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Phase-Amplitude Method in Atomic Physics. II. Z Dependence of Spin-Orbit Coupling*

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The spin-orbit interaction for p electrons is shown to occur in the K shell for all atoms and to vary with atomic number Z according to $\Delta\mu \propto H\alpha^2(0, Z)/Z$, where $\Delta\mu$ is the difference in quantum defect between the fine-structure levels evaluated at the series limit, $\alpha(0, Z)$ is the amplitude function for a nonrelativistic zero-energy p wave at $r = 0$, and H is a relativistic correction factor. The quantity $\Delta\mu$ is evaluated and found to vary as $Z^{2.33}$, which is in remarkable agreement with experiment. In addition to this gross behavior, the variation of $\alpha^2(0, Z)/Z$ exhibits a structure tied to the Periodic Table. This structure derives from the influence of the valence region of the atomic potential, which affects the spin-orbit interaction through the normalization factor $\alpha(0, Z)$. Neither inner screening effects, embodied in Casimir's $\sigma(Z)$ parameter, nor deviations of the atomic potential from Zr^{-1} in the interaction region appear very relevant to this problem.

I. INTRODUCTION

The study of spin-orbit (SO) interaction is a very old subject, historically dealing with the analysis of the optical spectra of particular atomic configurations. A recent advance[1] employing quantum-defect theory (QDT) has led to an empirical law by which the strength of SO interaction of p electrons for all atoms can be expressed approximately as a power law in Z, the atomic number. In the present paper, the phase-amplitude method (PAM)[2] is used to show that the SO interaction for p electrons can be expressed as the product of two factors. One factor originates from a *purely hydrogenic* interaction that takes place within the atomic K shell in the field of the *unscreened* nucleus and the other factor depends on the spin-independent potential outside the K shell. This latter factor is the amplitude function of the PAM and constitutes an electron optical transmission function that connects the amplitude of a radial wave function at $r = 0$ to that in the ionic field beyond the valence region of the atom. This application of PAM to the Z dependence of SO interaction is a prototype for applications to other inner-shell

phenomena, such as K-shell photoabsorption, which can be usefully separated into a factor arising from interactions localized near the nucleus and a normalization factor that depends on transmission properties of the entire atomic field.

Before proceeding, we will review briefly the aspect of the PAM to be exploited here. As shown in an earlier paper,[2] hereafter referred to as I, the radial wave function $P(r)$ for an electron in the field of an ion can be conveniently expressed in terms of an amplitude function $\alpha(r)$ and a phase function $\delta(r)$:

$$P(r) = \alpha(r)\{f\cos[\delta(r)] - g\sin[\delta(r)]\}, \qquad (1)$$

where (f, g) are independent Coulomb functions defined in I. The utility of the amplitude function derives from the fact that $\delta(r)$ depends solely on the range $[0, r]$ whereas $\alpha(r)$ depends on the entire range $[r, \infty]$. Hence, for an interaction taking place at small r, the part of Eq. (1) in braces is characteristic of a purely Coulomb field and should scale with atomic number in a simple way. Therefore, all nonhydrogenic behavior is isolated in the factor $\alpha(r)$, which we will show depends strongly on the field in the valence shells of atoms. This

dependence not only determines the over-all Z dependence of spin-orbit coupling, but also produces a periodic structure in this function that has the characteristic periods of the Periodic Table.

II. PARAMETERS FOR SPIN-ORBIT COUPLING

There are two alternative parameters in the problem of SO coupling. One is the spectroscopic strength parameter ζ_{nl}, which is accurately given by first-order perturbation theory as[3]

$$\zeta_{nl} = \frac{1}{2}\left(\frac{\hbar}{mc}\right)^2 \int_0^\infty \frac{1}{r}\left(\frac{dV(r)}{dr}\right)P_{nl}^2(r)\,dr, \quad (2)$$

where $V(r)$ is the electron's potential energy at a distance r from the nucleus, and $P(r)$, the radial wave function of a discrete state nl, is normalized to unity, i.e.,

$$\int_0^\infty P_{nl}^2\,dr = 1.$$

This parameter has the dimension of energy and is directly related to the energy splitting of fine-structure levels. For the simple case of a single electron outside a closed shell, the fine-structure interval is given by

$$E_{l+1/2} - E_{l-1/2} = (l + \tfrac{1}{2})\zeta_{nl}. \quad (3)$$

For more complex spectra, routine spectroscopic techniques lead one to determine values of ζ_{nl} for each (core)nl configuration. The disadvantage of this quantity is that it depends strongly on the degree of excitation of the electron, vanishing at the limit of a Rydberg series. Therefore, while ζ_{nl} is directly applicable to calculation of fine structure, it is not suited for characterizing SO coupling as a function of Z.

The parameter used by Fano and Martin[1] was $\Delta\mu_{nl}$, the change in the effective quantum number between the fine-structure states. In the context of quantum-defect theory, $\Delta\mu_{nl}$ is the change in quantum defect due to spin-orbit coupling; when $\Delta\mu_{nl}$ is extrapolated into the continuum, $\pi\Delta\mu$ is the phase difference between the states with $j = l \pm \tfrac{1}{2}$. This parameter is dimensionless and equally relevant to discrete and continuous spectra. It is approximately independent of the degree of excitation and varies smoothly through the threshold for ionization. Therefore, we have dropped the subscript nl. The quantity $\Delta\mu$ is given by an expression like Eq. (2), except that the radial wave function is normalized per unit energy. This representation reveals the significance of $\Delta\mu$ as the spin-orbit energy per unit energy range. Using the known conversion[2] from discrete normalization to energy normalization, we can relate the two quantities by

$$\Delta\mu = \zeta_{nl}\left[\frac{n^{*3}}{2R} + \left(\frac{d\mu}{d\epsilon}\right)_{\epsilon = \epsilon_n}\right], \quad (4)$$

where n^* is the effective quantum number of the state and ϵ_n is its eigenvalue, or simply

$$\Delta\mu \sim \zeta_{nl}n^{*3}/2R \quad (5)$$

for Rydberg levels for which $d\mu/d\epsilon \simeq 0$. The parameter $\Delta\mu$ is very well suited for the study of the Z dependence of spin-orbit coupling since the effects of excitation may be removed by determining the value of this parameter at the ionization limit.

Using this parameter, we will now focus our attention on p electrons. The dependence of $\Delta\mu$ on atomic number determined by Fano and Martin from experimental energy levels is shown in Fig. 1. The over-all power law in Z determined from a straight-line fit to the log-log plot of the data is[1]

$$\Delta\mu = 2.05 \times 10^{-6} \, Z^{2.33}. \quad (6)$$

This plot was constructed from ζ values that result from fitting intermediate coupling theory to experimental energy levels. The effect of excitation was removed as completely as possible by extrapolating the quantity ζn^{*3} toward the series limit when enough data were available. Squares indicate points for which this is done and lines connect points that represent different degrees of extrapolation.

III. Z-DEPENDENT FACTOR IN SPIN-ORBIT COUPLING

In order to study the variations of $\Delta\mu$ with Z, we plotted for several atoms the integrand appearing in the definition of $\Delta\mu$,

$$\Delta\mu = \frac{1}{2}\left(\frac{\hbar}{mc}\right)^2 \int_0^\infty \frac{1}{r}\left(\frac{dV}{dr}\right)P_\epsilon^2(r)\,dr, \quad (7)$$

where the subscript ϵ denotes that the radial wave function is *normalized per unit energy*. The integrands for $Z = 18$, 20, 30, and 36 calculated with zero-energy p waves computed in a Herman-Skillman (HS) field[4] are shown in Fig. 2. These curves contain one very important piece of information: The interaction profile is located in the K shell and has a maximum remarkably close to $r = 1/Z$ a.u. (marked by arrow). The fact that the SO interaction occurs in the K shell for p electrons deserves emphasis since earlier discussions[1,5] have not appreciated this fact. This result is likewise obtained by assuming that the SO interaction occurs in a pure Coulomb field. That is, when one uses a $2p$-like function $P_\epsilon \propto r^2 e^{-(Zr/2a_0)}$ and $V \propto Z/r$, the integrand of Eq. (7) has a maximum at $r = Z^{-1}$. Therefore, Fig. 2 shows us that, in the region contributing to Eq. (7), the p electron is governed by the Coulomb field of the nucleus and is screened by at most the electrons of the K shell. Consequently, the value of $\Delta\mu$ should scale smoothly with the nuclear charge except for any dependence of the normalization of P_ϵ upon the outer part of the
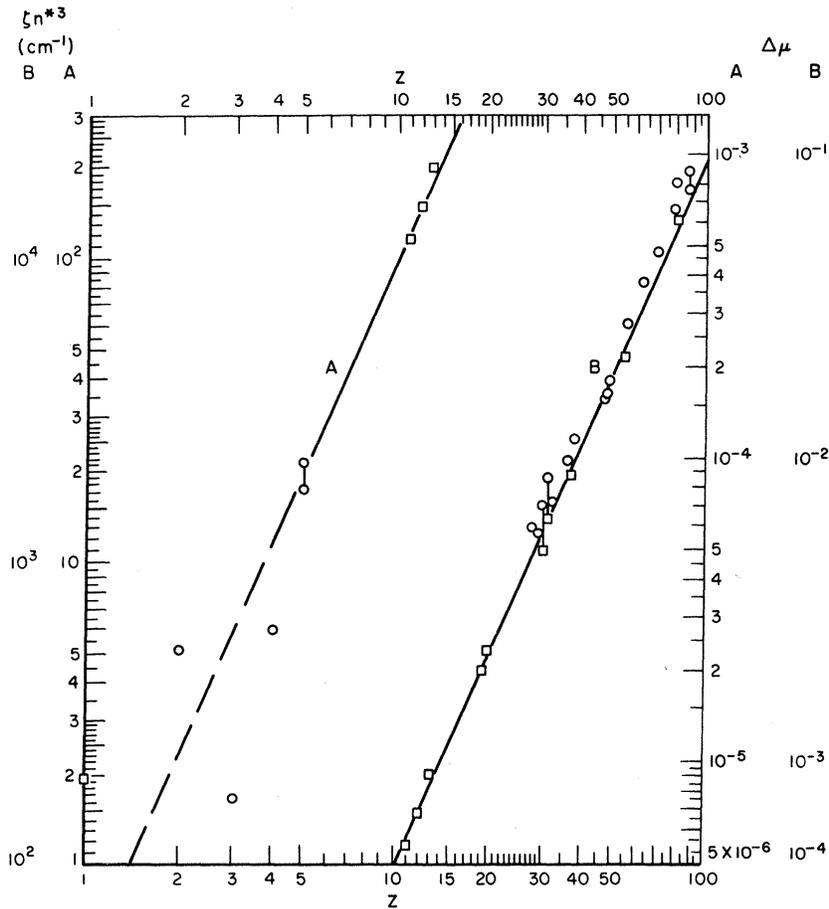
FIG. 1. Experimental Z dependence of spin-orbit interactions for p electrons in neutral atoms expressed as a change in quantum defect (from Ref. 1). The squares denote values of $\Delta\mu$ obtained by extrapolating this quantity to the series limit.

potential. This normalization effect can be represented, in the language of the PAM, by $\alpha(0, Z)$, where we have added the argument Z to emphasize the dependence of α on nuclear charge. We therefore replaced P_ϵ by $P_\epsilon/\alpha(0, Z)$ and replotted the

integrand of Eq. (7) as a function of Zr. The integrands for $Z = 18$ and 36, so modified, are shown in Fig. 3. The curves for $Z = 20$ and 30 would lie between these two curves. From this figure it is clear that we have factored out the main depen-
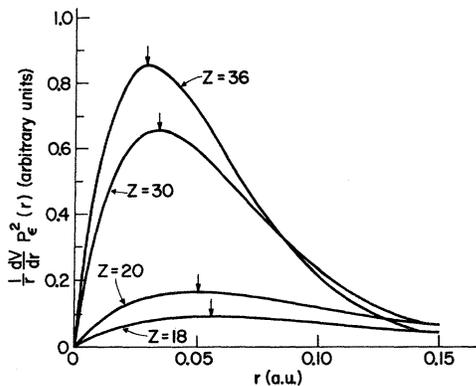

FIG. 2. Integrand of Eq. (7) for $Z = 18$, 20, 30, 36, and $\epsilon = 0$. The arrows correspond to the radial distances $r = Z^{-1}$. All curves are referred to a common ordinate scale with arbitrary units.
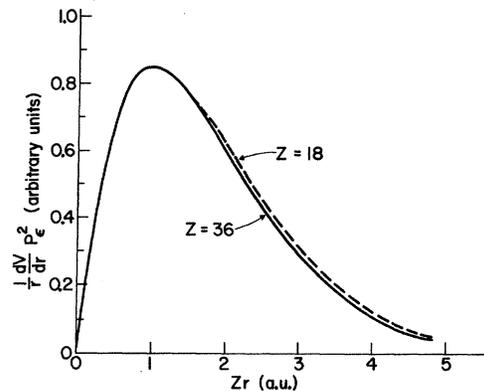

FIG. 3. Integrand of Eq. (7) for $Z = 18$ and 36, divided by $\alpha^2(0, Z)$ and plotted as a function of Zr. Both curves are referred to a common ordinate scale with arbitrary units.

dence on atomic number. This dependence may be expressed by

$$\Delta\mu = C\alpha^2(0, Z)/Z, \tag{8}$$

where C is evaluated starting from Eq. (7) by renormalizing P_ϵ by dividing by $\alpha(0, Z)$ and evaluating the integral as a function of Zr. This is just the area under the curves in Fig. 3 and has approximately the same value for all atoms. The slight deviation between the curves in Fig. 3 at larger r indicates that the part of the interaction that extends out of the K shell into the L shell does not scale in exact accordance with Eq. (8). Alternatively, this deviation might be due to a systematic error in the procedure used to produce these curves.[6] However, for the purposes of this discussion, we assume that Eq. (8) describes the scaling law of $\Delta\mu$ with sufficient precision, and do not discuss the 1–2% deviations further since they cannot significantly affect the power law in Z.

Before taking up the calculation of $\alpha(0, Z)$, we discuss the relation of Eqs. (4)–(8) to various hydrogenic approximations. First, the Coulomb wave function $P_\epsilon(r)$ for a p electron with $\epsilon \sim 0$ in the field of a nucleus of atomic number Z has the form (1) with $\alpha(0, Z) \propto Z^{3/2}$. Assuming this hydrogenic form for P_ϵ would yield

$$\alpha^2(0, Z)/Z \to Z^2 . \tag{9}$$

According to Rose,[7] assumption of this hydrogenic $\alpha(0, Z)$ in problems of this type (which include β-ray emission) is equivalent to applying a WKB approximation throughout the nonhydrogenic region of the atomic field. Therefore, any departure of a calculated value of $\alpha^2(0, Z)/Z$ from a Z^2 behavior serves as an index of the failure of WKB approximation.

Hydrogenlike formulas were used in the past to fit spin-orbit coupling data in a semiempirical way. An early Landé formula[8] was generalized by Casimir[9] to a form equivalent to

$$\Delta\mu_{nl} = \frac{1}{6}\frac{Z_i}{137}\frac{dn^*}{dn}H, \tag{10}$$

where Z_i indicates an effective nuclear charge, dn^*/dn coincides with the factor $1 + (2R/n^{*3})(d\mu/d\epsilon)$ in (4), and H is a relativistic correction defined by Casimir. Fitting of experimental data was achieved by Casimir, starting from Eq. (10) by defining

$$Z_i = Z - \sigma(Z), \tag{11}$$

where $\sigma(Z)$ is an empirical "inner screening" number. By equating Eq. (10) and the Fano-Martin power law, we find that the parameter σ increases from approximately 2 to 9 as Z increases from 5 to 90. Figures 2 and 3 support the remark of Fano and Martin that Casimir's interpretation of

σ is rather unrealistic since only a limited range of r contributes to the integral in Eq. (7) and this many electrons could not fit inside it. However, these same authors then concluded that the deviations from Coulomb behavior, which are grouped into Casimir's σ, were probably due to departure of $V(r)$ from Coulomb form. We can now see that the deviation is actually due to the influence of the outer regions of the potential that is manifested in the interaction region via the quantity $\alpha(0, Z)$, rather than to departures of $r^{-1}dV/dr$ from Ze^2/r^3 at the low r values that contribute to the matrix element.

IV. RESULTS AND DISCUSSION

The theoretical Z scaling law for spin-orbit coupling was calculated by evaluating the quantity $H\alpha^2(0, Z)/Z$ for atomic numbers between 5 and 103, using HS atomic potentials. The relativistic correction H takes into account the fact that in the K shell, p electrons acquire a velocity that is greater than $c/10$ for the heaviest atoms. This circumstance brings about some increases in the average spin-orbit interaction because it enables an electron of given energy and angular momentum to approach the nucleus more closely than one would expect in the absence of relativistic considerations. The resulting increase of $\Delta\mu$ is represented[9-11] by the factor H in Eq. (10), which rises monotonically from unity for $Z \lesssim 50$ to 1.27 for $Z = 92$. This correction is based on hydrogenic functions, which are very suitable for this application. The results are plotted in Fig. 4. In this logarithmic plot, the calculated points cluster along a straight line, $\ln H\alpha^2(0, Z)/Z = -2.10 + 2.33 \ln Z$. Evaluating the factor C in Eq. (8) by using a $2p$-like function, we can straightforwardly transform this representation of $H\alpha^2(0, Z)/Z$ into a final expression for $\Delta\mu$:

$$\Delta\mu = 2.90 \times 10^{-6} Z^{2.33}. \tag{12}$$

By comparing Eqs. (6) and (12) we find that the power of Z has been predicted exactly. This exact agreement is, of course, somewhat fortuitous, but demonstrates the suitability of this approach in studying the Z-dependent part of interactions that occur near the nucleus. The lack of agreement between the coefficient in Eq. (12) and the experimentally determined coefficient shows that the use of the HS model potentials and the explicit correction for relativistic effects does not permit the accurate determination of absolute magnitude of the function $\Delta\mu(Z)$. The calculation of this coefficient lies outside the scope of this paper and will not be treated further here. For present applications, therefore, it is better to use the experimental coefficient in Eq. (6), together with the values of $H\alpha^2(0, Z)/Z$ in Fig. 4, to determine $\Delta\mu$
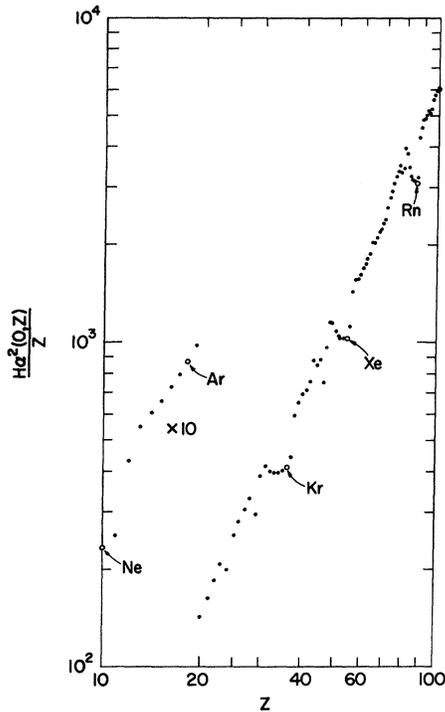
$$\times \overline{P}[\delta(r)] \; \overline{P}[\delta(r) + \tfrac{1}{2}\pi] dr\}. \qquad (13)$$

As in I, $U(r, Z)$ is the effective potential for the electron, minus a unit charge Coulomb potential. This modified potential has a finite range for the case of an electron in a neutral system and there-fore the integration in Eq. (13) is stopped at r_0. The quantity $\overline{P}[\delta(r)]$ is just the radial wave function divided by the amplitude function, i.e., $P(r)/\alpha(r)$. Since $\alpha(r)$ only modifies the amplitude of $\overline{P}$ to give P, these two functions resemble each other in that they have the same nodes and total phase $\phi(r)$, where

$$\phi(r) = (\text{Coulomb phase}) + \delta(r). \qquad (14)$$

In order to extract the physical significance of Eq. (13), we schematize it by setting $\overline{P}[\delta(r)] = \sin[\phi(r)]$. Since $\overline{P}$ appears again in Eq. (13), this time phase shifted by $\pi/2$, we set $\overline{P}[\delta(r) + \tfrac{1}{2}\pi]$ equal to $\cos[\phi(r)]$. Using this simplified model for $\overline{P}$, we can rewrite Eq. (13) in a more transparent way:

$$\alpha(0, Z) \propto \exp[\tfrac{1}{2}\pi \int_0^{r_0} U(r, Z)\sin(2\phi)dr]. \qquad (15)$$

Since U is a monotonic function, it is now apparent that the integrand in Eq. (15) will oscillate twice as often as the radial wave function, represented by $\sin\phi$. That is, during each loop (or orbit) of the radial wave function, there will be a positive and negative contribution to the integral in Eq. (15), corresponding, respectively, to the first half-loop (odd quadrant of ϕ) and to the second half-loop (even quadrant of ϕ) of the wave function. We can therefore interpret the substructure in Fig. 4 by considering the number of even and odd quadrants of the wave function in the region $[0, r_0]$ over which the modified potential $U(r)$ is nonzero. To be more precise, Eq. (15) dictates that the amplitude at the nucleus will be largest when the region $[0, r_0]$ includes an odd number of quadrants, and will be smallest when it includes an even number of quadrants, or integral number of loops. Note that these same remarks apply to the transmission coefficient for a plane wave passing over a square-well potential.[13] Here we are concerned, in effect, with the transmission coefficient of a realistic p wave over the potential U.

In applying these elementary properties of the transmission coefficient, we can take advantage of another property of atomic wave functions. The integral in Eq. (15) covers a range defined by the electron density of the atom. However, in the closed shell region of the atom, the potential energy is large and the inner loops of the wave function vary smoothly as a function of Z. Each loop contributes a positive and a negative contri-bution to the integral. These contributions tend to cancel each other and will not produce any periodic dependence on Z of the function $\alpha(0, Z)$. They will

FIG. 4. Theoretical Z dependence for spin-orbit coupling, given by $H\alpha^2(0, Z)/Z$, for $\epsilon = 0$, $l = 1$, and $10 \le Z \le 100$.

for a particular atom or set of atoms.

We now take up the distinct periodic substructure that is evident in Fig. 4. It seems that by virtue of calculating the value of $H\alpha^2(0, Z)/Z$ for every Z and always at the series limit, the curve in Fig. 4 exhibits a pattern in the deviations from a straight line mentioned by Fano and Martin. This pattern, which is not discernible in the sparser experimental data,[12] is quite clearly correlated to the Periodic Table. Specifically, the "local slope" of the curve in Fig. 4 depends on the angular momentum of the atomic subshell that is filling: The slope in the immediate vicinity of the alkali metals and alkaline earths is always approximately equal to 10. On the other hand, when an np sub-shell is filling, the slope is always less than 1.1 and becomes negative during the filling of the $4p$, $5p$, and $6p$ subshells. For all other Z, the points do not deviate significantly from the $Z^{2.33}$ law and are regarded here as a single class whether an nd or an nf subshell is filling.

The periodic deviation from the average $Z^{2.33}$ behavior observed in Fig. 4 is most clearly under-stood in terms of the definition of the amplitude function. It was shown in I that $\alpha(0, Z)$ for a con-tinuum wave function is given by

$$\alpha(0, Z) = 2^{-1/2} \exp\left\{ -\tfrac{1}{2}\pi \int_0^{r_0} U(r, Z) \right.$$

only cause a smooth increase in the integral as these inner orbits move to lower r with increasing Z. To find contributions to $\alpha(0, Z)$ that are not smooth with Z, we must examine the valence region of the potential. It is this region of space, outside of closed shells but inside the region of finite electron density, in which the atomic shell structure manifests itself.

As a specific example, we focus on one period of the variation, that is, on one row of the Periodic Table. At Kr, the $4p$ subshell has just become full. The $4p$ orbit defines the extent of the electron distribution, and exactly three loops of the wave function overlap the potential inside $r = r_0$. Between Kr and Y, the $5s$ subshell fills. These valence electrons occupy diffuse orbits. This extends r_0, while the additional nuclear charge pulls the fourth loop of the p wave toward the nucleus. The end result is that the seventh quadrant of the p wave now overlaps with U. Therefore, the steep slope of $\alpha(0, Z)$ in the vicinity of alkali metals and alkaline earths derives from this rapid movement of an odd quadrant of the wave function into the region $r < r_0$. In the following group of transition elements, the points in Fig. 4 lie close to the best straight line. In this range of Z, a high-angular-momentum state of an inner shell is filling so that the outer p orbit is almost completely screened from the increase in nuclear charge by the additional valence electron. Therefore, the relative positions of the outer p orbit and of r_0 do not change appreciably between $Z = 39$ and 48. The intermediate rate of increase of $\alpha(0, Z)$ is due to the general contraction of the electron distribution. Finally, after the end of the transition series, the $5p$ subshell becomes stable and fills between $Z = 49$

and 54. In so doing, the even quadrant of the $5p$ loop moves onto the potential U, and the amplitude function decreases, thus completing this particular period of variation in Fig. 4.

The motion of the zero-energy p wave described above is consistent with the phase-shift calculations of Manson.[14] Using HS potentials, Manson computed scattering phase shifts for zero-energy p waves as a function of Z. He found that the phase shift increases only by approximately $\frac{1}{2}$ rad during the long transition series, and then increases by more than 2 rad while the np and the $(n+1)s$ subshells are filling.

There is one more characteristic substructure in Fig. 4 which occurs during the transition series. For instance, as the $3d$ subshell is filling, there are sudden dips in $\alpha(0, Z)$ at Cr and Cu. The origin of these dips is presumably the promotion of a $4s$ electron to form a half full and full $3d$ shell in Cr and Cu, respectively. This promotion contracts the outer shell and eliminates a positive contribution to Eq. (15). (The effect may be overemphasized by artifacts of the HS model potential.) Likewise, irregularities at higher Z arise from changes in the outer part of the effective potential brought on by the discontinuous order of filling of atomic subshells.

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