ionization $\sigma_{fi}^{(0)}$ is differential in the energy of the final electronic state. $R_\perp(0)$ is the distance of closest approach. Although arbitrary, the trajectory is assumed to be symmetric about the y axis so that $d\vec{R}_\perp(0)/dZ = 0$. The symmetry approximation is good as long as the energy transfer is much less than the particle energy. If $N=1$, Eqs. (11) and (12) bear a close similarity to Bang and Hansteen's[5] Eq. (3.3) for the ionization cross section of a one-electron atom by a charged point moving along a straight-line trajectory with $\vec{R}_\perp(0)=\vec{b}$.

The interpretation of the quantities appearing in

Eqs. (11) and (12), however, is quite different from that of the corresponding quantities occurring in Bang and Hansteen's formula, which considers only eigenfunctions and energies of the unperturbed atom and is restricted to straight-line trajectories. The present treatment includes the possibility of strong perturbations of these quantities. Moreover, it derives the prescription to evaluate all energies and eigenfunctions at the position of closest approach of the incident particle moving along an arbitrary trajectory. This is so because Eqs. (11) and (12) employ atomic wave functions $u_{i,f}(\vec{R}_\perp(Z), Z)$ which are solutions to the time-independent Schrödinger equation at the place and time of closest approach of the particle to the target nucleus, namely,

$$[H_a + V(0)]u_{i,f}(\vec{R}_\perp(0), 0) = W_{i,f}(\vec{R}_\perp(0), 0)u_{i,f}(\vec{R}_\perp(0), 0) \quad . \tag{13}$$

The eigenfunctions and energy eigenvalues are those of the target atom perturbed by a point charge at rest at the distance $R_\perp(0)$ from the nucleus. Thus they are the same type of states employed in molecular-orbital calculations. It is precisely the initial energy value $W_i(\vec{R}_\perp(0), 0)$ that is calculated by BLS through first-order bound-state perturbation theory as an augmented electron ionization energy at low particle velocities, and applied to the calculation of K-shell ionization cross sections as prescribed by Eqs. (11) and (12). An additional distinction from the Bang and Hansteen formula is the reference not to v_1 but to the particle velocity evaluated at the distance of closest approach, $v_1(0)$.

One retrieves the usual semiclassical formula from the PSS approximation if unperturbed eigenfunctions and eigenenergies are employed with a straight-line trajectory in Eqs. (11) and (12), since all terms for $s > 0$ vanish.[9]

We note in passing that the perturbing influence of the particle on the atomic states described in Eq. (13) is also the origin of the Z_1^3 polarization effect.[10] It contributes to the cross sections only in the high-velocity regime[11] and is therefore not developed here.

Consider next the error incurred by neglecting all except the first term in Eq. (10). To this end, it is necessary to make some definite assumption about the form of $W_{if}(\vec{R}_\perp(Z), Z)$ and the matrix element appearing in Eq. (6). Assume for purposes of simplicity that K-shell ionization of an atom can be described though the perturbation by the particle of only K-shell electrons, that the K-electron wave function retains its spherical symmetry even though the energy of the level may be affected appreciably by the presence of the particle, and that transitions occur only to S-wave continuum final states. Transitions to such states are known to predominate as v_1 becomes very small.[1,12] In this limit the matrix element of the density operator is given approximately by[1]

$$\rho_{fi} = (e^{-i\vec{p}\cdot\vec{r}})_{fi} \simeq \frac{1}{[(Z_2^*)^2 R_\infty]^{1/2}} \frac{2^{7/2}}{(pa_{2K})^4} \quad , \tag{14}$$

where R_∞ is the Rydberg constant and a_{2K} is the radius of the K-shell orbit. Both a_{2K} and Z_2^* may be considered functions of the distance of the particle from the nucleus; they, as well as the central quantity $W_{if}(\vec{R}_\perp(Z), Z)$, might be determined variationally for a given $(\vec{R}_\perp(Z), Z)$ and Z_1. But for the purposes of estimating the errors of truncation, we assume a straight-line trajectory for the projectile and neglect the dependence of a_{2K} and Z_2^* on $(\vec{R}_\perp(Z), Z)$ and Z_1.

Substituting Eq. (14) into Eqs. (6), (9), and (10), and carrying out the differentiations, we find that $a_f^{(1)} = 0$ and

$$a_f^{(0)} = \frac{iZ_1 e^2}{\hbar v_1} \frac{2\sqrt{2}}{[(Z_2 - S_{2K})^2 R_\infty]^{1/2}} \frac{x^2 K_2(x)}{[q_0(0) a_{2K}]^4} \quad , \tag{15}$$

$$a_f^{(2)} = \frac{1}{6} \frac{b}{W_{if}(b)} \frac{dW_{if}(b)}{db} \frac{H(x)}{x^2 K_2(x)} a_f^{(0)} \quad , \tag{16}$$

with $x \equiv q_0(0)b$ and

$$H(x) \equiv (96 + 9x^2)K_0(x) + (2/x)(96 + 21x^2 + \tfrac{1}{2}x^4)K_1(x),$$

where K_0, K_1, and K_2 are modified Bessel function of the second kind. We use $W_{if}(b) \equiv W_{if}(\vec{b}, 0)$ as derived by BLS, namely,

$$W_{if}(b) = W_i^{(0)} \left(1 + \frac{2Z_1}{Z_2 - S_{2K}} \frac{1}{W_i^{(0)}} \beta^{-1}[1 - (1+\beta)e^{-2\beta}]\right) - W_f^{(0)}, \tag{17}$$

where $\beta = b/a_{2K}$. Z_2^* has been chosen to be $Z_2 - S_{2K}$ where $S_{2K} = 0.3$ is the screening constant of Slater for hydrogenic wave functions, and $a_{2K} = a_0/(Z_2 - S_{2K})$ with $a_0 = \hbar^2/me^2$. $W_i^{(0)}$ and $W_f^{(0)}$ denote the energy of the initial and final electronic states, respectively, in the absence of the particle. We perform the integration over impact parameters to first order in $a_f^{(2)}$:

$$\frac{d\sigma_f}{dW_f^{(0)}} = 2\pi \int_0^\infty b\,db\,|a_f(\infty)|^2$$

$$\simeq 2\pi \int_0^\infty b\,db\,(|a_f^{(0)}|^2 - 2a_f^{(0)} a_f^{(2)}) \quad . \tag{18}$$

Note $a_f^{(0)}$ and $a_f^{(2)}$ are purely imaginary.

The integration in Eq. (18) shows that for 20-keV protons on aluminum, for example, the cross term contributes 23%. At lower energies this

contribution diminishes monotonically and thus demonstrates the convergence of the expansion in the limit of small velocities. The effect of the change in the binding energy on the term $|a_f^{(0)}|^2$ of Eq. (18) is to *reduce* the cross section by 85% for 20-keV protons on aluminum. The inclusion of the cross term, which is zero in the Bang and Hansteen calculation, gives a reduction of 88%. Quantitative comparison with observed values is outside the scope of this paper. To compare experiment with theory a calculation must be undertaken which includes trajectory deflection and sums over all final electronic states. This, in effect, has already been accomplished.[2,3,6]

We conclude that for straight-line trajectories in the low-velocity regime where one expects the PSS method to be accurate, the series in Eq. (10) is dominated by the first term.

On the other hand, when unperturbed atomic states and energies are used with a straight-line trajectory the first term dominates again since it is the only nonzero term. The Bang and Hansteen cross section, valid at high velocities, is then obtained. This cross section is also obtained at high velocities in the BLS approach since the binding effect disappears in this limit. Thus it might be expected that the leading term in the PSS theory, dominant in the low-velocity limit, also gives the correct cross section at high velocities. One makes the conjecture that in Eq. (10) the contribution of the sum of terms $a_f^{(s)}$ for $s>0$ is small for all velocities in the case of a straight-line trajectory.

The BLS approach *via* Eq. (13) is expected to remain valid for straight-line trajectories even if more accurate expressions for $W_{if}(\vec{R}_\perp(Z), Z)$ and $u_{i,f}(\vec{R}_\perp(Z), Z)$, and hence for the quantity ρ_{fi} [Eq. (14)] are developed. For instance at low incident velocities where the important range of impact parameters is $(b/a_{2K}) \ll 1$, most K-shell excitations or ionizations occur when the incident particle is deep within the shell. Under these conditions the radial electronic charge distribution specified by $ru_{i,f}(\vec{R}_\perp(0), 0)$ is mainly outside the region where the particle is found and thus should be insensitive to variations in Z near $Z=0$. It is this constancy of $W_{if}(\vec{R}_\perp(Z), Z)$ and ρ_{fi} with Z that ensures convergence of the expansion in terms of derivatives with regard to Z. Since this feature should be independent of the particular model used for calculations, the validity of the BLS approximation is expected to persist if more accurate expressions for $W_{if}(\vec{R}_\perp(0), 0)$ and ρ_{fi} are used. It might be worthwhile to employ variational methods to obtain better values of these quantities for the comparison of Eqs. (11) and (12) with experiment.

Thus our result constitutes a formal derivation of the BLS binding effect. If the restriction to a straight-line trajectory is dropped, Coulomb deflection appears here in a form somewhat different from that of Bang and Hansteen,[5] presumably because we expand the probability amplitudes in terms of the wave-number variable P. In the evaluation of the truncation error one finds $a_f^{(1)} \neq 0$, and it is not obvious that the series will converge. Nonetheless the resulting prescription for treating Coulomb deflection in the leading term is physically appealing. The "straight-line" Coulomb-deflection approach of Hansteen and Mosebekk,[13] where b is replaced by $R_\perp(0)$, is shown here to occur naturally as part of the exact description found in the first term of the expansion in P. However, one should also replace v_1 by $v_1(0) = [b/R_\perp(0)]v_1$.

In light of the only remaining uncertainty in the formal theory, viz., the series convergence in the case of an arbitrary trajectory, it is practical to retain the Bang and Hansteen hyperbolic Coulomb deflection as derived and applied by BLS.

We summarize the procedure for obtaining a cross section from the leading term of Eq. (10). It is assumed that wave functions are available for describing the atom in the presence of a point charge located at the distance of closest approach $R_\perp(0)$. These wave functions, solutions to Eq. (13), are used to calculate the matrix element M_b [Eq. (12)] needed in the integration over impact parameters to obtain the cross section Eq. (11). In practice a one-electron model for the atom, $N=1$, is used. One can take a final electron state with unperturbed wave function $u_f(\infty, 0)$ and energy $W_f(\infty, 0) = W_f^{(0)}$ under the assumption that only the perturbation of the initial state, leading to $u_i(\vec{R}_\perp(0), 0)$ and $W_i(\vec{R}_\perp(0), 0)$, is important.

IV. CONCLUSIONS

The exact time-dependent wave function for atomic excitation and ionization under the influence of a slowly moving heavy charged particle on an arbitrary trajectory can be systematically expanded in a series such that the leading term contains the dominant perturbation of the particle on the target atomic states between which the transitions take place. The binding effect which Brandt, Laubert, and Sellin[6] described and incorporated into the theory of inner-shell ionization is derived *ab initio*. Our approach formally unifies the Coulomb deflection of the particle trajectory in the field of the target nucleus with the perturbation of the atomic states in their effect on the ionization cross section.

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Resonances in Photoelectron Angular Distributions*

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Photoelectron angular distributions should show pronounced variations with energy across autoionization resonances. This prediction applies quite generally to both atomic and molecular autoionization. Examples illustrate both the magnitude of the spectral variation and the inability of the Cooper-Zare model to account for the phenomenon. Calculations are reported for autoionization in xenon between the fine-structure levels $5p^5\ ^2P^o_{3/2}$ and $5p^5\ ^2P^o_{1/2}$ of the ion ground-state doublet. An analysis is given of the recent measurements by Niehaus and Ruf on autoionizing levels of the mercury Rydberg series $5d\ ^96s\ ^2(^2D)np$ and $5d\ ^96s\ ^2(^2D)n'f$ below the $Hg^+\ 5d\ ^96s^2\ ^2D_{5/2}$ threshold.

I. INTRODUCTION

The determination of the spectral variation of photoelectron angular distributions through autoionization resonances is a new and essentially untapped resource for photoelectron spectroscopy. Here this class of spectroscopic measurements is theoretically analyzed. The analysis predicts quite generally not only sharp spectral variations of the angular distributions across resonance features, but more importantly, angular distributions that should depart markedly from those predicted by direct (nonresonant) ionization models, such as the Copper–Zare model.[1] Deviations from direct ionization predictions arise owing to the enhancement by the autoionization process of the effects of just those forces that are often sufficiently weak as to go undetected in nonresonant photoionization. Accordingly, these resonances in photoelectron angular distributions are a sensitive new probe of photoejection dynamics.

This study rests on the angular-momentum-transfer formulation of angular correlations, given recently by Dill and Fano.[2] It also draws on extensive experience in analyzing the dynamical origin and significance of the various angular momentum transfers allowed in any given ionization process. This paper reports the most important implications and results for autoionization of the general dynamical analysis, whose full description is deferred to a separate report.[3]