fit the region of importance, it requires a trial wave function which is an exact eigenfunction of a demonstrable Hamiltonian. Consequently, this method becomes difficult to employ when dealing with wave functions using different variational parameters for inequivalent electrons, whereas the technique discussed in Sec. II can be modified to treat this situation.[16]

A distinct advantage of the Aranoff and Percus method is that a minimum rather than a stationary point must be determined. A better function for ψ_{1T} can be obtained by choosing a form with a large number of parameters and minimizing M' numerically, if necessary. Another promising possibility is to use a more accurately tabulated function for ψ_{0T} which is not parametric. For example, the Hartree-Fock solution for helium could be used, and ψ_{1T} determined by numerical integration. If the average value of the operator taken between the Hartree-Fock states is in error by $O(\delta)$, the variational expression should generate a result in error by $O(\delta^2)$. This work is currently in progress.

A disadvantage of the procedures discussed here is that they do not provide a bound for the expectation value. Techniques for calculating rigorous lower bounds have been developed by Weinhold,[17] and although such investigations are vital and deserve thorough study, his results are generally much farther from the correct value than are those given here. Furthermore, to obtain a good lower bound, his calculation requires the use of wave functions whose overlap integral $\langle \psi_{0T} | \psi_0 \rangle \approx 1$ which, especially for many-particle systems, is a difficult condition to satisfy.

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Minima in Atomic Continuum Generalized Oscillator Strengths

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Minima in continuum generalized oscillator strengths for atoms are found to exist, and their position as a function of energy is discussed. It is shown that at increased energy loss they occur at larger momentum transfer. Calculations are performed for the Na $3s \rightarrow \epsilon p$, K $4s \rightarrow \epsilon p$, and Ar $3p \rightarrow \epsilon d$ transitions.

I. INTRODUCTION

A knowledge of the details of inelastic collisions between fast charged particles and an atom or molecule is important in a number of areas, including astrophysics, plasma physics, space and atmospheric physics, and radiation physics. The theory for such a process was developed by Bethe nearly forty years ago[1,2]; it was here that the idea of the generalized oscillator strength $f_n(K)$, hereafter referred to as GOS, was introduced as an essential factor in the differential (first) Born cross section[3] $d\sigma_n$ for the inelastic excitation of an atom or molecule from the initial state 0 to the final state n by particles of charge ze and velocity v:

$$d\sigma_n = \frac{8\pi a_0^2 z^2}{mv^2/R} \frac{f_n(K)}{E_n/R} \, d\ln(Ka_0)^2 , \tag{1}$$

where a_0 is the Bohr radius, m the electron mass, R the rydberg energy, E_n the excitation energy, and $\vec{K}\hbar$ the momentum transfer. The GOS is defined as

$$f_n(K) = (E_n/R)(Ka_0)^{-2} |I_n(K)|^2 , \tag{2}$$

where the matrix element

$$I_n(K) = (n|\textstyle\sum_j e^{i\vec{K}\cdot\vec{r}_j}|0) , \tag{3}$$

$\vec{r}_j$ being the position vector of the jth electron of the target.

We can extend the definition of the GOS to continuum (ionizing) transitions where the Born cross section is differential in both K and ϵ, the kinetic energy of the ionized electron:

$$d^2\sigma_n = \frac{8\pi a_0^2 z^2}{mv^2/R} \left(\frac{df_n(K)}{d(\epsilon/R)} \Big/ \frac{E_n}{R} \right) \times d\ln(Ka_0)^2 \, d\epsilon , \tag{4}$$

where

$$\frac{df_n(K)}{d(\epsilon/R)} = \frac{E_n}{R}(Ka_0)^{-2}|I_n(K)|^2 , \tag{5}$$

with the state n interpreted as a continuum wave function normalized per unit energy in rydbergs, and $I_n(K)$ as defined in Eq. (3). The sign of $I_n(K)$ depends upon the wave functions and K. Assuming the continuity of $I_n(K)$, if it changes sign as K varies, the GOS $f_n(K)$ [or $df_n(K)/d(\epsilon/R)$ for ionization] must go through a zero minimum.

Such minima have been known for some time in the case of excitation[4-7] but only recently has it been demonstrated how often they occur.[8-13] It was also pointed out that minima would be expected in continuum transitions as well.[8] For discrete transitions the limit of $f_n(K)$ as $K \to 0$ is just the optical oscillator strength[3] f_n; for continuum transitions this becomes

$$\frac{df_n(K)}{d(\epsilon/R)} \to \frac{df_n}{d(\epsilon/R)},$$

which is related to the photo-ionization cross section σ_n^{photo} by[14]

$$\sigma_n^{\text{photo}} = 4\pi\alpha a_0^2 \frac{df_n}{d(\epsilon/R)} . \tag{6}$$

Recent studies[14-17] have shown that photo-ionization cross sections in many cases exhibit minima, known as Cooper minima, at certain energies corresponding to the change of sign of the dipole matrix element. This in turn implies a minimum in the GOS at $K=0$ at the same energy. The behavior of this minimum as a function of energy

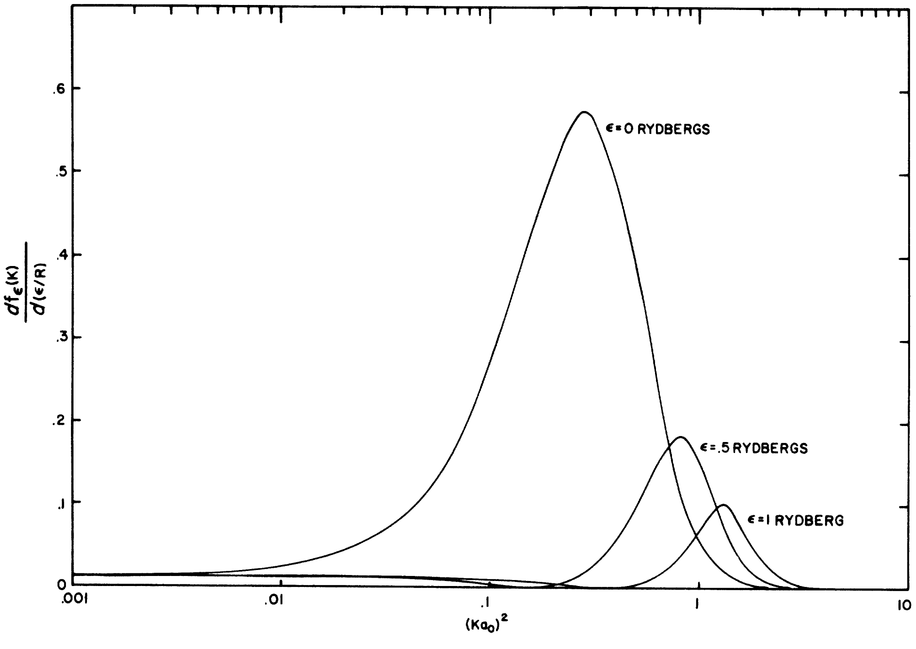

FIG. 1. Generalized oscillator strength of Na for the $3s \to \epsilon p$ transition.

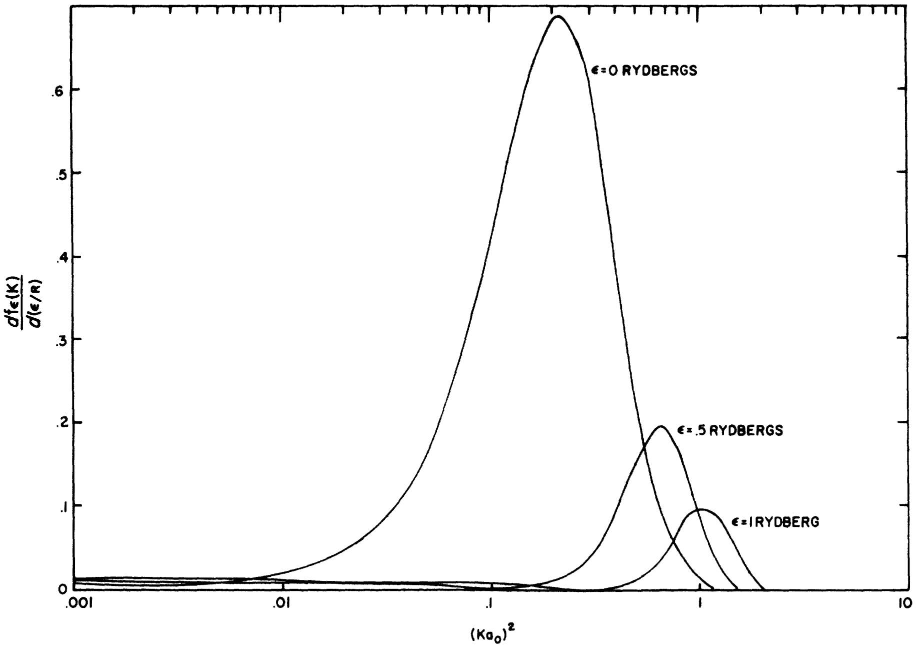

FIG. 2. Generalized oscillator strength of K for the $4s \rightarrow \epsilon p$ transition.

has been looked at only in preliminary studies.[18,19] In an effort to provide some more detailed information on the behavior of minima in the GOS for ionization we have performed calculations on the transitions $3s \rightarrow \epsilon p$ in Na, $4s \rightarrow \epsilon p$ in K, and $3p \rightarrow \epsilon d$ in Ar, all of which have pronounced minima in photo-ionization.

II. METHOD OF CALCULATION

We have employed antisymmetrized products of one-electron wave functions of the Hartree-Slater[20] (HS) type as tabulated by Herman and Skillman[21]

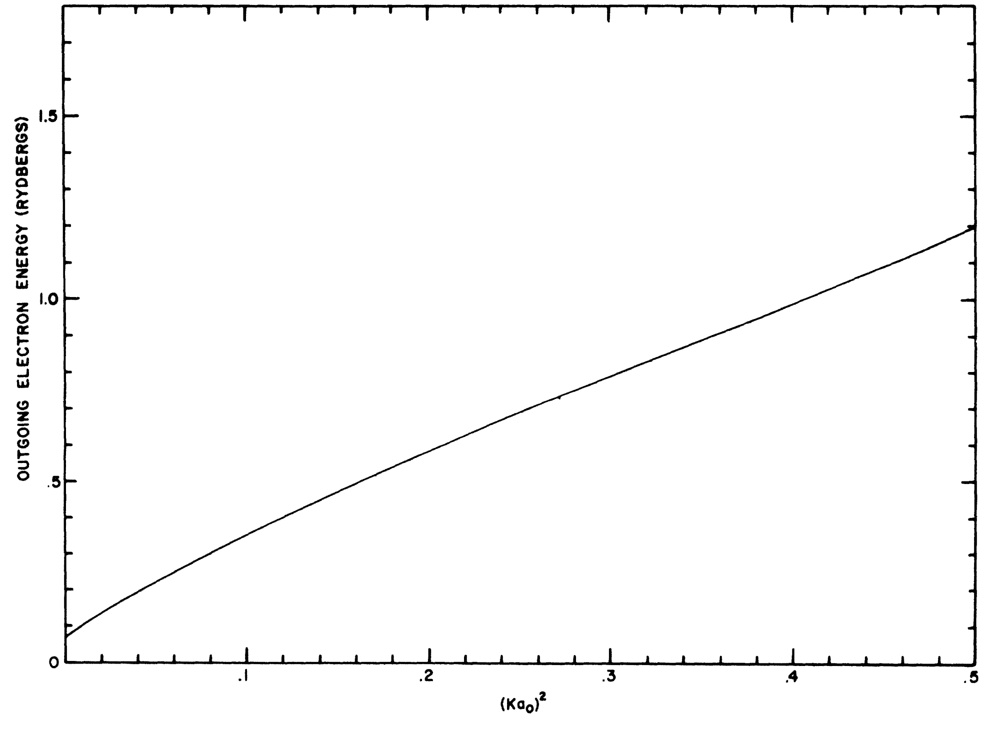

FIG. 3. Trajectory of the minimum in the generalized oscillator strength of Na for the $3s \rightarrow \epsilon p$ transition.

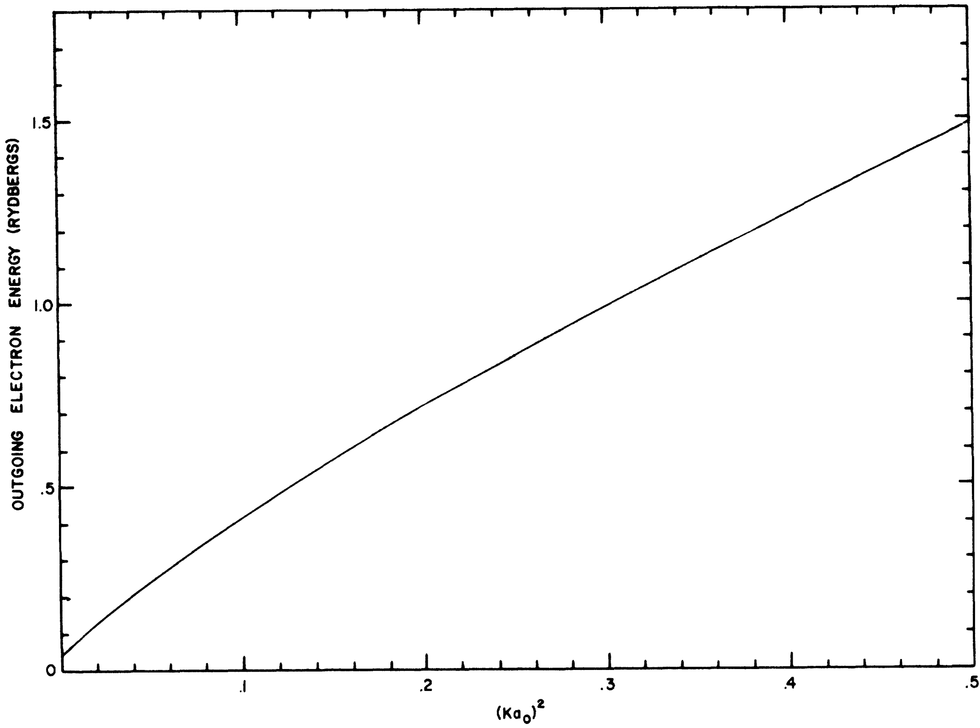

FIG. 4. Trajectory of the minimum in the generalized oscillator strength of K for the $4s \rightarrow \epsilon p$ transition.

which have proved to be adequate for photo-ionization.[14,22] The initial state for the electron undergoing ionization, $P_{nl}(r)$, is taken directly from the tabulation while its final continuum state of energy ϵ, $P_{\epsilon l'}(r)$, is obtained by numerically integrating the Schrödinger equation with the same potential

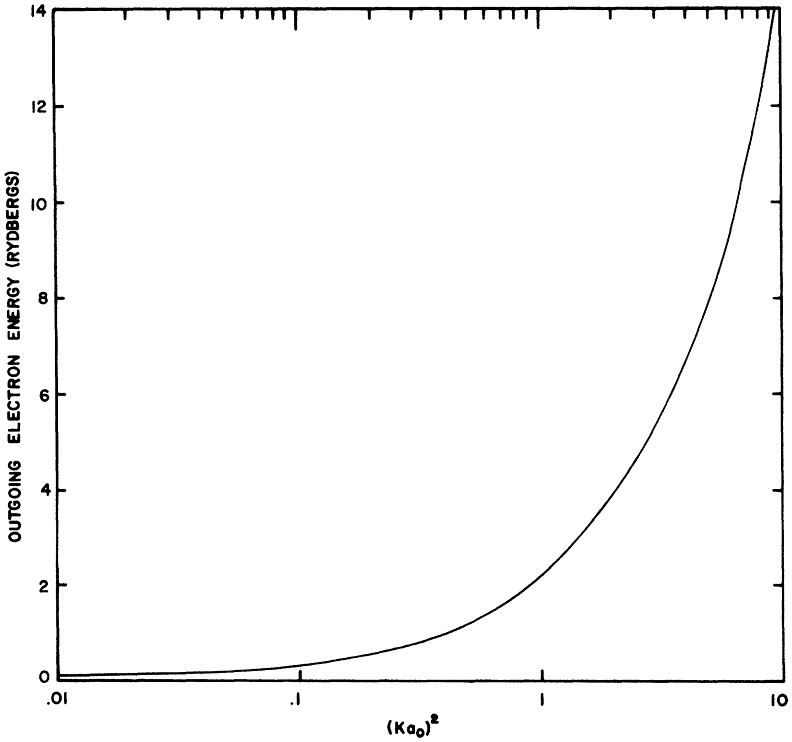

FIG. 5. Trajectory of the minimum in the generalized oscillator strength of Na for the $3s \rightarrow \epsilon p$ transition.

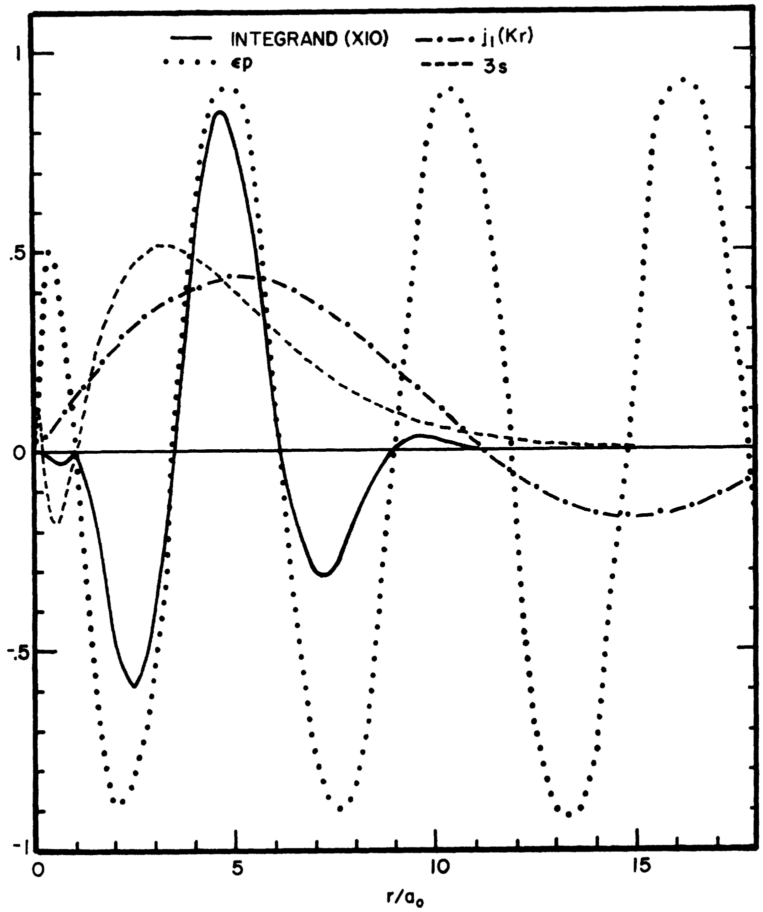

FIG. 6. Integrand of the matrix element [Eq. (8)] of the generalized oscillator strength of Na for the $3s \to \epsilon p$ transition for $Ka_0 = 0.4$, $\epsilon/R = 1$. Also shown are the $3s$ and ϵp wave functions in Na and $j_1(Kr)$. The product of these three functions is the integrand.

as the initial state. The details of this integration and subsequent normalization of the continuum wave function can be found in Refs. 14 and 15.

In order to carry out the integration of the matrix element [Eq. (3)] we use the well-known expansion

$$e^{i\vec{K}\cdot\vec{r}} = \sum_\lambda (i)^\lambda (2\lambda+1) j_\lambda(Kr) P_\lambda(\cos\theta) \ , \qquad (7)$$

where θ is the angle between $\vec{K}$ and $\vec{r}$, P_λ is the Legendre polynomial of order λ, and $j_\lambda(Kr)$ is the spherical Bessel function of the first kind of order λ. Then, since we are using one-electron wave functions, when the angular variables are integrated out, the matrix element becomes a linear combination of

$$R^\lambda_{nl,\epsilon l'}(K,\epsilon) = \int_0^\infty P_{nl}(r) j_\lambda(Kr) P_{\epsilon l'}(r)\, dr \ , \qquad (8)$$

where λ is limited to $l+l'$, $l+l'-2, \ldots, |l-l'|+2$, $|l-l'|$. The general expression for the GOS of a transition $nl \to \epsilon l'$ (or $n'l'$) is quite messy so we present the results only for the types of transitions we calculate, $ns \to \epsilon p$ and $np \to \epsilon d$. In these cases

$$\frac{df_{ns\to\epsilon p}(K)}{d(\epsilon/R)} = 3N_{ns}(\epsilon+\epsilon_{ns})[R^1_{ns,\epsilon p}(K,\epsilon)]^2 (Ka_0)^{-2} \qquad (9)$$

and

$$\frac{df_{np\to\epsilon d}(K)}{d(\epsilon/R)} = N_{np}(\epsilon+\epsilon_{np})\{2[R^1_{np,\epsilon d}(K,\epsilon)]^2 + 3[R^3_{np,\epsilon d}(K,\epsilon)]^2\}(Ka_0)^{-2} \ , \qquad (10)$$

where N_{nl} is the number of electrons in the initial state and ϵ_{nl} their binding energy. To obtain these equations we have averaged over the degenerate initial magnetic substates and summed over the final which are also degenerate. The calculations were carried out on an IBM 7094 computer.

III. RESULTS AND DISCUSSION

The results of our continum GOS calculations for the $3s \to \epsilon p$ transition in Na and the $4s \to \epsilon p$ transition in K are shown in Figs. 1 and 2. In each case the GOS at threshold has no minimum, but it has a zero minimum at energies 0.5 and 1 Ry above threshold. This minimum occurs at higher momentum transfer K at the higher energy. Between threshold and 0.5 Ry there is a minimum at $K = 0$ as indicated

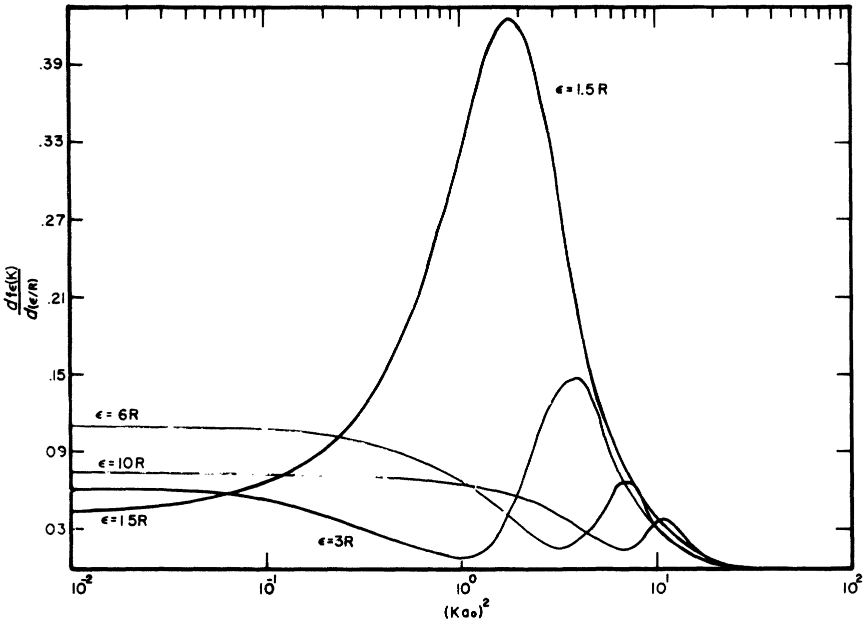

FIG. 7. Generalized oscillator strength of Ar for the $3p \rightarrow \epsilon d$ transition.

by the Cooper minimum in the photo-ionization cross section just above threshold in each case. Thus we see that, in these cases, the minimum moves to larger momentum transfer at increasing outgoing electron energy. This is further substantiated by calculations at many more energies; the results are shown in Figs. 3 and 4 in which the path of the minimum in the K plane for Na and K near threshold is plotted and Fig. 5 where the path of the minimum is shown for Na to much higher ionized electron energies.

To explain this behavior, it is first necessary to investigate the conditions which produce minima in the GOS, in this case the vanishing of the matrix element $R^1_{ns,\epsilon p}(K, \epsilon)$. This can be understood by considerations similar to those employed in explaining the minima in photoabsorption cross sections.[14-17] The initial- and final-state radial wave functions as well as the spherical Bessel functions are oscillatory so that the product of the three can be either positive or negative. If the positive contribution to the integral (8) is just equal to the negative, the net result is the vanishing of the matrix element. This is illustrated in Fig. 6 for the zero in the Na $3s \rightarrow \epsilon p$ GOS at $\epsilon/R = 1$, $Ka_0 = 0.4$. At higher energy the nodes in the ϵp function occur at smaller r, i.e., the continuum wave function becomes more oscillatory. This tends to destroy the equality of the positive and negative contributions to the matrix element so that it no longer vanishes. However, with increasing Ka_0, $j_1(Kr)$ moves in toward the nucleus as well, restoring the balance and causing a minimum at this new (higher) value of Ka_0.

This argument is not restricted to the particular case we have discussed since *all* spherical Bessel functions move in with increasing momentum transfer. Further, this argument can be easily extended to minima in discrete GOS's where increasing energy means increasing principle quantum number n which leads to more oscillatory final-state wave functions. Thus, the general behavior of minima in the GOS is to move to greater Ka_0 at higher excitation energy in both discrete and continuum cases.

As another example of the phenomenon, the results of our GOS calculations for the ionization of argon $3p$ to the ϵd continuum, which has been studied to a certain extent previously,[23,24] are shown in Fig. 7. Here the GOS has no minimum at the lowest energy shown, but it does at all of the higher energies. The minimum moves to larger Ka_0 for increased energy, as expected from the discussion above. The path of the minimum in the K plane is shown in Fig. 8. The minimum is, however, not a zero minimum as the previous cases discussed.

This can be explained by noting that the expression for the GOS, in this case given by Eq. (10), is the sum of two terms. Thus, when one term goes to zero the other term, in general, does not. For the $3p \rightarrow \epsilon d$ GOS in argon, the first term $R^1_{3p,\epsilon d}$, which is generally the larger, goes through zero while $R^3_{3p,\epsilon d}$ varies rather smoothly. The result is the occurrence of the nonzero minima shown and Fig. 8 is a plot of the path of the zero in the matrix element $R^1_{3p,\epsilon d}$.

At this point it is worthwhile to note that for ionizing transitions an experiment can only measure the sum of the GOS's to *all* of the degenerate continuum channels, i.e., all final-state angular momenta. In practice, for small ionized electron

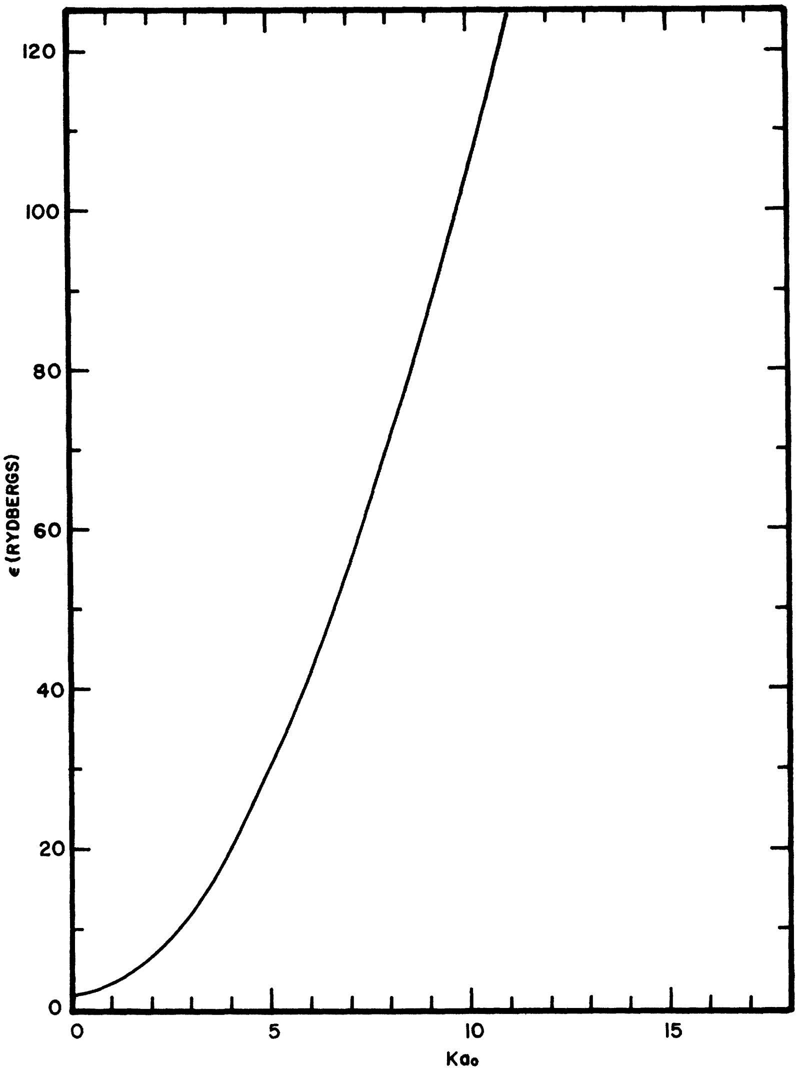

FIG. 8. Trajectory of the minimum of the generalized oscillator strength for the $3p \rightarrow \epsilon d$ transition in Ar.

energies, only a few low-l continuum states have GOS's of any appreciable magnitude. Thus, these minima may not be obervable experimentally; they may be overshadowed by the GOS's for the other continuum states. As a matter of fact, it is very likely that the minima discussed in Na and K would not show up experimentally. On the other hand, the minimum in the Ar $3p \rightarrow \epsilon d$ GOS will likely appear. In fact recent experimental evidence[25] seems to indicate a minimum in the GOS for the ionization of argon. This will be studied more extensively in a future paper.

Whether or not the minimum is observable, if it occurs in a particular atom or molecule at or near $Ka_0 = 0$ for a dipole-allowed transition, the optical oscillator strength will be zero or anomalously small at this energy loss. This has consequences for the ionization of the atom or molecule by high-energy charged particles at this same energy loss which goes as[26]

$$A(\ln T)/T + B/T, \qquad (11)$$

where T is the incoming particle kinetic energy, B is a constant, and A is proportional to the optical oscillator strength. Hence, a minimum at or near $Ka_0 = 0$ implies that A is zero or very small, thus drastically affecting this high-energy ionization cross section.

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Lamb Shift and Binding Energies of *K* Electrons in Heavy Atoms * †

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The self-energy of *K* electrons in atoms with atomic numbers in the range $70 \leq Z \leq 90$ is determined numerically. Detailed theoretical evaluations of *K*-electron binding energies including all effects of $O(\alpha mc^2)$ are given for the four heavy closed-subshell atoms – W, Hg, Pb, and Rn – in the range considered. With the present values of the electron self-energy, the theoretical *K*-shell binding energies for these elements are found to agree with experimental determinations to better than 1 part in 10^4.

I. INTRODUCTION

Since the appearance of the first Dirac-Hartree-Fock (DHF) calculations of atomic energy levels for heavy atoms,[1] various attempts have been made to understand quantitatively the discrepancies between theoretically determined eigenvalues[2-5] for inner electrons and experimentally determined inner-electron binding energies. A great impetus has been added to this work over the last few years because of the highly accurate analysis of electron binding energies by Bearden and Burr[6] based on precise electron spectroscopy[7] (ESCA) measurements.

It is the purpose of the present paper to analyze the electromagnetic effects of lowest order in the fine-structure constant α, in an attempt to bring the theoretical and experimental understandings of these inner-electron binding energies into closer agreement. The (somewhat surprising) result of our study is that, considering only lowest-order electromagnetic corrections to the *K*-shell binding energies, we are able to reduce the discrepancy between theoretical and experimental values to less than 0.4 Ry (1 part in 10^4) for each of four closed-subshell atoms – W, Hg, Pb, and Rn – in the range of atomic numbers considered ($Z = 70-90$).

For these heavy atoms the principal electromagnetic effect on inner-electron binding is certainly the nuclear Coulomb field. The Coulomb binding energies are appreciably modified by electrostatic screening; these screening effects are accurately described for heavy closed-shell atoms by DHF calculations. We take as a basis for the discussion of electromagnetic effects the bound-interaction representation of quantum electrodynamics,[8] in which it is assumed that the electron-positron field satis-